ISSN 2079-1372 Problems of Tribology, V. 31, No 1/119-2026, 86-91

Problems of Tribology
Website: http://tribology.khnu.km.ua/index.php/ProbTrib
E-mail: tribosenator@gmail.com

DOI: https://doi.org/10.31891/2079-1372-2026-119-1-86-91

Equipment and technology for gas fluorination of polymers to improve their wear resistance under micro-impact loads

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Received: 05 February 2026: Revised 25 February 2026: Accept: 10 March 2026

Abstract

The article addresses the problem of improving the cavitation–erosion wear resistance of polymer materials operating under micro-impact loads in corrosive environments. It is shown that material degradation under such conditions has a complex mechano-corrosive nature, while corrosion processes can significantly accelerate the degradation of surface layers. In this regard, the use of polymers with high chemical resistance and inertness to aggressive media is relevant. However, the application of such highly resistant polymers is often economically impractical, which necessitates the development of methods for surface modification of available structural polymers to improve their performance properties. he aim of this work is to develop and scientifically substantiate a laboratory installation and technological parameters of the direct gas fluorination process for polymer materials in order to form a modified surface layer without altering the surface microgeometry and to increase their wear resistance. Polypropylene grade 21060, widely used in mechanical engineering, agricultural machinery, and food equipment due to its sufficient strength, chemical resistance, and processability, was selected as the object of the study. A laboratory installation for direct gas fluorination of polymers was designed using a gas mixture of 1% F_2 and 99% Ar followed by treatment with nitric oxide to neutralize active radicals. Experimental studies showed the formation of a modified surface layer about 5 µm thick with increased chemical inertness. It was established that fluorination significantly reduces the intensity of cavitation–erosion wear of polypropylene in various environments, confirming the effectiveness of the method for improving the durability of polymer components.

Keywords: gas fluorination, polypropylene, surface modification, cavitation–erosion wear, aggressive environments, micro-impact loads.

Introduction

The cavitation–erosion wear resistance of metallic alloys in corrosive environments is determined by both mechanical and corrosion-related factors of material degradation. Corrosion itself does not usually cause significant mass loss; however, it acts as a catalyst for fatigue failure of metallic surfaces subjected to micro-impact loading in corrosive media. Therefore, corrosion resistance, and in many cases complete chemical inertness to aggressive environments, has stimulated the interest of researchers and practitioners in the use of polymer components that operate in contact with corrosive media, particularly under friction and cavitation conditions [1].

On the other hand, polymers characterized by high chemical resistance or complete chemical inertness are relatively expensive and their application is often limited at elevated temperatures [2]. Therefore, from an economic perspective it is advantageous to manufacture equipment components from inexpensive and readily available polymers and subsequently modify only their surface layer in order to obtain the required performance characteristics [3]. One of the effective methods of surface modification of polymers is the method of direct gas fluorination [3].

The term direct fluorination of polymers usually refers to the process of heterogeneous interaction between polymer surfaces and gaseous molecular fluorine (F_2) or gas mixtures containing fluorine together with N_2, He, Ar, O_2, etc. Direct fluorination has several important practical advantages: the process occurs at room temperature with a sufficiently high rate and does not require heating or additional activation by ultraviolet radiation, catalysts, or γ-radiation. At the same time, only a thin surface layer of polymers with a thickness of approximately 0.01–10 μm is modified, while the geometric dimensions of the polymer remain unchanged [3].

The direct fluorination process is widely used on an industrial scale to improve the barrier properties and chemical resistance of polymer automotive fuel tanks [3–5]. However, studies investigating the effect of direct fluorination on improving the cavitation–erosion resistance of polymers under cavitation–erosion wear are practically absent.

On the other hand, in the food industry and the agro-industrial sector, polyethylene and polypropylene (polyolefins) and their modifications are most widely used for manufacturing equipment components [6]. This is explained by the fact that polypropylene, in particular, exhibits high chemical inertness, is approved for full contact with food products, and can be readily processed both by machining and by molding [6].

Therefore, the aim of this work is to develop and scientifically substantiate the design of an installation and the technological parameters of the gas fluorination process for polymer materials in order to form a modified surface layer without altering the surface microgeometry and to increase their wear resistance under micro-impact loading in corrosive environments.

