Influence of Nonionic Surfactant Hydrophobicity on the Tribological Properties of Microemulsion Systems Aimed at Cutting Fluid Applications

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The development of new environmentally-friendly cutting fluids is an important technological advancement. The aim of this study was to assess the tribological behavior of microemulsions (W/O) developed with epoxidized soybean oil and nonionic surfactants with different degrees of ethoxylation (NP4EO, NP6EO and NP9.5EO). The tribological performance of the microemulsion systems was assessed in a High Frequency Reciprocating Rig (HFRR) tribometer. Microemulsions showed Newtonian fluid behavior, with viscosities compatible with conventional cutting fluids. In addition, contact angle values above 90º indicate spherical-shaped drops on the surface on which they are deposited, due to their hydrophobic nature. The microemulsions formulated using surfactants with lower ethoxylation numbers and 20% concentration exhibited greater stability, lower viscosity and better friction reduction during tribological contact between surfaces, given that the average wear scar diameter was 118 µm with smooth surfaces exhibiting slight slippage wear caused by abrasion, as identified by SEM/EDS analyses.

Keywords: *Tribological performance, Microemulsion, Nonionic surfactant.*

1. Introduction

In recent decades, the scientific and industrial communities have shown greater environmental awareness due to the increase in pollution, restrictive laws and growth in demand for green products. Machining, one of the most widely applied manufacturing processes, uses cutting fluids due to their superior tribological performance. The use of fluids for machining aims at increasing the shelf life of the tool, minimizing heat generation during the process and removing chips from the working area, thereby improving the efficiency of the production system. By contrast, its generalized use has had negative effects on human health and the environment, given the presence of oils and chemical agents that contaminate surface and groundwater, pollute the air, contaminate the soil, agricultural products and food items[1]. In addition, around 80% of all occupational diseases in operators occur by their inhaling fumes and skin contact with cutting fluids, primarily those of mineral origin[2].

To overcome these challenges, formulating new cutting fluids is an important field in the development of scientific and technological research, in pursuit of low-cost, environmentally friendly cutting fluids that ensure the efficiency of their tribological properties[3]. The restrictions imposed by environmental laws limit the use of conventional cutting fluids, thereby prompting the discovery of viable and competitive technologies from an environmental standpoint[4-9]. Aqueous cutting fluids are developed by dispersing oil in water using a surfactant on the oil-water interface in order to reduce interfacial tension and promote emulsion stability[10], in addition to forming a hydrodynamic film more efficiently[6]. These fluids are widely used in industrial applications, given that they provide lubrication and dissipate heat during tribological contact[11].

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Studies on the tribological practices of microemulsion systems for cutting fluids continue to grow, heightening interest in aspects related to stability, the environment and industrial applications[12]. The development of stable cutting fluids is one of the greatest challenges in microemulsion studies, since there are several factors that contribute to system destabilization, such as the different densities between phases, coalescence, flocculation, droplet size in the dispersed phase, continuous phase viscosity, among others[13]. Microemulsions are considered an anisotropic transparent mixture, with drop sizes between 5 and 50 nm and thermodynamically stable, consisting of oil in water (O/W) or water in oil (W/O) and stabilized by a surfactant, which is used to reduce interfacial tension between the two liquids[14]. Short and medium-chain alcohols are used as cosurfactant to more markedly reduce interfacial tension, thereby increasing interface fluidity and entropy of the system[15].

Microemulsion stability is obtained using surfactants, primarily the nonionic variety, since their adsorption on the oil droplet surface produces electric repulsion between them. These repulsive forces act against the Van der Waals forces, preventing the aggregates from approaching one another, coalescing and forming flocs[16]. In addition, these amphiphilic molecules improve the rheological properties of the medium, and their micelles form a mono or bilayer that interacts strongly with metal surfaces, reducing friction and wear and therefore protecting the metal[17].

Numerous studies have reported that vegetable oil is a viable and promising alternative to mineral oils in the formulation of microemulsion fluids, since it has the following characteristics: renewable, biodegradable, non-toxic, good compatibility with the skin, high flash point and compatibility with different additives[18,19]. Vegetable oils also exhibit compatible viscosity as a biolubricant capable of preventing friction between the two metal surfaces in contact[20]. In addition to all the aforementioned properties, vegetable oils are renewable and compatible with environmental protection policies[21]. As such, the purpose of the present study was to assess the performance of the tribological properties of microemulsions (W/O) formulated with epoxidized soybean vegetable oil and nonionic surfactants with different degrees of ethoxylation aimed at cutting fluid applications for lathe machining.

2. Materials and Methods

2.1. Materials

The water in oil (W/O) microemulsions were prepared using ethoxylated nonionic commercial surfactants (NP4EO, NP6EO and NP9.5EO), with NP representing nonylphenol and nEO the average number of ethylene oxide units

present in the polar part of the surfactant. The surfactants used did not undergo any purification process and all were acquired from Oxiteno (São Paulo, Brazil)[22]. The epoxidized soybean oil was supplied by Inbra Indústrias Químicas Ltda (São Paulo, Brazil)[23]. Distilled water was used in the microemulsion formulations (W/O). Table 1 shows the following nonionic surfactant properties: chemical structure, molecular mass (MM) and hydrophilic/lipophilic balance (HLB). Table 2 presents the physicochemical properties of the epoxidized soybean oil (ESO).

2.2. Methods
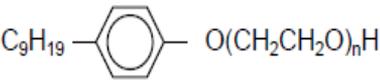
2.2.1. Microemulsion system

The ternary phase diagrams of the microemulsions were prepared according to the titration methodology, using the mass fractions of all the components. Initially, a binary solution of epoxidized soybean oil (ESO) with the surfactant was prepared at proportions of 10, 20, 30, 40, 50, 60, 70, 80 and 90% by weight. The Winsor regions were obtained using drop-by-drop titration under moderate mechanical agitation with the pure component of the opposite vertex. Phase changes were detected by visual inspection using a clear, transparent and/or homogeneous solution. The phase diagrams were built with the help of a high-precision digital analytical balance (SHIMADZU, model AUY220), microprocessor-controlled centrifuge (QUIMIS, model Q222TM), vortex mixers (FOUR E'S SCIENTIFIC) and an ultrathermostatic bath (SOLAB, model SL-152/10).

