

Investigation of Thermal Degradation of Polyethylene–Polypropylene-Based Grease

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Synopsis

Thermal degradation of polyethylene–polypropylene-based lubricating grease was studied in a differential scanning calorimeter under static air atmosphere, while weight loss with increase in temperature under inert atmosphere of nitrogen gas was recorded thermogravimetrically. The polymer-based grease exhibited higher thermal stability when compared to that of a soap-derived multipurpose lubricating grease based on lithium 12-hydroxystearate.

INTRODUCTION

Lubricating greases are the products of the dispersion of a thickening agent in a liquid lubricant. Most thickening agents are metal soaps of long chain fatty acids and constitute about 10–15% of the composition^{1,2}.

The use of polymers as gellants for lubricating oils has been reported in patent literature, and a number of polymer-based greases have attained commercial importance.³ The most widely used polymeric gellants are the linear polyolefins.⁴ For example, the oil-soluble atactic or amorphous type of polyolefins, having molecular weights of about 1000–20,000 tend to give stringiness characteristics to lubricating greases while the oil-insoluble isotactic or crystalline type, having molecular weights of 20,000 to about 100,000 give adhesive properties to greases.⁵ Thus a blend of the two types will confer both characteristics to lubricants in proportion to the amount used. Other types of polymers, such as polyureas and perfluoroalkylpolyethylenes have also found commercial application as gellants for lubricating oils especially where more severe conditions are encountered.⁶ In addition to their use as sole gellants, polymers are often used as supplements to other types of thickening agents in order to improve the adhesion and cohesion characteristics of lubricating greases.⁷

Thermoanalytical techniques, such as differential thermal analysis (DTA), differential scanning calorimetry (DSC), thermogravimetry (TG), and differential thermogravimetry (DTG) have been used extensively in recent years for studying the thermal behavior and decomposition patterns of many polymeric and petroleum-derived products under different atmospheric conditions.^{8,9}

In the work described in this paper, thermal property and degradation of a polyethylene–polypropylene-based grease were studied in a differential scanning calorimeter and thermogravimetrically employing different atmospheric conditions. Results obtained were compared to that of a soap-based multipurpose lubricating grease based on lithium 12-hydroxystearate studied under the same conditions.

EXPERIMENTAL

Materials. The low viscosity index (LVI) lubricating oil of grade 60 (additive free) and lithium 12-hydroxystearate of 97% purity were obtained from a local refinery. Polyethylene (low density) and isotactic polypropylene with densities of 0.92 and 0.85, respectively, were purchased from the Aldrich Chemical Co.

Instrumentation. Thermal measurements were carried out in a Heraeus TA 500 thermal analyzer. Pure benzoic acid and tin were used in calibrating the DSC apparatus.

Sample Preparation. Lubricating greases were prepared at elevated temperatures by dissolving the appropriate thickening agent in the mineral oil. The thickening agent input by mass for the polymer-based grease was 6% polyethylene and 2% polypropylene. These proportions yielded the product possessing excellent characteristic properties. The lithium 12-hydroxystearate input in the soap-based grease was 10% by mass. The lubricating greases were thoroughly homogenized prior to their investigation in the thermal analyzer. Specifications of the two prepared greases are presented in Table I.

Thermal Degradation Measurements. The DSC measurements were carried out by placing a thin film of grease sample weighing 5–10 mg in an aluminium crucible and heated at a rate of $10^{\circ}\text{C min}^{-1}$ under static air atmosphere. The reference cell was left empty. TG and DTG curves were recorded simultaneously by placing a thin film of grease sample weighing

TABLE I
Specifications of the Prepared Lubricating Greases

Specification of the grease	Polymer-based	Soap-based
1. Visual color	Brown	Brown
2. Texture	Smooth	Smooth
3. Dropping point of lubricating grease ($^{\circ}\text{C}$), ASTM ^a D2265	149	197
4. Cone penetration of lubricating grease (0.1 mm.), IP ^b 310	305	310
5. Grade number	1	1
6. Acidity of grease (wt %) of oleic acid, IP 37	Nil	0.27
7. Ash determination of lubricating grease (wt %), ASTM D128	Nil	0.64
8. Wear preventive characteristic of lubricating grease (four ball method), scar diameter (mm), IP 239	0.75	0.6
9. Measurement of extreme-pressure properties of lubricating grease (four ball method), ASTM D 2596		
a. mean Hertz load	39.2	21.2
b. welding point (K/g)	200	126
10. Oxidation stability of lubricating grease by the oxygen bomb method, ASTM D 942	552 h	300 h

^a ASTM: standard methods of the American Society of Testing and Materials.

