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Formulation of Sustainable Water-Based Cutting Fluids with Polyol Esters for Machining Titanium Alloys

Elisabet Benedicto [1,2,*,†], Eva María Rubio [1], Laurent Aubouy [2] and María Ana Sáenz-Nuño [3]

1 Department of Manufacturing Engineering, Industrial Engineering School, Universidad Nacional de Educación a Distancia (UNED), St/Juan del Rosal 12, E28040 Madrid, Spain; erubio@ind.uned.es
2 Department of Surface Chemistry, Leitat Technological Center, C/Innovació 2, E08225 Terrassa, Spain; laubouy@leitat.org
3 Department of Manufacturing Engineering, Instituto de Investigación Tecnológica, IIT (Comillas Pontifical University), St/Alberto Aguilera 25, E28015 Madrid, Spain; msaenz@comillas.edu
* Correspondence: ebenedict6@alumno.uned.es; Tel.: +34-660-127-618
† Programa de Doctorado en Tecnologías Industriales.

Abstract: The machinability of titanium alloys still represents a demanding challenge and the development of new clean technologies to lubricate and cool is greatly needed. As a sustainable alternative to mineral oil, esters have shown excellent performance during machining. Herein, the aim of this work is to investigate the influence of esters' molecular structure in oil-in-water emulsions and their interaction with the surface to form a lubricating film, thus improving the efficiency of the cutting fluid. The lubricity performance and tool wear protection are studied through film formation analysis and the tapping process on Ti6Al4V. The results show that the lubricity performance is improved by increasing the formation of the organic film on the metal surface, which depends on the ester's molecular structure and its ability to adsorb on the surface against other surface-active compounds. Among the cutting fluids, noteworthy results are obtained using trimethylolpropane trioleate, which increases the lubricating film formation (containing 62% ester), thus improving the lubricity by up to 12% and reducing the torque increase due to tool wear by 26.8%. This work could be very useful for fields where often use difficult-to-machine materials—such as Ti6Al4V or γ-TiAl – which require large amounts of cutting fluids, since the formulation developed will allow the processes to be more efficient and sustainable.

Keywords: cutting fluid; esters; lubrication; tool wear; titanium alloys

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1. Introduction

Titanium alloys, particularly Ti6Al4V, are used extensively in the aeronautic, aerospace, automotive, chemical, and biomedical industries due to their unique mechanical properties (Table 1), such as high specific strength, hardness, corrosion resistance at high temperatures, and biocompatibility [1]. Despite these exceptional properties, Ti6Al4V is classified as a difficult-to-cut material because of its high chemical affinity, low thermal conductivity, and work hardening. The poor machinability of these alloys leads to excessive tool wear and catastrophic tool failure, resulting in decreased tool life and low productivity.

Due to the low conductivity of Ti6Al4V, the heat generated during machining cannot be dissipated throughout the workpiece and chips effectively. Therefore, the application of lubrication/cooling systems is extremely important. In most difficult-to-machine alloys, cutting fluids are employed in the machining process by providing lubrication under boundary friction at the workpiece-tool interface, or, more specifically, at the chip-tool interface, eliminating heat from the cutting zone and removing abrasive particles from the contact area [2]. The creation of the lubricating film depends on the media composition, particularly the absorption and chemisorption of polar or metal-active additives on the surface of the workpiece, while the coolant and cleaning capacity depends on the physical properties of the cutting fluids (e.g., specific heat capacity, vaporization heat, viscosity, and surface tension) [3]. Additionally, the cutting fluid protects the workpiece, the tool, the machine tool, and other metal surfaces from corrosion.

Table 1. The main properties of the Ti6Al4V alloy [4–6].

Property	Ti6Al4V
Density (g/cm^3)	4.42
Young's modulus at RT (GPa)	120 ± 10
Yield Strength (MPa)	800–1100
Tensile strength (MPa)	900–1200
Ductility at RT (%)	13–16
Creep limit (°C)	385
Oxidation limit (°C)	400
Hardness (HV10)	360 ± 30
Thermal conductivity (W·mK)	7.5–8.6

However, the use of conventional mineral oil-based cutting fluids has been thoroughly reviewed because of their environmental and health hazards [7]. Many investigations have aimed to improve the machinability of titanium alloys using sustainable lubrication/cooling systems. The advantages and drawbacks of the most common systems are summarized in Table 2.

