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Polymer additive analysis by pyrolysis–gas chromatography III. Lubricants

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Abstract

Lubricants are widely used in thermoplastic polymers to increase the overall rate of processing or to improve surface release properties. Because of the low level of lubricants normally used in a polymer, it may not be possible to analyze the additive directly by common spectroscopic or thermal chemical techniques. However, lubricants as well as other additives in the polymer can be qualitatively analyzed by pyrolysis–gas chromatography (Py–GC) after extraction. In this work, several lubricants have been studied to demonstrate that Py–GC is a viable tool to investigate lubricants. The advantages of using Py–GC in the analysis of lubricant have also been discussed. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Lubricants are substances that when compounded in a small quantity into a polymer, will provide a significant increase in the movement of polymer chains or segments without notable influence in other observable properties [1]. Essentially, lubricants are added to polymers to increase the overall rate of processing or to improve surface release properties during extrusion, injection molding, compression molding, etc., [2]. The factors which will be considered during the selection of lubricants are: compatibility with the host polymer, no adverse effect on other physical properties, easy introduction, no retarding effect on the gelation process, no reduction in

melt strength and extensibility, good transparency, improved plate-out performance and cost [3].

According to the lubricant action, they may be divided into two basic groups based on function, external and internal lubricants [4]. A main function of lubricants is to prevent polymers that have a tendency toward tackiness from sticking to metallic parts of processing machinery. This is termed external lubrication. Another important function is to provide lubrication to the polymer under processing to improve the free flow of the melt bulk polymer by reducing friction between chain segments; this is termed internal lubrication. These two functions facilitate mold release and also give a better output from the processing equipment. Lubricants may appear to have only one function in a polymer system. However, if the additive behaves according to one function under one set of conditions and in another function in different circumstances, it is considered to be a dual function lubricant. In many

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applications, when a balance among various lubricating functions is required, a lubricant package that is a mixture of several different materials is used to satisfy the lubrication demand. This lubricant package is called a multifunction lubricant.

Because a plasticizer is also an additive that promotes movement of chains and segments of a polymer, what is the difference between lubricants and plasticizers especially in terms of purpose and function of internal lubrication? Normally, plasticizers are used in more than trace amounts and are expected to provide significant change in observable physical properties. They may, in addition, provide improved processibility and may be chosen partly for that purpose. The term “the change of observable physical properties” addresses the difference between lubricants and plasticizers. The major purpose of using plasticizers as an additive is to change the physical properties of a polymer; in contrast, the major purpose of using lubricants is to change the processibility of the polymer.

There are many different ways to classify lubricants. Based on their action, lubricants may be classified into two basic groups, external lubricants and internal lubricants. However, from the point of view of the analysis of lubricants, they may be categorized by their chemical structure. They can be divided into:

1. Saturated hydrocarbons [5]: paraffin waxes, microcrystalline wax, earth wax, polyethylene waxes and oxidized polyethylene waxes are several important examples.
2. Fatty acids [6]: stearic acid is the one mostly used because of its low price and its availability.
3. Metallic soaps: the most common example in this category is zinc and calcium stearate.
4. Fatty acid esters [6]: the butyl stearate, octyl stearate, and fatty acid glyceryl esters are typical examples.
5. Fatty acid amides: the typical examples are stearamide, erucamide, ethylene bisstearamide (EBS) and ethylene bisoleamide (EBO).

The level of lubricants used in the polymer is rather low. Normally, the concentration is between one tenth of 1% to several percent depending on the type of polymers and the processing conditions. The direct analysis of lubricants in the polymer by spectroscopic or thermal techniques is difficult be-

cause of low concentration and interference of the parent polymer matrix. The typical approach of lubricant analysis is first to separate the polymer and additives, follow with appropriate gas chromatography (GC) or liquid chromatography (LC) methods to separate and identify the lubricants from the additive mixture. Since the lubricants are rather large molecules with polar functional groups, the choice of GC or LC to achieve the separation and detection/identification is difficult when facing an unknown. It always requires several trial-and-error tests in order to induce the correct approach. However, there is another technique that may be applied to simplify this lubricant analysis task.

Pyrolysis–gas chromatography (Py–GC) [7] is an important technique for polymer as well as large molecule analysis. Py–GC is a technique that uses thermal energy (pyrolysis) to break down a polymeric chain or large molecule to monomers, oligomers, and other fragments, followed by the separation of the pyrolysates with GC and detection with appropriate detectors. Flame ionization detection (FID) is one of the most frequently used detection methods for quantitative analysis of pyrolysates. Mass spectrometry (MS) is one of the most commonly used detection methods for identification. The intensities of monomers or monomer-related fragments are commonly used to obtain compositional data [8]. The oligomers or oligomer-related fragments are used to elucidate microstructure as well as compositional information [9].

Lubricants as well as other additives in the polymer can be qualitatively analyzed by Py–GC after separating the polymer and additives. In this study, several different types of lubricants have been studied to demonstrate that Py–GC is a good tool to investigate the lubricants in polymers. The advantages of using Py–GC for lubricant analysis are also discussed.

2. Experimental

2.1. Polymers

Paraffin wax (catalog No. 32,720-4), stearic acid (99+%) (catalog No. 26,830-0), stearamide (85%) (catalog No. O-60-1), zinc stearate (catalog No.

30,756-4), and *N,N'*-ethylenebistearamide (EBS) (catalog No. 43,467-1) were purchased from Aldrich (Milwaukee, WI, USA). The technical grade of stearic acid, butyl stearate, butyl oleate, butyl palmitate, polyethylene (PE) wax, and earth wax were obtained from various polymer additive distributors. Spartech 14575, a PE, was obtained from Spartech (Washington, PA, USA). All lubricant samples and thermoplastic resin were used as they were received without any further purification.

2.2. Additive extraction

The additives in the polymer were extracted before Py-GC study. The additives extract from Spartech 14575 was prepared by following steps. (1) Weigh 0.5 g resin to 20 ml toluene and 10 ml chloroform, heat to 105°C and shake until the resin is completely dissolved. (2) Add 20 ml methanol to the solution to precipitate out the polymer. (3) Separate the solid and solution; concentrate the solution to several drops. (4) Deposit those drops into a quartz tube for pyrolysis experiment.

