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Friction and wear behavior of near-frictionless carbon coatings in formulated gasolines

J. Hershberger*, J.B. Woodford, A. Erdemir, G.R. Fenske

Energy Technology Division, Argonne National Laboratory, 9700 S Cass Ave, Argonne, IL 60439, USA

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Abstract

Million-cycle reciprocating wear tests have been carried out to determine the ultimate wear lifetime of near-frictionless carbon (NFC) coatings applied to production fuel-injector tips. Wear tests were performed in existing and reformulated gasolines as part of a study to improve fuel systems for spark-ignited, direct-injected (SIDI) engines. Ball-on-three-disc (BOTD) tests were performed to determine the lubricity of the gasolines, and the wear surfaces were analyzed using Raman spectroscopy. NFC coatings reduced friction and total wear by up to 48% and 39%, respectively. No evidence was seen of coating graphitization, the formation of transfer films from the coatings, or the presence of chemical protective films originating from the gasolines.

Keywords: Amorphous; Profilometry; PACVD; Carbon

1. Introduction

Previous work [1] established that the friction and wear performance of fuel injectors coated with near-frictionless carbon (NFC) was good compared to parts coated with commercial diamond-like carbon coatings (DLCs) when tested in gasoline. In this work, reciprocating tests have been used to determine the durability and wear lifetime of the NFC coatings in regular and reformulated gasolines. This series of tests was performed for two reasons. First was to assess durability: while the reciprocating tests in the previous study indicated that the performance of the NFC coatings was good, they did not address whether this performance would last the lifetime of the part, or what would happen once the coatings wore through. If coating removal were followed by immediate catastrophic failure of the part, extra attention would have to be paid to the component design, and use of the coating might be precluded. As a result, the duration of the reciprocating tests was extended from the 100 000 cycles used in the previous study to 1 000 000 cycles. The stroke length of 1 mm gave a total sliding distance of 2 km.

The second reason for performing these tests was that the coatings were intended to be used in spark-ignited, direct-injected (SIDI) engines, which, when introduced to the market, will ultimately require reformulation of the North American gasoline supply. Early port fuel injected (PFI) systems suffered from deposits on the injectors in much the same way that current SIDI injectors do, and efforts by the oil industry produced gasolines which were more compatible with the designs [2]. Therefore, several varieties of regular gasoline and candidates for reformulated gasoline were acquired for wear testing. Table 1 lists the gasolines tested and their characteristics. Winter and summer gasolines differ in the amount of water they contain; premium and regular gasolines have different octane numbers. The additive put into some of these gasolines was proprietary; therefore, details on its composition were not available, but it was not a compound designed for wear reduction.

Spark-ignited, direct-injected engines deliver fuel to the combustion chambers without mixing it with air beforehand. Spark-ignited engines typically run on gasoline, whereas compression-ignited (or CI) engines typically run on diesel fuel. Direct injection (DI) is to be contrasted with PFI, the most common type of fuel system found in passenger vehicles, in which fuel and air are premixed before introduction to the cylinder.

*Corresponding author. Tel.: +1-630-252-7361; fax: +1-630-252-4798.

E-mail address: jhersh@anl.gov (J. Hershberger).

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Table 1
Fuels used in long-term reciprocating tests

Name	Season	Type	Grade	Additive?
Ethanol	–	–	–	–
Gasoline A	Winter	Conventional	Premium	Yes
Gasoline B	Winter	Conventional	Premium	No
Gasoline C	Winter	Reformulated	Premium	Yes
Gasoline D	Summer	Reformulated	Premium	No
Gasoline E	Winter	Conventional	Regular	Yes
Gasoline F	Winter	Conventional	Regular	No
Gasoline G	Summer	Conventional	Regular	No

Gasoline engines are used in applications ranging from handheld landscaping tools to municipal electrical power facilities. Direct injection is in use in electrical generators and was first included in motor vehicles by Mitsubishi Corp. The objective of developing DI fuel systems in SI motors is to increase fuel efficiency while maintaining the low emissions of SI engines. However, DI is highly sensitive to formation of solid deposits on the fuel injectors. Other issues in SIDI development include tailpipe emissions, which are not yet an improvement over PFI systems, and injector design challenges (such as tribological issues) posed by the low lubricity of gasoline and the high fuel injection pressures required for proper dispersal of the fuel in engine cylinders. When researchers overcome these obstacles, SIDI technology promises greatly improved fuel control compared to PFI systems.

