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Study on the Tribological Properties of Porous Sweating PEEK Composites Under Ionic Liquid Lubricated Condition

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ABSTRACT: The tribological behaviors of novel porous Polyetheretherketone (PEEK) composites under 1-hexyl-3-methylimidazolium tetrafluoroborate ionic liquid lubricated condition were investigated. The effect of sliding velocity and applied load on the sweating tribological properties and the stability of lubricating oil film was also studied. Results indicated that when the sliding velocity was 0.69 m/s and the applied load was 250 N, the friction coefficient and wear rate of the ionic liquid lubricated porous sweating activated carbon fiber/polytetrafluoroethene/PEEK composites showed the minimum values, were 0.0197 and 4.145×10^{-15} m^3/Nm, respectively. The friction coefficients fluctuated in a narrow range of 0.0162–0.0215. It was found that the porous sweating PEEK composites under ionic liquid lubricated condition showed good low-friction and antiwear performance, especially under the condition of high sliding velocity and applied load. The formed transfer film due to the tribo-chemical reaction as well as boundary lubricating film is effective in improving the carrying capacity and antiwear properties of the porous sweating PEEK composites. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40989.

KEYWORDS: friction; ionic liquids; morphology; porous materials; resins; wear and lubrication

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INTRODUCTION

The study on friction and wear behaviors of polymer composite materials has been the focus of interest in both material science and tribology of materials.[1,2] However, with the rapid development of science and technology, it is still difficult for polymer composites to satisfy the tribological requirements under harsh conditions, such as high sliding velocity, high applied load, and corrosive conditions. Owing to its high friction coefficient and wear rate of polymer composites, it is rarely used for self-lubricating material under rigorous conditions in industry. To overcome above problems, some researchers pursue the preparation of porous polymer composites for tribological performances.

Porous polymer self-lubricating material is a polyporous functional material, which can be prepared by the use of moulding-leaching and high temperature vacuum melting technologies.[3] The pores are interconnected and easily connect to the sliding surface of tribo-materials.[4,5] The intricate porous structures of porous composites can be used to store lubricants for self lubricating. During tribological testing, the prestored grease will be squeezed out of the porous structure to the sliding surface under the effect of load and generated temperature.[6,7] Therefore, it may be a feasible way to absorb lubricating oil into porous Polymer composites to achieve synergistic improvement in tribological properties.[8] Some efforts have been made to investigate the effects of internal solid and/or oil lubricants on tribological behaviors of porous polyamide,[9] polyimide,[10] polyetheretherketone (PEEK),[6] and ceramics composites.[11] Studies indicated that porosity of composites has obvious effects on the excurrent quantity of lubricant and compressive behavior of matrix.[4]

PEEK is a typical high-performance thermoplastic polymer. In recent years, there are many studies on improving wear resistance and decreasing friction coefficient of PEEK composites.[12–14] In this article, PEEK is selected as the skeleton of porous self-lubricating composites owing to its outstanding merits of high mechanical strength, elastic modulus, and thermal stability.[15,16]

In recent years, ionic liquids have received extensive attention owing to their unique properties, such as negligible volatility, high thermal stability, low melting point, and nonflammability, in the fields of organic synthesis, electrochemistry, and catalysis.[17,18] An increasing attention has been given to study ionic liquids as lubricants by the researchers worldwide. Studies indicate that ionic liquid lubricants have excellent tribological properties which are not only used for potential lubricants with high performance, but also used as additives for some base oil.[19–22] Additionally, ionic liquid lubricants offer several advantages over traditional lubricants, especially for the steel-