Materials and Methods for Experimental Studies

Polypropylene grade 21060 (hereinafter referred to as PP) was selected for the study because this material is one of the most widely used structural thermoplastics. It is extensively applied in mechanical engineering, agricultural machinery, and transport equipment due to its combination of sufficient mechanical strength, chemical resistance, low density, and good processability. Polypropylene is characterized by relatively low surface energy and limited wear resistance under impact–friction loading, which makes modification of its surface layer advisable. Gas fluorination enables modification of the chemical composition and structure of the polymer surface without significantly affecting its bulk properties, making polypropylene a promising material for investigating the effectiveness of such modification aimed at improving wear resistance under micro-impact loading.

For cavitation–erosion testing, a laboratory setup with a magnetostrictive vibrator (MSV) was designed and manufactured. The system includes an ultrasonic vibration generator UZDN-A, a container for the working media with a specimen mounting unit, and a cooling system. The generator power is 130 W, the operating frequency is 22 kHz, and the amplitude of the concentrator oscillations ranges from 22 to 65 μm (Fig. 1) [6].

For experiments in aggressive environments, the container for the working media (1) and the specimen mounting unit (2) were made of fluoroplastic F4. Two coil-type heat exchanger circuits with counter-directional flows of tap water were installed inside the container (Fig. 1). The first heat exchanger (3) maintains stabilization of the average temperature of the working medium throughout the entire volume of the container, while the second heat exchanger (4) is located directly in the cavitation zone. To increase the heat transfer coefficient, the pitch of the turns of circuit 4 was experimentally selected to be 4–5 mm (Fig. 1). This pitch ensures free movement of differently heated volumes of the working medium between the turns of the coil during different phases of incident and reflected ultrasonic waves. In addition, the opposite directions of the coil turns provide counterflow of cooled and heated volumes of the working solution. As a result, countercurrent flow is achieved, increasing the heat transfer coefficient and improving the efficiency of temperature stabilization of the working medium [1,6,7].

Stabilization of the temperature in the cavitation zone at the ambient temperature increases the reliability and accuracy of evaluating cavitation–erosion wear resistance, bringing the experimental conditions closer to the real operating conditions of components and assemblies of hydraulic machines [1,6-8].

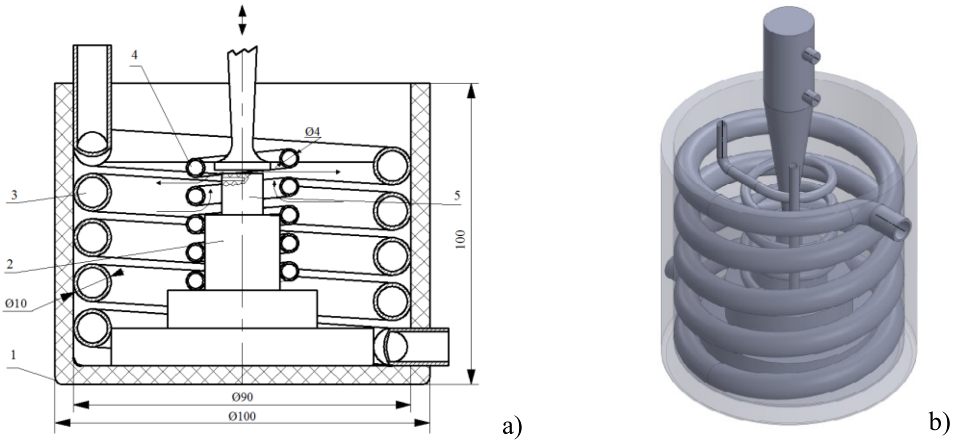

Fig. 1. Capacity for working environments with a sample attachment unit and a two-circuit cooling system: a) installation diagram; b) general view of the installation. 1 – container, 2 – sample attachment unit, 3 – external cooling circuit, 4 – internal cooling circuit, 5 – sample.

The wear resistance of the samples was tested in neutral (3% sodium chloride solution), alkaline (calcium oxide CaO – 250 g/L + sucrose – 15% by mass of CaO), and acidic (disodium phosphate Na_2HPO_4 – 10 g/L + citric acid $C_6H_8O_7$ – 5 g/L) environments, which are typical model solutions used in the food industry and the agro-industrial sector [7].

Results and Discussion

A laboratory setup for direct gas fluorination of polymers was designed and fabricated for the experimental studies (Fig. 2).