Density was obtained using a DMA 4500 M digital densimeter (Anton Paar, USA). After the densimeter was calibrated with distilled/deionized water at a temperature of 20 ºC, the surfactant and microemulsion system samples were injected into the inner compartment of the device in order to obtain a density reading of the samples (g/cm^3).

The viscosities of the nonionic surfactants and microemulsions were measured in a Brookfield digital rheometer (Middleboro, MA - DV-III ultra+) equipped with a small SSA SC4-18/13Rb sample adaptor and SC4-45YD water jacket. Temperature was controlled using a thermostatic bath (MGW LAUDIA, model S-1). A volume of 6.7 mL of each sample was allocated to the rheometer chamber and readings were taken, varying the shear rate between 5 and 100 s^{-1}, at temperatures of 25, 40, 60, and 80 ºC.

The contact angle was determined by the method reported by Nascimento et al., 2015[24], using a goniometer (Krüss, DSA 100). Drops with a volume of 5 μL were automatically deposited on the central surface of a steel disk. The measurements were monitored using a high-resolution camera installed in the device (25 frames per second). An LED diffusor with white background was used as light source.

Table 1. Nonionic surfactants used and their properties[22].

Surfactant	Chemical structure	Molecular mass (g/mol)	HLB value
NP4EO		396.0	8.9
NP6EO	C_9H_{19} —⬡— $O(CH_2CH_2O)_nH$	484.0	10.9
NP9.5EO		622.0	13.0

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A screen was placed between the light source and the drop in order to minimize heating and provide uniform lighting and good contrast without losing mass during deposition. The software (DSA100) instantly calculated the apparent contact angles, producing a contact angle curve as a function of time. The measurements were carried out in triplicate.

2.2.2. Assessment of the tribological performance of the microemulsion

The ability of the microemulsions to reduce the friction and wear of the tribosystem was assessed using a PCS Instruments High Frequency Reciprocating Rig (HFRR). Table 3 summarizes the tribological pair description; both ball and disc were made of AISI 52100 steel, whose chemical compositions were determined using X-Ray Fluorescence (XRF) (Table 4). The disc (AISI 52100) was smoothed from 220# to 1200# and polished to reach a roughness (Ra) of 0.02 μm. The tribological pair were cleaned by immersion in toluene for 10 minutes in an ultrasound bath and then dried with hot air. Analysis consisted of a ball-on-disc test to measure friction and wear under lubrication conditions using a ball tensioned against a disc. The steel sphere slides against the steel disk with a stroke length of 1 ± 0.02 mm, at a frequency of 50 ± 1 Hz and sliding velocity of 0.01 m/s for 75 ± 0.1 min. The sphere and disk in contact are totally submerged in 2.0 ± 0.2 mL of lubricant with a normal load of 2.0 ± 0.01 N. The lubricant temperature was maintained at 60.0 ± 1.0 °C. Contact pressure was 1.4 GPa. All the tests were performed in triplicate. The coefficient of friction was measured with a piezoelectric force transducer. Contact resistance (Ω) between the friction test specimens was measured using the electrical contact resistance (ECR) technique. The tribological pair (sphere and disk) was cleaned by immersion in acetone for 7 min. using an ultrasonic bath and then dried with hot air. The tests were conducted in triplicate in order to provide average coefficient of friction and wear scar diameter (WSD) values. After the test, the dimensions of the wear scar formed on the surface of the sphere were measured by an optical microscope calibrated to measure up to 1000 μm with 100 X magnification, obtaining the wear scar diameter (WSD). High WSD values indicate greater sphere wear and therefore, less fluid lubricity[25]. The standards that assess the lubricity of a lubricant only consider the scar wear diameter calculated from its size (X and Y) and analyzed under an optical microscope[26]. Thus, it is important to analyze the image of the sphere after the HFRR test. The lengths of the scars formed on the disks were determined by scanning electron microscopy (SEM), and chemical analysis of surface wear was performed using electron dispersive scanning (EDS).

3. Results and Discussion

3.1 Microemulsion system

3.1.1 Ternary diagrams

The phase diagrams were plotted from the ternary mixtures (surfactant, oil phase and water phase) to delimit the borders and transition regions between the emulsion and microemulsion. Several types of dispersions were observed, including translucid systems such as liquid and viscous microemulsions, opaque systems (murky), biphasic systems and emulsions. The microemulsions were classified as transparent and homogeneous systems. Figure 1 presents the ternary phase diagrams obtained for the systems containing NP4EO (Figure 1a), NP6EO (Figure 1b) and NP9.5EO (Figure 1c). These diagrams show the borders of the regions with the presence of each surfactant and the regions of the microemulsion selected (Table 5). The compositions of microemulsion systems M1, M2 and M3 are compatible with cutting fluid applications, confirmed by determining their properties. On the other hand, a comparison between the microemulsion regions obtained and the three surfactants demonstrated that the points selected are close together, indicating that the ethoxylation of the surfactants studied did not compromise the formation of the microemulsion, that is, their hydrophilic nature maintained the same type of microemulsion (W/O). NP9.5EO provided the most pronounced emulsion region, and the ethylene oxide molecules (hydrophilic) hindered system stabilization (W/O), favoring the formation of larger droplets, which may lead to phase separation. The microemulsions have numerous advantages over their conventional counterparts, such as smaller structure, thermodynamic stability, low interfacial tension, combined with a high interface area between immiscible fluids, among others.

Table 2. Physicochemical properties of epoxidized soybean oil (ESO)[23].