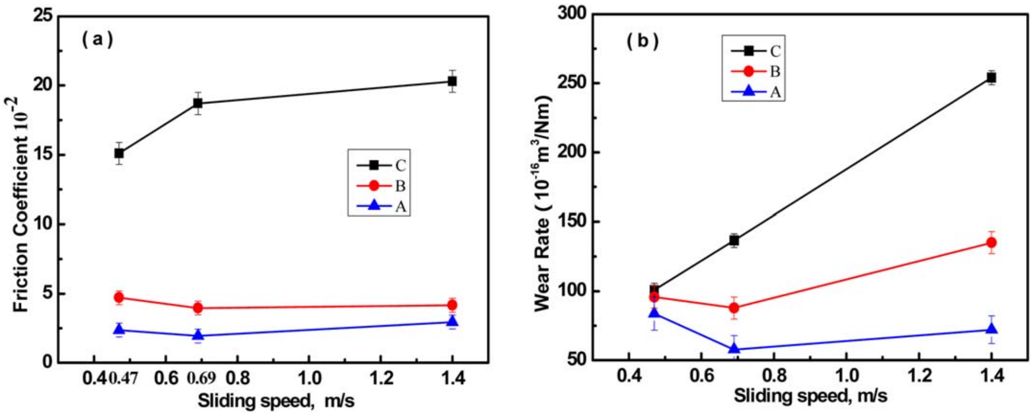

Figure 1. Effect of sliding speed on the tribological performances of A, B, and C composites under 100 N loads. (a) Friction coefficients and (b) wear rates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

aluminum friction pair which is a commonly difficult task to lubricate.[23–25]

To the best of our knowledge, however, no literature is available regarding porous polymer composites containing ionic liquid as self-lubricating agent for tribological application. In this study, the design and fabrication of porous PEEK composites incorporating polytetrafluoroethene (PTFE) as solid lubricant, NaCl as micron pore-forming agent, and the activated carbon fiber (ACF) as nanometer pore forming was investigated based on the mechanism of human sweating. Furthermore, the tribological behaviors of ionic liquid lubricated porous PEEK composites were studied. Moreover, the micromorphology of worn surface is examined by scanning electron microscope (SEM) and the wear mechanism of porous PEEK composites was discussed. This article provides a valuable reference for the development of sweating self-lubricating polymer composites under harsh conditions with unique low friction and high wear resistance.

EXPERIMENT

Materials

PEEK powder in 160-mesh size (supplied by Jilin University High-Technology Co., Changchun, China), was used as the polymer matrix material. PTFE powder (7AJ, mean diameter 25 μm) was provided by Dupont Co., USA. NaCl (food grade, the mean diameter of 109 μm) used in this work was homemade and sieved, which plays the role of micron pore-forming agent. Multipurpose lithium base grease (SL3141, containing MoS_2) and ACF felt (, SY-ACF-1000, S = 900–1000 m^2/g) were provided by American CRC and Nantong Senyou Company, respectively. 1-Hexyl-3-methylimidazolium tetrafluoroborate ($C_{10}H_{19}BF_4N_2$, purity $\geq$99%) was supplied by Lanzhou Chemical Institute of Chinese Academy of Science.

Samples Preparation and Characterization

The PEEK powder, ACF, and NaCl were dried at 120°C for 4 h, and then mixed mechanically. The PEEK samples were produced by molding in a press mold, followed by sintering at 360°C for 2 h. Finally, the samples were cut into a shape with an external diameter of 32 mm, an inner diameter of 22 mm, and a shoulder height of 2.5–3 mm. The cut sample is immersed in a deionized water maintained at temperature of 80°C, followed ultrasonic vibration to allow the leaching out of the porogen leaving behind a porous polymer structure.

Then, the process of steeping the ionic liquid or lithium base grease to the hierarchical porous ACF/PTFE/PEEK composites was carried out by the high-temperature vacuum melting technology (0.01–0.2 bar, 120°C for 2 h). The tribological properties of the porous PEEK composite lubricated by the ionic liquid (named A), the porous PEEK composite lubricated by the lithium base grease (named B), and the porous ACF/PTFE/PEEK composites without lubrication (named C) were investigated, respectively.

The wear tests were performed on pin-on-disk tribological testing machine (Xuanhua Co., Hebei province, China) and the sliding wear was carried out in a ring-on-ring configuration. The material of counterpart surface is 1045 steel with quenching (HRC hardness = 56). Before each test, the counterpart surface was polished with 1000-grit SiC abrasive paper to an average roughness of 0.15–0.3 μm and then cleaned with anhydrous ethanol. Test conditions were sliding velocity of 0.49, 0.69, and 1.4 m/s, applied load of 100–300 N, respectively, and test duration was 120 min. The friction coefficient was calculated by friction torque continually collected with a computer during the tests. The mean friction coefficients and wear rates were obtained after three tests under the same condition. The mass loss of samples (accuracy to 0.1 mg) after the test was measured with the FA2004 electronic analytical balance (Shanghai Jingke Co.). The morphologies of the worn surfaces were analyzed by QUANTA-200 SEM and the surface elements were characterized by using Fourier transform infrared spectroscopy (FTIR).

