

**INTERNATIONAL JOURNAL OF ADVANCES IN
PHARMACY, BIOLOGY AND CHEMISTRY****Research Article****EFFECT OF RECYCLED PLASTIC WASTE ON
RHEOLOGICAL MODIFICATION OF CALCIUM
GREASES****E. A. Ismail¹, R A. El-Adly¹, Modather F. Hussein², H. I. Al-Shafey¹.**¹Egyptian Petroleum Research Institute, Nasr city, Cairo, Egypt²Faculty of science, chemistry department Al-Azhar University.**ABSTRACT**

There is a growing interest on the development of new materials based on recycled polymers from plastics waste, since the use of such plastics represents a low-cost source of raw material. The aim of the present work is to prepare and evaluate calcium lubricating greases based on mineral oil and recycled high density polyethylene. On this way, the influence of recycled HDPE concentration on the rheological, thermal and mechanical properties of prepared greases was explored. The flow and viscoelastic properties of the prepared calcium greases with and without recycled HDPE have been studied by programmable Rheometer HADV-III ultra system. This system operates either in a steady rotation or in an oscillatory mode. Data reveals that, the flow behavior depends on a large extent of the contents of the recycled polymer. Mathematical models based on Herschel-Bulkley, Bingham and Casson equations were applied for fitting the experimental data. It was concluded that the values of both apparent viscosity and consistency index increases with recycled HDPE concentrations. Also, recycled HDPE was found to be an effective additive to modify the rheological properties of prepared calcium grease.

Keywords: Calcium lubricating grease, Flow behavior, Rheological modifier, Recycled polyethylene**1. INTRODUCTION**

Lubricating greases are generally highly structured colloidal dispersions, consisting of a thickener dispersed in mineral or synthetic oil. Fatty acid soaps of lithium, calcium, sodium, aluminium and barium are most commonly used as thickeners. These thickeners form an entanglement network, which traps the oil and confers the appropriate rheological and tribological behaviour to the grease^{1,2}. Grease lubrication is dependent on the base oil being released slowly and sufficiently under load and the delivery depends strongly on temperature³. Grease, by its nature, cannot dissipate heat by convection like circulating oil. Consequently, without the ability to transfer heat, excessive temperatures result in accelerated oxidation or carbonization, where grease hardens or forms a crust. The presence of these oxidation products in lubricating greases may lead to an increase in viscosity which might be detrimental to

the gel structure causing an adverse effect on lubrication^{4,5}.

In some cases, it is desirable to incorporate polymers into a grease formulation, such as polyisobutylene, styrene-butadiene copolymer, styrene-isoprene block-copolymers or ethylene-propylene copolymers. These usually play a significant role as additives in greases for modification of some performance characteristics such as dropping point, appearance, tackiness, water resistance and bleed⁶, all of these related to the ability to act as rheological properties modifiers^{7,8,9}. The selection of a suitable polymer as additive may offer added advantages; thus by proper matching of polymer, thickener and base oil, it should be possible to obtain an optimized formulation with maximum performance characteristics⁶. These polymeric additives can be usually added at the final stage of grease manufacturing process. The

rheological modification induced by polymeric additives affects the viscoelasticity of lubricating greases, which is important for preventing loss of lubricant or reinforcing sealing properties, but also the flow properties under working conditions^{10,11}. The use of recycled polymers is continuously increasing; the problem of post-consumer recycling of these materials has become an important issue for economic and environmental reason^{12,13,14}.

Accordingly, the aim of the present work is to prepare and evaluate calcium lubricating greases based on heavy base mineral oil and recycled high density polyethylene. On this way, the influence of recycled HDPE concentration on the rheological, thermal and mechanical properties of prepared greases was investigated

2. MATERIALS AND METHODS

2.1. Materials:

Stearic acid, rosin (colophony) and calcium hydroxide were kindly supplied by Morgan Co. Heavy base oil was kindly supplied by Suez oil Processing Company. The recycled HDPE was obtained from local company of recycled waste polymers.