Parameters	Specifications
Density	0.99 g/cm³ (25°C)
Acidity index	0.70 mg KOH/g.max
Iodine index	3.50 g I/100 g.max
Epoxy index	6.50 g O/100 g.min
Viscosity (μ)	480.00 cP (25°C)
Flash point	280.00 °C
Volatiles	0.20% max

Table 3. Characteristics of the tribological pair[9]

Properties	Ball	Disc
Hardness (HV)	570-750	190-210
Diameter (mm)	6.0	10.0
Roughness (μm)	0.050	0.008

Table 4. Chemical composition by weight (wt.%) of the AISI 52100 steel disc[9]

Fe	C	Mn	Cr	S	Si	Al	Ca
Bal	0.900	0.413	1.567	0.127	0.546	0.105	0.154

Table 5. Composition of the microemulsions selected.

Microemulsion	Surfactants (%)	ESO (%)	Water (%)
M1	20	70	10
M2	30	60	10
M3	40	50	10

3.1.2 Density

The API (American Petroleum Institute) gravity of the ESO and surfactant samples is presented in Table 6. The results indicate that ESO is above ANVISA (Brazilian Health Regulatory Agency) specifications[27], which stipulate that the density of vegetable oils should be between 0.9150 and 0.9200 g/cm³ at 25 °C. This increase is due to the epoxidation reaction, which changes its physical and chemical properties, but does not preclude its use in the formulation of microemulsion systems. With respect to the surfactants, density rose as a function of the polar chain length of the surfactant, in the following order: NP4EO > NP6EO > NP9.5EO, demonstrating that an increase in the degree of surfactant ethoxylation makes the amphiphilic molecule more voluminous and concentrated. Commercial cutting fluids OP30 and Dromus exhibited densities of 0.9133 g/cm³ and 0.9140 g/cm³, respectively, similar to the substance values (ESO, NP4EO, NP6EO and NP9.5EO), which make up the new formulations[28].
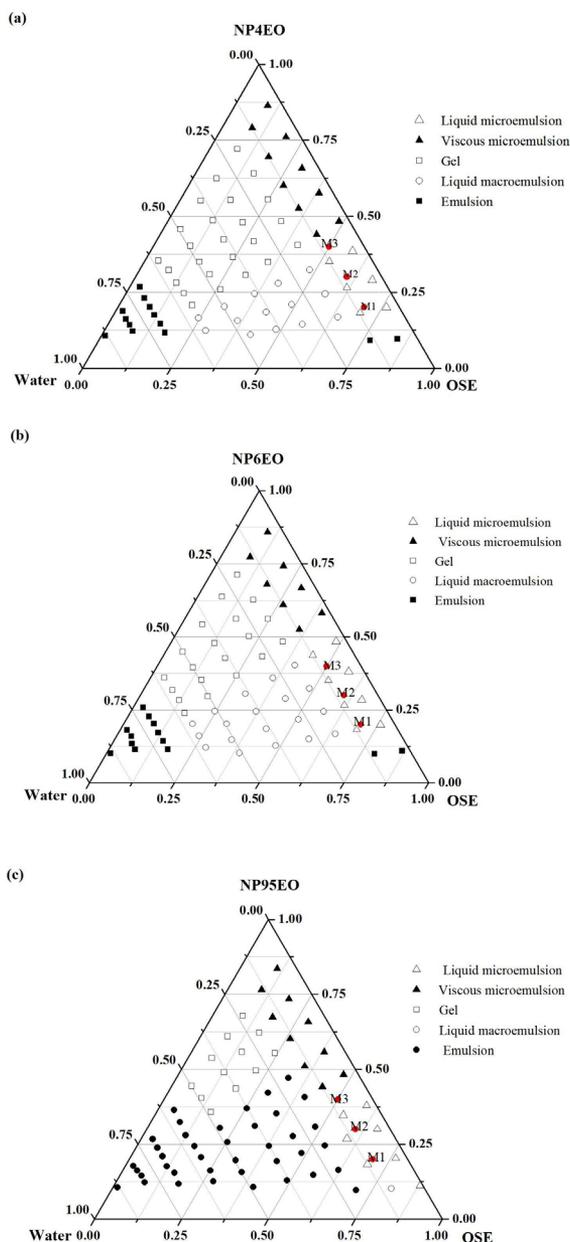
3.1.3 Contact angle

The hydrophobicity of a surface is generally expressed as wettability, which can be quantified by the contact angle. Figure 2 demonstrates that the contact angle of the microemulsion systems (M1, M2 and M3) is considered high ($\theta > 90°$), indicating low wettability, confirming that the microemulsions exhibited a spherical format on the surface where they were deposited, with low humectation. This occurs due to the high surface tension, causing minimal drop spreading on the surface. This behavior is more evident with the insertion of hydrophilic groups (EO), owing to the repulsive interactions between the microemulsion and the solid surface, which decreases their affinity for nonpolar surfaces[29]. Microemulsion M3 showed no significant variation in contact angle, likely because of the high surfactant concentration (40%), underscoring the predominance of its amphiphilic nature.

3.1.4 Rheological behavior

Initially, the behavior of epoxidized soybean oil (ESO) flow was assessed over a shear range of 5-100 s⁻¹ at temperatures of 25, 40, 60 and 80 °C (Figure 3). As expected, the increase in temperature caused a significant decline in viscosity, demonstrating a decline from 480.70 cP (25 °C) to 36.01 cP (80 °C). The rise in lubricant temperature produces lower viscosity due to the higher potential molecular energy with

Figure 1. Ternary diagram for systems at 25 °C: OSE, water and (a) NP4EO, (b) NP6EO and (c) NP9.5EO.

Table 6. Density of ESO and surfactants (NP4EO, NP6EO and NP9.5EO).