Table 2. The advantages and drawbacks of sustainable lubrication/cooling systems used in titanium alloy machining [1,8,9].

Lubrication/ cooling systems	Advantages	Drawbacks
Dry cutting	No need for cutting fluid Easier chip collection for recycling Minimal environmental impact	High cutting temperature generation High tendency of workpiece microstructural alterations Reliable results for limited cutting parameters Poor tool life and surface finish Problematic chip evacuation
MQL	Reduction in cutting fluid Less costly method in comparison to other systems Good results in terms of cutting forces, tool wear, surface roughness are noted	Poor chip evacuation Poor cooling capacity Mist formation Very sensitive to MQL supply system
Cryogenic cooling	Eliminate the use of cutting fluid No need to clean the chips and improved chip breakability Promote improvements in surface integrity Improved tool life	Highly sensitive to tool–material pairs. The production cost of the cryogen is very high compared to cutting fluids Special Dewar is needed for cryogenic supply Overcooling lead to embrittlement of workpiece
Cold compressed air	Absence of cutting fluid Chips can be collected in dry form	Additional energy is required to produce compressed air
Sustainable cutting fluids	Can be totally biodegradable and renewable Less costly compared to cryogenic cooling Chip evacuation Effective removal of heat	Vegetable oils have low oxidation stability Formulation difficulties

A great improvement in the machining of titanium alloys is observed when different lubrication/cooling systems are combined. Noteworthy results were obtained with a minimum-quantity lubrication (MQL) and a cryogenic cooling hybrid system. The poor cooling capacity and lack of chip evacuation in the MQL system can be enhanced using compressed air or cryogenic cooling [10]. Moreover, vegetable oils or even recycled oils can be used as MQL fluid, thus increasing not only its efficiency but also reducing its environmental impact [11].

In order to ensure high levels of productivity whilst meeting the surface integrity of the machined parts, industrial companies still employ cutting fluids, especially in the most demanding operations. More than 2,000,000 m^3 of cutting fluids are used globally each year, the majority of which (85%) are petroleum-based [12]. Hence, these cutting fluids are non-renewable and toxic. Therefore, introducing new sustainable materials for the formulation of environmentally friendly cutting fluids as an alternative to mineral oil-based fluids is one of the main future trends in the machining of titanium alloys [10].

When selecting the type of cutting fluid to use, there are several aspects to consider, such as the machining operation, the workpiece material, the cutting tool material, the mode of application, the cutting fluid, and the environment friendliness [13]. The excellent heat dissipating properties of water and its cleaning capacity to remove chips of water-based cutting fluid, make it suitable for machining titanium alloys [14]. Moreover, the components of the cutting fluid and its physico-chemical properties determine the wetting and adsorption properties on the metal surface, which further affect the quality and performance of the machined surface. Chemical reactions can result in the loss of effective alloying elements thus damaging the surface [15].

Sustainable cutting fluids is a commonly used term for products that meet the following characteristics: good biodegradability; low eco-toxicity; risk of low contamination for water, air. and soil; low consumption; a long shelf life; recyclable; an ability to produce less waste; and an ability to promote energy saving [16]. There is a trend towards the use of vegetable or synthetic based oils and against the formulation of environmentally hazardous mineral oils [17], as well as the elimination or reduction in hazardous substances in the formulation of cutting fluids.

The most commonly used sustainable base fluids as alternatives to mineral bases are low molecular weight polyalphaolefins, polyalkylene glycols, vegetable oils, and synthetic esters [18]. This research addresses synthetic esters, which have attracted wider interest from both academic researchers and industrial users due to their high polarity and excellent lubricity in the boundary lubrication [19]. Synthetic esters perform well over a large temperature range, have a high viscosity index, possess a high lubricity, provide corrosion protection, and have a high oxidative stability [20]. In general, synthetic esters meet the requirements for aquatic biodegradability and toxicity, although they tend to be less readily biodegradable than vegetable oil-based lubricants.

There is a wide range of synthetic esters with properties that vary greatly depending on their chemical structure. A synthetic ester in its simplest form consists of an alcohol and a fatty acid. In lubricants, esters are usually made with two or more carboxylate groups. Due to the large number of different alcohols and fatty acids available for ester formulation, esters can be synthesized to suit a specific application [21]. In particular, this study is focused on polyol esters obtained from the reaction of fatty acids and polyhydric alcohols, also known as polyol, which are less susceptible to hydrolysis [22]. The fatty acids most commonly considered in the synthesis of polyol esters are caprylic acid, oleic acid, rapeseed oil, olive oil, animal fats, and palm oil. Examples of commonly used polyols are trimethylolpropane, neopentylglycol, and pentaerythritol [23].