2.3. Py-GC conditions

Samples of lubricant (approximately 0.5 mg) were carefully deposited into a quartz tube. The quartz tube was inserted into a 300°C interface connected to the injection port of a Hewlett-Packard (HP) Model 6890 gas chromatograph equipped with an FID system. The samples were pyrolyzed (CDS 2000 Pyroprobe, Pt coil) at a calibrated temperature of 950°C. The coil was heated to the calibrated temperature at 20°C/ms and held at the set temperature for a 20-s interval. The pyrolysates were split in the 300°C injection port, with 250:1 split ratio. The GC system was set up with a fast flow program (15 p.s.i./0.2 min, 75 p.s.i./min, to 90 p.s.i./8.8 min; 1 p.s.i.=6894.46 Pa). The separation was carried out on a fused-silica capillary column (J&W Scientific DB-5, 10 m×0.10 mm I.D., 0.4 μm film) using a fast temperature (maximum heating rate allowed) ramping program (50°C/0.2 min, 100°C/min, to 100°C/0 min; 80°C/min, to 140°C/0 min; 60°C/min, to 200°C/0 min; 50°C/min, to 280°C/0 min; 40°C/min, to 320°C/5.2 min).

2.4. Py-GC-MS conditions

The sample preparation and pyrolysis in the Py-GC-MS experiments were the same as Py-GC experiments. The GC system used is a HP Model 5890 gas chromatograph. The pyrolysis products were split in the 300°C injection port, with 10 p.s.i. head pressure, and 30:1 split ratio. The pyrolysates were separated on a fused-silica capillary column (J&W Scientific DB-5, 30 m×0.25 mm I.D., 1.0 μm film) using a linear temperature program (40°C/4 min, 10°C/min, to 320°C/18 min); and detected by a HP 5791 mass-selective detector. The GC transfer line to the mass-selective detector was kept at 300°C. An electron ionization mass spectrum was obtained every second over the *m/z* range of 15 to 650. The results of Py-GC-MS are used mainly for identification of pyrolysates.

3. Results and discussion

The lubricants have been classified into five different groups according to their structure. However, there are really two general types of compounds involved. The first type includes fatty acids and their related esters, amides and metallic salts. The fatty acid most often is stearic acid. The other type includes waxes from petroleum refinery products that is in general a mixture of hydrocarbons from C₂₀ to C₅₀ or higher. When analyzing lubricants from an additive extract of a polymer sample by Py-GC, it is easy to distinguish these two types of compounds by the series of hydrocarbon pyrolysates produced. Under Py-GC, stearic acid and its related family will generally produce a set of alkenes from C₃ to C₁₇ to reflect the degradation of the aliphatic hydrocarbon chain portion of the stearic acid. In contrast, the petroleum wax family will produce extra hydrocarbon pyrolysates of C₂₀ to C₅₀ or higher in addition to the C₃ to C₁₇ series as a result of its composition. Depending on the retention time and the identities of the aliphatic hydrocarbon series, the types of lubricants often can be quickly discerned.

Fig. 1 shows a low-molecular-mass PE wax. The pyrolysates produced are similar to the pyrolysis of a polyethylene. In the pyrolysis of polyethylene, the

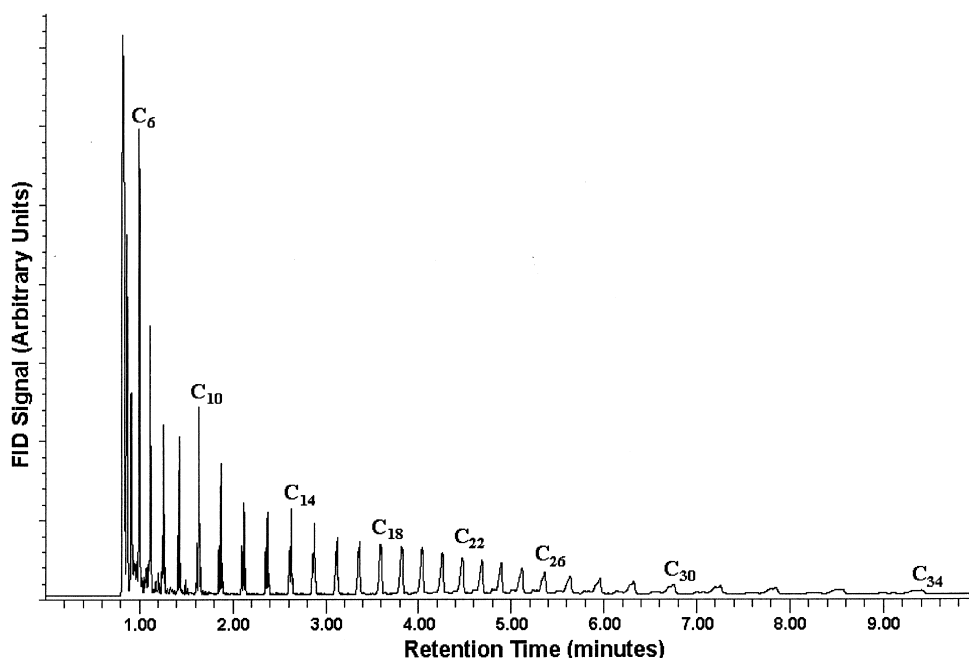


Fig. 1. The pyrogram of PE wax. Each peak consists of three major pyrolysates, dialkenes, straight-chain terminal alkenes and alkanes. The C number labeled in the peak indicates the hydrocarbon chain length of that pyrolysate, for example, C_{14} means the hydrocarbon chain consists of 14 carbons.

identification of the pyrolysates that are produced and the relative intensity of different pyrolysates have been discussed in the literature [10]. To distinguish PE wax from other waxes as a lubricant, it is important to recognize that the relative peak intensity of the pyrolysates as well as the trend of the peak intensity is a function of the chain length in the pyrogram. In PE wax, there is a trend of a smooth descending intensity in the pyrolysates after C_{20} .