^b IP: standard methods of the Institute of Petroleum.

10–15 mg in a platinum crucible and heated at a rate of $20^{\circ}\text{C min}^{-1}$ under an atmosphere of nitrogen gas flowing at a rate of $50\text{ cm}^3\text{ min}^{-1}$. All measurements were carried out in triplicate.

RESULTS AND DISCUSSION

The DSC traces of the polymer-based and soap-based lubricating greases performed between room temperature and 270°C under static air atmosphere are displayed in Figures 1 and 2, respectively. The DSC trace of the polyethylene–polypropylene-based grease exhibited two major endothermic transitions, the first occurring between 80 and 115°C and the other between 137 and 155°C . The first endothermic peak with a maximum at 100°C is associated with a change in the state of the polymeric constituents of the grease such as specific heat, thermal expansion coefficient, and free volume. The second endothermic peak (137 – 155°C) is due to the softening/melting of the grease with a maximum transition temperature of 148°C . This temperature is nearly similar to the dropping point value (149°C) of the same grease measured according to the standard procedure and as shown in Table I. The dropping point is usually defined as the temperature at which a grease sample passes from the semisolid into the liquid phase.¹⁰ The endothermic offset from the base-line recorded in the DSC trace after melting, between 160 and 270°C , is related to the change in the heat capacity resulting from the transformation of the lubricating grease into the liquid phase and also to the evaporation of the lighter fractions present in the mineral oil constituent.

DSC technique has been used extensively in studying the oxidation stability of petroleum-derived products.¹¹ On heating a sample of the product in air, an exothermic effect resulting from oxidative degradation is recorded. The onset temperature of the exotherm can be taken as a measure of its thermal stability. The higher the onset temperature, the more stable is the product, and conversely.¹² In the DSC trace of the polymer-based grease, no exothermic effect due to oxidative degradation was recorded up to a temperature of 270°C .

The DSC curve of the lithium 12-hydroxystearate-based grease indicated the presence of a minor endothermic peak occurring between 95 and 110°C

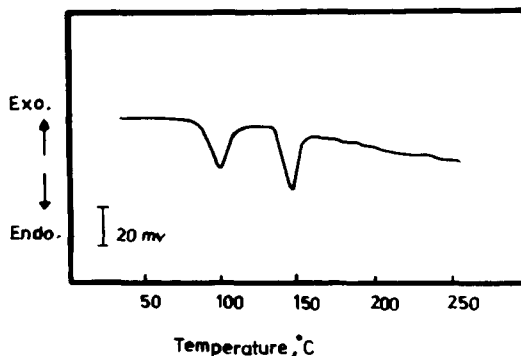


Fig. 1. DSC trace of polyethylene–polypropylene-based grease.

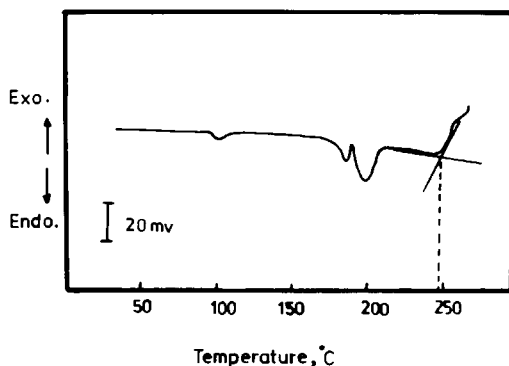


Fig. 2. DSC trace of lithium 12-hydroxystearate-based grease.

and a shouldered major endothermic peak occurring between 175 and 205°C with a maximum transition temperature at 198°C (Fig. 2). The former peak is associated with phase transition due to structural changes, while yet again the latter is related to softening/melting of the soap-based grease. The corresponding dropping point of the same grease measured according to the standard procedure was 197°C (Table I).