The model of the designed setup is shown in Fig. 2. The installation operates as follows: the reactor 2 (fluorination chamber), made of stainless steel 12X18H10T (hereinafter stainless steel), is mounted on the platform 1. The gas mixture is supplied to the reactor through the inlet pipe 3 and evacuated through a cascade of filters for fluorine neutralization by a fore-vacuum pump via the outlet pipe 4.

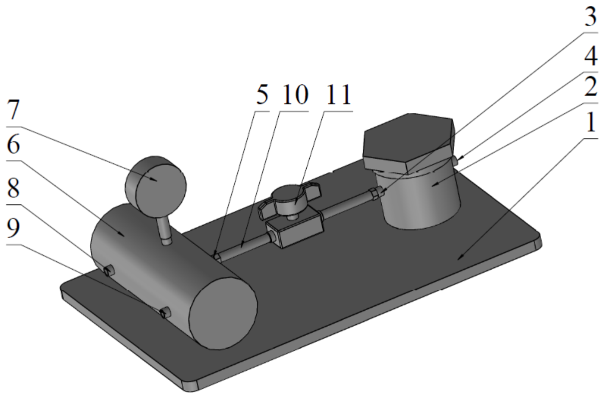

Fig. 2. Model of the laboratory setup: 1 – mounting plate; 2 – reactor; 3 – flange for fluorinating mixture inlet; 4 – flange for fore-vacuum pump; 5 – flange for fluorination supply; 6 – mixing container; 7 – pressure sensor; 8 – flange for Ar and NO supply; 9 – flange for F_2 supply; 10 – connecting pipes; 11 – valve.

The fluorinating mixture is prepared in the container 6, with gas pressure monitored by a manometer 7. Gases are fed into the container through inlet pipes 8 (Ar and NO) and 9 (F_2). Check valves installed in pipes 8 and 9 prevent backflow of the mixture after disconnecting the supply lines.

Once the mixture is prepared, the container is placed on the platform, and via pipe 10 it is connected from the outlet flange 5 (valve not shown in the figure) to valve 11 (type Ду), which is fixed on the frame and connected to the reactor via a stainless steel pipe.

Inside the reactor (Fig. 3), four polymer samples 2 are installed into copper sleeves 1 soldered with silver into the reactor body. This configuration ensures that only the wear surface of each sample is fluorinated. Such placement significantly reduces fluorine (F_2) consumption and also serves as a heat sink and catalyst for the sample during fluorination.

After the samples are installed, the reactor 3 is closed with a lid 5 sealed with a fluoroplastic gasket 4. Additionally, the threaded connection between the lid and reactor body is sealed with a fluoroplastic tape (FUM tape). Flanges 6 and 7 for mixture supply and evacuation are soldered to the reactor body with silver.

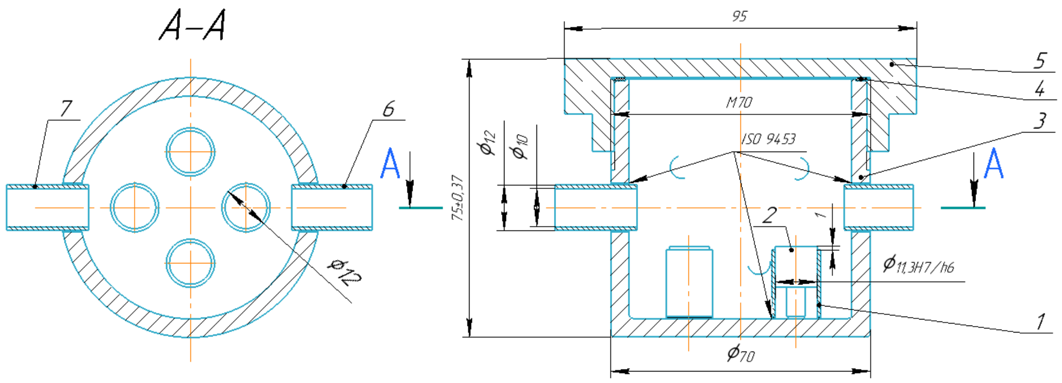

Fig. 3. Reactor (fluorination chamber) of the fluorination setup: 1 – sleeve; 2 – sample; 3 – reactor body; 4 – fluoroplastic gasket; 5 – lid; 6, 7 – outlet and inlet pipes, respectively.