An excellent review of the history of research and literature on SIDI was performed by Zhao et al. [3]. Li et al. studied hydrocarbon emissions from SIDI engines and found that a strong contribution came from the liquid fuel that reached the cylinder walls and piston [4]. They also concluded that, while wetting on the exhaust side of the liner was worst from an emissions standpoint, all liner locations were probably highly undesirable because of oil-layer dilution and subsequent wear of the liner and rings.

The literature on SIDI systems emphasizes the combustion and the motion of fuel and air, or mixture preparation. Lee et al. analyzed the shape of the gasoline spray from an injector as a function of various parameters and found that the injection pressure of the fuel is an important factor [5] in that higher pressure sprays are more effective. In this paper, pressures of only 5–7 MPa were considered, whereas other papers investigated considerably higher pressures. The flow of fuel inside a high-pressure swirl-type DI injector was investigated by Cousin et al. using simulations [6]. They found that the spray-cone sheet thickness near the orifice strongly affects the mixture preparation. This finding argues for careful control of the orifice geometry against effects such as deposit formation and wear. A presentation on optical flow characterization by Hentschel described in detail the droplet size and other aspects of in-cylinder mixing [7]. The injectors he discussed were also of the high-pressure swirl type and used pressures up to 12 MPa. Optical diagnostics were also used by Wicker et al. in a paper on fuel spray structure [8]. They noted that SIDI engines require more precise control of both fuel and spark than do conventional PFI engines. They discussed the inhomogeneities of jets and sprays caused by the flow of liquid within the injector. They also noted that preferential concentration and directed motions of fuel in SIDI engines are significant, suggesting a need for attention to the geometry of the internal surfaces of the injector and its orifice.

Tribology is also a significant concern in the SIDI literature. Several papers have been published on fuel lubricity, especially since the experience of Sweden and Canada after reformulation of diesel fuel caused fuel pump failures. Wei et al. discussed the lubricity of gasolines and found that the poor wear-protection properties of gasoline relative to diesel was primarily due to gasoline's low viscosity [9]. Ping et al. compared the lubricating properties of gasoline and diesel, as well as the effects of detergents and other additives [10]. Diesel lubricity additives were found to have a similar function in gasoline. In 1999, Nikanjam reviewed the work to date on providing a specification for the lubricity of diesel fuel [11]. The discussion centered around the effects which removal of environmentally harmful components such as sulfur would have on the lubricity of diesel. This information is highly relevant to discussions of SIDI engines since diesel fuels also operate in direct injection. A standard for assessment of diesel lubricity was given by ISO 12156-1 and -2, which specified a set of wear test conditions in a high-frequency reciprocating rig (HFRR) tester and a maximum wear scar size for acceptable lubricity [12]. Further remarks on wear in injectors due to the lubricity of fuels appear in a study by Lacey [13]. That work found that oxidative corrosion was the predominant mechanism of wear in very highly processed fuels, leading to catastrophically high wear rates. The source of the oxygen causing corrosion in that study was water dissolved in the fuel. In 1999, Bardasz et al. compared the lubrication and wear performance in a test study of several SIDI and PFI engines [14]. They observed significant piston bore wear under some conditions, and suggested that soot was the cause.

Many investigations of friction, wear, and lubrication have been performed for non-DI gasoline-engine applications. Tung and Tseregounis developed a method for simulating piston liner-ring wear in an HFRR wear tester [15]. Using direct measurement techniques, Wakuri et al. studied the total frictional loss in an engine, as well as the friction in the piston assembly and between the cam and follower [16]. A study on valve seats and inserts for heavy duty diesel engines by Wang et al. was notable for its encyclopedic coverage of failures [17].

They performed microscopy on over 100 valves from 47 engines. Wear and failure due to adhesion, corrosion, abrasion and delamination from mechanical or thermal fatigue were observed. Ito et al. studied cam wear using an engine-mountable device for friction measurement [18]. Many novel experimental techniques such as these have been adopted to reduce the dependence of engine manufacturers on full-scale engine tests, which are time-consuming and expensive.