RESULTS AND DISCUSSION

The Effect of Velocity on the Tribological Properties of Porous PEEK Composites

Figure 1 shows the effect of sliding velocity on the friction coefficients and wear rates of ionic liquid lubricated porous PEEK composite (A), lithium base grease lubricated porous PEEK composite (B), and porous PEEK composites without lubrication (C). It can be seen that the friction coefficient and the wear rate of C increase gradually with the increase of sliding speed. Whereas, the friction coefficients and the wear rates of B and C reduce at first and then increase. When the sliding

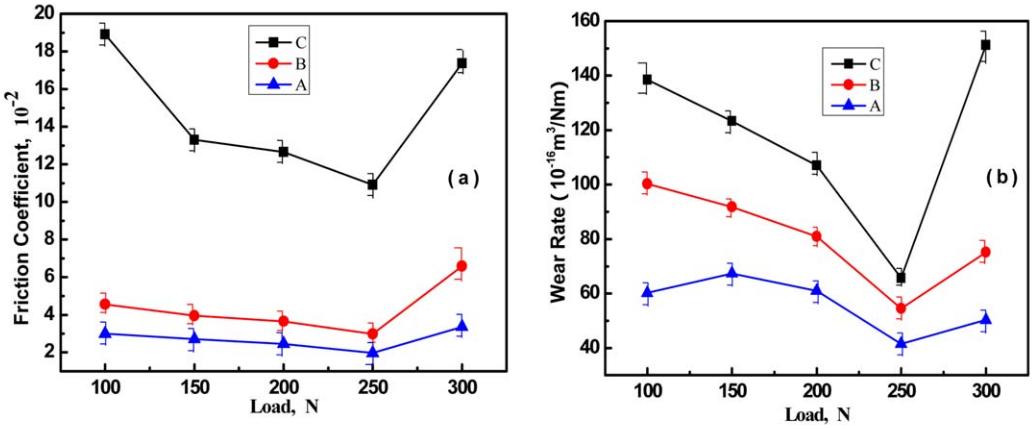

Figure 2. Effect of load on the tribological performances of A, B, and C composites under 0.69 m/s. (a) Friction coefficients and (b) wear rates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

velocity is 0.69 m/s, the friction coefficient and the wear rate reach the minimum values. At this time, ionic liquid lubrication (for composite A) decreases the friction coefficient and the wear rate of Sample C with 9.7 and 2.4 times, respectively. It indicates that ionic liquid exuded from pores shows higher capacity of decreasing the friction coefficient and increasing the wear resistance than that of grease.

As Sample C is considered, there is no lubricant during the process of friction to protect the material from being worn. The wear rate of C is sensitive to the sliding speed. It indicates that the wear of the porous PEEK composite becomes comparatively serious with the increasing of sliding speed, which leads to the increasing of friction coefficient and wear rate.

However, as the porous sweating PEEK composites of A and B for consideration, when the sliding speed is 0.69 m/s, the ionic liquid or grease could be exuded out under the effects of load and temperature through the micrometer-sized and nanometer-sized pores, and continuously formed stable oil film on the sliding surface. Therefore, the friction coefficient and wear rate of porous sweating PEEK composites decrease under the ionic liquid or grease lubrication.

The Effect of Load on the Tribological Properties of Porous PEEK Composites

Figure 2 shows the effect of load on friction coefficients and wear rates of Samples A, B, and C. It can be seen that the friction coefficients and the wear rates of these three porous PEEK composites all decrease at first and then increase, respectively. When the load is less than 250 N, the friction coefficients and the wear rates of the three materials obviously reduce with the increase of the applied load. Nevertheless, when the applied load is over 250 N, the friction coefficients and the wear rates of the three materials increase fleetly. Under the load of 250 N, the friction coefficients and the wear rates of the three porous composites reach the minimum values. It means that increasing load properly can improve lubricating effect on the friction surface, which is favorable to get low friction coefficient and wear rate. However, under the condition of high load, due to metamorphose, growth of superfine crack in composite and leakage of grease, it was difficult to retain lubricants in the pores. In this case, it would lead to higher friction coefficient and higher wear rate.

