

DEVELOPMENT OF HIGH PERFORMANCE LUBRICANT THROUGH THE COMPATIBILIZATION OF POLYALPHAOLEFIN, POLYUREA AND IRRADIATED POLYTETRAFLUOROETHYLENE

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ABSTRACT

High performance lubricants are essential for shipping and oil exploration industries for working under severe conditions of temperature, pressure and contamination. Polytetrafluoroethylene (PTFE) is widely used as a lubricating additive in greases for presenting the lowest known coefficient of friction, is commercially found irradiated in air, by this way can be grinded and oxygenated terminal groups can be formed. PTFE processed by ionizing radiation with 4 μ average particle size was supplied by Uniflon and compared with the ultraviolet-irradiated PTFE with the same average particle size, from Dupont. The characterization of functional properties by drop point, oil separation and four ball test was conducted with a polyurea base grease additive with both types of PTFE. The chemical characterization was done with Differential Scanning Calorimetry (DSC). The drop point and oil separation tests showed that the Uniflon irradiated PTFE improved the thermal resistance and stability of polyurea grease due to the greater presence of the end groups increase the compatibility of the additive with the fluid. Four ball tests showed that the grease with Uniflon irradiated PTFE also has a better antiwear and extreme pressure performance because of the greater polarity of the molecules improving the dispersion and anchoring of the PTFE in metal surface voids, reducing wear. The PTFE processed by ionizing radiation showed greater compatibility with polyurea grease and polyalphaolefin fluid and the grease functional characteristics met the requirements for a high performance lubricant.

1. INTRODUCTION

According to Carteiro and Moura (1998)^[2], the earliest manifestation of lubrication was found in Egypt in the tomb of RA-EM-KA, in 1700 BC, where a picture show a type of sled carrying a stone monument and a man is pouring a liquid (animal fat) to lubricate the slides of the sled, but a grease material was really found on the axis of a carriage buried in the tomb of Yuua Thuui dating around 1400 BC. The petroleum products began to be better explored, refined and applied only by the 18th century. Nowadays lubricants have a great importance for the industries, not only to keep the process running continuously, but also to avoid excessive maintenance, machine breakdown, excessive costs, poorly finished and the waste of products.

The basic principle of lubrication is when a surface moves on to another surface causes a force opposing the movement, called the frictional force. The friction hampers movement, consumes energy without producing corresponding work and promotes wear. According to Souza^[1], the lubricant has to form a film between the parties in order to reduce friction to a minimum and avoid the problems arising such as excessive wear, poorly finished,

overheating, breakdown of equipments, including others. Lubricants can be liquid, semi-solid (greases) or in very specific cases, dry solids (powders).

The annual global grease manufacturing in 2005 was 250 million pounds, according to the National Lubricating Grease Institute (NLGI), broke the record in 2011 to nearly 1.1 billion pounds, highlighting the importance of new developments of more specific and cost-effective lubricants. According to studies by Carreteiro and Moura ^[2], greases are used where the oils are not effective in the face of its natural drain tendency, even being high viscous. The main greases advantages regarding oils are: sealing lubricated point, higher adhesion, longer usage life and use in inaccessible places. The main disadvantages according Pires ^[5], are the limitations at high speeds due to the high viscous, less resistance to oxidation and less cooling power. The main difference between the liquid and semi-solid lubricant, according to Carter and Belmiro ^[6], is that the grease has thickener.

Based on the Lubarsa ^[7] and Runge ^[8] datas, the thickener may be defined as a structure-modifying agent lubricating fluid promoting consistency. The consistency of the grease varies depending on the percentage and type of thickener used. The chemical nature and thickener concentration provides certain characteristics such as: drop point, structure, behavior in the presence of water and high temperature resistance. Thickeners are divided into two basic types: soap and non-soap. According Moteurs ^[4] non-soap thickeners are inorganic or organic compounds, which are insoluble in the lubricating fluid, however they are able to stabilize in the oil because of its porous surface structure. The most commonly non-soap thickeners used are polyurea (PUR), bentonites, silica and plastics such as polytetrafluoroethylene (PTFE) and polyethylene (PE). The polyureas are formed by reaction of isocyanates with amines, these reaction is very fast and do not require catalysis. The polyurea-thickened grease is widely used to lubricate electric motors, having high dielectric strength points or exposed to moisture and sea air, as it has excellent anti-corrosion characteristics.