Fig. 2 shows a pyrogram of paraffin wax. These waxes consist of mixtures of alkane hydrocarbons, most of that are linear alkanes with the chain length varying from about C_{20} to C_{50} . The chain length distribution in a paraffin wax has a close relation with its melting point. For example, a paraffin wax possessing a chain length distribution between C_{20} and C_{45} has an average melting point between 60 and 62°C. As indicated in Fig. 2, there is another pyrolysate distribution of C_{20} to C_{34} in addition to the normal descending peak intensity as for pyrolysis of a long chain hydrocarbon, indicating that this paraffin wax is a mixture of hydrocarbons with chain length from C_{20} to approximately C_{35} . There is a

small peak before each major straight-chain peak after C_{22} indicating that there is a small portion of branched isomers in the wax.

Fig. 3 shows a pyrogram of earth wax. This wax is also a mixture of hydrocarbons that are obtained by purification of ozokerite. Although the PE wax and paraffin wax are all mixtures of aliphatic hydrocarbons, the trend of intensity variations along the different hydrocarbon chain lengths is the key to distinguish them. In earth wax, there is an alternation in the intensity of pyrolysates between C_{20} and C_{34} suggesting that the relative intensity and distribution between C_{20} and C_{34} chain length is unique. This difference in the chain intensity and distribution can be used as an identity to distinguish it from PE wax and paraffin wax.

Fig. 4 shows a pyrogram of stearic acid. Stearic acid is a fatty acid with a saturated C_{17} aliphatic hydrocarbon chain. The pyrogram indicates a series of hydrocarbon pyrolysates up to C_{17} and a large amount of stearic acid that was vaporized in the pyrolysis interface before pyrolysis. The series of hydrocarbon pyrolysates is an indicator that an

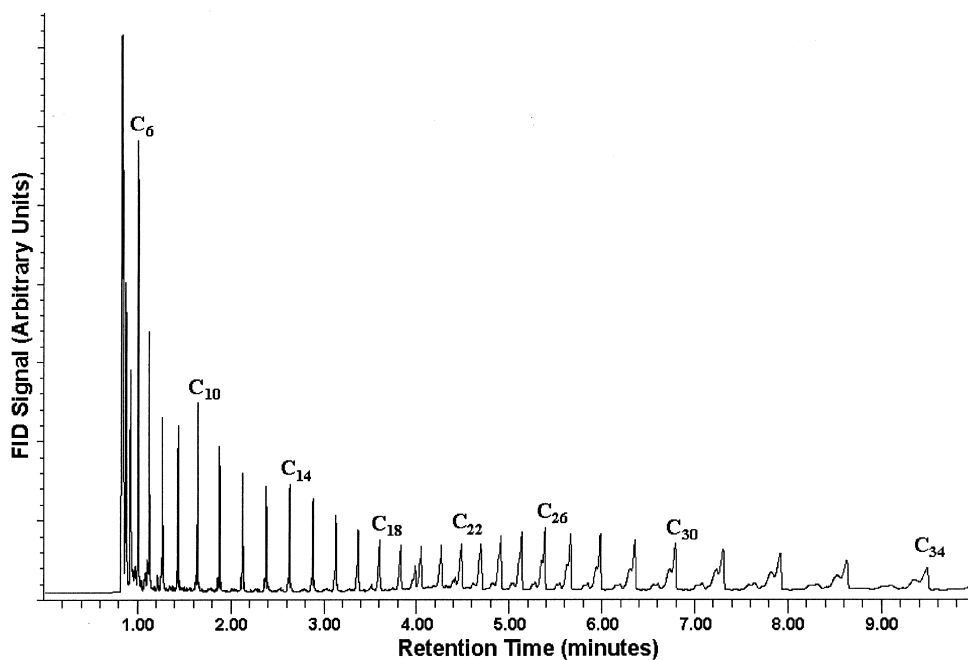


Fig. 2. The pyrogram of paraffin wax. An increased intensity of hydrocarbon chains from C₂₀ to C₃₄ indicates that this wax consists of a distribution of hydrocarbon chain lengths from C₂₀ to C₃₄.

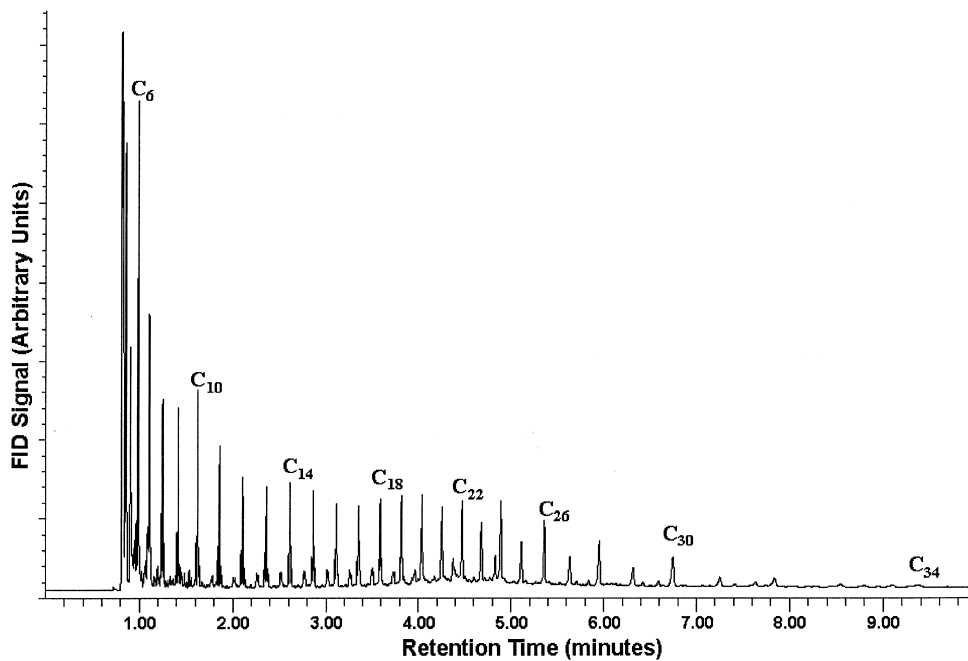


Fig. 3. The pyrogram of earth wax. An alternate intensity of peaks from C₂₀ to C₃₄ suggests that this wax consist of a different distribution of hydrocarbon chains. This difference in the chain intensity and distribution can be used as an identity to distinguish it from PE wax and paraffin wax.