2.4. Grease Preparation:

Four grades of calcium grease designated G₀%, G₂% and G₄%, G₆% were prepared based on the ingredient concentrations of heavy base oil, lime, colophony as mentioned in Table (1). The prepared greases were made in batches of one liter in an open kettle with a capacity of 2 liter, fitted with a mechanical stirrer. The saponification process was performed on a mixture of heavy base oil and stearic acid with calcium hydroxide, at 100-110°C. The reaction time for each saponification process to achieve a soap structure was found to be dependent on the type of constituent. After the completion of the reaction, the different concentrations from of recycled HDPE were added, the reaction mixture was cooled gradually while heavy base oil was added to get NLGI-2. The consistency and drop point of the prepared greases were then determined. A penetration test was done using the standard ASTM D-217 method, the dropping point was assessed with ASTM D-566 Oil Separation (ASTM D-1724) and Copper Corrosion Test (ASTM D-4048).

Rheological measurements, this test was performed on a Brookfield programmable Rheometer HV DV-III ULTRA used in conjunction with Brookfield software, RHEOCALC V.2, through RHEOCALC all Rheometer function (rotational speed, instrument % torque scale time interval, set temperature) are controlled by a computer. The corresponding shear

stress shear rate, dynamic viscosity, mathematical model and confidence of fit consistence index were also recorded by the software.

3. RESULT AND DISSECTION

3.1. Physicochemical Properties of the Prepared Greases:

Table (2) shows that the Physicochemical and mechanical properties for prepared greases under investigation. Dropping point generally determines the thermal stability of the lubricating greases. The experimental data in this table show that the prepared greases G₀%, G₂%, G₄%, and G₆% had dropping points 95, 100, 110, and 120°C, respectively. We noted that the better thermal performance of greases is G₄% and G₆%, which they have dropping points are 110 and 120°C respectively. On other hand, oil separation test has tendency of lubricating grease to separate during storage. In this respect, experimental data of oil separation for prepared greases in table (2) show that greases G₀%, G₂%, G₄%, and G₆% have percentages of oil separation less than 5%. Also, data of copper strip corrosion test of the prepared greases under study showed that greases G₀%, G₂%, G₄%, and G₆% didn't corrode copper parts.

The apparent viscosity of prepared greasers was clearly increased with increasing of recycled HDPE concentrations as presented in Table 2. So, this reveals that the high content of recycled HDPE acts as a rheological modifier for the prepared greases^{18,19}.

3.2. Mechanical Stability of Prepared Greases:

The effect of mechanical work at different double strokes from 1000 to 5000 strokes on penetration for the prepared greases (G₀%, G₂%, G₄%, G₆%) was illustrated in Figure (1). This figure shows that the role of recycled HDPE for prepared greases under investigation. Also, the penetration values of these greases increased in the following order G₆% < G₄% < G₂% < G₀%.

3.3. Thermal Stability of Prepared Greases:

The measurement of dropping point generally determines the thermal stability of grease. In this respect, structural changes in lubricating greases due to temperature are mainly due to phase changes in the thickening agent. As the temperature lubricating greases is raised, the thickener softens stepwise due to phase transitions. At lower temperature, such softening may be great enough to permit the grease to flow²⁰. Figure (2), shows that the variation of the dropping point with the mechanical work at different double strokes from 1000- 5000 as a function of binding forces between ingredients and degree of compatibility of recycled HDPE with calcium soap.

It shows that with the increase of the mechanical work the dropping points decrease in the following order: $G_6\% > G_4\% > G_2\% > G_0\%$. This explanation consistent with the apparent viscosity and penetration values for greases under investigation.

3.4. Rheological Characterization:

In order to predict the role of lubricating greases in the lubrication of moving parts, knowledge of their rheological properties within a wide range of temperature and stress is essential, because these properties are major factors that determine the strength of the three-dimensional network of lubricating greases. The lubricating greases are two phase colloidal suspensions consisting essentially of mineral oil in addition to a metal soap and additives. The additives are widely used in the industry as rheology modifiers at both low and high temperatures^{21,22}. In this respect, the rheological behaviors of prepared greases were determined at 80 °C, 90 °C, and 100 °C and at different concentrations from recycled HDPE polymer. The viscosities of prepared grease are affected by the concentration of recycled HDPE as shown 5650, 8246, 11380, 15333 for $G_0\%$, $G_2\%$, $G_4\%$, $G_6\%$., respectively.