A slight endothermic offset from the base line due to evaporation of the lighter parts of the mineral oil constituent and heat capacity changes associated with phase transformation was again recorded beyond 205°C in the DSC trace of the soap-based grease. However, a sharp exothermic effect due to oxidative degradation of the grease melt was recorded with an onset temperature of 246°C. The onset temperature was evaluated from the intersect of the extrapolated tangents of the DSC curve as shown in Figure 2. It is clear from the results obtained that the melt of the polymer grease possessed higher oxidation stability compared to that of the soap-based grease. These results correlated well with those obtained from the oxidation stability standard test method which are presented in Table I, i.e., the same pressure drop in the oxygen bomb was achieved in 552h for the polymer-based grease and 300h for the soap-based grease.

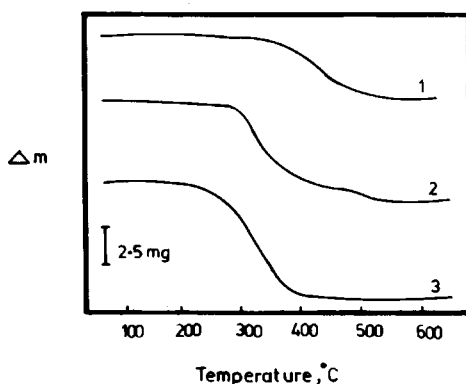


Fig. 3. TG curves of: (1) polymer-based grease; (2) soap-based grease; (3) 60 LVI base oil.

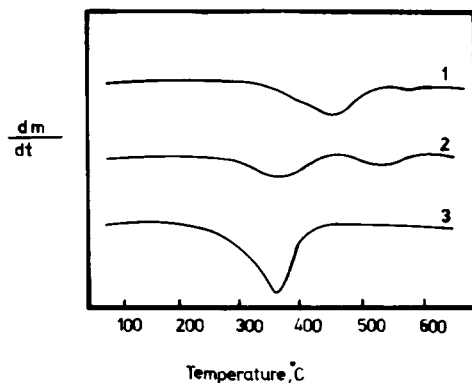


Fig. 4. DTG curves of: (1) polymer-based grease; (2) soap-based grease; (3) 60 LVI base oil.

TG and DTG measurements were recorded between 30 and 650°C under nitrogen gas for the two lubricating greases together with the individual oil as shown in Figures 3 and 4. It is clear from these figures that, under the inert atmosphere of nitrogen gas, the main feature of the thermogravimetric curves of the studied greases corresponds mainly to the volatilization of the mineral oil constituent followed by degradation of the thickening agent. It is also obvious that both types of thickeners retarded the volatilization of the base oil. However, the polyethylene-polypropylene composition was more effective than the lithium 12-hydroxystearate in raising the initial temperature of oil volatilization, i.e., by 110°C in the case of the polymer-based grease and by 65°C in the case of the soap-based grease. The initial temperature of oil volatilization was 220°C. This behavior may be attributed to the tight enclosure of the hydrocarbon oil molecules within the longer chain polymeric structure which is interlocked in a three-dimensional network.

From these results, it can be concluded that the polymer-based grease exhibited higher thermal stability compared to that of the soap-based grease. These results correlated well with those obtained from standard methods of testing. In addition, the thermal methods employed, proved to be simple, quick and reproducible.

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References

1. C. J. Boner, *Modern Lubricating Greases*, Scientific Publications, Broseley, U. K., 1976, p. 1.3.
2. D. Al-Sammerrai and E. Said, *Analyst*, **109**, 403 (1984).
3. B. W. Hotten, *Advances in Petroleum Chemistry and Refining*, Wiley-Interscience, New York, 1964, Vol. 9, Chap. 3.
4. J. L. Dreher, U. S. Pat. 3,234,372. (1966).
5. B. Mitacek, U. S. Pat. 3,169,114 (1965).
6. H. Gisser and J. Messina, U. S. Pat. 3,640,859. (1972)
7. B. Mitacek, U. S. Pat. 3,112,270 (1963).
8. J. Chiu, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **14**, 486 (1973).
9. F. Noel, *J. Inst. Pet.*, **57**, 354 (1971).

10. Institute of Petroleum Standard for Petroleum and Its Products, Standard Method of Testing for Dropping Point of Lubricating Greases, IP Method 132, Applied Science, London, 1982.

11. F. Noel, *Thermochim. Acta*, **4**, 377 (1972).

12. M. Barbooti and D. Al-Sammerrai, *Thermochim. Acta*, **76**, 221 (1984).

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