Properties	ESO	NP4EO	NP6EO	NP9.5EO
Density (25 °C, g/cm³)	0.9845	1.0206	1.0355	1.0468
Density (API)	12.23	7.14	5.15	3.67
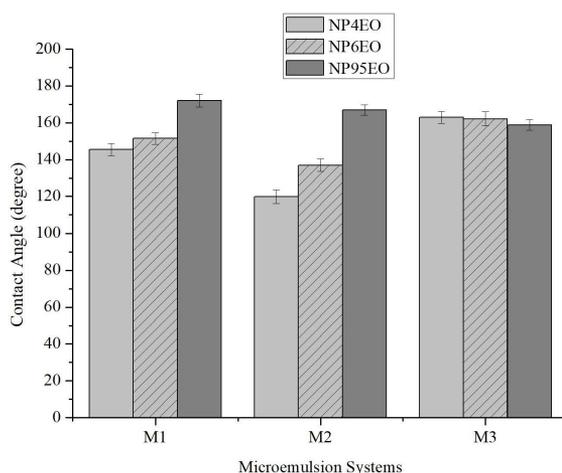
Figure 2. Contact angle behavior for the microemulsion systems.

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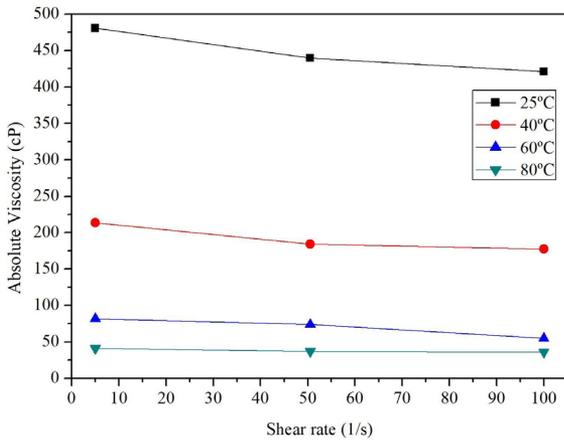Aimed at Cutting Fluid Applications

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Figure 3. Influence of temperature on OSE rheology.

a reduction in intermolecular forces[30]. At low temperatures, the high viscosity value of ESO may be attributed to the fact that the epoxidation reaction increased the molecular weight of the epoxidized oil, in addition to forming a more polar chemical structure than that of oil with no chemical change, resulting in a stronger intramolecular interaction. The epoxidation reaction eliminates the unsaturation from vegetable oils, thereby supporting broader and more hostile operating conditions[19]. The viscosities of commercial fluids OP39 and Dromus are 42.50 cP (40 °C) and 39.80 cP (40 °C), respectively[28].

The rheological behavior of surfactants (NP4EO, NP6EO and NP9.5EO) was investigated over a shear range of 5-170 s^{-1} at temperatures of 25, 40, 60 and 80 °C (Figure 4). As observed for ESO, the increase in temperature caused a significant decline in the viscosity of all the surfactants and the rise in intermolecular movements and decrease in friction between molecules (as a function of free movement) lowered viscosity. In regard to the influence of the degree of ethoxylation on viscosity, the increase in the hydrophilic nature of the surfactant raised viscosity at a temperature of 25°C, as follows: 251.95 cP (NP4EO) < 274.94 cP (NP6EO) < 315.13 cP (NP9.5EO). Adding ethylene oxide molecules [(4EO, MM = 396), (NP6EO, MM = 484) and (NP9.5EO, MM = 622)] transforms the surfactant into an amphiphilic molecule with increased polarity, more volume and capable of establishing stronger interactions with metal surfaces, thereby providing greater resistance to shear deformation.

Figure 5 shows the viscosity behavior of microemulsion systems M1, M2 and M3, which contain the same constituents, but with different compositions, particularly the nonionic surfactants (NP4EO, NP6EO, and NP9.5EO) and epoxidized soybean oil. The results demonstrated that the viscosity of the microemulsions formulated with NP4EO (Figure 5a) and NP6EO (Figure 5b) declined slightly with an increase in surfactant concentration and decrease in the amount of oil (Table 5). On the other hand, the viscosity of microemulsions formulated with NP9.5EO (Figure 5c) increased as the surfactant concentration rose (M1-M3) (Table 5), likely as a function of the balance of its amphiphilic nature (HLB), showing greater capacity in stabilizing different liquids (water and oil). The HLB reflects the balance of the amphiphilic
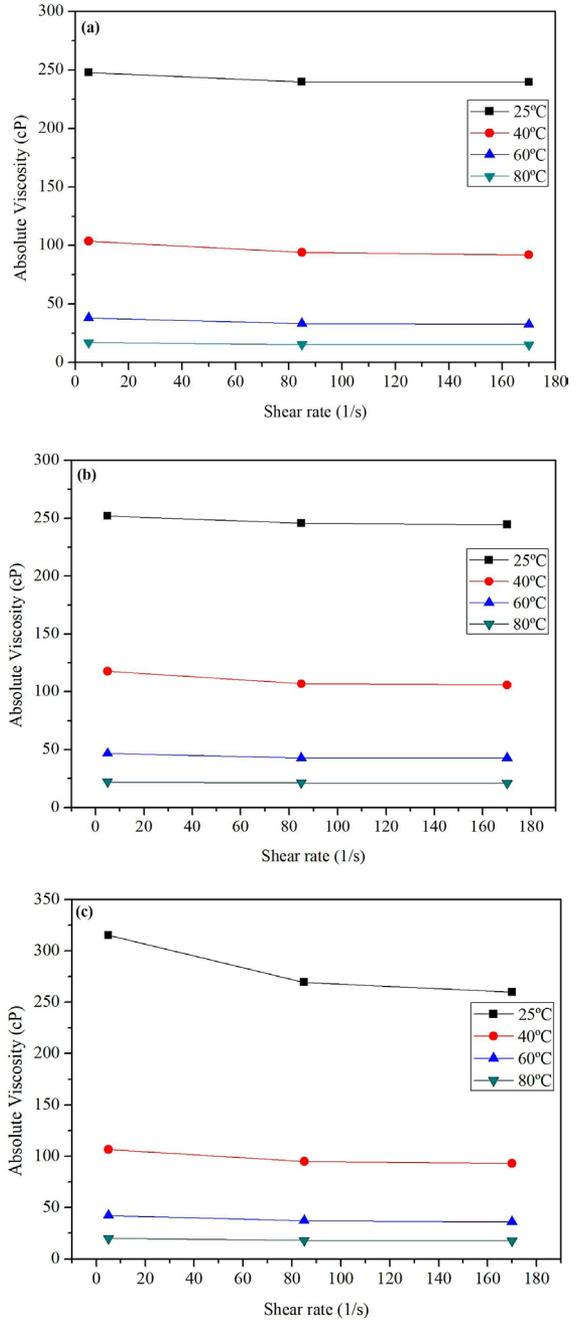