The challenges in formulating water-based cutting fluids continue to increase as end users demand a better performance over longer periods of time and under harsh conditions [24]. Currently, vegetable oils and the synthetic esters obtained from them are emulsified as additives in water-based cutting fluids [25]. However, there are few studies that describe the lubrication/cooling results obtained in the machining of difficult-to-cut materials [26].

In contrast to oils, water has many unique properties due to its polarity, which makes aqueous lubrication much more complicated than traditional oil lubrication. Water-based lubrication mechanisms are not yet well known due to the diversity and complexity of aqueous solutions. In addition, some traditional lubrication theories are not applicable to aqueous lubrication due to the complex physical and chemical properties of water [27]. In the case of water-soluble cutting fluids, the effect of hydrolysis must be considered. Emulsions contain significant amounts of water, which can cause ester hydrolysis and variation of the chemical composition in the lubrication film, resulting in a completely different tribochemical mechanism between the water-based emulsion and the ester [28].

The aim of this work was to study the influence of the polyol ester on the development of a sustainable cutting fluid for titanium alloys. Oil-in-water (O/W) emulsions were formulated with several polyol esters and the ability to form a lubrication film was analyzed on Ti6Al4V strips. Finally, the lubricity performance was tested using a tapping process and evaluated with design of experiments (DOE) software.

2. Materials and Methods

2.1. Materials and Sample Preparation

To carry out the study, five cutting fluids were prepared by adding a mixture of nonionic and anionic surfactants to stabilize the O/W emulsions. Oleyl/cetyl propoxylated alcohol (BASF, Ludwigshafen, Germany) and oleth-10 carboxylic acid (Kao Chemicals GmbH, Emmerich, Germany) were mixed in deionized water at 0.8 mmol/l and 1.2 mmol/l, respectively. The mixture was adjusted to the recommended pH 9.2 with monoethanolamine.

Four commercial esters synthetized by Industrial Química Lasem (IQL, Castellgalí, Spain) were used to formulate the cutting fluids. All of them were commercialized as environmentally adapted lubricants [29] and were recommended for the formulation of lubricants. The esters were obtained from a reaction of oleic acid and the number of ramifications were varied, modifying the alcohol group. The esters were added in a concentration of 1.0 mmol/l and stirred in order to obtain a homogeneous mixture. The same molar concentration for all esters was used to easily compare the effect of the molecular structure of the polyol esters. The cutting fluids prepared were:

- without an ester;
- C18:1 × 1 using isopropyl oleate;
- C18:1 × 2 using neopentylglycol dioleate;
- C18:1 × 3 using trimethylolpropane trioleate;
- C18:1 × 4 using pentaerythrityl tetraoleate.

Moreover, the cutting fluids were prepared without the addition of anti-wear and extreme pressure chemical additives to prevent interference with the lubricity performance of the mixtures.

2.2. Determination of Lubricating Film on Ti6Al4V Surface

The lubricity performance is related to the capability to form a lubricating film on the surface, providing a layer that protects the surface from wear. The schematic diagram of the experimental setup is shown in Figure 1. Tests were conducted with Ti6Al4V (grade 5) panels (special metals and products, Spain) with dimensions of 17 × 75 × 0.8 mm^3, and the chemical composition shown in Table 3. Panels were immersed in the cutting fluid at room temperature and stirred for 10 min. The film formation was determined according to the method developed by Benedicto et al. [30]: 1) measuring the total organic carbon (*TOC*) with RC612 (Leco, St Joseph, MI, USA) to quantify the milligrams of carbon adhered to the Ti6Al4V panel and 2) calculating the ratio of the ester, analyzed by infrared reflection absorption spectroscopy (IRRAS) (Vertex 70 Bruker, Ettlingen, Germany)

