Polymer Tribology in Safety Medical Devices: Retractable Syringes

WITOLD BROSTOW, DOROTA PIETKIEWICZ

Laboratory of Advanced Polymers & Optimized Materials (LAPOM), Department of Materials Science and Engineering, University of North Texas, P.O. Box 305310, Denton, TX 76203-5310

STEVEN R. WISNER

Retractable Technologies, Inc., P.O. Box 9, Little Elm, TX 75068-009

Received: December 18, 2006 Revised: April 11, 2007

ABSTRACT: We analyze an example of the application of polymer tribology to create a safety medical device, namely a retractable syringe. In service at various stages either low- or high-dynamic friction is needed. Our work focuses on a VanishPoint[®] nonreusable safety syringe manufactured by Retractable Technologies, Inc., Little Elm, TX. Different medical-grade materials strongly affect the performance of this product. Extant tribological testing methods developed for flat surfaces are of little use. A functionality test that provides static and dynamic friction between rounded and cylindrical parts moving one inside the other gives us data not obtainable from the earlier techniques. These results combined with the liquid blowout force results (also for cylindrical surfaces) tell us that a polyolefin elastomer imparts better properties to a polypropylenecontaining resin than does silica as an additive. Data-based selection of appropriate polymeric materials for components of the syringe thus becomes possible. © 2007 Wiley Periodicals, Inc. Adv Polym Techn 26: 56–64, 2007; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/adv.20084

KEY WORDS: Additives, Elastomers, Friction, Medical device, Polypropylene

Correspondence to: Witold Brostow; e-mail: brostow@unt.edu.



Introduction

/ / e do not need to argue that plastics play a key role in human life, from materials for packaging to clothing, from transportation to communication, from security to healthcare.^{1,2} In recent years, there has been rapid growth in using polymer-based materials (PBMs) for medical applications such as drug delivery systems, human organ supplements, and medical devices. Materials from which medical products are composed must adhere to very rigid standards: they must be able to function over the expected shelf life of the product; they must be nontoxic and biocompatible; they must survive without property loss at least one method of sterilization (e.g., gamma radiation, ethylene oxide). The benefits of using PBMs in medical devices include the following: a wide variety of rigidity ranging from soft rubbers to hard plastics; light weight; noncorrosive nature; clarity; transparency or opacity; easy coloring; sterilizability and low cost. However, the use of PBMs in medical devices often involves problems with friction. Tribology is well developed for metals but not for polymers. The problems for metals can be solved by external lubrication; in polymers, strong interaction with such lubricants is possible, resulting in some cases in swelling, making the situation worse. While there has been progress in PBM tribology,³ much remains to be done.

Over the past few years development of safety medical devices has continued to progress. The problem is of considerable interest on a large scale. Each year only in the United States nearly 5.6 million healthcare workers suffer as many as 800,000 "sharps injuries," mostly by needlesticks. At this rate, around one out of every seven workers is accidentally struck by a sharp needle whereas only one out of three incidents is reported.⁴ Approximately 2.7% of the needlestick injuries each year result in HIV exposure. About 80% of such injuries may be prevented by the use of safety needles.⁵ Therefore, new products designed to prevent spreading of blood-borne pathogens and help to reduce sharps injuries. Medical companies around the globe are trying to develop new safety and innovative products, including sharps safety medical devices to protect healthcare workers. The International Healthcare Worker Safety Center at the University of Virginia lists 12 companies offering retractable needles/syringes.⁶ The products involve a variety of technologies, for example, a safety needle device has a needle encapsulation sleeve after it has been used; the sleeve automatically resheathes the needle and locks it so that it cannot be exposed. Blunt safety devices have two needles, one inside the other: the inside needle is hollow and has a flat, blunt end; the outside sharp needle is used to access the vein. The inner needle moves forward and past the sharp needle to insure safety before it is removed from the patient. Such devices are known as first-generation safety products.

Retractable syringes are considered secondgeneration safety products. The retractable syringe is a unique device requiring *no change* in the basic procedure of delivery of the medication by healthcare workers. After injection, the needle safely retracts from the patient into the syringe barrel; thus, there is no risk of accidental needlestick injuries that can transmit HIV, hepatitis, or other infections to healthcare workers.