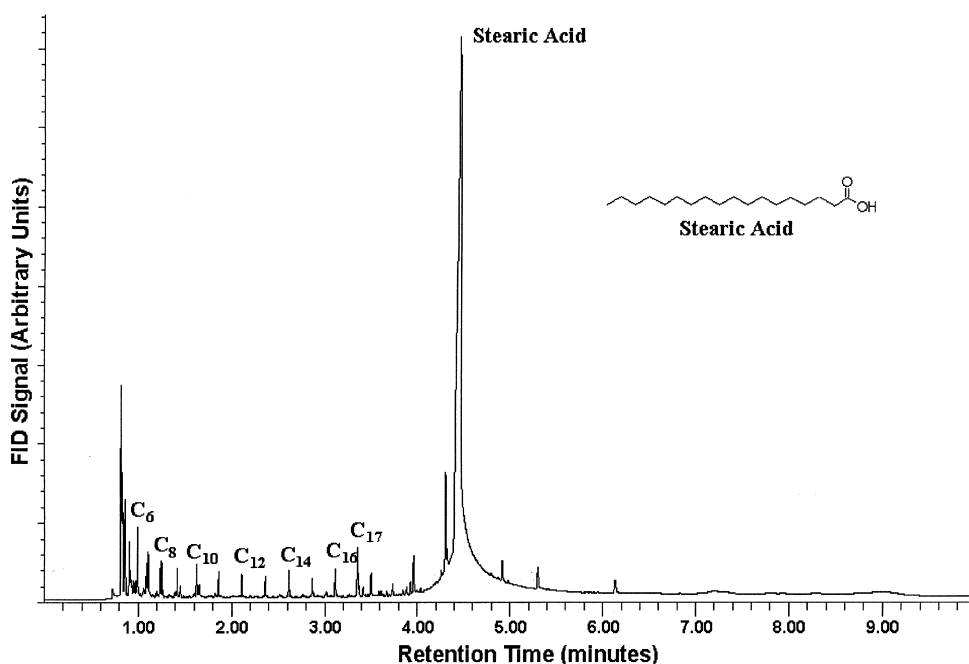


Fig. 4. The pyrogram of stearic acid. The pyrogram indicates a series of hydrocarbon pyrolysates up to C_{17} and a large amount of stearic acid that has vaporized in the pyrolysis interface before pyrolysis.

aliphatic hydrocarbon chain exists in the parent molecule and the chain length is equal to the highest hydrocarbon chain pyrolysate. In this case, the stearic acid can be eluted by GC and can be detected/identified by an appropriate GC detector.

Fig. 5 shows a pyrogram of technical-grade butyl stearate. Butyl stearate is one of the commonly used fatty acid monoesters in lubricant applications. The series of hydrocarbon pyrolysates show that the hydrocarbon pyrolysates up to C_{17} proves the sample is a stearate. The extraordinary intensity of the C_4 peak indicates the contribution of the butyl ester portion of the molecule. The identification of butyl stearate is based on the detection of the parent molecule that was vaporized in the pyrolysis interface before pyrolysis. Butyl palmitate ($C_{15}H_{31}COOC_4H_9$) and butyl myristate ($C_{13}H_{27}COOC_4H_9$) also exists in the sample. Most of the alkyl stearate or other fatty acid monoesters can be detected and identified by a GC method. The Py-GC analysis of fatty acid or fatty acid monoester not only depends on the vaporized parent molecules to determine the types of alkyl ester, but also on the

series of hydrocarbon pyrolysates to determine the aliphatic chain length of the fatty acid.

An awareness of the level of purity of the technical-grade lubricants as well as the composition of the common fatty acid in the lubricants is important. For example, technical grade stearic acid may contain up to 50% of other fatty acids that are mainly palmitic acid and myristic acid. The existence of other fatty acids just reflects the natural distribution of these fatty acids in the oils that were used for manufacturing lubricants. Fig. 6 shows a pyrogram of technical-grade stearic acid. When a noticeable level of palmitic acid has been detected along with stearic acid, further tests are necessary before drawing the conclusion that the palmitic acid is the major constituent of the lubricant mixture. Sometimes, the same chemical produced by a different manufacture may vary in composition because it may be produced by different methods. For example, the relative abundance of different carbon chain lengths of paraffin waxes will depend on the source of raw materials and the collection during petroleum refinery. It is important to know the possible variation in

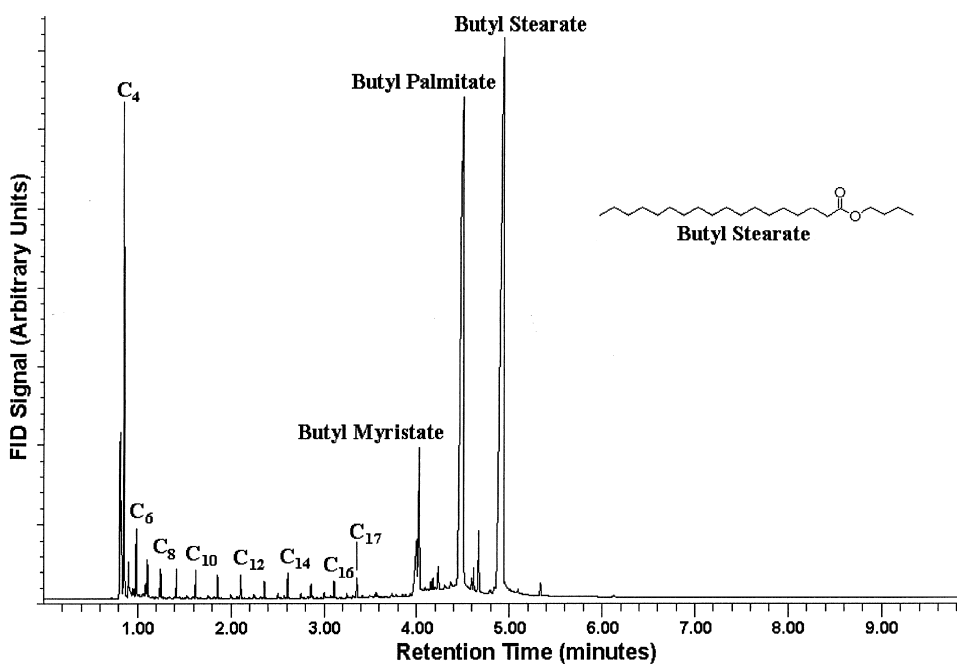


Fig. 5. The pyrogram of butyl stearate. The series of hydrocarbon pyrolysates up to C₁₇ in the pyrogram indicates that this is a stearate. The other components in this sample are butyl palmitate and butyl myristate.