Figures (3-5) show that there are two distinct flow regions the first region, at low shear rate up to 5 s^{-1} reveal that the apparent viscosity decreases with shear rate increase, indicating that the rheological flow (deformation) of greases with different concentration of recycled HDPE polymer. But the flow curves at high shear rate show steady state in the second region, this reflect that the greases exhibits less dependence on shear after shear rate 5 s^{-1} ^{15,16}.

From a rheological point of view the development of a grease formulation should consider both the linear viscoelastic and viscous responses. Thus, greases must be designed to prevent loss of lubricant but also

they cannot yield a significant increase in the resistance of the motion of rubbing surfaces.

3.4.1. Rheological Models:

The rheological models have been proposed to describe the calcium greases behavior:

$$\text{Bingham model} \quad \tau = \tau_y + \eta \dot{\gamma}^n \quad (1)$$

Herschel – Bulkley model

$$\tau = \tau_y + K \dot{\gamma}^n \quad (2)$$

Casson model

$$\tau^{1/2} = \tau_0^{1/2} + \eta_c^{1/2} \dot{\gamma}^{1/2} \quad (3)$$

Where, τ is shear stress

The results from the Rheometer calc measurement are presented in the tables (3) as results from fitting the rheological model of the measurement. Confidence % for each of the rheological models, it can to observe that the most appropriate models for prepared greases are Herschel-Bulkle. From the same point of view, the rheological models with the smallest Confidence % are the Bingham and casson models¹⁷.

CONCLUSIONS

From the above result obtained, it can be deduced that the recycled HDPE can be potentially used as an effective rheological modifier of calcium lubricating greases. Apparent viscosity and linear viscoelasticity functions increase with increasing recycled HDPE polymer concentrations. The bulk rheology of calcium greases can be described in optimum conditions by Herschel-Bulkle model.

Table 1
Ingredients of the prepared greases

Type of Grease Ingredient, Wt%	$G_0\%$	$G_2\%$	$G_4\%$	$G_6\%$
Heavy base oil	80.0	80.2	81.4	81.5
Stearic acid	12.0	10.5	8.0	6.5
Calcium hydroxide	3.0	2.8	2.6	2.4
Colophony (Rosin)	5.0	4.5	4.0	3.6
Recycled HDPE	0.0	2.0	4.0	6.0

Table 2
Physicochemical properties of the prepared greases

Test	Prepared greases				Test method
	G ₀ %	G ₂ %	G ₄ %	G ₆ %	
Penetration at 25°C					
Unworked	295	291	288	280	ASTM D-217
worked	300	296	290	290	
Dropping point, °C	95	100	110	120	ASTM D-566
TAN, mg KOH/gm, @72h	1.3	1.6	1.8	1.0	ASTM D-664
Oil separation, Wt%	2.5	2.0	1.7	1.2	ASTM D-1724
Oxidation Stability at, 99°C, 96h, pressure drop, psi	3.5	6.9	8.5	3.4	ASTM D-942
Copper Corrosion 3h/100°C	Ia	Ia	Ia	Ia	ASTM D-4048
Code Grease According to					
NLGI	2	2	2	2	
Egyptian Standard	LB	LB	LB	LB	
Apparent Viscosity, cP @ 80 °C	5650	8246	11380	15333	ASTM D-189
Yield stress, D/cm ²	86.9	188.7	257	319	

Table 3
Viscoelastic parameters for selected prepared greases, of Herschel Buckley at different temperatures

Test	@ 80 °C				@ 90 °C			
	G ₁	G ₂	G ₃	G ₄	G ₁	G ₂	G ₃	G ₄
Consistency index	1068	7186	23729	17903	2800	7067	17326	10228
Yield stress, D/cm ²	96.1	112.9	32	152.3	775	839	62.4	0.10
Flow Index	1.1	055	028	037	0.78	0.46	0.31	0.5
Confidence	99.8	99.3	99.4	99.6	99.5	99.8	99.3	99.5
Test	@ 100 °C							
	G ₁		G ₂		G ₃		G ₄	
Consistency index	1196		1428		1149		10253	
Yield stress, D/cm ²	77.8		15		88.9		72.8	
Flow Index	0.99		0.34		0.47		0.46	
Confidence	99.8		99.5		99.9		99.6	