Our work focused on VanishPoint® automated retraction safety syringes manufactured by Retractable Technologies, Inc. (RTI), Little Elm, TX.^{7–14} RTI is the only U.S. maker of nonreusable safety syringes to receive a contract under the President's Emergency Plan to supply its patented automated retraction syringes to Haiti and several African nations.¹⁵ From the materials science point of view, a more compelling reason is in the nature of the design; it is entirely based on friction of polymeric components in motion.^{7–14} In service, at some stage *low*-dynamic friction is needed and achieved, whereas at a later stage *high* friction serves the purpose. In a comprehensive book on friction by Rabinowicz, polymers are mentioned only twice,¹⁶ whereas a collective Swiss book on tribology only lists polymer friction values without an explanation.¹⁷

To develop PBMs with appropriate dynamic friction values for retractable syringes of the second generation, we need to consider now the design of such a syringe. The VanishPoint[®] syringe can be used only once; a second time use is impossible since the needle safely retracts from the patient into the barrel of the device^{7–14}; see Fig. 1.

A patented needle retraction mechanism has been designed to withdraw the needle from the patient and safely encapsulate it within the syringe barrel in one action. The retraction is based on a friction mechanism and depends on the molded components of the syringe, namely plunger plug and friction ring as shown in Fig. 1. The latter clearly owes its name to the fact that a certain narrow range of friction values determines whether the ring will fulfill its function.



FIGURE 1. Photo of 3-cc VanishPoint[®] syringe: (a) before activation and (b) after the needle safety retraction. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

In this particular design, the friction ring has two interference fits: inner diameter has an interference fit with the needle holder outer diameter, and outer diameter has an interference fit with the syringe barrel inner diameter. These two interference fits must prevent premature needle retraction before the medication has been dispensed fully—and also must ward off liquid medication leak around the syringe components.

The plunger plug outer diameter has an interference fit with a plunger handle inner diameter. Needle retraction is activated by dislocating the plunger plug and the friction ring at the time when user applies the force.

In such a design, polymer tribology plays multiple roles. First, during the injection of the medication, friction between the syringe piston and the barrel has to remain within a certain range; too high friction would prevent injection of the medication whereas too low friction would be accompanied by leaks. The plunger plug has to resist dislocation until all medication has been transferred to the patient. Thus, there is friction when needed to assure the integrity of the syringe components; then there is virtually no friction when the needle is backwards and locked inside the syringe barrel. Quite important is comfort of the patient during the injection.

Apart from the fact that for a long time, tribology was applied mostly to metals,¹⁶ methods of tribo-

logical testing have been developed for *flat* surfaces. As Fig. 1 instantly tells us, such tests are of little (if any) use for the syringes under consideration, or for that matter for any devices with cylindrical barrels. To quantify the appropriate dynamic friction ranges and the forces needed to overcome them, a *functionality test* has been designed. We explain the performance of the test in the section "Functionality Tests and Their Results" along with some results it produced. Functionality is defined as the force needed to operate the syringe. As noted above, the required forces are different at different stages of the process. The requirements are based on avoidance of leaks and also on the fact that too high forces would require unusual strength of the medical personnel. The friction ring and the plunger plug belong to the key elements of the innovative RTI syringe design.

To improve the properties that enable the syringe to function correctly and fulfill the performance requirements, our study was conducted to identify polymeric materials for components of the VanishPoint[®] syringe by comparing a variety of medical-grade materials, or else their modification by several kinds of additives (equally approved for medical use). The investigated materials have code names since a nondisclosure agreement is involved. There is no implication that the materials studied in this project are actually used by RTI.

Experimental

MATERIALS

The VanishPoint[®] syringes are classified as the three-part disposable syringes. The syringes contain a barrel, a piston, and an "o" ring-type gasket. The list of materials for the VanishPoint[®] syringes includes polypropylene (barrel and plunger handle) and synthetic elastic materials (plunger plug, friction ring, and plunger seal). These synthetic rubbery components act similarly as natural rubber; they create good seal with the polypropylene syringe barrel. A medical-grade silicone oil is used as the lubricating agent to provide low friction and avoid a sticking action.

Commercially available medical-grade thermoplastic rubbers, which can be processed by conventional thermoplastic methods, such as injection molding, have been selected for our study. Some of their initial characteristics are listed in Table I.