Figure 4. Viscosity versus shear rate at different temperatures for surfactant: (a) NP4EO, (b) NP6EO and (c) NP9.5EO.

structure (polar and nonpolar) of the surfactant and is important for microemulsion stability and efficiency as a cutting fluid. In all the cases, an increase in temperature caused a decline in viscosity.

3.2 Tribological behavior

3.2.1 Coefficient of friction

Figure 6 shows the behavior of the coefficient of friction of surfactants NP4EO, NP6EO, NP9.5EO and epoxidized
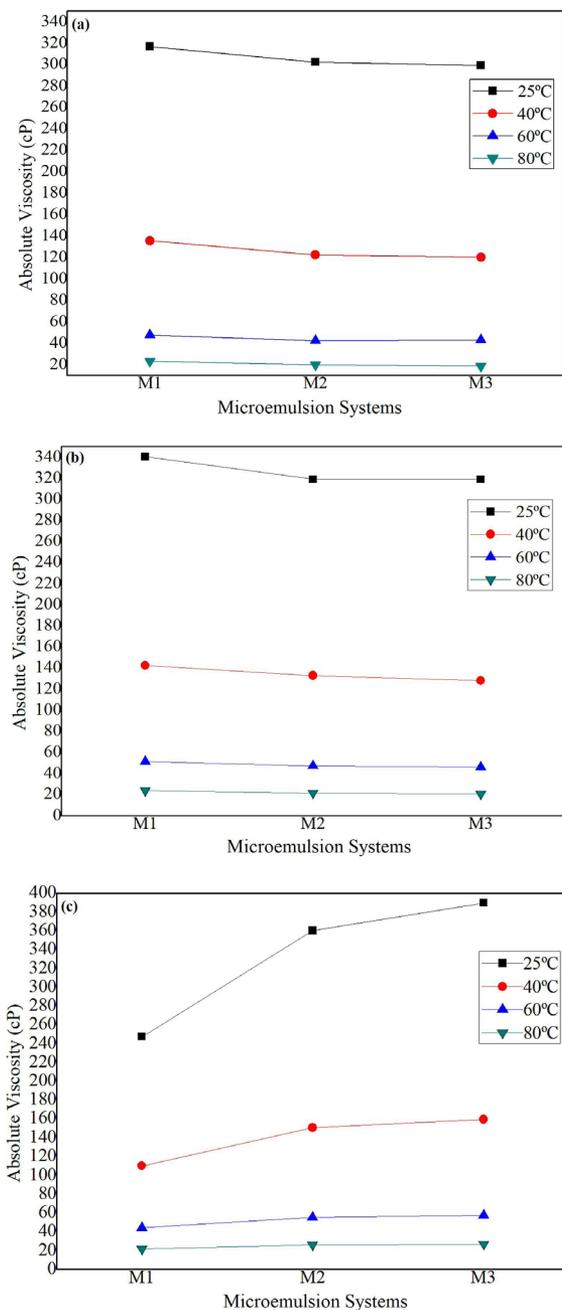
Figure 6. Coefficient of friction behavior for individual surfactants and pure ESO.

Table 7. Coefficient of friction obtained with the OSE and nonionic surfactants.

Compounds	Average coefficient of friction	HLB
OSE	0.034 ± 0.002	-
NP4EO	0.088 ± 0.001	8.9
NP6EO	0.066 ± 0.001	10.9
NP9.5EO	0.055 ± 0.001	13.0

Figure 5. Absolute viscosity versus surfactant concentration: (a) NP4EO, (b) NP6EO and (c) NP9.5EO.

soybean oil (ESO). There was a clear increase in the coefficient of friction (COF) as the HLB of the nonionic surfactants declined (Table 7). COF behavior did not achieve the expected stability. However, despite the disturbances presented, COF evolution provided an acceptable average, since the tests were performed in triplicate and with good reproducibility using HFRR. The surfactants with the highest viscosities exhibit the lowest coefficients of friction: NP9.5EO (μ = 315.13 cP, COF = 0.055), NP6EO (μ = 274.94 cP, COF = 0.066), NP4EO (μ = 251.95 cP, COF = 0.088). In general, nonionic surfactants with a higher degree of ethoxylation exhibit greater
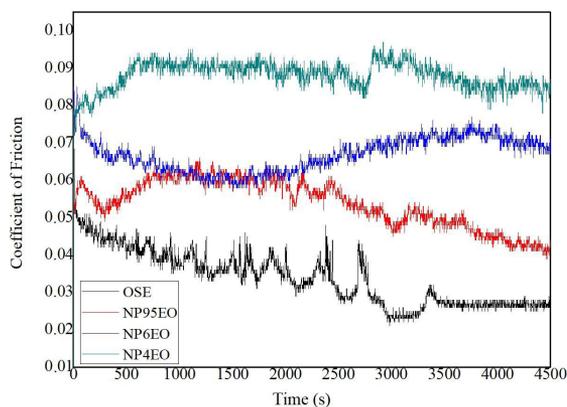
antiwear efficiency[31]. In addition to its amphiphilic nature, the functional group of the surfactant establishes a stronger interaction with the metal surface during tribological contact, producing a more stable lubricant film. One of the basic criteria to reduce friction during contact between surfaces is the polarity of these surfactants. In regard to ESO, the coefficient of friction values are lower than those obtained with the surfactants, likely because of its chemical nature, polarity and greater viscosity. Nevertheless, its adsorption onto the metal surface is demonstrated by the formation of a thin layer of oil, preventing metal-metal contact, thereby reducing wear and friction[32-34].