As the tribological properties of the three kinds of materials are concerned, the friction coefficient and wear rate of C are much higher than those of A and B. Among them, Sample A shows the lowest friction coefficient and wear rate. It indicates that ionic liquid is efficient in decreasing the friction coefficient and wear rate of porous composites. During the sliding wear, the ionic liquid could be released uniformly from interconnected porous structure to sliding surface to generate lubricating oil film protecting the samples surface from being directly damaged. Additionally, tribo-chemical reaction generated on the counterpart surface leads to form a boundary lubricating film which contributes to the decrease of friction and wear.

The Stability of Friction Coefficients with Different Lubricants

Figure 3 shows the stability of friction coefficients of porous PEEK composites lubricated by ionic liquid and grease under the sliding velocity of 0.69 m/s and the applied load of 250 N. It can be found that the friction coefficient of A is the least, which hovers in a narrow range of 0.0162–0.0215. The friction coefficient of Sample A is almost 2/3 of Sample B, and 1/8 of

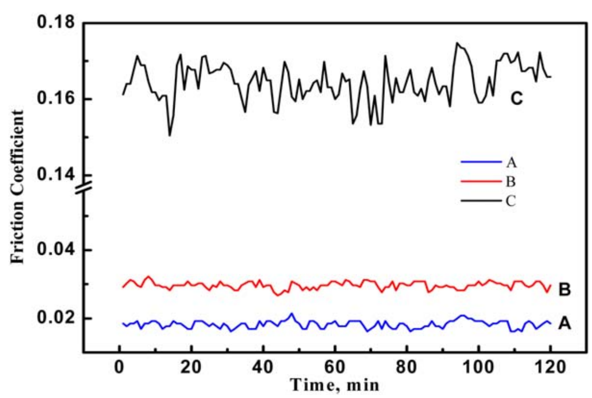

Figure 3. Effect of ionic liquids on the friction coefficient under the condition of 0.69 m/s and 250. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. The Characteristic Comparison of Porous Composites with Different Lubricants Under the Condition of 0.69 m/s and 250 N

Materials and condition	Oil content (%)	Temperature of sliding face (°C)
Sample A	1.29	27.1
Sample B	0.407	38.2

Sample C. The friction coefficient of C is much higher than those of A and B, and its fluctuation is obvious. Therefore, conclusion can be drawn that the ionic liquid lubricant is quite effective in decreasing the friction coefficient of porous PEEK composites, achieving super low-friction material. Prestored ionic liquid in the porous PEEK composites is capable of being released uniformly and forming thin oil film on the sliding surface, which leads to the distinct decrease of the friction coefficient of the porous composites.

The Characteristic Comparison of Porous Composites with Different Lubricants

The oil content in porous PEEK composites and the temperature on the worn surfaces for A and B are compared in Table I. The adsorption content of the ionic liquid lubricated porous PEEK composites is 2.2 times higher than that of lithium base grease lubricated porous PEEK composites. The reason is that the viscosity of ionic liquid is lower than that of grease. Therefore, it is more facilitated to achieve higher content absorption of ionic liquid into porous structure. At the same time, the pre-absorpted ionic liquid is easier to be released from those porous structure to sliding surface to generate lubricating oil film. Moreover, fractional ionic liquid reacted chemically with the counterpart surface to generate the absorbed transfer film which also contributes to the enhancement of the wear resistance and decrease of friction coefficient.

Surface Analysis

To obtain further comparison of the tribological properties of Samples A, B, and C, the observations of counterpart surfaces of A, B, and C were carried out by the SEM (Figure 4). It can be seen that the counterpart surface of A is comparatively smooth with slight signs of wear. It is deduced that the ionic liquid involves a complicated series of reactions with the coupling metal, which leads to the generation of the transfer film on the counterpart surface protecting the worn surface from being scratched. The counterpart surface of B is also quite smooth, only some nicks can be seen on the surface. However, the situation on the counterpart surface of Sample C is in a different manner. It is plucked and ploughed, which represents results of higher abrasion.

SEM is also used to characterize the morphology of the worn surfaces of A, B, and C samples, as shown in Figure 5. Typical SEM image of Sample A reveals that the worn surface is relatively smooth. Obvious oil film can be found around the pores. It indicates that owing to the effect of applied load and temperature, the ionic liquid is released uniformly and formed lubricating oil film on the sliding surface. The formed lubricating oil film leads to the stable sliding operation of the porous materials no matter at high or low temperature. From Figure 5(b) for composite B, it can be seen that some pores are not completely filled and the worn surface is not as smooth as Figure 5(a), which is the main reason for grease to be inferior to ionic liquid in decreasing the friction and wear of porous PEEK composites.