Three cubic centimeters plunger plugs and friction rings were prepared by injection molding from a variety of polymeric materials. The injection molding was performed in accordance with suggested processing conditions of each material. The 3-cc VanishPoint[®] syringes of each material were assembled on a 3-cc Sortimat machine (Sortimat Automations GmbH, Winnenden, Germany) at the RTI.

Influence of an inorganic and a polymeric additives on the performance of syringe components has been studied; silicon dioxide (SiO₂) and Engage 8180, respectively. SiO₂ was supplied by U.S. Silica Company (Berkeley Springs, WV). The average particle size is 10 μ m. Engage 8180 was provided by DuPont Dow Elastomers (Wilmington, DE). Engage is a polyolefin elastomer, an ethylene–octene copolymer with convenient flow characteristics: it has a low density 0.863 g/cm³ and a low-melting point 49°C.

The polymer blends were prepared by mixing the materials in a Brabender Preparation Station at 190°C and 120 rpm for 5 min.

The 3-cc VanishPoint[®] syringes of each group were exposed to gamma sterilization with the most commonly validated dose used to sterilize medical devices, 18–30 kGy. A number of test methods were used to verify whether the material fulfills all the requirements for use in this application. The methods include RTI inspection test methods, such as functionality force and liquid blowout force.

INSTRUMENTS

The functionality and liquid blowout forces of the 3-cc syringes were recorded by using a United universal tensile testing machine, model number SSTM-1 (United Calibration Corp., Huntington Beach, CA) with a computer program Datum version 3.0. Figure 2 shows a schematic diagram of test apparatus used to determine the functionality force and the liquid blowout force. To some extent, the tests are similar to standard compression tests. Namely, a force is applied from above to the syringe piston with the syringe placed vertically. In contrast to standard compression, however, there is no support below the tested specimen. In each case, the needle cap was removed from the syringe and the syringe was placed in an appropriate insert fixture with the needle facing downward. The tests were carried out at room temperature of 25°C, with relative humidity was kept within a narrow range of $75 \pm 3\%$. The

TABLE I				
Symbol of Material	Specific Gravity (g/cm ³)	Hardness Shore (A)	Tensile Strength (MPa)	Elongation at Break (%)
VP-1				
Plunger plug	0.95	94	14.3	625
Friction ring	0.95	91	15.0	638
VP-2				
Plunger plug	0.96	89	9.0	440
Friction ring	0.97	90	12.8	500
VP-3				
Plunger plug	0.90	94	10.3	708
Friction ring	0.91	97	11.7	663



FIGURE 2. Schematic diagram of test apparatus used to determine the functionality force and liquid blowout force.

crosshead speed was 1.00 in./min (25.4 mm/min) for the functionality force and 3.00 in./min (76.2 mm/min) for the liquid blowout force; a load cell of 100 lb (45.4 kg) was used.

The functionality is defined as the highest force required to activate the needle safety mechanism.

The test as described above was performed and repeated until all specimens were tested. Plots of force (lb) versus extension (%) were recorded and compared with acceptable limits.

The liquid blowout test is somewhat similar to the functionality test. The same machine and fixtures are used, and the same syringe orientation is applied. As the name implies, the minimum force that will cause a blowout and the liquid flowing out is measured. The test data were collected according to the following procedure: each syringe was filled with appropriate amount of colored water; in the case of the 3-cc syringe, the volume of fluid in the barrel was 0.5 cc; air bubbles were removed from the liquid by tapping the syringe with a finger; the tip of needle was blocked to prevent leaking; then the syringe with the needle facing downward was placed in the appropriate fixture; the test was performed and repeated until all specimens were tested. Plots of force (lb) versus extension (%) were recorded. A specification limit of liquid blowout force for the 3-cc syringes has been defined; in practice the forces applied by users of the syringe never reach that value.

The universal testing machine MTS-QTEST[™]/5 with a frictional device (Fig. 3) was used to perform the friction test. A 10.2-kg load cell, a sled with the nominal weight of 431 g, and a Teflon surface were used. The testing speed was 150 mm/min. The results reported here are the averages of 20 tests conducted at room temperature (25°C). Resistance required starting to move one surface over another and resistance required to sustain continuous movement of one surface over another have been measured to determine static and dynamic friction, respectively.