The laboratory setup is equipped with two interchangeable containers (Fig. 2, position 6), which serve for preparing the fluorination mixture and for storing nitric oxide (NO), respectively.

The samples were treated with nitric oxide for 20 minutes to neutralize free radicals formed during the fluorination process. This treatment was carried out at atmospheric pressure and room temperature [3].

For the fluorination process, a fluorine–argon gas mixture was used, consisting of 1% F_2 (fluorine) and 99% Ar (argon) [9]. Argon was chosen due to its relatively low cost and because it ensures a more stable reaction during mixture preparation [9]. Before introducing the fluorinating mixture into the reactor, air was evacuated from the reactor to a residual pressure of $(3–4) \times 10^{-2}$ Pa. The reactor was then filled with the fluorine-containing mixture. Experimental conditions (fluorination area, reactor volume, etc.) were selected so that the fluorine consumption did not exceed 5% of the reactor volume.

After a set period, the fluorinating mixture was removed from the reactor, and the fluorine was neutralized in a filter. The pressure was again reduced to the same residual level, and nitric oxide was introduced into the chamber to neutralize remaining free radicals. Afterward, the NO was evacuated, the pressure stabilized, and the samples were extracted for further testing.

All parts of the laboratory setup that come into contact with fluorine or its gas mixtures are made of stainless steel and copper. Pipes and their connections are made of fluoroplastic F4, and all metal and threaded connections are sealed with fluoroplastic FUM tape [9-10]. To ensure safe operation with fluorine and nitric oxide, the setup was installed inside a specially equipped fume hood.

Cavitation–erosion wear resistance tests were performed on two types of samples: original polypropylene 21060 and polypropylene after surface fluorination. Tests were conducted in three environments: alkaline, acidic, and neutral. The thickness of the modified fluorinated layer was approximately 5 μm.

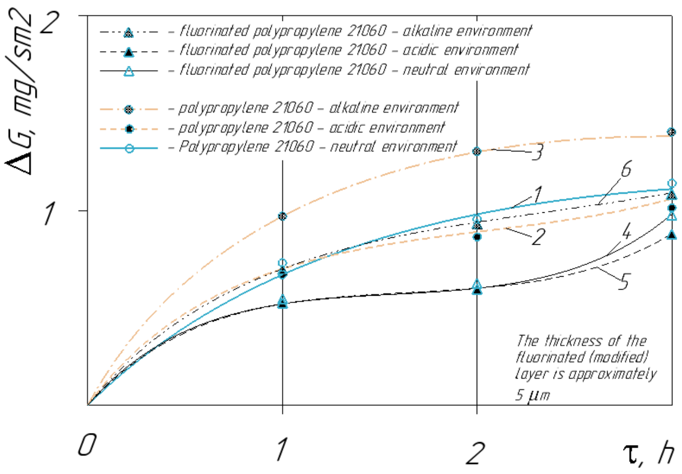

Fig. 4. Wear resistance kinetics of polypropylene 21060 and fluorinated polypropylene 21060 under micro-impact loading in neutral, acidic, and alkaline environments

The analysis of the experimental data (Fig. 4) shows that for all tested samples, the mass loss ΔG increases systematically with the duration of cavitation loading in neutral, acidic, and alkaline environments. The change in ΔG is nonlinear, reflecting the characteristics of the cavitation–erosion wear processes in the polymer material. In the initial stage, ΔG increases relatively rapidly due to active destruction of the surface layer caused by micro-impacts generated during the collapse of cavitation bubbles. Subsequently, the mass loss rate gradually decreases, indicating partial stabilization of the surface and the approach of the wear process to a quasi-stationary regime.

It was found that unfluorinated polypropylene 21060 exhibits the highest intensity of cavitation–erosion wear in an alkaline environment. Under such conditions, the polymer matrix interacts more actively with the components of the medium, and in combination with micro-impact loads induced by cavitation, this leads to accelerated surface degradation. In acidic environments, surface degradation occurs less intensively, resulting in a more moderate increase in ΔG. In neutral media, the mass loss also gradually increases, with wear intensity intermediate between alkaline and acidic conditions. These results demonstrate the significant influence of the chemical nature of the environment on the cavitation–erosion behavior of polypropylene 21060.