2. Experimental procedures

2.1. Coating deposition

Deposition of NFC coatings has been described in detail elsewhere [1] and will be summarized in brief below. Depositions were performed in a Perkin–Elmer 2400 sputtering system using plasma-assisted chemical vapor deposition (PACVD). Before introduction to the chamber, the metal substrates were ultrasonically degreased and solvent cleaned. Once they were arranged in the chamber, the system was sealed and pumped down to a base pressure of 10^{-6} Torr (1.3×10^{-4} Pa) using a turbopump. Argon gas was used to perform RF sputter cleaning of the sample surfaces. An amorphous hydrogenated silicon bond coat, approximately 100 to 200-nm thick, was deposited on the sample via PACVD from a source gas of silane. The NFC films were then formed by PACVD from source gases consisting of a mixture of methane and hydrogen. The ratio of H2 to methane was different for different types of NFC [1]. The resulting coatings were 2 to 3-μm thick.

2.2. Wear tests

A Falex ball-on-three-disc (BOTD) tester measured the lubricity of the gasolines in this study. In the absence of a standard for gasolines (analogous to ISO12156-1 and -2 for diesel fuels) the BOTD test was chosen because of its low expense and common availability. The tester output its friction force signal to a computer for continuous recording and analysis. The test conditions were as follows: load, 24.5 N (10 N between the ball and each flat due to geometry); speed, 60 rev./min; temperature, 25–30 °C; duration, 45 min; and environment, laboratory air. The discs were AISI 52100 (UNS# G52986) steel with a ground finish (surface roughness R_a=0.1–0.2 μm) hardened to 57–63 Rockwell C (R_c) hardness, and the counterfaces were Al_2O_3 balls with a diameter of 0.5 inch (1.3 cm) and a surface roughness R_a of 0.008–0.01 μm. Before testing, the ball, discs, and the parts of the tester which contact the gasoline were ultrasonically degreased and solvent rinsed. After testing, the discs were inspected in an optical microscope, and the diameter of the wear scar (WSD) was recorded for all three discs from each test.

Reciprocating wear was measured using a custom-built system called the Fretting Tester. It was designed for sealed operation with very small to moderate track lengths and has been described elsewhere [1]. The samples were ultrasonically degreased and solvent rinsed, dried, and placed in the cup inside the chamber, and then the chamber was sealed. The air in the chamber was exchanged with dry nitrogen for 30 min at a flow rate of 10 standard l/min. At that point the flow rate was reduced to under 2 standard l/min, gasoline was added to the sample cup without opening the chamber, and the test was started. The normal load was sensed by a load cell on the mechanism used to raise the sample cup to the counterface. For each test, the load required to raise the cup was zeroed out, the sample and counterface were brought into contact, and the normal load between them was increased to the desired value. After the test, both the flat and counterface were inspected by optical microscopy and three-dimensional optical surface profilometry. The profilometry system measured the volume of the areas, which were below the plane of the sample surface, in cubic micrometers. In the case of injectors and balls, whose unworn surfaces are spherical, the system mathematically subtracted the curvature of the sphere from the data set of three-dimensional heights. The flats of AISI 440C (UNS# S44004) steel with hardness 60 R_c were polished to R_a=0.010–0.015 μm. The production fuel injectors had a spherical AISI 440C steel tip of diameter 2.85 mm.

2.3. Raman spectroscopy

Samples were analyzed using visible-light Raman spectroscopy, a structural characterization method highly sensitive to the presence of sp^2-hybridized carbon and to the degree of amorphization of the carbon films. This method allowed determination of changes in film structure during the wear process. The instrument used had a spatial resolution on the order of a few micrometers, so it was also possible to characterize particles of wear debris embedded in wear scars. The NFC film, initially amorphous in structure, has been thought to undergo partial crystallization to graphite during the wear process, and Raman spectroscopy was used to investigate this possibility.