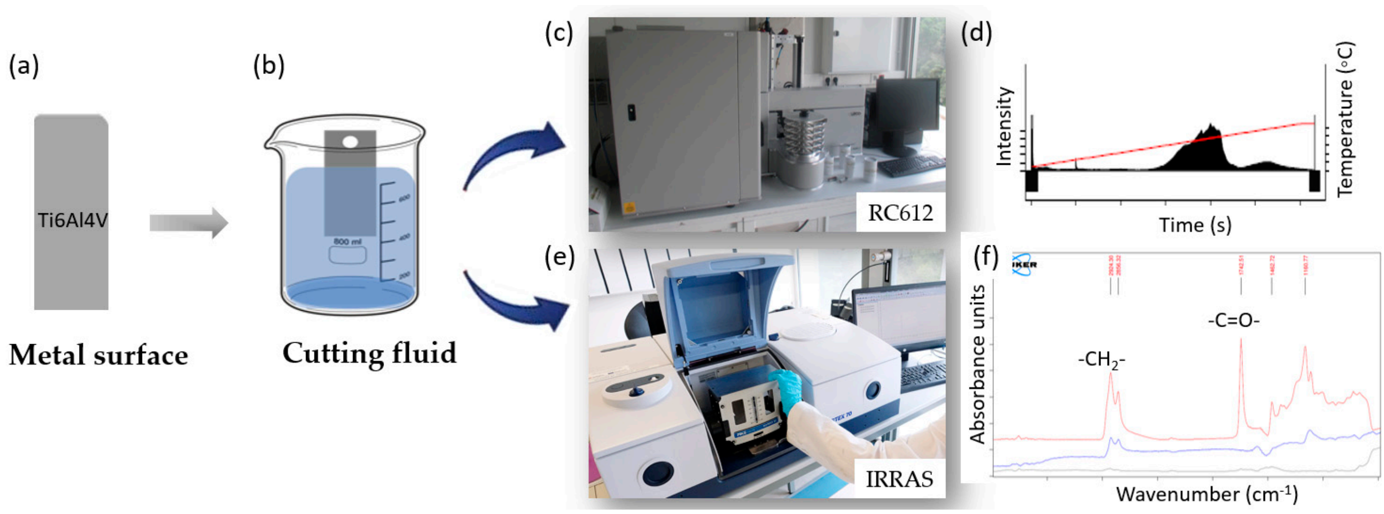


Figure 1. The experimental setup to study the lubrication film formed on the panel surface: (**a**)Ti6Al4V panel, (**b**) cutting fluid, (**c**) RC612 equipment, (**d**) the total carbon rate of evolution as a function of temperature, (**e**) IRRAS equipment and, (**f**) IRRAS spectra with C=O and CH_2 stretching vibration peaks.

Table 3. The chemical composition of Ti6Al4V (grade 5) (wt%).

Ti	Al	V	Fe	O
89.75%	6%	4%	0.25% max.	0.2% max

Following this method, four calibration curves were built for each ester, varying its concentration in the O/W emulsion and using a Fourier Transform infrared spectrophotometer (Iraffinity-1S Shimadzu, Nagoya, Japan). The regression line provided the ratio (*REO*) between the integrated absorbance under the C=O peak (1735–1750 cm^{-1}) and under the CH_2 stretching vibration peaks (2850–2925 cm^{-1}). The following regression equation allowed the percentage of ester (wt%) to be given a *REO* value from a spectrum and the correlation coefficient (R^2) measured the strength of the relationship between them:

$$\% \text{ ester} = A + B \cdot REO. \quad (1)$$

Finally, the amount of ester adhered to the Ti6Al4V panels was calculated by multiplying the percentage of ester by the milligrams of *TOC*, taking into account the molecular weight and the average of number of carbons on the organic layer for each cutting fluid.

2.3. Lubricity Performance of Polyol Ester Cutting Fluids

To gain a better understanding of the behavior of the polyol ester in water-based cutting fluids, a tapping torque test was conducted in Labtap G8 (Microtap, Munich, Germany). This cutting operation is highly sensitive to lubrication [31]. The material used for the machining was a Ti6Al4V with pre-drilled holes (Figure 2). A TTT_M4C coated tool, size M4 (0.7 mm pitch, 3.3 mm tapping diameter) with helical channels was used for each cutting fluid.