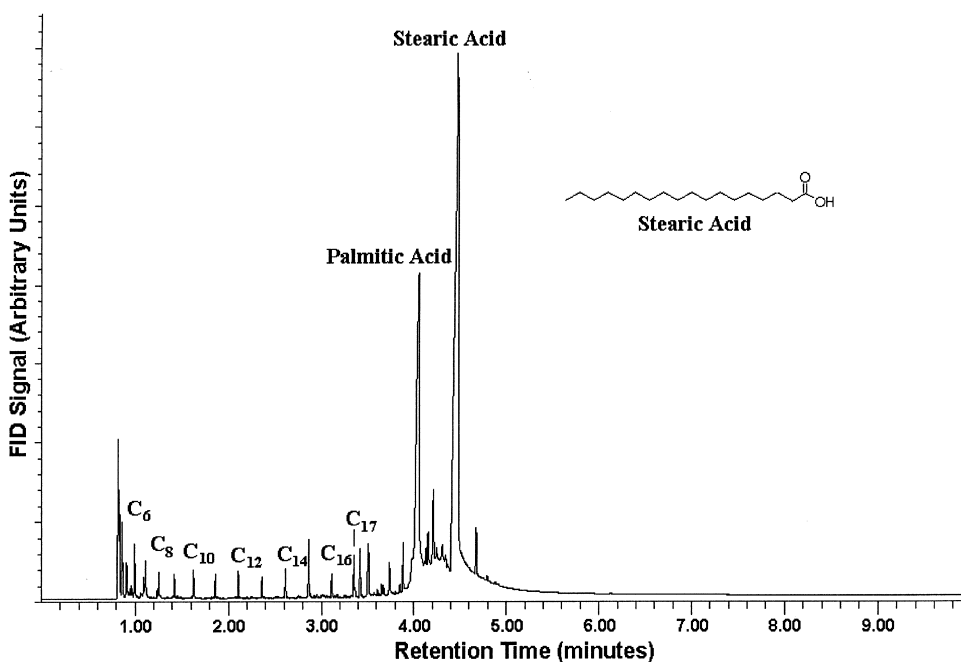


Fig. 6. The pyrogram of a technical grade of stearic acid. Technical-grade stearic acid may contain up to 50% of other fatty acids, mainly palmitic acid.

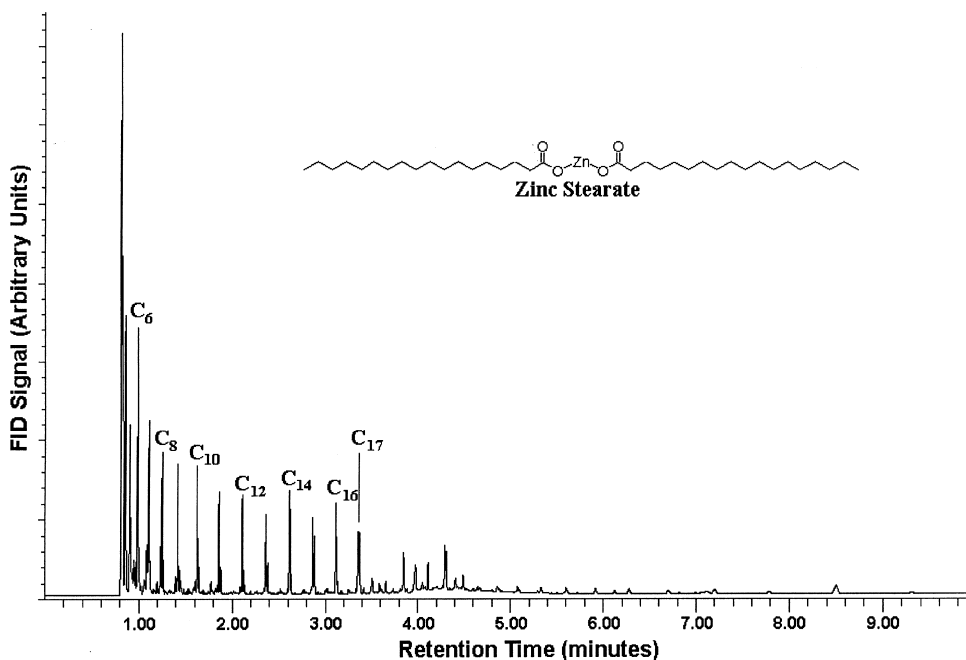


Fig. 7. The pyrogram of zinc stearate, a popularly used metallic salt of stearic acid. The series of hydrocarbon pyrolysates up to C_{17} in the pyrogram indicates that this is a stearate. The identification of the metal of the metallic salt of the fatty acid will have to rely on another inorganic method.

different brand samples in order to make the correct identification.

Fig. 7 shows a pyrogram of the zinc stearate. Zinc stearate is one of the popularly used metallic salts of stearic acid for the lubricant applications. The series of hydrocarbon pyrolysates up to C_{17} in the pyrogram clearly demonstrates that this is a stearate. The parent molecule, zinc stearate ($C_{17}H_{35}COO$)₂Zn, is not volatile enough to be analyzed by GC. This is a common phenomenon for most esters, amides, or metallic salts of saturated fatty acids. Again, the Py-GC is only suitable for the organic portion. The metal part of metallic salt of the fatty acid will have to rely on other inorganic methods for identification.

Because the series of hydrocarbon pyrolysates is so important in the identification of the (aliphatic portion) chain length in the esters, amides, or salts of saturated fatty acids, it is necessary to test that this degradation pathway is unique and reproducible. Fig. 8 is a pyrogram of butyl oleate. Instead of having a continuous saturated hydrocarbon chain in the molecule such as stearate, the oleate has a double bond between the ninth and tenth carbons. The existence

of this double bond has a great effect on the degradation mechanism. The degradation pathway of an aliphatic hydrocarbon chain will not proportionally produce all possible hydrocarbon chain lengths that are equal to or lower than the original hydrocarbon chain in the parent molecule. Instead, all possible hydrocarbon chains produced will be based on the longest saturated hydrocarbon chain in the parent molecule. The series of hydrocarbon pyrolysates up to C_9 in the pyrogram indicates that the longest saturated chain length is C_9 . Even though the structural difference between the stearate and oleate is only one double bond, there is a dramatic difference in the pyrolysate pattern produced. Py-GC is very sensitive in distinguishing the saturated or unsaturated aliphatic hydrocarbon chains. Fig. 9 shows a pyrogram of butyl palmitate. The series of hydrocarbon pyrolysates stopped at C_{15} . This indicates that the longest hydrocarbon chain in the molecule is C_{15} . In butyl palmitate, the hydrocarbon chain length of the aliphatic portion is exactly C_{15} . The pyrolysate series in the pyrogram completely reflects this feature.