3. Results

A set of BOTD tests was performed with uncoated steel discs to measure the lubricity of each of the gasolines used in the long-term reciprocating tests. Fig. 1a shows friction measured for Gasolines A through G, plus ethanol and regular gasoline. Fig. 1b gives the wear scar diameter from the tests. The friction and wear results were consistent with each other, with the low friction fuels also providing low wear. However, the

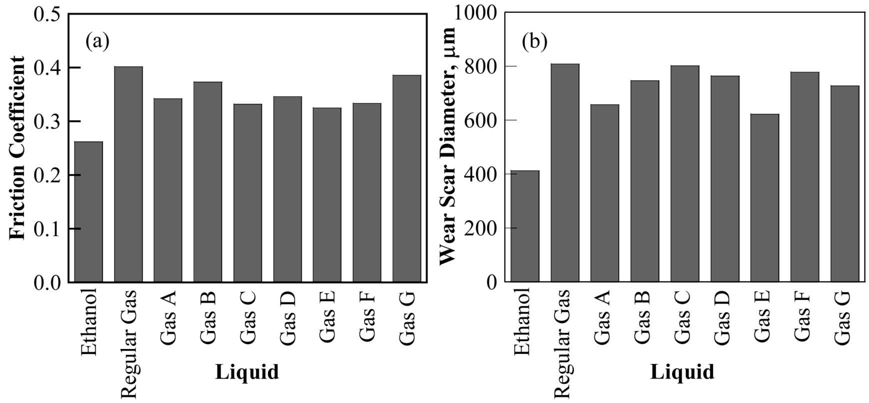

Fig. 1. Friction coefficient (a) and wear scar diameter (b) from BOTD tests using uncoated discs and formulated gasolines.

differences in friction and wear among the fuels were relatively small.

Fig. 2a, b and c show, respectively, the friction coefficient, the wear rate of the uncoated flats, and the wear rate of the coated injectors. The tests were carried out for uncoated, NFC2-coated, and NFC6-coated injectors, submerged in ethanol and seven types of gasoline; the surface treatments and liquids provide the *X*-axis and *Y*-axis, respectively, for each of the plots in Fig. 2. Trends in the friction data were found by averaging the friction results for each coating over the seven gasolines used, and by averaging the friction results for each gasoline over the three surface types used. Table 2 shows the friction results for the three surface types averaged over the seven gasolines. The NFC coatings provided clear friction improvements over the uncoated fuel injectors. NFC6 gave 27% lower friction, while NFC2 resulted in an average friction reduction of nearly a factor of two. Averaging the friction data from all coatings for each of the gasolines gave tightly grouped results, each of which had a large standard deviation (surface-to-surface variability). In other words, the major factor influencing friction was the coating, not the gasoline.

Similarly, trends in the wear data were analyzed by averaging results for each coating over the seven gasolines and for each gasoline over the three surface types. Attention to the differences among injector wear, flat wear, and the total wear revealed additional information. Table 3 shows the trends. Applying NFC coatings on the injectors again provided reductions in total wear rate and wear rate of the flats compared to the uncoated injectors. In the case of the coated injectors themselves, NFC6 provided a wear rate slightly greater than that of the uncoated surface, while the NFC2 coating, surprisingly, wore significantly faster than NFC6 and the uncoated part. Comparing the wear results of different gasolines by averaging the data for different coatings, we saw trends similar to those in the friction. Gasolines A and B and ethanol produced somewhat higher wear on both flats and injectors, while Gasolines C and D lowered wear, but in general, the major factor influencing wear was the surface treatment, not the gasoline.

A wear scar from a million-cycle reciprocating test is shown in Fig. 3a. This image is a plan view of a three-dimensional surface profile. The curvature of the spherical injector tip was mathematically removed from this data set to give the appearance of a plane with an indentation. The scar was from a wear test of an NFC2-coated injector worn in gasoline B. The coating wore smoothly, while the areas of exposed steel and the coating next to it were rough. Only a very small amount of substrate wore off in this experiment. Fig. 3b gives a standard optical micrograph of part of the wear track from the steel flat against which the injector of Fig. 3a was worn. The differences between the areas worn by NFC and the areas worn by the exposed substrate were clearly visible, despite the fact that the entire sample shown in Fig. 3b was steel. Fig. 4 shows the friction trace collected during a test which produced similar wear morphologies. The friction was stable throughout the first half of the test, but a sudden increase occurred at 500 000 cycles. This was followed by a less rapid drop; during the second half of the test, the noise in the friction was much greater. Repeatedly, sudden small increases in friction were followed with slower decreases.