Compared with worn surface image of Sample A, the worn surface of Sample C shows rough morphology with obvious scraps. The reason leading to the severe damaging may be that the porous materials cracked and formed scraps during the process of sliding without lubricating. In the following wear test, the worn surface and the scrap interact with each other to get the worn surface rough and jagged, which leads to the highest wear rate and friction coefficient of Sample C.

The Analysis and Discussion of Wear Mechanism

The adsorption schematic diagrams of ionic liquid on the counterpart surface (steel substrate) is presented in Figure 6. According to the tribological results and the analysis of the morphology of counterpart surface, it indicates the low-energy electrons emitted from the tiny contact convex points on metal surface and formed positive charges due to the electrostatic attraction during the process of sliding friction.[26] Then, it is easier for the fluoroborate ion in the ionic liquid to adsorb on the positive charge sites of metal surface, whereas the imidazolium cation adsorbs on the anion of the alkyl chain to stay away from the metal surface.[27]

In addition, the second layer of ionic liquid could subsequently form on the first adsorption layer via tail-to-head self assembly on counterpart surface. The Van Der Waals chain-chain interaction between the alkyl chains in the ionic liquid may arrange

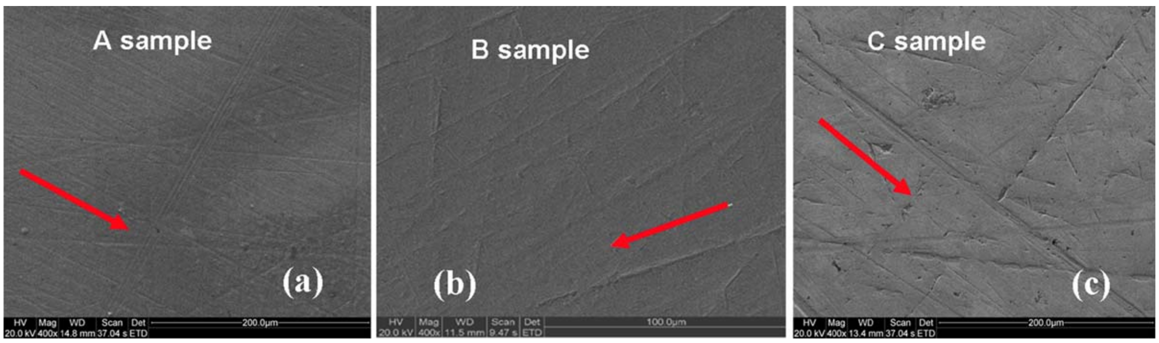

Figure 4. SEM images of the counterpart surfaces of samples. Red arrow indicates sliding direction. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

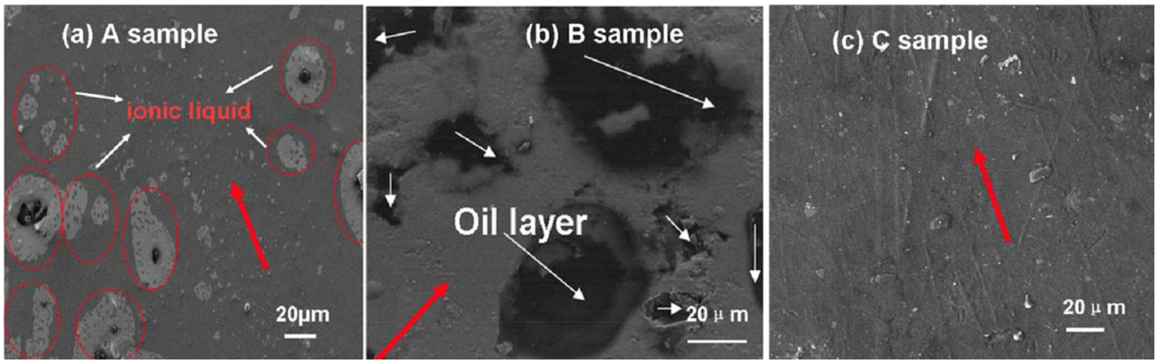

Figure 5. SEM mirographs of the worn surfaces of composites. Red arrow indicates sliding direction. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

more orderly and compactly, at which the interdigitated alkyl chains are separated by imidazolium cation. Therefore, the ionic liquid formed a double-layer or multilayer-structure has stronger adsorption on the metal surface to form uniform and robust boundary lubricating films. As a result, it exhibits good friction-reducing and antiwear performance.