Table 8 shows the mean and standard deviation of the average coefficient of friction (COF) obtained with the microemulsion systems (M1, M2 and M3), indicating the influence of surfactants with different degrees of ethoxylation on the coefficient of friction (Figure 7). Microemulsion systems (M1, M2 and M3) formulated with NP4EO obtained the lowest coefficients of friction. The M1 microemulsion system containing surfactant NP4EO (Figure 7a) produced the lowest coefficient of friction, remaining stable for almost the entire test. This demonstrated an affinity with the metal surface, guaranteeing film formation and preventing metal-metal friction during lubrication. Microemulsion systems M2 and M3 exhibited similar coefficient of friction behaviors, showing a decline after 1500 s due to the formation of a lubricant film. However, the perceived instability on the friction curve throughout the test indicates that the film did not completely adhere to the metal surface. Assessment of the microemulsions formulated with NP6EO (Figure 7b) revealed a smaller coefficient of friction using microemulsion M1 containing the lowest surfactant concentration. The region

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Table 8. Coefficient of friction obtained with the microemulsion systems.

Nonionic surfactant	Microemulsion	Average coefficient of friction
NP4EO	M1	0.018 ± 0.000
	M2	0.045 ± 0.005
	M3	0.068 ± 0.001
NP6EO	M1	0.027 ± 0.002
	M2	0.057 ± 0.002
	M3	0.061 ± 0.002
NP9.5EO	M1	0.033 ± 0.001
	M2	0.035 ± 0.002
	M3	0.048 ± 0.002
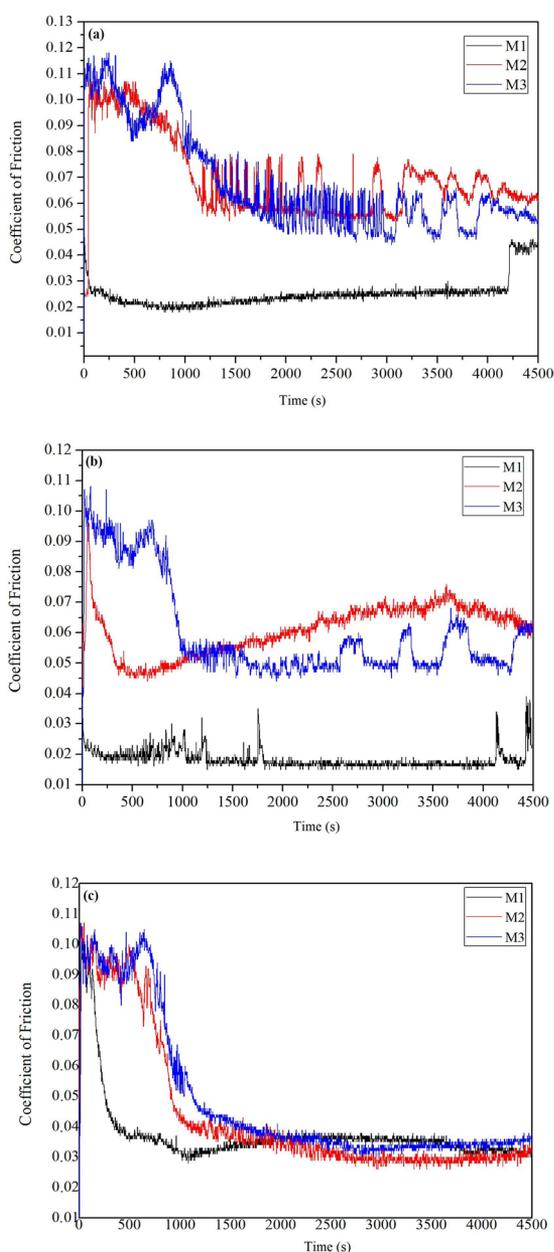
Figure 7. Behavior of the coefficient of friction for microemulsion systems using surfactants: (a) NP4EO, (b) NP6EO and (c) NP9.5EO.

extending up to 1750 s shows a slight oscillation, followed by a stable region. However, above 4000 s, the film may have torn, thereby increasing the COF. Microemulsions with higher concentrations in the surfactant (M2 and M3) caused an increase in the coefficient of friction, exhibiting irregular behavior, without reaching a permanent regime, indicating difficulty in forming a stable lubricating film and promoting greater friction between surfaces. With respect to the microemulsions (M1, M2 and M3) formulated with NP9.5EO (Figure 7c), all the systems are stable from 1500 s onwards, demonstrating the formation of a stable film due to the higher degree of surfactant ethoxylation, which increases interaction between ethylene oxide molecules and the steel, benefitting surfactant adsorption onto the metal surface. It is important to underscore that nonionic surfactants are temperature-sensitive and that their solubility declines as a function of hydrophilic chain dehydration (nEO). This can cause microemulsion instability, especially in surfactants with lower hydrophilia at smaller concentrations[35], which may have caused the oscillations observed in the coefficient of friction (Figures 7a-b).

It is important to note that the decrease in the number of ethylene oxide groups in the polar chain of the surfactant reinforces its hydrophobic nature, favoring the wetting of steel surfaces, which, in turn, makes lubrication more efficient[24,31]. In addition, the lower coefficients of friction between the sphere and the steel surface occur with microemulsion systems, exhibiting the lowest surfactant concentrations. The M1-NP4EO microemulsion system provided a larger reduction in the coefficient of friction compared to pure OSE and nonionic surfactants (Table 5 and Table 6). This may be attributed to micellar morphology, acting as thermodynamically stable spherical aggregates, ensuring strong adhesion to the metal surface[35]. Alves et al.[36] reported that the addition of CuO (0.50 wt%) nanoparticles provides little reduction in the coefficient of friction (from 0.124 to 0.114) compared to pure synthetic oil.