Distinct trends were observed for polypropylene samples modified by direct gas fluorination. In all tested environments, ΔG values for fluorinated samples were lower than for the unmodified material, indicating increased resistance to cavitation–erosion wear due to surface modification. In alkaline media, mass loss of fluorinated samples occurs much more slowly, demonstrating the effectiveness of the modified layer in resisting simultaneous micro-impact and chemically aggressive action. Similar trends were observed in acidic and neutral media, where cavitation–erosion processes proceed more stably and less intensively.

Comparative analysis confirms that surface fluorination reduces cavitation–erosion wear intensity in all tested environments. This effect is attributed to the formation of a thin fluorinated layer on the polymer surface, which exhibits increased chemical inertness, lower permeability to aggressive components, and a reduction of free radicals in the near-surface layer. This layer decreases surface destruction under micro-impacts and slows diffusion and chemical processes at the polymer interface.

Furthermore, the most intense cavitation–erosion wear occurs during the initial stage of cavitation exposure. The subsequent decrease in mass loss rate may be associated with changes in surface morphology and the establishment of quasi-stationary wear conditions.

Thus, the results confirm the effectiveness of surface fluorination as a promising method for enhancing the resistance of polypropylene to cavitation–erosion wear in various aggressive environments. This modification method reduces surface degradation under cavitation and increases the service life of polymer components during operation.

Conclusions

1. It was established that under cavitation loading, polypropylene 21060 exhibits a systematic increase in mass loss with increasing cavitation duration. The cavitation–erosion wear process is nonlinear, with more intensive mass loss occurring during the initial stage of testing.
2. The chemical nature of the environment significantly affects the intensity of cavitation–erosion degradation of polypropylene. The highest wear intensity for unfluorinated samples is observed in alkaline media, while in acidic and neutral environments, degradation processes occur less intensively.
3. Surface modification of polypropylene by direct gas fluorination reduces the intensity of cavitation–erosion wear in all tested environments. This effect is due to the formation of a thin fluorinated layer on the material surface, which has increased chemical inertness and a stable structure.
4. A laboratory setup for surface fluorination of polymer materials was developed, providing controlled gas-phase processing and enabling surface modification of samples with minimal fluorine consumption.
5. The proposed reactor design and fluorination technology ensure localized surface treatment of samples, efficient heat removal, and neutralization of active radicals after fluorination, which enhances the operational resistance of polymer materials to cavitation–erosion wear.

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Мартинюк В., Стечишин, М., Федорів В., Ярошенко П., Люховець В. Установка та технологія газового фторування полімерів для підвищення їх зносостійкості при мікроударних навантаженнях

У статті розглянуто проблему підвищення кавітаційно-ерозійної зносостійкості полімерних матеріалів, що працюють в умовах мікроударних навантажень у корозійно-активних середовищах. Показано, що руйнування матеріалів у таких умовах має складний механіко-корозійний характер, а корозійні процеси можуть значно прискорювати деградацію поверхневих шарів. У зв'язку з цим актуальним є застосування полімерів із високою хімічною стійкістю та інертністю до агресивних середовищ. Проте використання таких матеріалів часто є економічно недоцільним, що обумовлює необхідність модифікації поверхні доступних конструкційних полімерів. Метою роботи є розроблення та наукове обґрунтування лабораторної установки і технологічних параметрів процесу прямого газового фторування полімерів для формування модифікованого поверхневого шару без зміни мікрогеометрії поверхні та підвищення їх зносостійкості. Об'єктом дослідження обрано поліпропілен марки 21060, який широко застосовується у машинобудуванні, сільськогосподарській техніці та харчовому обладнанні. У роботі спроектовано лабораторну установку для прямого газового фторування полімерів із використанням суміші 1% F_2 та 99% Ar з подальшою обробкою монооксидом азоту. Експериментальні дослідження показали формування модифікованого шару товщиною близько 5 мкм, що характеризується підвищеною хімічною інертністю. Встановлено, що фторування суттєво знижує інтенсивність кавітаційно-ерозійного зношування поліпропілену в різних середовищах, підтверджуючи ефективність методу для підвищення довговічності полімерних деталей.

Ключові слова: газове фторування, поліпропілен, поверхнева модифікація, кавітаційно-ерозійне зношування, агресивні середовища, мікроударні навантаження.