Several Raman spectroscopy studies were performed to assist interpretation of the wear tests. In order to allow detection of any films which may have formed on the wear surfaces, the gasoline from the wear test was not rinsed away with solvent. Fig. 5a shows the Raman intensities measured after a reciprocating test of an NFC2-coated injector worn in Gasoline A. Displayed are spectra for a worn area of the coating, exposed steel substrate, and wear debris. The response from the worn area of NFC2 coating shows the two broad peaks typical of diamond-like carbon coatings. In contrast, the area of

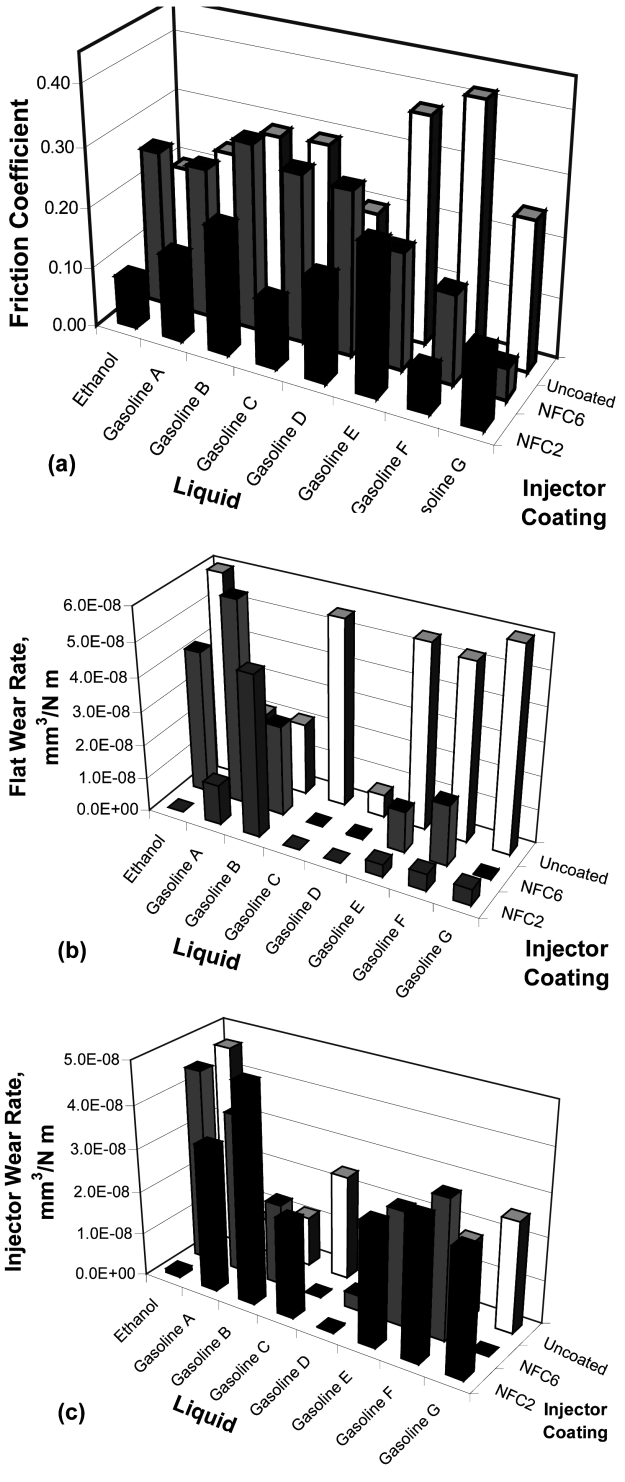

Fig. 2. Friction (a) and wear rates of uncoated flats (b) and fuel injector tips (c) for 10^6 -cycle reciprocating tests in fuels. The coating applied to the injectors is shown on the *X*-axis, while the test fluid is shown on the *Y*-axis.

the injector where the steel substrate was exposed exhibits the approximately linear response characteristic of steel. There is also no indication of any transfer film on that steel. The wear debris found on the steel flat exhibits two low, broad peaks, indicating that this material is NFC. Fig. 5b shows the Raman intensity from both worn and unworn areas of an NFC2-coated injector tested in Gasoline B. The two traces are substantially the same, indicating that the degree of amorphization of the NFC was not changed by the wear process.