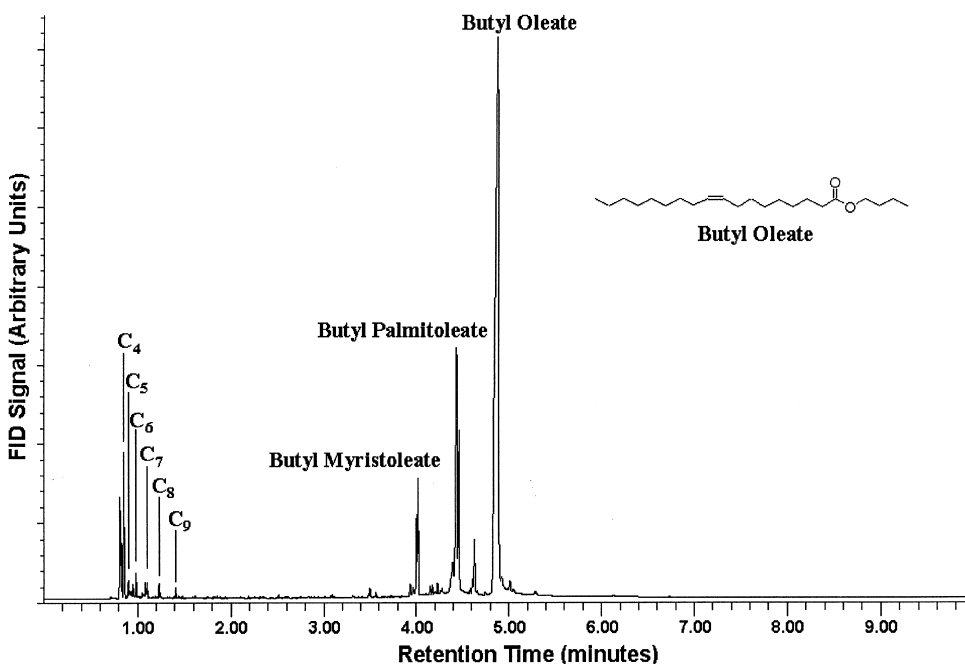


Fig. 8. The pyrogram of butyl oleate. The existence of the double bond between the ninth and tenth carbons has a great effect on the series of hydrocarbon pyrolysates produced. The series of hydrocarbon pyrolysates up to C_9 in the pyrogram indicates that the longest saturated chain length is C_9 .

Py-GC analysis of lubricants in a polymer requires a pre-separation of the additives and polymer because level of lubricants is usually low. The choice of different separation techniques such as extraction, dissolution-precipitation, swelling, etc. will depend on the types of polymers and additive packages used. In addition to the separation techniques, the sequence of separation techniques applied is almost equally important. For example, the metallic salts of stearic acid may be used as lubricants, however, in the same additive package, other stearate ($C_{17}H_{35}COO$) containing compounds may be used for other purposes such as stearyl citrate, used as a stabilizer or plasticizer. If the dissolution-precipitation procedures are not applied in the right sequences, the metallic salt of stearic acid may be lost in the separation process or the total stearate detected will not match the level of metal detected to back-calculate the metallic salt of stearic acid.

Fig. 10 is a pyrogram of stearamide ($C_{17}H_{35}CONH_2$). Stearamide is another type of stearic acid derivative that is widely used as a lubricant in polymers. The pyrogram of stearamide

will be similar to that of stearic acid. The identification is based on the series of hydrocarbon pyrolysates up to C_{17} and a large amount of stearamide that has vaporized in the pyrolysis interface before pyrolysis. Again, because the additive is produced from natural oils, it consists of a distribution between stearamide and palmitamide ($C_{15}H_{31}CONH_2$).

Fig. 11 is a pyrogram of EBS, or AcraWax C. This is another fatty acid amide commonly used in polymers as a lubricant. The series of hydrocarbon pyrolysates up to C_{17} indicates that stearates are in the molecule. The molecule is too large to be analyzed by GC, but the pyrolysate produced by this molecule provides strong evidence that the parent molecule is EBS. One pyrolysate has been identified as 1H-2-heptadecyl-4,5-dihydroimidazole which can be attributed to the rearrangement of the dehydrated parent molecule after loss of one stearate side chain.

A PE resin, Spartech 14575, has been used to test of lubricant or mode release agent to evaluate this pyrolysis-GC approach. Fig. 12 shows the pyrogram of this additives extract. The direct detection of