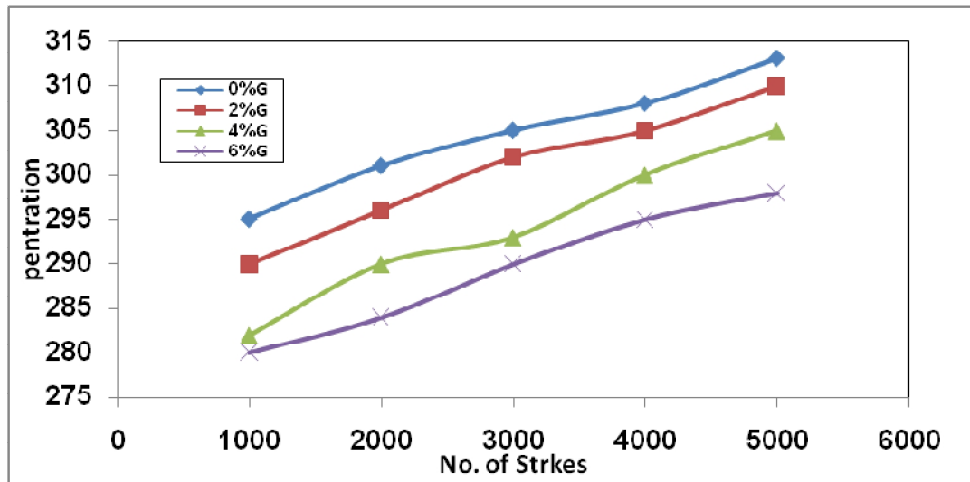


Figure1
Effect of mechanical working on the penetration for prepared greases

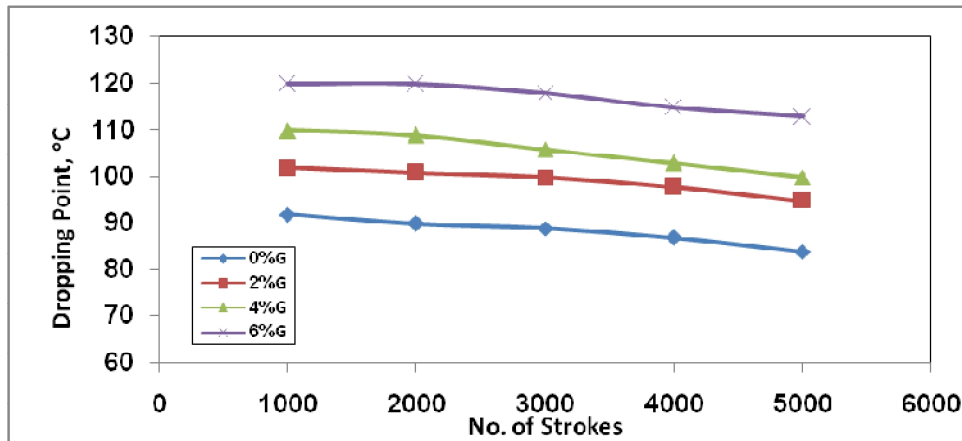


Figure 2
Effect of Mechanical working on dropping point for prepared grease

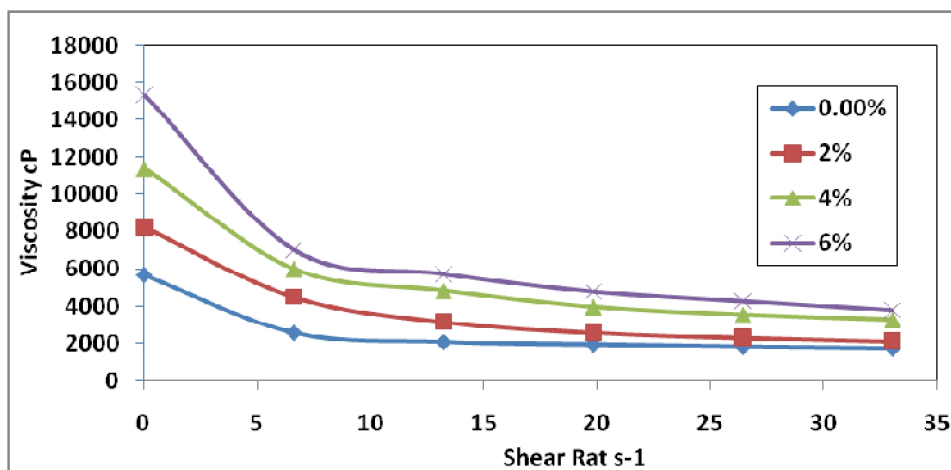


Figure 3
Variation of Viscosity with shear rate for prepared grease at different Concentration and temperature 80 °C