Functionality Tests and Their Results

Figure 4 shows an example of the functionality force test results for the VanishPoint® syringe as a function of distance traveled by the syringe piston (also called the plunger handle). Two main peaks occur during the needle retraction. The first peak is characteristic for the plunger plug pushout force, that is, the force required to dislodge the plunger plug from the plunger handle. Following the first peak, we have a region representing stick-slip behavior. Its presence can be explained by the fact that a polymer surface is never smooth on the microscopic scale. Both the syringe barrel and the syringe piston are polymeric materials, with polypropylene (PP) as the main constituent because of important advantages of PP discussed by Karger-Kocsis and his colleagues.¹⁸ There are quantitative methods of evaluation of polymer surface roughness.^{19,20} Techniques such as scanning electron microscopy (SEM),²¹ a combination of SEM and focused ion beam application,²² or else profilometry²³ allow us to see how uneven polymeric surfaces are. What happens during the functionality test is a series of stops because of stickiness. By definition of static friction,³ moving from such a stop we need to overcome static friction. When the movement starts, a lower force is needed to overcome dynamic friction.³ Thus, we observe slip behavior, whereas both static and dynamic





FIGURE 4. Schematic representation results of a functionality test, plotted as the friction force versus distance traveled by the piston; F_s = static friction and F_d = dynamic friction.

friction manifest themselves during the stick-slip test region.

As seen in Fig. 3, the third and final region in the functionality test consists of a second large peak. It represents the force needed to dislodge the friction ring from its original position. At that time, the medication has already been injected; in fact, the largest force is needed at this stage to prevent the dislodging of the ring *before* the medication has been injected fully. It is the final displacement of the friction ring that allows the retraction spring to move—together with the needle—into the syringe barrel. It is at this point that the needle becomes nonreusable.

A number of methods are used to minimize or prevent stick-slip behavior.²⁴ One approach is to choose a friction pair, so that the difference between static and dynamic friction is small; another is covering one of the component surfaces by a lubricant film.

A thin layer of silicone oil is sprayed into the PP barrel of the VanishPoint[®] syringes during the manufacturing process. Also, the plunger plugs and friction rings are lubricated to facilitate the assembly process. We recall that caution is needed since the external silicone oil can cause swelling of the synthetic rubber components, thus softening and causing shape deformation—resulting in a need for higher activation forces.

Comparison of Selected Materials

As noted in the Introduction, polymeric components of a syringe have to fulfill a variety of requirements defined by the application. Given the design displayed in Fig. 1 and characterized in the previous section, particular stringent requirements pertain to the plunger plug and the friction ring. In this work, we have found that the syringe performance can be greatly affected by the characteristics of the polymeric resins.

Let us first report an interesting observation made during the functionality force test. The material VP-2 did not show the usual stick-slip behavior. The friction dropped to a much lower value as sliding progressed and then remained constant. Thus, stickslip behavior while frequent is by no means universal. The VP-2 material fulfilled the specifications in the functionality test; forces lower than specification limit were obtained. However, the liquid blowout

POLYMER TRIBOLOGY IN SYRINGES

force was 18% below the required minimum. VP-2 showed lower trigger forces (second peak) than the VP-1; reduction of this force caused failures by liquid blowout.

As noted, the components of the syringe are lubricated before assembly. In the case of VP-3 material, the lubricant was absorbed by VP-3 components and swelling occurred. This caused softening of the parts, their deformation, and resulted in higher activation forces needed. As already pointed out in the Introduction, a lubricant applied to polymeric components constitutes a two-edged sword. In this case, the swelling disqualified VP-3.

Let us focus now on the plunger plug pushout force (first peak). That force can be the primary culprit for too high functionality. An increase in the plunger plug pushout force was observed when the polymeric resin (PP030-1) was changed to a slightly stiffer one (PP030-2); the force needed was 90% higher than for PP030-1. The stick-slip region in the friction force versus displacement diagrams was pronounced with significant chatter; the syringes showed poor performance. To improve the functionality, a series of materials were prepared by adding varying amounts of SiO₂ or Engage.

Static and dynamic friction for raw polymeric resins, for example, PP030-1 and PP030-2, and also for PP030-2 with different concentration of inorganic or elastomeric additive, have been determined. Figures 5 and 6 show results for the PP030-2 blends as a function of SiO₂ and Engage concentration, respectively. The results presented in both these figures are for components that have *not* been lubricated. As Fig. 5 shows, PP030-2 has a lower static friction and higher dynamic friction than the resin PP030-1. This is interesting since, as has been pointed out, PP030-2 is stiffer.