4. Discussion

At first glance, the differences in friction and wear among the fuels in the BOTD results appear inconsistent with the observation that the gasolines have a relatively minor effect on friction and wear rate for injector-on-flat contacts. However, closer examination revealed that the differences were a result of inclusion of the coated materials in the reciprocating tests. Taking into account only the data from the uncoated injectors, for comparison to the uncoated BOTD discs, we find general consistency between the BOTD and reciprocating test results.

Differences were attributable to a number of factors. First, the peak and average Hertzian contact pressures in the BOTD tests were approximately half those in the reciprocating tests. Second, the average velocities were similar, but the local thermal situations in the two tests were very different. In the BOTD test the counterface was made of Al_2O_3 and was rotating; the Al_2O_3 was cooled because of its moderate thermal conductivity and exposure to liquid. In the reciprocating tests, only one area of the counterface was worn, and that area was in constant contact with the flat. Flats in the BOTD tests, on the other hand, were in constant contact with the counterface, while in the reciprocating tests they were not. Third, the BOTD tests were performed in laboratory air and the reciprocating tests were performed under nitrogen to better simulate the operating conditions of fuel injectors. The presence of water vapor and oxygen could have significantly affected wear. Finally, in reciprocating tests, debris tends to remain in the wear track unless pushed out the ends, while in BOTD tests debris generally joins the circulating fluid.

In long-duration tests designed to determine the ultimate wear lifetime of the NFC coatings on injectors, we found that the NFC2 coating wore significantly faster than NFC6 and the uncoated part. Taking into

Table 2
Friction results for three surface treatments averaged over seven gasolines

Surface treatment	Friction average	Improvement
Uncoated	0.29	Baseline
NFC-6	0.22	27% reduction over uncoated
NFC-2	0.15	48% reduction over uncoated

Table 3
Wear rates for three surface treatments averaged over seven gasolines, stated in terms of change from the uncoated case

Surface treatment	Flat wear	Injector wear	Total wear
NFC-6	−56% from uncoated	+13% from uncoated	−39% from uncoated
NFC-2	−77% from uncoated	+89% from uncoated	−36% from uncoated

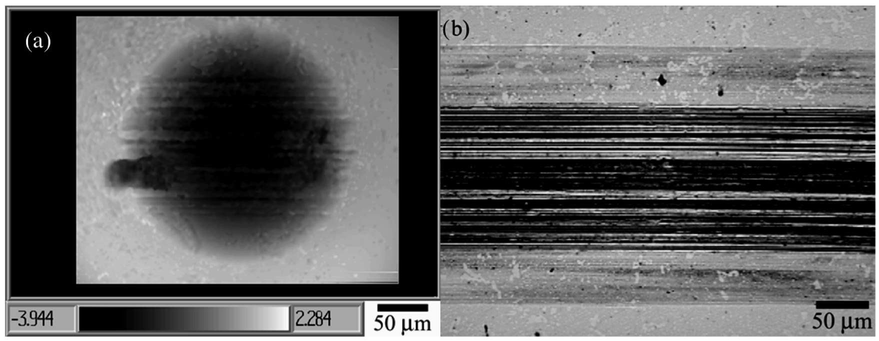

Fig. 3. Plan view of three-dimensional optical surface profile of worn injector (a) and plan view optical micrograph of wear flat (b). In (a), the curvature of the spherical injector tip has been subtracted from the data set, and the gray scale corresponding to image heights is shown at the lower left (see text).