Additives can also be added to grease, which according to Hissa ^[3] are compounds that give special properties to lubricants, absent or present in insufficient degree in pure oil. Some examples are: anti-wear, extreme pressure, lubricity and antioxidants additives. PTFE is widely used as a lubricity additive being the lowest friction coefficient already known material. In general it is irradiated in air to obtain smaller particles which can penetrate better in the surfaces pores, making them smoother, making the movement easier and to occur the formation of oxygenated terminal groups, increasing the compatibility of the polymer with fluids and metal surface. Some of the most common high performance greases are produced with synthetic base oils, with irradiated polytetrafluoroethylene (PTFE) and are thickened with polyurea.

2. MATERIALS AND METHODS

With the advancement of technology and the constant environmental concern, the lubricants market has been increasingly targeting specific products to better meet the special needs of each industrial process with minimum damage to the environment. Some processes need extremely resistant lubricants due to work under severe conditions such as high and low temperatures, extreme pressure and high abrasive or corrosion contamination, to meet these special procedures were developed the high-performance lubricants, usually formulated from

synthetic raw materials, in mostly part polymers, which have excellent lubricating characteristics and high thermal and mechanical resistance.

Polyalphaolefin is widely known as a synthetic fluid, has an excellent thermal property, antioxidant resistance and is a great lubricant, because of its inert chemical property can be used as a vehicle for a reaction to obtain a grease thickener. The soap based greases are the widely used, because it only works in normal conditions processes, doesn't handle severe conditions, the most common grease is lithium soap based, but non-soap greases are used when especial characteristics are required, the most known non-soap thickener is polyurea. It has especial characteristics as good anticorrosion property, excellent antiwear and great pumpability. For those reasons in this present study was used Polyalphaolefin as lubricant oil and Polyurea as thickener.

The polyurea of this study was obtained from the reaction of an aliphatic long chain monoamine (approximately 12 carbons), an aliphatic short chain diamine (less than 4 carbons) and an aromatic diisocyanate, using the polyalphaolefin as vehicle for the reaction. One third of the polyalphaolefin was maintained under heating ($\sim 60^{\circ}\text{C}$) and constant mixing, the reagents were added simultaneously, amines in a third and diisocyanate in the other third, resulting in a viscous and milky white mixture as following picture.



Figure 1: Polyurea grease obtained by reaction of long chain monoamine, short chain diamine and an aromatic diisocyanate.

To provide a greater lubricant characteristic to polyurea grease, was added Polytetrafluoroethylene (PTFE) as additive, because it is the solid with the lowest friction coefficient, is very inert, does not react with other additives, the only need is to improve its compatibility with other polymers.

The main factor about materials compatibility is the chemical affinity; some examples are polarity, electronegativity, organic function, size chains, atomic radius, number and types of branches, among others. In the case of polymers specifically, its molecular weight, its structure and its branches are crucial factors in determining compatibility with other polymer. Polymers, by having long chains and high saturation degree are more inert compared to other chemicals with smaller chains. What may come to interact in their chains are the halogens or oxygen atoms present. To make two polymers more compatible between themselves, in other

words, increase their attraction potential, we can modify branches, degree of saturation and the chain length, by this way their mixture became more stable.

The polymers used in greases must have affinity with the fluid and have a structure propitious to the absorption of same, in other words, the more porous the polymer surface is the more stable the mixture will be. The polyurea has oxygen atoms and polyalphaolefin has some unsaturated links those increase their polarity, but PTFE being that inert needs to be processed to improve its compatibility with the others polymers, as its chain is very resistant the PTFE needs to be processed by radiation.