Both static and dynamic friction of PP030-2 were reduced by adding different amounts of additives; see Figs. 5 and 6. As expected, both the nature of the additive and its concentration are important.

We see in Fig. 5 that the largest friction lowering is achieved for 2% SiO₂. Thus, 1 or 2% of silica causes "bumps" on the surface that lower the effective contact area. At 5%, the contact area was increased again. There is also another factor pertinent for the application: the additive is visible to the naked eye as agglomerates and also to the medical personnel.

Addition of Engage also causes lowering of both static and dynamic friction. Similarly, as for silica, there is also an increase in friction for higher additive concentrations; here it is above 2%. Thus, curves of static and dynamic friction as a function of the



FIGURE 5. Static and dynamic friction for the materials: PP030-1, PP030-2, and PP030-2 with several concentrations of SiO₂.

additive concentration have minima. The explanation of these diagrams is analogous to silica. However, Engage has an advantage over silica; as a polymer, Engage is distributed more evenly in the matrix and there is no agglomeration.

We now move to discuss the functionality test results. Because of nondisclosure, we do not provide absolute values, only percentages of changes with respect to the base material. We have found that adding 2 wt% of SiO₂ practically does not affect the plunger plug pushout force results. However, a significant improvement occurs when 5 wt% of SiO₂ or at least 2% of Engage 8180 is added to the PP030-2 material. The plunger plug pushout force is reduced



FIGURE 6. Static and dynamic friction for the materials: PP030-1, PP030-2, and PP030-2 with several concentrations of Engage 8180.

by $\approx 35\%$ by 5 wt% of SiO₂ added or reduced by 23% by 2 wt% of Engage added. The performance of the syringe is clearly improved. Thus, PP030-2 with an adequate concentration of an additive provides acceptable functionality and liquid blowout force without performance problems. SiO₂ is much stiffer than Engage; our investigations have shown poor performance in the RTI syringes when a too stiff material was used for molded components.

We found that determination of the functionality combined with the liquid blowout force determination is sensitive to differences in chemical and mechanical properties of materials used for molded parts of the syringe. These parameters allow prediction of satisfactory performance or else failures in service. Apparently, relatively small variations in the characteristics of materials used for molded components of the syringe can affect the manufacturing process, lower productivity, and result in final products that do not provide satisfactory operation of the safety device.

General Discussion

Polymeric constituents required for needle retraction in the RTI syringes to assure nonreusability^{7–14} rely on polymer tribology. Our results reported above show that creating polymer-based components with improved tribological properties for new applications is doable. Details on nonreusable syringes can be found in various patents,^{7–14} whereas there are also related patents^{25–27} for catheters and systems for blood collection.^{28,29} While the liquid blowout force has been used to evaluate syringes before, we find that the functionality test is a very useful tool for discerning between candidate materials for syringe components. For a given PP030-2 base polymer, our work has shown that the Engage 8180 polyolefin elastomer is a better additive than silica.

In the usual friction tests, such as we performed in our earlier work,³⁰ there is an interaction between flat surfaces. Tribological techniques include scratch resistance determination,³¹ sliding wear,^{32–34} and the surface evaluation techniques such as SEM analyzed in detail by Michler²¹ as well as atomic force microscopy used among others by us.³⁴ Finally, the pin-on-disk tribometry belongs also to the list.³⁵ Interactions between round and cylindrical parts evaluated in the functionality test thus complements the earlier tribological techniques. There is one report in the literature of computer simulation of scratch testing of polymers,³⁶ analyzed also in an instructional article,³⁷ Molecular dynamic approach has been used in these simulations, and they have been also made for flat surfaces. However, there is nothing in the molecular dynamics method that would prevent simulation of curved or cylindrical surfaces.

Acknowledgments

Discussions with Dr. Georg Broza, Composites Group, Technical University of Hamburg, and several colleagues on an earlier part of these results at the POLYCHAR-14 Annual World Forum on Advanced Materials in Nara, Japan, in April 2006 are gratefully acknowledged.