3.2.2 Wear scar diameter

Figure 8 shows the wear scar diameter for the epoxidized soybean oil (ESO), ethoxylated nonionic surfactants (NP4EO, NP6EO and NP9.5EO) and microemulsion systems (M1, M2 and M3). All the WSD values are in line with European regulations[37], that is less than 460 μm. The lowest WSD values were obtained with OSE (176 μm) and NP4EO (181 μm), when used in their pure form. Microemulsions M1 formulated with the surfactants (NP4EO, NP6EO, and NP9.5EO) obtained the lowest WSD values. The best result was obtained for M1-NP4EO (WSD = 118 μm). In all the systems, WSD values increased as the hydrophilic nature of the surfactant rose, in the following order: NP4EO < NP6EO < NP9.5EO. All values compared to European WSD regulations consider a value lower than 460 μm to be adequate[37]. The images obtained with M1, M2 and M3 formulated with NP4EO displayed greater oxidation (dark stains), likely due to the lower solubility in water, revealing greater surface activity. However, the system formulated with NP9.5EO showed fewer signs of oxidation and clearer, more uniform grooves with a smaller diameter. The efficiency of a microemulsion as a lubricating agent also depends on
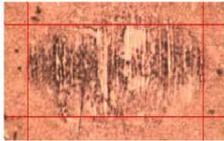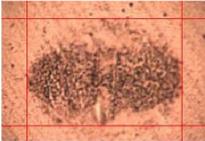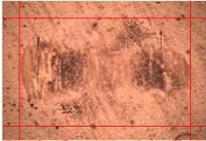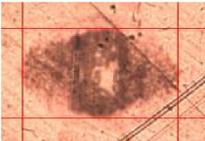
Systems	Wear scar diameter of ball after tribological tests		
Epoxidized soybean oil (ESO)	WSD = 176 μm		
Nonionic Sufactant	nEO - number of ethylene oxide units		
	4EO	6EO	9.5EO
NPnEO (nonylphenol)	WSD = 181 μm	WSD = 199 μm	WSD = 206 μm
Microemulsion Systems	nEO - number of ethylene oxide units		
	4EO	6EO	9.5EO
M1	WDS = 118 ± 3.555 μm	WSD = 123 ± 3.333 μm	WSD = 135 ± 3.111 μm
M2	WSD = 145 ± 2.516 μm	WSD = 201 ± 1.555 μm	WSD = 210 ± 2.666 μm
M3	WSD = 185 ± 2.888 μm	WSD = 208 ± 5.333 μm	WSD = 254 ± 4.888 μm

Figure 8. Images of wear scar on steel ball AISI 5210. The average scar diameter for epoxidized soybean oil (ESO), ethoxylated nonionic surfactants (NP4EO, NP6EO and NP9.5EO) and microemulsion systems (M1, M2 and M3).

the capacity of the hydrophobic chain of the surfactant to drag oil droplets to the surface of the metal, which are then microemulsioned with the surfactant and water in the form of spherical inverse micelles. The mechanism of this adsorption process can be attributed to electrostatic and hydrophobic interactions between the surfactant (anphiphillic nature) and metal surfaces. In this respect, the wettability of the oil and the formation of a stable tribofilm on the interface of the tribological pair can protect the surface from friction, high pressures and elevated temperatures[17,38].

In general, the differences in WSD values can be easily explained by the chemical nature of the substances (OSE, nonionic microemulsioned surfactants). OSE acted as an antiwear additive, obtaining a WSD of 176 μm, indicating the formation of a protective layer. With respect to the

nonionic surfactants, the WSD values were higher than those obtained by OSE, and rose with an increase in ethylene oxide molecules because of the higher polarity with a decline in hydrophobicity, compromising the affinity for the metal surface. In the case of microemulsions, point M1 (20% - Surfactants, 70% - ESO and 10% - Water) produced the lowest WSD values, highlighting the NP4EO surfactant (WSD of 118 μm), indicating that its high hydrophobicity (HBL – 8.9) stengthened OSE solubilization in the microemulsion, ensuring the formation of a protective film with greater stability on the metal surface.