The irradiation process is a widely known method and is used to modify polymers structures. When this radiation interacts with the polymer matrix, its energy is absorbed and species are activated, radicals are produced and start various chemical reactions near by, the molecular chains can propagate through the radical species that are generated inside and outside the film by radiation.

The effects of radiation on polymers are:

- 1) Crosslinking: arises when the polymer chains are interconnected and form a chain of crosslinks;
- 2) Decomposition: the result is a decrease in polymer molecular weight due to chains fission (break);
- 3) Grafting: occurs when a new monomer is polymerized and grafted onto the polymer chain.

When the monomers are irradiated, their polymerization can also be initiated.

The most expected results from radiation in PTFE are the decrease of its chain and the occurrence of oxygenated terminal groups, normally peroxides and carboxylic acids. These terminal groups increase the anchorage of the PTFE molecules on the lubricated surface.

On lubricants market is easy to find at least two types of irradiated PTFE, one virgin wherein its polymerization process is already scheduled for a particular size of chain and subsequently processed with ultraviolet and other coming from the recycling of machining wastes or unused materials, this in turn is already obtained with a certain degradation degree because of its various previous processes, this recycled PTFE is processed with ionizing radiation, which has a stronger degrading effect. In this study was tested the lubricating characteristics of both types of irradiated PTFE to determine the advantages of each one. Dupont company ceded the PTFE irradiated by ultraviolet with the trademark Zonyl MP 1100 and the PTFE processed by ionizing radiation was provided by Uniflon, with trademark Unilub L 400, both with 4 μ average particle size. Were also analyzed compatibility features with other polymers of polyurea grease.

2.1. Functional characterization

The polyurea grease drop point (ASTM D566) was determined putting a little amount of grease in a metallic capsule inside a glass tube positioned in a controlled heated silicon bath and observing the temperature that the polyurea grease drips for the first time. The oil separation (ASTM D6184) was determined by positioning a pre-determined amount of the grease in a metallic strainer into a glass, submitting the grease at 100°C for 30 hours and after

is determined the oil amount by weigh in the glass. The four ball test is processed in a specific machine that makes a metallic ball turns around over more 3 balls and after each 5 seconds a determined weigh is increased making pressure and is observed how many kilos the lubricant bears before the balls be welded (ASTM D2596), and to determine the wear characteristic (ASTM D2266), the weigh is fixed and the ball turns around over the others for 1 hour, after that the wear is measured in millimeters. Finally the grease penetration (consistency) was measured by the penetration of a determined metallic cone into the grease (ASTM D217), this measure is gave in tenth of millimeters.

2.2. Physical-chemical characterization

To study the structural differences between ultraviolet and ionizing irradiated PTFE, both polymers were submitted to Differential Scanning Calorimetry (DSC) test. The DSC curves were obtained with a DSC 822 Mettler-Toledo equipment under nitrogen atmosphere from 30 to 400°C, at 10°C m⁻¹. The equipment is allocated in CQMA, IPEN/CNEN-SP.

To calculate the W_c (crystalline percentage) was used the following formula:

$$W_c = (\Delta H_f / \Delta H_{f100}) \times 100$$

Where ΔH_f is the change in fusion enthalpy of the sample and ΔH_{f100} is the fusion enthalpy of a 100% crystalline polymer. For PTFE the ΔH_{f100} is 82,9.

3. RESULTS AND DISCUSSIONS

The polyurea grease with both types of irradiated PTFE was submitted to functional proprieties tests, those the values are described as following table 1.

