

Estudio Del Poder Lubricante De Mono Di Tri Acetil Glicerol Aditivados Con Nanopartículas De Oxido De Zinc

Study Of The Lubricant Power Of Mono Di Tri Acetil Glycerols Additivated With Zinc Oxide Nanoparticles

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Arnoldo Emilio Delgado-Tobón 

Universidad Militar Nueva Granada. Bogotá, (Colombia)
arnoldo.delgado@unimilitar.edu.co

Esperanza Rodríguez-Carmona 

Universidad Militar Nueva Granada. Bogotá, (Colombia)
esperanza.rodriguez@unimilitar.edu.co

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Resumen

Introducción: Mono, di, tri acetil glicerol fueron obtenidos por esterificación de glicerina grado técnico con ácido acético en presencia de resina de intercambio iónico a escala laboratorio. Se empleó tolueno como agente de arrastre. La mezcla de acetil glicerol fue aditivada con nanopartículas de óxido de zinc aplicando dispersión por ultrasonido, se ensayaron concentraciones equivalentes a 0.05; 0.1; 0.15; 0.2% en peso. Las dispersiones se sometieron a ensayo tribológicos de cuatro bolas. Se valoró el comportamiento lubricante en condiciones de baja carga por medio de la prueba de Desgaste Preventivo, con medición del diámetro de huella y el coeficiente de fricción. La morfología de las huellas fue analizada usando microscopía de barrido electrónico. El desempeño de las dispersiones en condiciones de lubricación a Presión Extrema fue evaluado mediante la cuantificación del punto de soldadura. Los resultados arrojados de la experimentación indican que mono, di, tri, acetil glicerol requieren de la adición de nanopartículas metálicas para mejorar su desempeño tribológico con la finalidad de usarlos en formulaciones de biolubricantes.

Objetivo: Estudiar el comportamiento de mono, di, tri acetil glicerol MDTAG desde en términos de la tribología, mezclándolo con nanopartículas para mejorar el poder lubricante.

Metodología: Las dispersiones fueron sometidas a ensayos de tribología cuatro bolas. Se evaluó el comportamiento lubricante en condiciones de baja carga aplicando la prueba de Desgaste Preventivo, se midió el diámetro de huella y el coeficiente de fricción.

Resultados: Los resultados arrojados de la experimentación indican que mono, di, tri, acetil glicerol requieren de la adición de nanopartículas metálicas para mejorar su desempeño tribológico con la finalidad de usarlos en formulaciones de biolubricantes.

Conclusiones: La mezcla de mono, di, tri acetil glicerol con la adición de nanopartículas de óxido de zinc permite utilizarlas posiblemente como aditivos en bases biolubricantes.

Palabras clave

Acetilación, mono di tri acetil glicerol, nanopartículas, tribología.

Abstract

Introduction: Mono, di, tri acetyl glycerols were obtained by esterification of technical grade glycerin with acetic acid in the presence of ion exchange resin on a laboratory scale. Toluene was used as a trawling agent. The mixture of acetyl glycerols was added with zinc oxide nanoparticles by applying ultrasound dispersion; concentrations equivalent to 0.05 were tested; 0.1; 0.15; 0.2% by weight. The dispersions were subjected to four-ball tribological tests. The lubricating behavior under low load conditions was assessed through the Preventive Wear test, with measurement of the footprint diameter and the friction coefficient. The morphology of the prints was analyzed using scanning electron microscopy. The performance of the dispersions under Extreme Pressure lubrication conditions was evaluated by quantifying the welding point. The results obtained from the experimentation indicate that mono, di, tri acetyl glycerols require the addition of metal nanoparticles to improve their tribological performance with the purpose of using them in biolubricant formulations.

Objective: study the behavior of mono, di, tri acetyl glycerols MDTAG in terms of tribology, mixing it with nanoparticles to improve the lubricating power.

Method: The dispersions were subjected to four-ball tribology tests. The lubricating behavior was evaluated under low load conditions by applying the Preventive Wear test, the footprint diameter and the friction coefficient were measured.

Results: The results obtained from the experimentation indicate that mono, di, tri acetyl glycerols require the addition of metal nanoparticles to improve their tribological performance with the purpose of using them in biolubricant formulations.