Figure 7 shows the infrared spectrum analysis of original ionic liquid, Samples A and C. It can be observed that the bands at 1120–1350 1/cm indicate the presence of $–F_2$ and $–F_3$ groups of ionic liquid, whereas the band at about 3207 and 3406 1/cm suggests the presence of amino acid groups. The results confirm that the thermal oxidation components of 1-hexyl-3-methylimidazolium tetrafluoroborate ionic liquid can form active polar group on the surface of composites during the friction process, which also contributes to the formation of transfer film on the counterpart surface. Therefore, the friction-reducing and antiwear properties of ionic liquid lubricated porous PEEK composites are higher than that of the initial porous polymer or grease lubricated porous PEEK composites.

CONCLUSIONS

In this study, inspired by the mechanism of human sweating, a novel ionic liquid lubricated porous PEEK composites was fabricated and its tribological behaviors were investigated. Conclusions can be drawn as follows:

1. The friction coefficient and the wear rate of ionic liquid lubricated porous sweating PEEK composites reach the minimum value under the condition of 0.69 m/s and 250 N, which is 0.0197 and $4.145 \times 10^{-15} m^3/Nm$, respectively. At this time, ionic liquid lubrication decreased the friction coefficient and the wear rate of initial porous PEEK composite by 9.7 and 2.4 times.
2. During the sliding process, the preabsorpted ionic liquid could be released uniformly from interconnected pores to sliding surface to generate lubricating oil film protecting the samples from being damaged, which contributes to the improvement of wear resistance and decrease of friction coefficient.
3. The ionic liquid can be adsorbed on the counterpart surface during the process of friction. Under the effect of temperature and applied load, partial ionic liquid between the contacting surface areas reacted with the steel counterpart surface by tribo-chemistry and formed the boundary lubrication film, which possesses higher carrying capacity, low friction, and antiwear properties for porous PEEK composite.

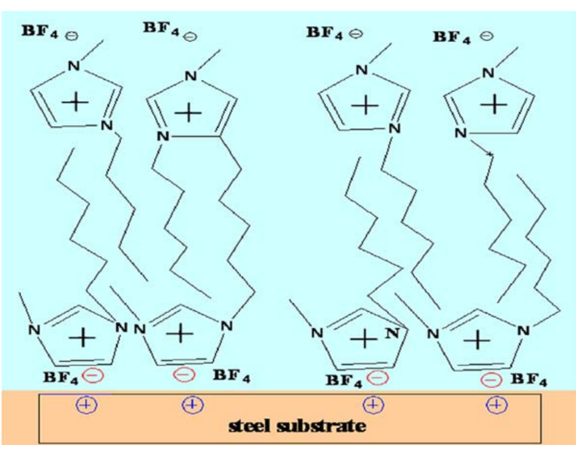

Figure 6. Schematic diagrams of 1-Hexyl-3-methylimidazolium tetrafluoroborate adsorbed on the steel counterpart surface. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

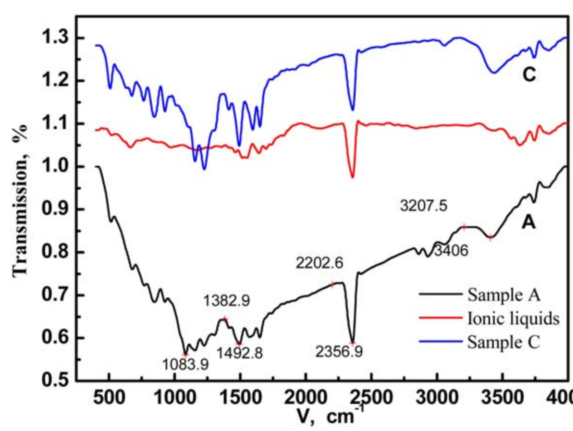

Figure 7. FTIR spectrum of ionic liquid and the friction surface composite materials. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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