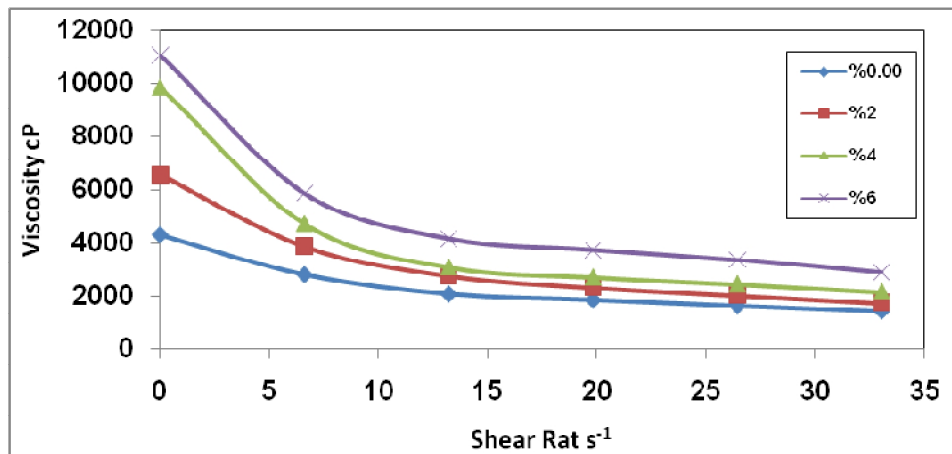


Figure 4

Variation of Viscosity with shear rate for prepared grease at different Concentration and temperature 90 °C

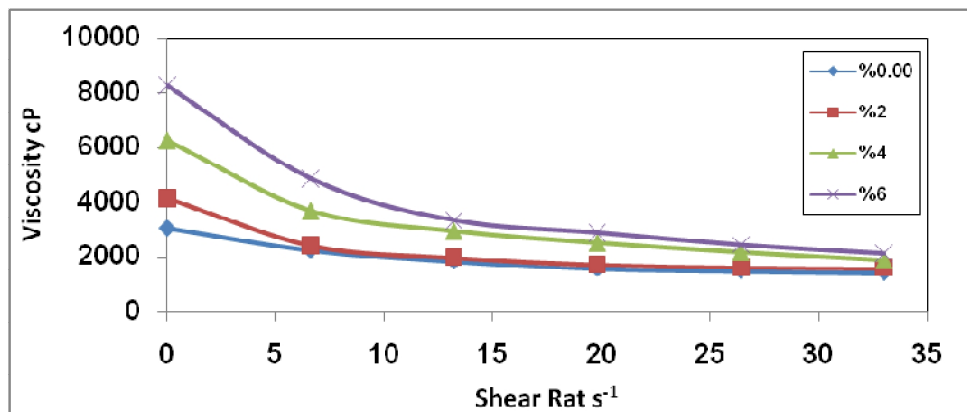


Figure 5

Variation of Viscosity with shear rate for prepared grease at different Concentration and temperature 100 °C