Conclusions: The mixture of mono, di, tri acetyl glycerols with the addition of zinc oxide nanoparticles allows them to possibly be used as additives in biolubricant bases.

Keywords

acetylation, monodi triacetyl glycerol, nanoparticles, tribology



INTRODUCTION

Various routes have been proposed to valorize the glycerin generated as a by-product of the biodiesel industry. There is an excess of technical grade glycerin which cannot be used as a raw material or additive to make food, pharmaceutical and cosmetic products because it does not have the required specifications (USP reference). Several studies emphasize that the cost to purify crude glycerin until it reaches a pharmaceutical grade is very high compared to that required to synthesize it, due to the complex processes required to eliminate undesirable traces of methanol, salts, fatty acids, soaps and other substances [1], [2], [3]. Actually, technical grade glycerin is used as a chemical precursor for the production of 1,3-propanediol, succinic acid, carbonated glycerin, acetins and biopolymers, among other products [3], [4].

An alternative use that has been widely studied consists of the chemical modification of glycerin with acetic acid or anhydride to produce mixtures of mono, di, tri acetyl glycerols (MDTAG). The reaction is verified using a heterogeneous catalyst, the most used industrially is an ion exchange resin [5], [6], the resins called Amberlyst®15 stand out commercially, Amberlyst®35. The glycerol/acetic acid molar ratio and the type of catalyst influence the selectivity of the reaction, while the reaction time and temperature influence the progress of the reaction (glycerol conversion). For example, a molar ratio of 1/9 of glycerol/a. acetic acid produces tri acetyl glycerol (TAG) in an amount greater than 45% with respect to mono acetyl glycerol (MAG) and di acetyl glycerol (DAG) [7], [8]. MDTAG are also called acetins (mono, di, tri acetins).

MAG and DAG are used for cryogenic applications and also as oxygenated additives for fuels (biodiesel, gasoline). TAG synthesized from glycerol USP is used in food, cosmetic and pharmaceutical industries. TAG obtained from technical grade glycerol is used as an additive in plastics [9].

Some physical characteristics that MDTAG have, are low melting point (-3°C to -30 °C) and high boiling point (258-280 °C) make them attractive to study as possible additives to improve the low temperature performance of biolubricants made from vegetable oils and their derivatives. However, there are not enough studies to quantify the lubricating capacity of MDTAG.

Therefore, in this research it is intended to study the behavior of MDTAG from the point of view of Tribology, for this purpose, MDTAG dispersions with nanoparticles will be prepared in order to improve their lubricating power, so that the addition of MDTAG dispersions in lubricant bases of vegetable origin improves the performance at low temperatures without detriment to the lubricating properties.

The scope of this research article is limited to the tribological characterization of MDTAG dispersions with nanoparticles.

Nanoparticles (Nps) have gained acceptance to improve the lubricating properties of oils, several studies indicate that Nps of Cu, CuO, Fe, Ni, TiO₂, Fe₂O₃, FeO, CuO, Cu₂O, Al₂O₃, Mo, Ti, MgO, MoS₂ and ZnO, reduce the coefficient of friction and improve the antiwear behavior and antiwear of biolubricants [10], [11], [12]. Nps are considered as candidates to replace the classic antiwear and extreme pressure additives which contain sulfur and phosphorus and are highly harmful to human health and the environment due to toxicity [13], [14] [15].

In this study, MDTAG will be synthesized from technical grade glycerin. Then, dispersions of MDTAG with zinc oxide nanoparticles (NpsZnO) will be prepared, which will be characterized by means of Preventive Wear and Extreme Pressure tests in a four-ball tribometer.

MATERIALS AND METHODS

Materials

Technical grade glycerin (97.5% purity), glacial acetic acid (98% purity) and the drag agent: toluene (99% purity) were purchased from El Alquimista® (Colombia). Catalyst for the acetylation reaction: Amberlyst15® ion exchange resin was purchased from Sigma Aldrich® (USA). Zinc oxide nanoparticles (NpsZnO) with average diameter of 50 nm were supplied by Anhui Elite® Industrial Co. Ltd. (China).