References

- Goldman, Y. Prediction of Determination Properties of Polymeric and Composite Materials; American Chemical Society: Washington, DC, 1994.
- 2. Brostow, W. (Ed.). Performance of Plastics; Hanser: Munich, 2000.
- 3. Brostow, W.; Deborde, J. L.; Jaklewicz, M.; Olszynski, P. J Mater Educ 2003, 25, 119.
- Strategic focus report on retractable syringes market outlook; available at http://www.giiexpress.com/products/fs22353, accessed on September 30, 2003.
- 5. Frost & Sullivan. U.S. safety devices and containers markets; available at http://www.frost.com/prod/servlet/reporthomepage.pag?repid=A455-01-00-00-00&ctxst=FcmCtxl& ctxht=FcmCtx2&ctxhl=FcmCtx3&ctxixpLink=FcmCtx4& ctxixpLabel=FcmCtx5; accessed on June 26, 2003.
- International Healthcare Worker Safety Center, University of Virginia. List of safety-engineered sharp devices; available at http://healthsystem.virginia.edu/internet/epinet/ safetxdevice.cfm; 2003.
- 7. Shaw, T. J. US Patent 5,120,310, 1992.
- 8. Shaw, T. J. US Patent 5,385,551, 1995.
- 9. Shaw, T. J. US Patent 5,389,076, 1995.
- 10. Shaw, T. J. US Patent 5,578,011, 1996.
- 11. Shaw, T. J. US Patent 5,632,733, 1997.
- 12. Shaw, T. J. US Patent 6,090,077, 2000.
- 13. Shaw, T. J.; Zhu, N. US Patent 6,221,055 B1, 2001.
- 14. Shaw, T. J.; Zhu, J.; Rutherford, D. US Patent 6,572,584, 2003.
- 15. Anonym. Dallas Business Journal, August 19, 2004.
- 16. Rabinowicz, E. Friction and Wear of Materials, 2nd ed.; Wiley: New York, 1995.

POLYMER TRIBOLOGY IN SYRINGES

- Zambelli, G.; Vincent, L. (Eds.) Materiaux et contacts: Une approche tribologique; Presses polytechniques et universitaires romandes: Lausanne, 1998.
- Karger-Kocsis, J. (Ed.). Polypropylene: A–Z Reference; Kluwer: Dordrecht, 1999.
- 19. Laurena, A.; Pinto, G. Mater Lett 1991, 11, 309.
- 20. El Fray, M.; Boccacini, A. R. Mater Lett 2005, 59, 2300.
- Michler, G. H. Kunststoff-Mikromechanik: Morphologie, Deformations- und Bruchmechanismen; Hanser: München, 1992.
- 22. Brostow, W.; Gorman, B. P.; Olea-Mejia, O. Mater Lett 2007, 61, 1333.
- 23. Brostow, W.; Chonkaew, W.; Rapoport, L.; Soifer, Y.; Verdyan, A. J Mater Res 2007, in press.
- 24. Bhushan, B. Introduction to Tribology: Wiley: New York, 2002.
- 25. Shaw, T. J. US Patent 5,817,058, 1998.

- 26. Shaw, T. J.; Duesman, K. US Patent 5,989,220, 1999.
- 27. Shaw, T. J.; Zhu, J. US Patent 6,872,193, 2005.
- 28. Shaw, T. J. US Patent 5,423,758, 1995.
- 29. Shaw, T. J. US Patent 5,810,775, 1998.
- 30. Brostow, W.; Cassidy, B. P. E.; Hagg, H. E.; Montemartini, P. E. Polymer 2001, 42, 7971.
- 31. Brostow, W.; Bujard, B.; Cassidy, P. E.; Hagg, H. E.; Montemartini, P. E. Mater Res Innovations 2002, 6, 7.
- 32. Brostow, W.; Damarla, G.; Howe, J.; Pietkiewicz, D. e-Polymers 2004, no. 025.
- Bermudez, M. D.; Brostow, W.; Carrion-Vilches, F. J.; Cervantes, J. J.; Pietkiewicz, D. e-Polymers 2005, no. 001.
- 34. Bermudez, M. D.; Brostow, W.; Carrion-Vilches, F. J.; Damarla, G.; Perez, J. e-Polymers 2005, no. 003.
- 35. Iglesias, P.; Bermudez, M. D. Wear 2004, 256, 386.
- 36. Brostow, W.; Simoes, R. J. J Mater Res 2004, 19, 851.
- 37. Brostow, W.; Simoes, R. J. J Mater Educ 2005, 27, 19.