REFERENCES

- Martín-Alfonso JE, Valencia C, Sa´nchez MC, Franco JM, Gallegos C, Development of new lubricating grease formulations using recycled LDPE as rheology modifier additive, *European Polymer Journal*, 2007; 43: 139–149
- Refaat A. El-Adly, Ahmed H. Beadier, Modather F. Hussein, Enas A. Ismail, Epoxidized Some Vegetable oils as Potential Source for Bio-Based Greases Part1: Epoxidized Jojoba oil as Potential Source of Bio-Based Greases, *International Journal of Fluid Power Engineering*, 2014; 20(1): 1145-1149.
- Martín-Alfonso JE, Valencia C, Sa´nchez MC, and Franco JM, Evaluation of Thermal and Rheological Properties of Lubricating Greases Modified with Recycled LDPE, *Tribology Transactions*, 2012; 55: 518-528.
- Grote KH. and Antonsson E K. *Handbook of Mechanical Engineering*, Springer: New York, 2009.
- Moreno G., Valencia C., De Paz V., Franco J.M., and Gallegos C., *Ind. Chem. Eng. Res.*, 2006; 45: 4001.
- Martín-Alfonso JE, Valencia C, Sa´nchez MC, Franco JM, and Gallegos C. Rheological Modification of Lubricating Greases with Recycled Polymers from Different Plastics Waste, *Ind. Eng. Chem. Res.*, 2009; 48: 4136-4144
- El-Adly RA, Ahmed H. Bedier, Modather F. Hussein, Enas A. Ismail and Mahmmod M. El-Emary, Jojoba and Castor Oils as Fluids for

- the preparation of bio greases: A Comparative Study, *International Journal of Scientific & Engineering Research*, 2014; 5(5).
8. Martín-Alfonso JE, Valencia C, Sánchez MC, Franco JM, and Gallegos C. Evaluation of Different Polyolefins as Rheology Modifier Additives in Lubricating Grease Formulations, *Materials Chemistry and Physics*, 2011; 128: 530-538.
 9. Garcia-Morales JA, Franco JM, Valencia C, Sánchez MC. and Gallegos C. Influence of processing variables on the rheological properties of lubricating greases manufactured in a stirred tank, *Journal of Industrial and Engineering Chemistry*, 2004a; 10(3): 368–378.
 10. NLGI (2006) *Lubricating Greases Guide*, National Lubricating Grease Institute, Kansas.
 11. Martín-Alfonso JE, Valencia C, Sánchez MC, Franco JM. and Gallegos C. Influence of some processing variables on the rheological properties of lithium lubricating greases modified with recycled polymers, *Int. J. Materials and Product Technology*, 2012; 43: Nos. 1/2/3/4
 12. Couronné I, Mazuyer D, Vergne P, Truong-Dinh N, and Girodin D. Effects of Grease Composition and Structure on Film Thickness in Rolling Contact, *Tribology Transactions*, 2003; 46: 31–36.
 13. Delgado MA, Valencia C, Sánchez MC, Franco JM, Gallegos C. *Ind Eng Chem Res*, 2006; 45: 1902–10.
 14. Pracella M, Pazzagli F, Galeski A. *Polym Bull*, 2002; 48: 67–74.
 15. Ismail EA, Ph.D. Thesis, A study on the utilization of Jojoba oil and Jojoba meal as additives for lubricating oil and greases, University of Ain Shams, Cairo, Egypt, 2009.
 16. Refaat A El-Adly and Enas A. Ismail, *Tribology - Lubricants and Lubrication, Lubricating Greases Based on Fatty By-Products and Jojoba Constituents*, *InTech*, 2011; 8: 201-222.
 17. Radulescu AV, Radulescu I, *Rheological models for lithium and calcium greases*, *Mechanika*, 2006; 3(59): 67-70.
 18. Franco JM, Delgado MA, Valencia C, Sánchez MC, and Gallegos C. *Mixing Rheometry for Studying the Manufacture of Lubricating Greases*, *Chemical Engineering Science*, 2005; 60: 2409-2418.
 19. Delgado MA, Valencia C, Sánchez MC, Franco JM, and Gallegos C. “Thermorheological Behavior of a Lithium Lubricating Grease, *Tribology Letters*, 2006; 23: 47-54.
 20. Modather FHA., PhD Thesis, Study on preparation and evaluation of biogreases based on renewable sources, Al-Azhar University, Cairo, Egypt, 2013.
 21. Moreno G., Valencia C., Franco J. M., Gallegos C., Diogo A., and Bordado J. C. M. Influence of Molecular Weight and Free NCO Content on the Rheological Properties of Lithium Lubricating Greases Modified with NCO-Terminated Prepolymers, *European Polymer Journal*, 2008; 44: 2262–2274.
 22. Sánchez M. C., Franco J. M., Valencia C., Gallegos C., Urquiola F., and Urchegui R. *Atomic Force Microscopy and Thermo-Rheological Characterisation of Lubricating Greases*, *Tribology Letters*, 2011; 41: 463-470.