Methods

1. MDTAG synthesis

The process was carried out in a 500 cm³ glass reactor with three ports, equipped with a heating mantle and magnetic stirring, mineral oil thermal bath, thermometer, vigreux fractionation tower, condenser with cooling water, dean stark accessory, it was used to continuously remove the water produced during the progress of the reaction, as shown in Fig 1. In the ball, 30 g of glycerin glycerol were mixed with 117.5 g of acetic acid, then 180 g of toluene were added. When the reaction mixture reached a temperature equal to 95 °C, 2.5 grams of Amberlyst®15 were added to start the reaction, which lasted up to four hours, the temperature slowly rose to a maximum of 110 °C. The product: MDTAG was washed with deionized water and then subjected to roto-evaporated to remove traces of moisture and acetic acid.

2. Preparation of MDTAG/NpsZnO dispersions

The ultrasound dispersion technique is primarily used to disperse nanoparticles in a liquid medium [16], [17]. Dispersions were prepared with the following concentrations of NpsZnO: 0.05; 0.1; 0.15; and 2.0% by weight.

A TOPT®500 ultrasound dispersion equipment manufactured by Toption® Instrument Co. Ltd (China) equipped with a transducer with a diameter equal to 6 mm was used.

Volumes of 60 cm³ with MDTAG + NpsZnO were subjected to dispersion according to the parameters: output power 500 W; frequency:20kHz; total sonication time 10 minutes, ON/OFF pulse: 3/2 (seconds).



Fig 1. Assembly for the synthesis of MDTAG.
Source: Authors

3. Preventive Wear Test (PW)

The measurement of the lubricating capacity of the MDTAG/NpsZnO dispersions under low load conditions it was performed in a four ball tribometer applying the ASTM D4172-94 standard. The dispersion sample was poured into a glass containing the spheres, then the accessory was placed in the equipment. Test conditions: dispersion temperature 75 °C, rotation speed: 1200 rpm, load: 147 Newton, time: 60 minutes. The lubricating capacity was evaluated by measuring the average tread diameter (DPH) of the spheres and the coefficient

of friction (f). AISI 52100 chromium alloy steel spheres were used, with a diameter of 12.7 mm and a hardness of 60–66 HRC.

4. Extreme Pressure (EP) Test

With this test, the lubrication capacity of the dispersions under high load conditions was determined. The ASTM D2783-03 Standard was applied using the four ball tribometer. Test parameters: variable load, rotation speed 1760 rpm, time 10 seconds, initial temperature 23°C. The welding point (load at which the spheres break) was determined. Spheres of the same reference to those used in the PW test were used.

5. Scanning Electron Microscopy (SEM)

The morphology of the wear tread of the spheres subjected to the PW test was analyzed by SEM. A JEOL® JCM-5000 NeoScope™ equipment was used. Images were taken with 15 kilowatt accelerating voltage and 800x magnification.

DISCUSSION OF RESULTS

Fig 2 shows DPH and coefficient of friction as a function of concentration (wt%) of NpsZnO dispersed in MDTAG. The larger the tread diameter, the greater the wear and therefore the lower the oil's ability to lubricate under low stress conditions.

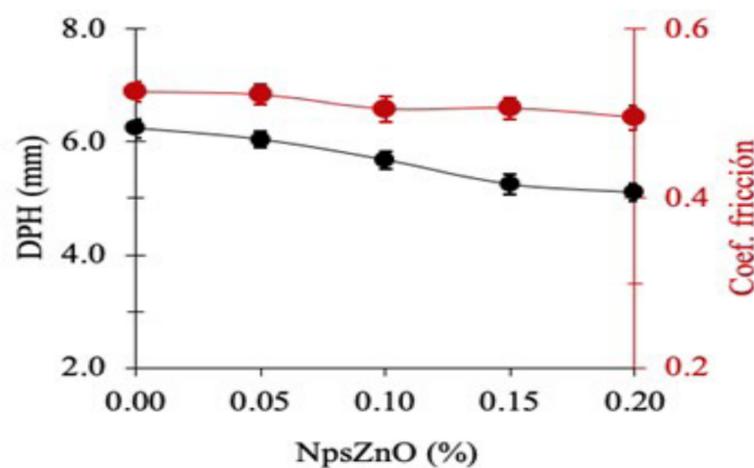


Fig 2. PW assay: DPH and f vs % NpsZnO dispersed in MDTAG.
Source: Authors

The MDTAG sample without NpsZn presented the lowest lubricating power (DPH: 6.24 mm). The addition of Nps slightly improved the lubricating performance of MDTAG. This result was expected because Nps of metal oxides smaller than 100 nm have been successfully tested as anti-wear agents in biolubricants, [13], [18], [19], [20]. Several studies indicate that Nps are deposited on surfaces and form a protective tribofilm [21], [22], [23].