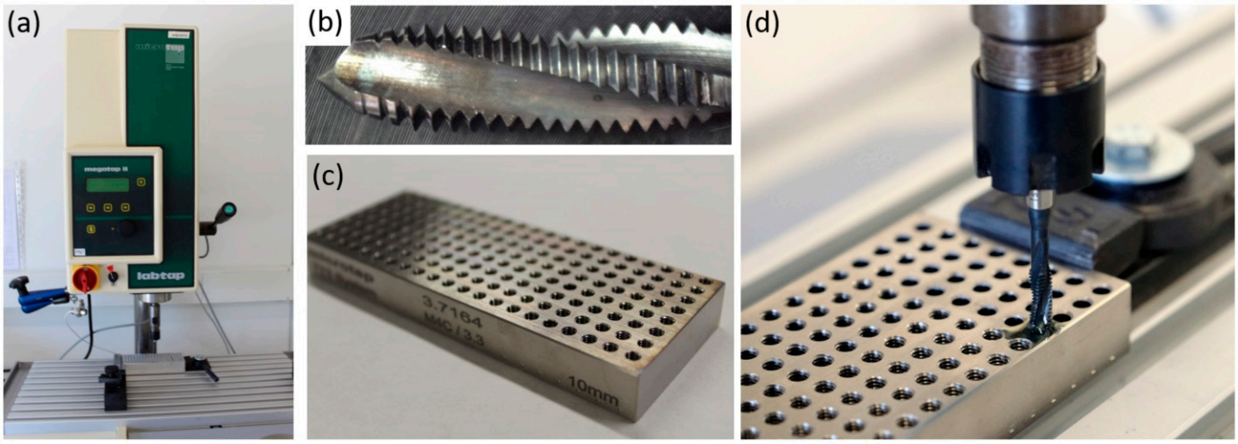


Figure 2. The experimental setup to study the lubricity performance using the Labtap G8: (**a**) Labtap G8 equipment, (**b**) TTT_M4C coated tool, (**c**) Ti6Al4V workpiece and, (**d**) cutting process.

The cutting fluid was poured in the holes to lubricate them during the tapping process at 300 rpm, with a 6 mm length of thread, as shown in Table 4 each tapping process was repeated 15 times or until the tool broke. Figure 3 shows the tapping procedure graphically where: (1) shows the beginning of the cut; (2) shows the tool penetrating the workpiece and the torque increasing due to the increasing contact surface between the workpiece and the tool; (3) shows the tool cutting with all its chamber teeth until the length's thread is achieved and (4) shows the beginning of the reversal of the spindle to bring the tool to the initial position [32]. Finally, the results were reported averaging the tapping torque values (N·cm) in the 1 mm to 6 mm range of cut.

Table 4. Cutting operation conditions.

Parameter	Value
Workpiece material	Ti6Al4V (grade 5) pre-drilled
Spindle speed (rpm)	300
Length of the thread (mm)	6
Hole diameter (mm)	3.3
Tapping tool	TTT_M4C coated tool. Size M4
Tap mode	Cutting

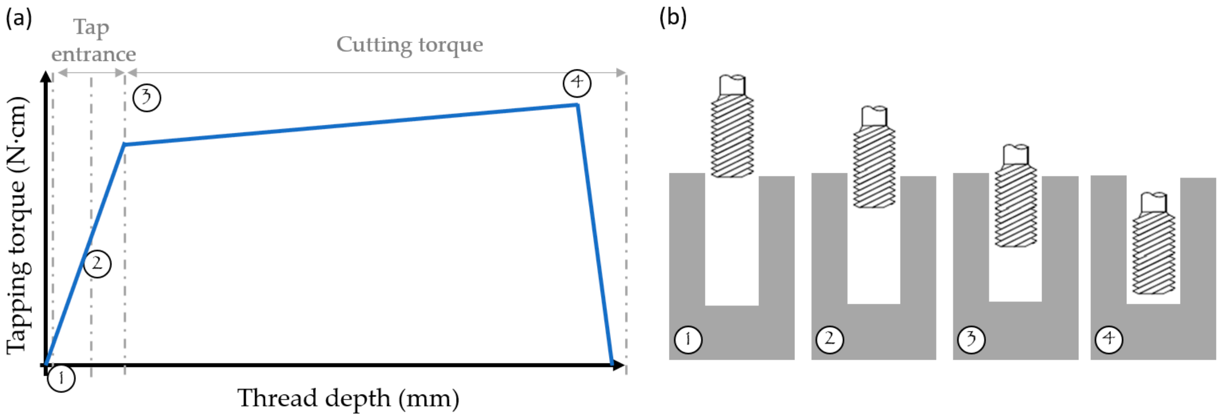


Figure 3. The tapping process: (**a**) graphical measurement of the tapping torque, (**b**) different positions of the tap during processing. (1) beginning of the cut, (2) tool penetrating the workpiece, (3) complete chamber teeth and (4) beginning of the reversal of the spindle.