Table 1: Functional properties of polyurea based grease compared with additive grease with both types of irradiated PTFE

Tests	Method	Polyurea	Polyurea with Unilub L400	Polyurea with Zonyl MP1100
Drop Point	ASTM D566	255°C	260°C	258°C
Oil Separation	ASTM D6184	1,87%	1,75%	1,83%
Four ball-Weld	ASTM D2596	160 kg	620 kg	315 kg
Four ball-Wear	ASTM D2266	0,448 mm	0,511 mm	0,475 mm
Unworked penetration	ASTM D217	278 mm/10	268 mm/10	270 mm/10
10.000x worked penetration	ASTM D217	300 mm/10	290 mm/10	295 mm/10

Analyzing functional properties in table 1, both PTFE have good compatibility with polyurea grease, the increase of drop point temperature indicates that polyalphaolefin fluid has a high viscosity index, not altering its viscosity significantly by varying the temperature, also show high compatibility with the thickener, which promotes high strength even at elevated temperatures, and can be safely applied to lubrication points subjected to temperatures up to 240°C. The presence of PTFE in the grease had a positive impact proved by being compatible with the thickener and fluid making the grease more stable at elevated temperatures also

show that the PTFE acts as a secondary thickener, maintaining the polialphaolefin in the system even at high temperature.

The decrease of oil separation shows the improvement of system stability when the grease is in rest, the migration of the oil to the surface makes the superior part of the grease be smoother than the inferior part, which promotes a difference of the thickness in the lubricating film being able to damage to the equipment. The penetration showed that the grease consistence is stable even during working, maintaining the lubricating film uniform; both PTFE improved those characteristics very similarly.

The most difference between irradiated PTFE is the resistance of the lubricating film when pressured during work, the four ball tests showed a greater resistance of the ionizing irradiated PTFE, this additive endured double pressure until the weld point, this result indicates that the ionizing irradiated PTFE particles have a better anchoring on the metal surface, this can be explained by the greater polarity and number of oxygenated terminal groups in the molecules, probably the molecules had a better dispersion and more attractive interaction strength with the metal surface even under pressure and shear. The four ball test to determinate wear showed a similar performance, both had a great result, what indicated that the difference is the anchoring under pressure and shear.

To determine the structural proprieties of both irradiated PTFE, they were submitted to DSC test that can help to discover the crystallinity of polymers. The values found are described as the table 2 below.

Table 2: DSC values for ultraviolet and ionizing irradiated PTFE

Sample	T_f (°C)	ΔH_f (J g ⁻¹)	W_c (%)
Ultraviolet irradiated PTFE	311	56	68
Ionizing irradiated PTFE	313	63	76

The polymers bear chain scission when irradiated below the melting temperature causing an increase in the alignment of the chains with an increase in its crystallinity and higher the fusion temperature become, so that based on DSC results is possible to observe that the ionizing irradiated PTFE has a greater crystalline value and an elevated fusion temperature than ultraviolet irradiated PTFE, reaffirming the fact that ionizing irradiated PTFE has a greater number of oxygenated terminal groups being more compatible with other polymers and has a better anchoring on metal surface.

Analyzing the functional proprieties is possible to observe how greater the lubricant grease becomes with PTFE additives, bearing more pressure under working with less wear and bearing more compatible with the metallic surface, anchoring better and being more stable in rest or under working. All these improved characteristics can also be explained through the DSC values those show the effects of irradiation in the polymers chain.

4. CONCLUSIONS

PTFE are a great lubricant additive and can be greater when irradiated. Ionizing radiation produced a greater number of oxygenated terminal groups, turned the PTFE structure lightly

more crystalline than the ultraviolet irradiated PTFE, being more suitable for PTFE grinding for the use in lubricants. The irradiated PTFE had a higher compatibility with other polymers and the PTFE processed by ionizing irradiated has a better dispersion and anchoring on the metal surface by the larger polarity of its molecules. Because of the functional properties, the grease with irradiated PTFE can be considered a high performance lubricating grease and the addition of irradiated PTFE makes a great difference, being extremely compatible with polyalphaolefin and polyurea, improving the thermal characteristics of the lubricating grease and providing greater stability to the system. A further study can show how much irradiated the PTFE can be until get its highest lubricating power.

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