In this investigation, a slight improvement in the lubricating performance of the dispersions was observed from NpsZnO concentrations above 0.1%. There were increases of 17.6% and 21.9% of the lubricating capacity for the MDTAG dispersions prepared with 0.15 and 0.20% of NpsZn respectively with respect to the MDTAG without Nps. Comparing the dispersions formulated with 0.15 and 0.20% Nps, no significant difference in DPH was observed.

However, the DPH values reported in this research are high, which means that the lubricating power of MDTAG in Preventive Wear conditions is lower when compared to mineral oil without additives and sesame oil [24].

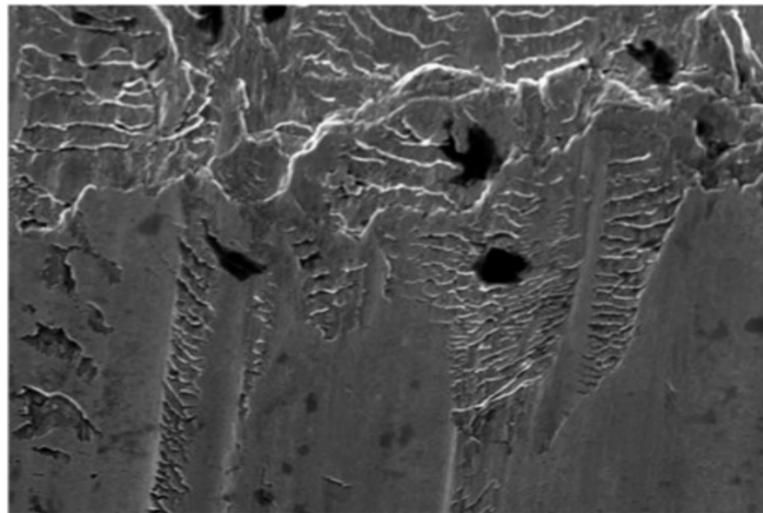


Fig 3. SEM 800x: DPH of MDTAG without NpsZnO.
Source: Authors

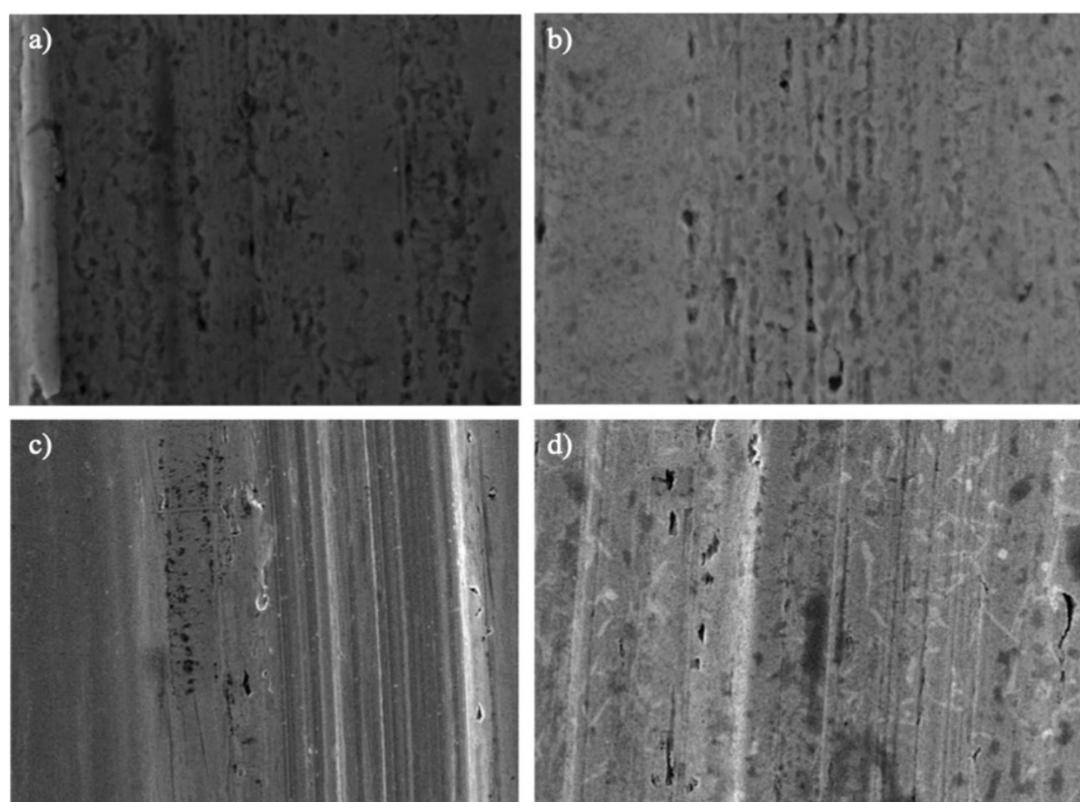


Fig 4. SEM 800x. DPH of MDTAG/NpsZnO: a) 0.05%; b) 0.01%; c) 0.15%; d) 0.020%.
Source: Authors

In Fig 3 and Fig 4 show the SEM images of the tracks generated in the DP test for each of the dispersions. When comparing the images, aggressive wear (high roughness) is observed for the MDTAG dispersion without nanoparticles (see Fig 3), this