3. Results and Discussion

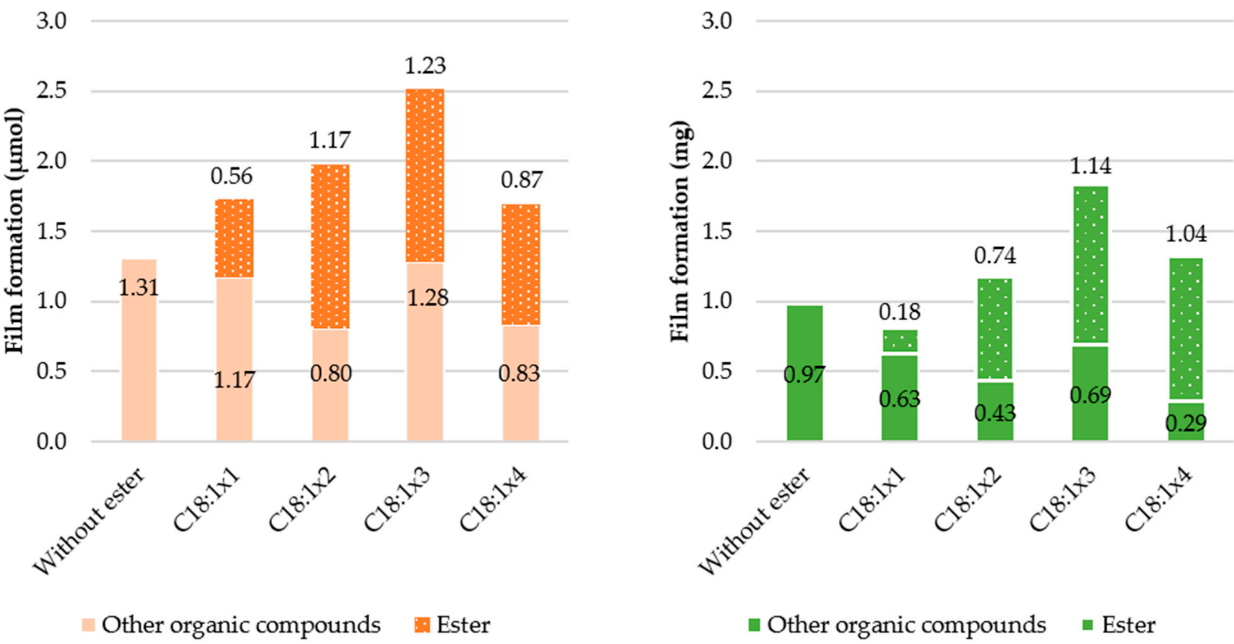
3.1. Film Formation on Ti6Al4V

The formation of the lubrication layer was calculated according to the equations of the regression line abstracted from the calibration curve of each polyol ester cutting fluid under study (Table 5.). The *REO* values were calculated with the IRRAS spectra on the Ti6Al4V panels and the total organic matter adhered to the surface, allowing the quantification of the lubrication layer formation.

Table 5. The *REO*, *TOC*, and equations of the regression line results of the cutting fluid formulated with polyol esters.

MWF	*REO*	*TOC* (mg C)	Equations of the Regression Line % ester = *A* + *REO* · *B*			% ester (w/w)	Organic Matter (µmol)	Ester (µmol)
			A	B	R^2			
C18:1 × 1	0.074	0.557	1.523	284.966	1.000	22.564	1.17	0.56
C18:1 × 2	0.219	0.860	2.077	279.079	0.999	63.166	0.80	1.17
C18:1 × 3	0.231	1.344	2.403	259.594	0.995	62.481	1.28	1.23
C18:1 × 4	0.304	1.200	2.474	250.050	0.999	78.408	0.83	0.87

Figure 4 shows the results of the organic film formed on the Ti6Al4V surface and the corresponding amount of ester after the panel was dipped in the O/W emulsions. The addition of esters in the cutting fluid resulted in lubrication layer growth. The ability to increase the film formation can be attributed to the stronger adsorption of polar functional groups on the metal surface. The molecular structure of such esters has a clear influence on the layer formed. Noteworthy results were obtained with C18:1 × 3. When the strip was dipped in the trimethylolpropane trioleate emulsion, a higher amount of organic matter was adhered, including both ester and surfactants.