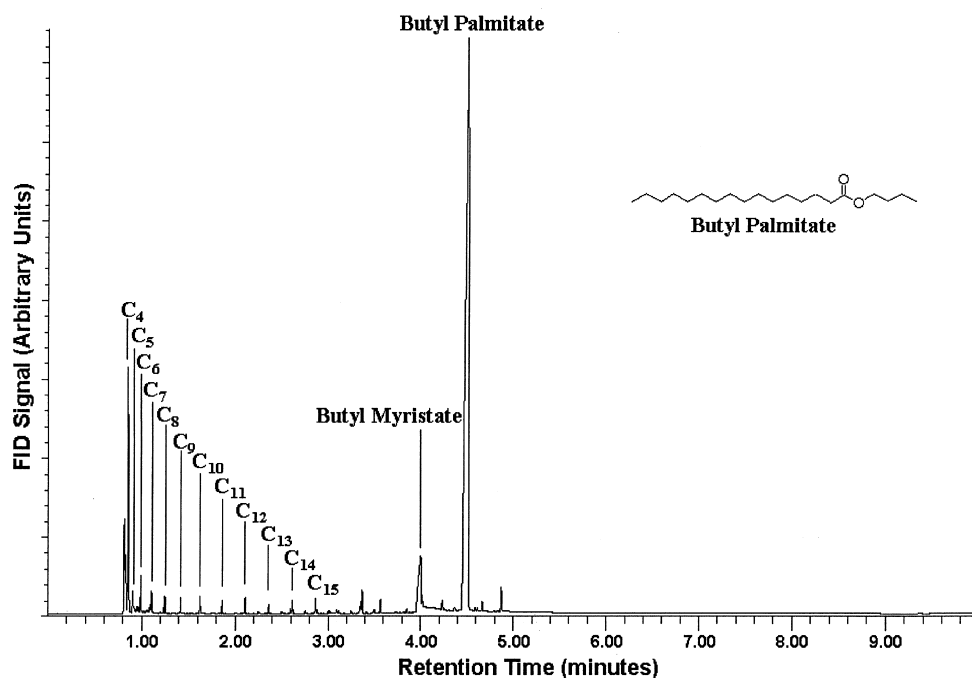


Fig. 9. The pyrogram of butyl palmitate. The series of hydrocarbon pyrolysates stopped at C_{15} , indicating that the longest hydrocarbon chain in the molecule is C_{15} . In butyl palmitate, the hydrocarbon chain length of aliphatic portion is exactly C_{15} . The pyrolysate series in the pyrogram completely reflects this feature.

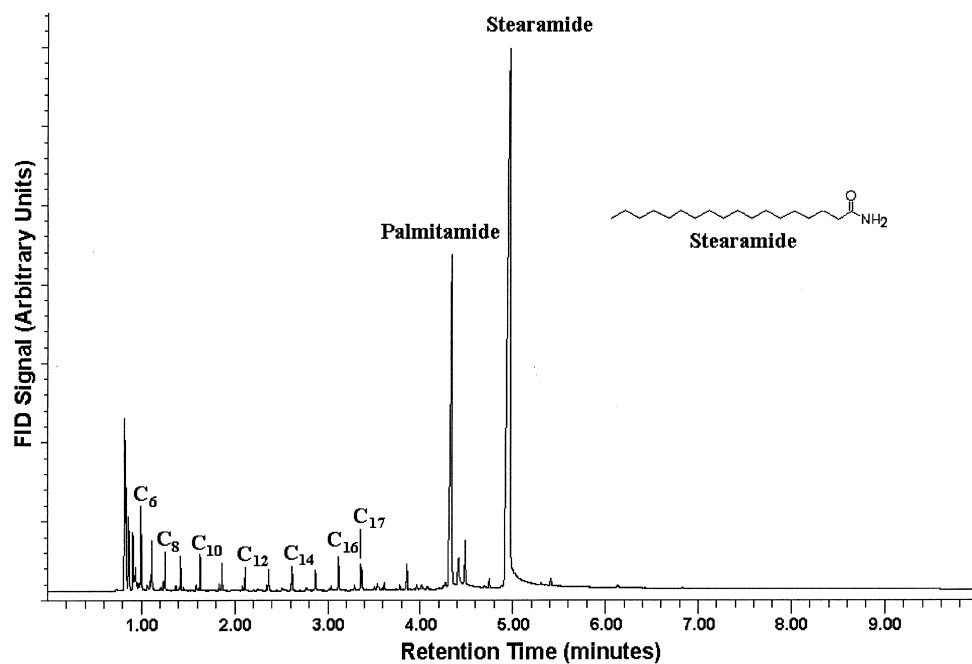


Fig. 10. The pyrogram of stearamide. The identification is based on the series of hydrocarbon pyrolysates up to C_{17} and a large amount of stearamide that has vaporized in the pyrolysis interface before pyrolysis.

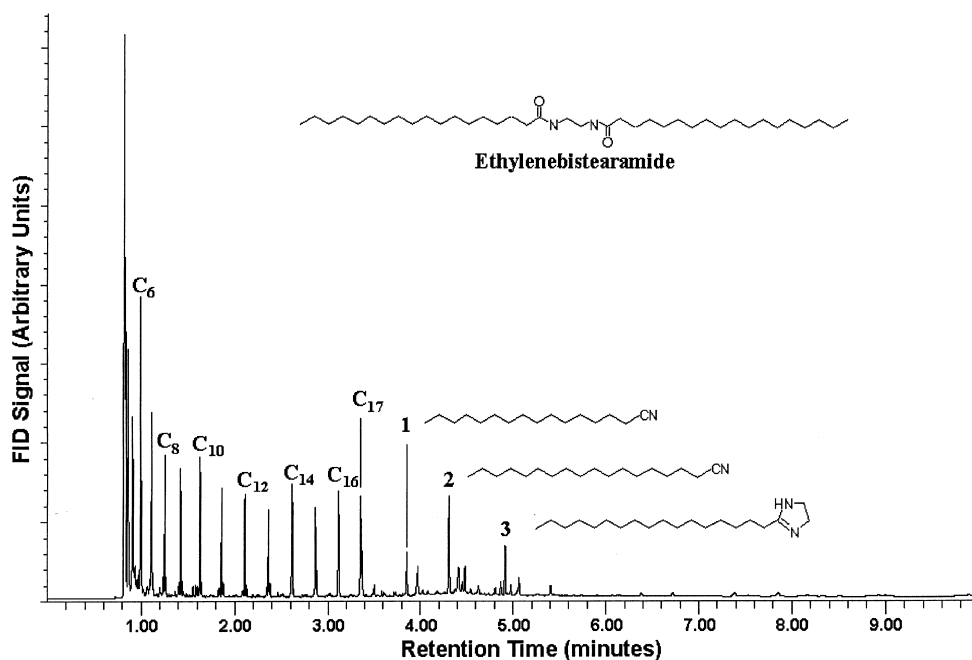


Fig. 11. The pyrogram of *N,N'*-ethylenebistearamide. The identification of peaks labeled in the pyrogram is 1=hexadecanenitrile, 2=octadecanenitrile, 3=1H-2-heptadecyl-4,5-dihydroimidazole.