3.2.3 Worn steel disc surface

Figure 9 shows the slippage direction, morphologies and distribution of the chemical elements of worn disk surfaces
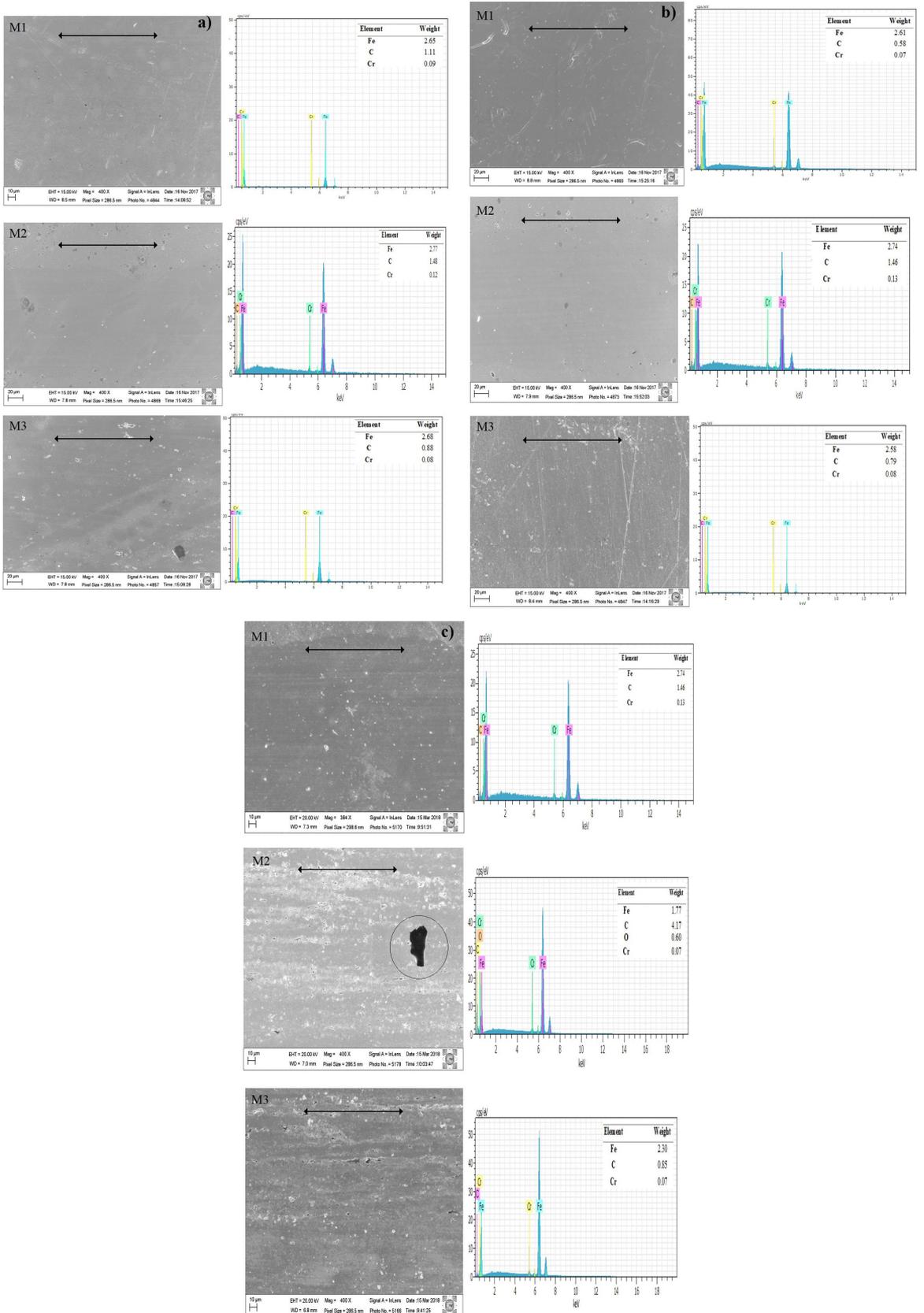
Figure 9. SEM/EDS analyses of worn surfaces lubricated with the microemulsion systems of different compositions (M1, M2 and M3) formulated with surfactants: (a) NP4EO, (b) NP6EO and (c) NP9.5EO.

analyzed by SEM equipped with electron dispersive spectroscopy (EDS). EDS enabled qualitative and semiquantitative chemical assessment, limited to the surface of the substance in order to estimate the concentration of the elements present. The tests carried out with low degrees of ethoxylation (Figure 9a) and (Figure 9b) and lower surfactant concentrations (20% and 30%) showed smooth surfaces with a slightly reduced wear diameter. Thus, it is suggested that more hydrophobic surfactants increase the wetting of steel surfaces, significantly improving lubrication[24,31,38]. Lubricant film formation likely fits from the polar part of the surfactant, which drags the oil droplet to the surface of the positively-charged metal. The adsorption process on the surface of the metal occurs spontaneously due to the amphiphilic characteristics of the surfactant, thereby guaranteeing the formation of a stable lubricating film capable of interacting strongly with the metallic surfaces, minimizing direct contact between these surfaces and attenuating the heat generated during contact[17]. On the other hand, the surface was well worn during the tests conducted with the more hydrophilic NP9.5EO surfactants (Figure 9c). The surface morphology of the disk exhibited more severe scratching during slippage contact, suggesting the occurrence of abrasive wear, confirmed by grooves and scratches on the wear track[39]. Figure 9c (M2) shows 0.6% oxygen, likely related to the dark stains present on the metal surface. Applying the energy-dispersive spectroscopy (EDS) technique made it possible to identify the chemical composition of worn surfaces (Figure 9). Based on the compositional profiles, the results demonstrated that the metallic surfaces contain chemical elements corresponding to the chemical surface of the surface analyzed, except for the presence of oxygen when the M2 microemulsion system formulated with the NP9.5EO surfactant was used (Figure 9c), suggesting the presence of the surfactant adsorbed to the surface.

4. Conclusion

This study demonstrated the evolution of the viscosity and tribological performance of microemulsions formulated with nonionic surfactants exhibiting different degrees of ethoxylation and epoxidized soybean oil. With respect to wettability, all the microemulsion systems had a contact angle above 90º, confirming that the formulations are compatible because of their spherical shape on the surface where they were deposited, characterizing low humectation capacity. The microemulsion systems were characterized as Newtonian fluids, showing classic viscosity behavior, that is, declining with a rise in temperature between 25 and 80 ºC. Additionally, the increase in the hydrophilic nature of the surfactant causes a rise in viscosity, highlighting surfactant NP9.5EO, with a viscosity of 315.13 cP, at a temperature of 25 °C. The coefficient of friction (COF) increases with a decline in the HLB (hydrophilic-lipophilic balance) of the surfactants. The physical and chemical properties of new microemulsion formulations demonstrated compatibility with commercial cutting fluids, especially microemulsion M1 formulated with surfactant NP4EO, due to its greater stability, lower viscosity, good friction reduction capacity and less wear on the metal surface. Analyses of flaws and the composition of worn surfaces obtained by SEM/EDS revealed that the most hydrophobic surfactants form a

more stable lubricating film, guaranteeing more effective adsorption between amphiphilic molecules and the metallic surface, reducing friction and wear. Thus, microemulsion systems may play the role of commercial cutting fluids from a technical and environmental standpoint.

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