(**a**) (**b**)

Figure 4. The film formation on the metal strips after the immersion of the panels in the cutting fluid: (**a**) in micromoles and (**b**) in milligrams.

At the same time, the presence of the ester interfered with the ability of other additives to attach to the metal surface. The results suggest that there is an adsorption competition on the surface between the surfactant and the ester molecules. The large molecular volume and polarity of pentaerythrityl tetraoleate prevents other molecules from being deposited on the metal, reducing the total organic matter. Therefore, it can be considered that the molecular structure of an ester in O/W emulsions has a substantial influence on its ability to form a lubricating film and on its conformation. The influence of the physico–chemical properties and the chemical composition, such as the branching structure and the polar functional groups on the film thickness has been observed by several authors [33], but unlike this study, they used neat esters.

When the Ti6Al4V strip was treated with C18:1 × 1 cutting fluid, the amount of ester that adhered to the surface was lower. This result can be attributed to the high stability of oil droplets in the emulsion, which are too stable to form a film. This relation between the oil droplet's stability and the film formation observed in this work was described by Ratoi-Salagean et al. [34], who correlated its incidence with a different emulsifier concentration.

3.2. Influence of Polyol Esters in the Lubricity of Cutting Fluids

To evaluate the lubricity of the cutting fluids, a tapping torque machine was used for experimental investigation. With this equipment, experiments are conducted by performing a tapping operation of a tool inside a hole with the cutting fluid and the torque is measured in situ. During the first tap, using deionized water as the cutting fluid, the tool welds in the Ti6Al4V workpiece. Comparing these results to the results from the cutting fluid without an ester, which showed that even after 15 taps the tool was not broken, it must be noticed that surfactants not only help to stabilize the emulsion, but they can also reduce the tapping torque. The lubricity properties of the surfactants observed in the present work were described by Benedicto et al. [35] who correlated their performance to the molecular structure of surfactants. Moreover, the addition of a polyol ester in the cutting fluid increases its lubricity and can reduce the tool wear by up to 37%.

The effect of the fatty acid ester in O/W emulsions on lubricity and wear is depicted in Figure 5 By comparing tapping torque values in the first tap, the ability of cutting fluids to lubricate can be studied. After the first tap, it is noted that the torque values increase with each tap due to tool wear.

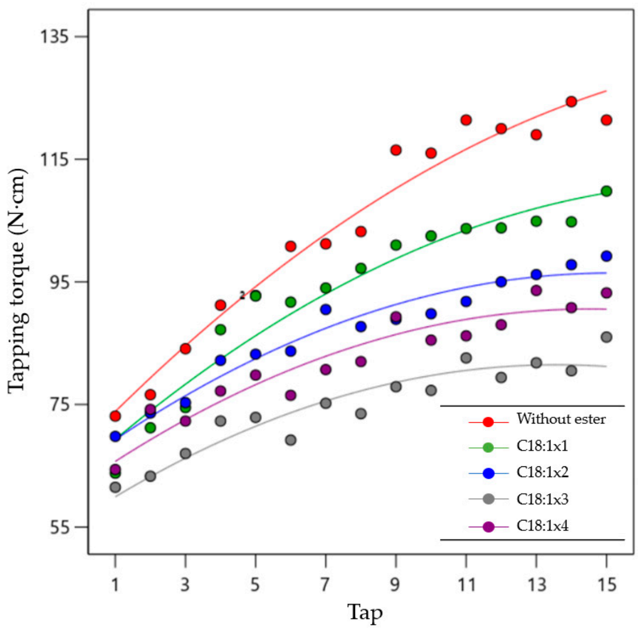


Figure 5. The effect of the addition of esters into an O/W emulsion on the tapping torque.

In order to analyze the effect of the cutting fluid on the tapping torque, a mathematical model was predicted by the design of experiments method (DOE). For each cutting fluid, a second order polynomial response has been fitted into the following equation:

$$Y = a + b \cdot X + c \cdot X^2, \quad (2)$$

where Y is the corresponding response (tapping torque) and X is the tap number.

The regression equations that have been obtained are collected in Table 6. The terms of these equations can be correlated with the lubricity performance (coefficient a) and the increase in tapping torque values in each consecutive tap due to the tool wear (coefficient b).