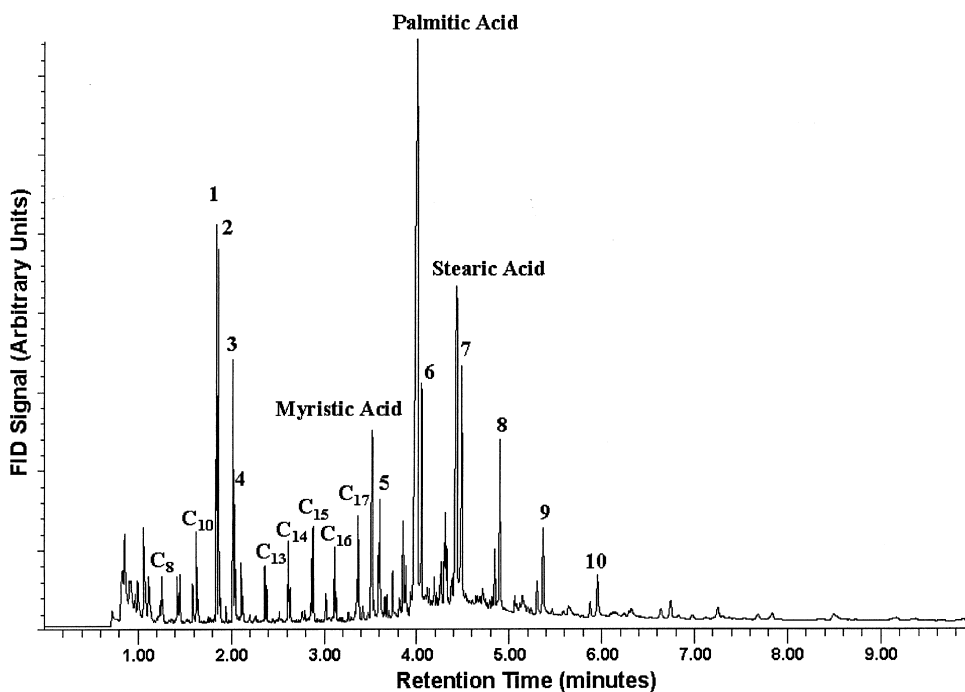


Fig. 12. The pyrogram of polyethylene (Spartech 14575). The identification of peaks labeled in the pyrogram is 1=1-isocyanato-2-methylbenzene, 2=2-methylaniline, 3=2-chloroaniline, 4=1-isocyanato-2-chlorobenzene, 5=octadecane, 6=eicosane, 7=docasane, 8=tetracosane, 9=hexacosane, 10=octacosane.

myristic acid, palmitic acid, and stearic acid and their relatively peak intensities in the pyrogram strongly indicates that technical-grade stearic acid has been used as the lubricant or mode release agent in this thermoplastic resin. The detection of the 1-alkene series all the way up to C_{17} is another proof that stearic acids or their related esters, amides or metallic salts has been used. The pyrolysates of 1-isocyanato-2-methylbenzene (peak 1) and 1-isocyanato-2-chlorobenzene (peak 4) are additives for other purposes. The pyrolysates of 2-methylaniline (peak 2) and 2-chloroaniline (peak 3) are the hydrolysis forms from previous compounds. The hydrolysis reaction is an often observed secondary reaction that takes place in the pyrolysis interface when the isocyanate functional group containing compound or polymer is pyrolyzed. The even number saturate alkane series detected from C_{18} to C_{28} (peaks 6–10) maybe belongs to another type of wax added for the lubrication or mode release purpose.

4. Conclusions

Lubricants used in polymers generally fall into two types of compounds. The first type includes fatty acids and their related esters, amides and metallic salts. The fatty acid mainly is stearic acid. The other type consists of the waxes derived from petroleum refinery products that are mixtures of hydrocarbons from C_{20} to C_{50} or higher. Py–GC can distinguish between these two general types by the series of hydrocarbon pyrolysates produced. Stearic acid and related lubricants generally produce a set of alkenes from C_3 to C_{17} to reflect the degradation of aliphatic hydrocarbon chain of stearic acid. In contrast, the petroleum wax family produces hydrocarbon pyrolysates of C_{20} to C_{50} or higher in addition to C_3 to C_{50} as a result of its composition. In order to distinguish esters, amides and metallic salts of the stearic acid family, auxiliary techniques may be

required along with Py–GC to achieve a complete identification. In addition, the analysis of lubricants requires a pre-separation of the additive package from the parent polymer that is a critical step in the lubricant analysis. In the Spartech 14575 thermoplastic resin study, Py–GC–MS was able to demonstrate that specific pyrolysates can be identified to correlate back certain lubricant or mode release agent used which in this case were technical grade stearic acid and other unknown type of wax. The advantages of Py–GC analysis of lubricants are the simplicity and quick turnaround time. In many instances, Py–GC may not be able to completely distinguish them in one experiment. However, the information generated from Py–GC is certainly very useful for the determination of further directions of the analysis. Py–GC definitely serves as a complete identification in some cases, and provides a screening tool in others.

References

- [1] J.T. Lutz, in: *Thermoplastic Polymer Additives*, Marcel Dekker, New York, 1989, p. 282.
- [2] J. Stepek, H. Daoust, in: *Additives for Plastics*, Springer-Verlag, New York, 1983, p. 23.
- [3] J. Murphy, in: *The Additives for Plastics Handbook*, Elsevier Advanced Technology, Oxford, 1996, p. 240.
- [4] T. Riedel, in: R. Gachter, H. Muller (Eds.), *Plastics Additives*, 4th ed., Hanser/Gardner, Cincinnati, OH, 1993, p. 424.
- [5] F. Jowett, F.A. Martin, in: J. Edenbaum (Ed.), *Plastics Additives and Modifiers Handbook*, Van Nostrand Reinhold, New York, 1992, p. 787.
- [6] D. Dieckmann, in: J. Edenbaum (Ed.), *Plastics Additives and Modifiers Handbook*, Van Nostrand Reinhold, New York, 1992, p. 858.
- [7] T.P. Wampler, in: T.P. Wampler (Ed.), *Analytical Pyrolysis Handbook*, Marcel Dekker, New York, 1995, p. 1.
- [8] F.C.-Y. Wang, P.B. Smith, *Anal. Chem.* 68 (1996) 3033.
- [9] F.C.-Y. Wang, B.B. Gerhart, P.B. Smith, *Anal. Chem.* 67 (1995) 3536.
- [10] H. Ohtani, S. Tsuge, T. Usami, *Macromolecules* 17 (1984) 2557.