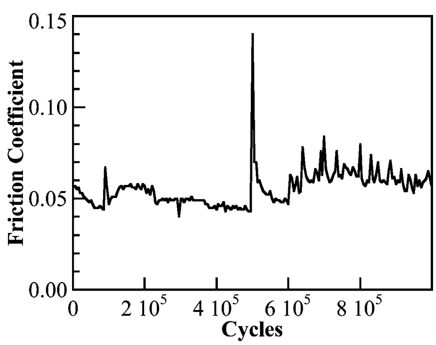

Fig. 4. The friction trace for million-cycle wear test between coated injector and uncoated flat in gasoline.

account the extremely low friction provided by NFC2 in the tests, we speculate that the NFC2 may have been slowly wearing away sacrificially to reduce both friction and counterface wear. In contrast, NFC6 reduced both friction and wear without accelerating its wear rate. Both NFC coatings considerably reduced the total wear rate and the wear rate of the flats compared to uncoated surfaces. In fact, NFC2 provided better flat protection than NFC6, almost a factor of four improvement over uncoated samples. This may be beneficial in applications where the geometry of the mating (uncoated) part is of paramount importance, for example, the nozzle of a fuel injector carefully shaped to control the fuel spray characteristics.

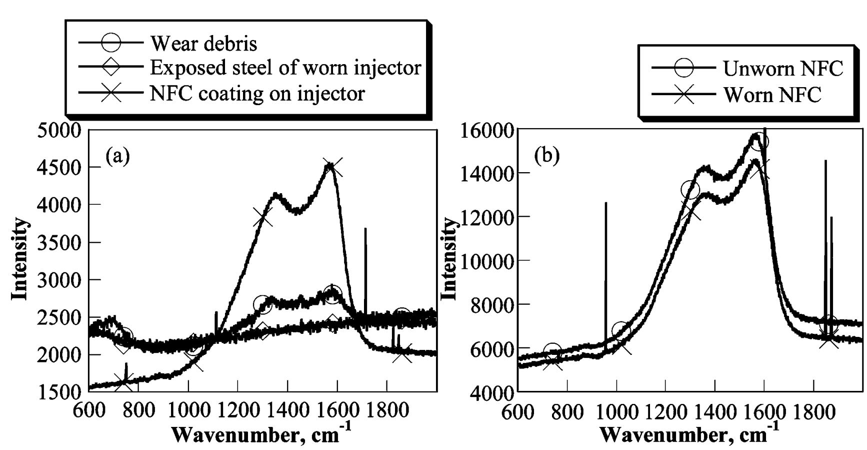

Fig. 5. Raman spectra for NFC-coated fuel injectors. In plot (a), data from an unworn area of coating are shown along with a spectrum from an area of exposed steel substrate in the centre of the wear scar, and a piece of wear debris which was attached to the flat. In plot (b), worn and unworn areas of NFC are compared.

The frictional trace of Fig. 4 and the morphological data in Fig. 3 can be interpreted as follows. During the first half of the reciprocating test, NFC was rubbing against steel, creating a smooth wear surface and stable friction. Halfway through the test, the NFC wore through, allowing steel-to-steel contact. The contacting steel surfaces quickly reacted with the gasoline, perhaps forming an oxide, and this reduced the friction. Additives in the gasoline could also have formed thin protective films on the exposed steel surfaces, which were wearing in the boundary-layer lubrication regime. Then, pieces of steel began to be torn off the surfaces, causing abrasive wear in the center of the scar; friction rose and fell as new steel was exposed and reacted. Raman characterization of worn and unworn surfaces did not produce any evidence of a transfer film originating from the NFC or a protective chemical film originating from the gasoline, either on the steel flat or on the exposed steel substrate. The Raman data also did not show any graphitization of the NFC during wear. Graphite would have appeared in Fig. 5 as much sharper peaks. Instead, NFC2 appeared to continue to protect against wear of the exposed steel simply by continuing to support the load around exposed substrate material.

5. Conclusions

Near-frictionless carbon coatings reduced friction and wear in million-cycle reciprocating wear tests performed with existing and reformulated gasolines. NFC2 produced extremely low friction and counterface wear sacrificially, while NFC6 provided low friction and counterface wear without excessive coating wear. Raman spectroscopy provided no evidence of coating graphitization, the formation of a transfer film from NFC, or the presence of a chemical protective film from the gasolines. Despite some minor differences, BOTD lubricity tests were consistent with customized reciprocating wear tests in showing the friction and wear reduction of NFC and the lubricity of the fuels.

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