Table 6. The regression equations for a quadratic model.

Cutting Fluid	Regression Line
Without ester	$68.07 + 5.91\ X - 0.14\ X^2$
C18:1 × 1	$64.41 + 5.04\ X - 0.14\ X^2$
C18:1 × 2	$65.31 + 4.11\ X - 0.14\ X^2$
C18:1 × 3	$56.40 + 3.69\ X - 0.14\ X^2$
C18:1 × 4	$61.90 + 3.94\ X - 0.14\ X^2$

The analysis of variance (ANOVA) with a F-value of 202.82 implies that the model is significant and there is only a 0.01% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate the model terms are significant. Additionally, the verification of the model was analyzed by R2, whose value is 0.969, very near to 1.

The results show a positive correlation between the lubricity and the total organic matter adhered and the amount of ester in the film layer. The ester was adsorbed to the metal surface with the fatty acid hydrocarbon end facing away from the metal surface, thus allowing a monolayer film formation. This is in accordance with the lubrication mechanism of the castor oil-in-water fluid described by Ni et al. [36]. Therefore, the fatty acid chain provided a sliding surface that reduced friction and facilitated chip evacuation through the tool's channels.

The wear protection was improved by increasing the ester, which resulted in stronger adsorption on the metal surface [37]. Remarkable results were obtained using C18:1 × 3. This can be attributed to the higher lubrication film that was formed on the metal surface, thus increasing lubricity and protecting the tool from wear. On the contrary, from the esters tested, C18:1 × 1 had the highest tool wear, corresponding to the polyol ester with the lowest ability to adhere on the Ti6Al4V surface. C18:1 × 3 improved the lubricity performance by 12.4% and decreased the tapping torque of consecutive taps by reducing the tool wear by 26.8% compared to the cutting fluid C18:1 × 1.

In comparison with C18:1 × 2, a slight decrease in the tapping values was detected using the cutting fluid C18:1 × 4. The molecule packing of C18:1 × 4 improves the deposition of the ester on the surface (1.04 mg of pentaerythrityl tetraoleate), increasing the lubricity properties of the cutting fluid. In terms of tool wear, the lowest indices were achieved with C18:1 × 4 fluid.

The results in this work demonstrate considerable potential for the introduction of the polyol ester as an alternative to mineral oil in water-based cutting fluids. Moreover, the associated environmental and health benefits of polyol esters make them more attractive substitutes. The characteristics of esters, such as their high biodegradability and the reduction in fossil carbon sources, reduces their contribution to global warming compared to mineral oil by approximately four times [38].

4. Conclusions

This study provides an evaluation of the influence of polyol esters in oil-in-water (O/W) emulsions on titanium alloys to overcome the challenges in formulating sustainable water-based cutting fluids. The emulsions were formulated by adding polyol esters with different molecular structures and surfactants to stabilize the O/W emulsion. The film formation on the surface and the tapping torque were measured to identify the factors that have a significant effect on lubricity performance.

Based on the results of the present experimental and analytical investigations, the following conclusions can be drawn:

- The molecular structure of esters influences the amount of the ester that adheres to the surface forming a lubricant film, which protects the tool from wear. By the addition of 1 mmol/L of ester in the water-based cutting fluid, trimethylolpropane trioleate ester can double the amount of ester adhered on the panel surface compared to isopropyl oleate.
- There is an adsorption competition on the surface between the ester and other additives. The molecular structure of esters has a high impact on the conformation of the lubricant film which, in turn, also has an impact on the lubricity properties of the cutting fluid.
- The increase in ester in the lubrication film improves the tribological performance and prolongs the tool life. The addition of a polyol ester in the cutting fluid increases the lubricity by up to 17% and can reduce the tool wear by up to 37%.
- From the polyol esters under study, C18:1 × 3 is preferred as a water-based cutting fluid for machining titanium alloys. It can double the amount of lubrication film formed compared to the rest of the cutting fluids. The best lubricity results were obtained with C18:1 × 3. In terms of tool wear, the lowest rate was achieved with the trimethylolpropane trioleate O/W emulsion.

This study may be used to develop new sustainable and environmentally friendly cutting fluids for titanium alloys to replace conventional mineral oil water-based cutting fluids. However, further work needs to be conducted to investigate the industrial potential of these cutting fluids for titanium alloys, comparing them with other lubrication and cooling systems, such as cryogenic cooling.

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