corroborates the poor lubricating performance of MDTAG. A change in the morphology of the tracks corresponding to the MDTAG/Nps-ZnO dispersions was observed. The surface of the tracks presented less roughness and more homogeneous morphology in the dispersions that have 0.15-0.20% of NpsZnO (Fig 4c-d), vertical lines are observed indicating a possible alignment of Nps.

The coefficient of friction reported in all the tests was high, in addition, it was not observed a significant decrease of the same when adding Nps. Contrary behavior expected. Some studies show a decrease in the coefficient of friction in oils added with nanoparticles [21], [22], [23].

Extreme Pressure of dispersions MDTAG/NpsZnO

The EP test measures the performance of lubricants under friction conditions supporting high loads. In a real situation, the test is related to oils that lubricate bearing materials, transmission chains, for example. Fig 5 and Fig 6 show the performance of MNDTAG/NpsZnO vs the Extreme Pressure test.

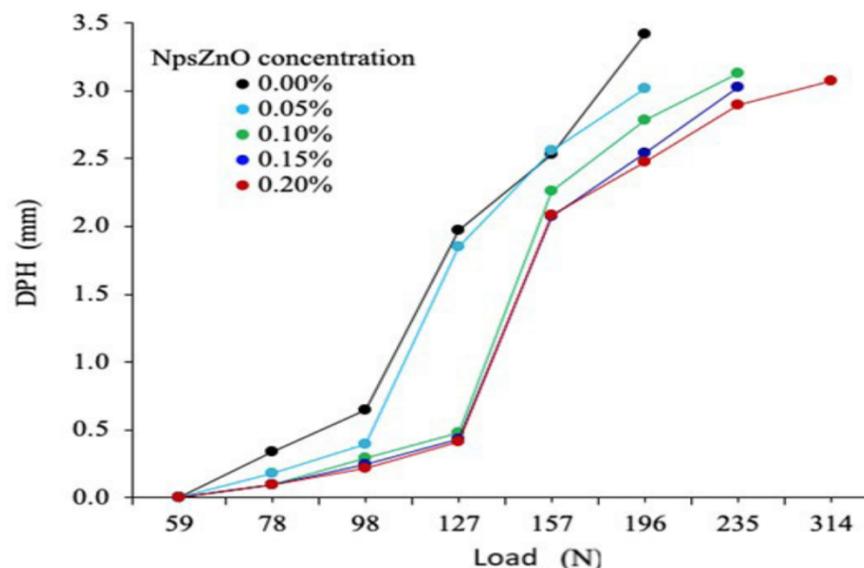


Fig 5. Extreme Pressure of MDTAG/NpsZnO dispersions vs applied load. Source: Authors

Weld point (WP) is the load at which the balls collapse. If the WP occurs at higher loads, it means that the oil has better performance in Extreme Pressure conditions. MDTAG at 0% and 0.05% of NpsZnO showed poor performance with WP= 196N. MDTAG is considered to have no lubricating ability under extreme pressure conditions. Nps concentrations equivalent to 0.1-0.15% slightly improved their behavior, being the dispersion formulated with 0.2% NpsZnO the one that showed the highest performance, with WP equal to 314 N.

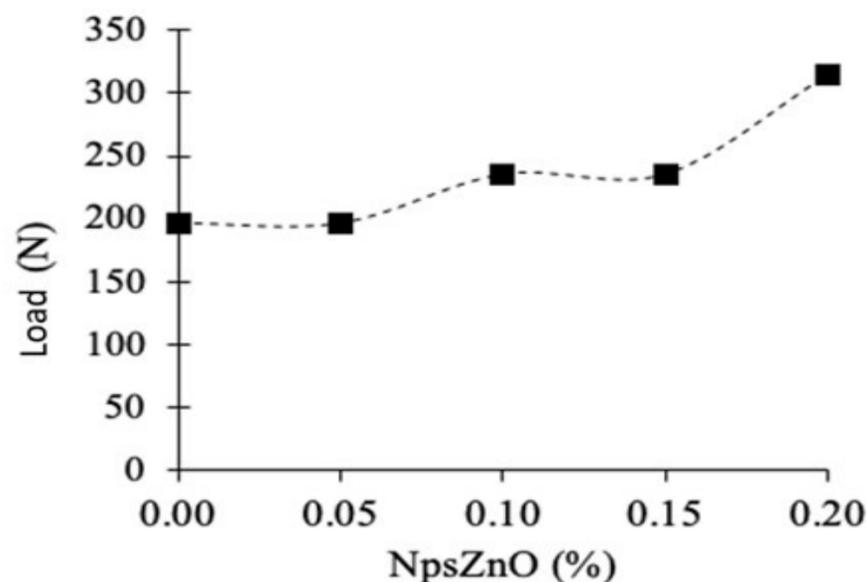


Fig 6. Weld point of dispersions vs the % of NpsZnO. Source: Authors

Nanoparticles allow to improve the lubricating capacity of acetyl glycerols, this result is consistent with several investigations that consider metallic nanoparticles as extreme pressure agents for the lubricant industry [21], [22], [20], [23].

CONCLUSIONS

The incorporation of zinc oxide nanoparticles to the mixture of mono, di, tri acetyl glycerols obtained by technical glycerin acetylation reaction, showed that at concentrations close to 0.2% slightly improved lubricating power under low load (Preventive Wear) and Extreme Pressure conditions. mono, di, tri acetyl glycerols without nanoparticles presented low lubricating power, however the addition of zinc oxide nanoparticles allows them to be possibly used as additives in biolubricant bases to improve behavior at low temperatures without negatively affecting lubricating properties.

CRediT AUTHORSHIP CONTRIBUTION STATEMENT

A. Delgado-Tobón: Conceptualization, Research, Methodology, Data Curation, Writing – Review & Editing. E. Rodríguez-Carmona: Research, Data Curation, Writing – Review & Editing.

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AUTHORS

Arnoldo Emilio Delgado Tobón, Performed his undergraduate studies in Mechanical Engineering in the Universidad Nacional of Colombia (UNAL) and MSc in Mechanical Engineering from the Universidad de Los Andes, Bogotá, Colombia. He is an Associate Professor on Mechatronic Engineering Program at Universidad Militar Nueva Granada, Bogotá. <https://orcid.org/0000-0002-8743-8958>

Esperanza Rodríguez Carmona, was born in Pereira (Colombia). She performed her undergraduate studies in Mechanical Engineering (1997) from the Universidad Tecnológica de Pereira (UTP). She is an Associate Professor on Industrial Engineering program at Universidad Militar Nueva Granada, Bogotá. <https://orcid.org/0000-0003-2915-6829>