1998

# Compatibility of Polymeric Materials with Low-Viscosity Refrigeration Lubricants

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# COMPATIBILITY OF POLYMERIC MATERIALS WITH LOW-VISCOSITY REFRIGERATION LUBRICANTS

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## ABSTRACT

*The desire to improve compressor energy efficiency ratings (EER) has driven refrigeration compressor manufacturers toward lower and lower viscosity lubricants. This is particularly true with regard to the small appliance, hermetic compressor market. The shift toward low viscosity lubricants has made the optimization of the lubricant system even more challenging. In addition to providing excellent durability, the lubricants must be compatible with all of the materials which comprise the refrigeration system. In general, however, the lower viscosity lubricants have proven to act as better solvents than their high viscosity counterparts. This enhanced solvency can result in the extraction of low-molecular weight components present in polyethylene terephthalate and other polymeric materials used in the manufacture of refrigeration compressors. Dissolution of polymer components can, in turn, lead to a wide range of system problems. Factors affecting the compatibility of several lubricants with polymeric materials have been systematically studied. The results of these compatibility studies as well as criteria for lubricant selection are discussed herein.*

## NOMENCLATURE

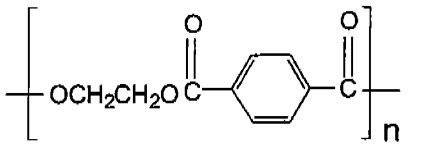
Energy efficiency rating (**EER**); Polyol ester (**POE**); alpha-branched POE ($\alpha$-**Br**); hydrofluorocarbon (**HFC**); monopentaerythritol (**MPE**), poly(vinyl) ether (**PVE**); polyethylene terephthalate (**PET**); Polybutylene terephthalate (**PBT**); end of test (**EOT**).

## INTRODUCTION

Previous studies on PET used as motor insulation have established that PET films are most stable in their driest state. Ester lubricants which contain ≤300 ppm water have been reported to protect PET by forcing water to migrate out of the film. The work of Harrington and Ward, among others, has suggested that the partial pressure of moisture in the vapor space of the hermetic milieu is likely to be a more important indicator of PET degradation than the water content of the lubricant itself. Thus, factors which affect the partitioning of water have been thought to be the most critical to PET integrity [1,2].

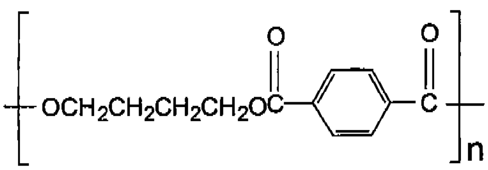
Many of the lubricant/polymer compatibility studies published to date have addressed the effect of ISO 22 to ISO 68 POEs on PET structural integrity [3-5]. In recent years, the shift toward low viscosity lubricants necessitates that lubricant compatibility with motor insulating materials be revisited. Slot liners, inter-phase and cover insulations, mufflers and cluster assemblies are comprised of polymeric materials which appear vulnerable to lubricants of greater solvency. Indeed, even systems which have exhibited very low lubricant water content after compressor life testing have shown severe polymer embrittlement and degradation. Our results indicate that embrittlement results from the extraction of the natural plasticizers (trimer, etc.) that are found in PET while degradation of the films occurs via interaction with water to result in film cleavage via a hydrolysis mechanism.

The work presented here addresses the compatibility concerns which must be taken into account when considering a move toward low viscosity lubricants [6,7]. The following studies reveal that dry POE lubricants (≤50 ppm $H_2O$) extract low molecular weight oligomeric components from PET and PBT motor insulating materials. The primary structures of the extractable materials have been characterized and are represented in Figure 1.



n = 3; MW = 576

A. Poly(ethylene Terephthalate) Trimer



n = 2; MW = 440

B. Poly(butylene Terephthalate) Dimer

**Figure 1. Low Molecular Weight Oligomers Extracted from PET and PBT**

## EXPERIMENTAL METHODS

***Extraction of Low Molecular Weight Oligomers from Polymeric Electrical Insulating Materials.*** Four different PETs were compared with respect to low molecular weight oligomer content. Polymer samples (10g PET/150 g $CHCl_3$) were refluxed in chloroform for 5 hrs. with stirring. Upon removal of solvent, the PET trimer was isolated as a grayish-white powder. The same type of experiment was also conducted with PBT obtained from compressor muffler material. Oligomer extracted from PBT was isolated as a deep yellow, amorphous solid. In each case, the extracted materials were subjected to characterization via Gas Chromatography-Mass Spectroscopy (GC-MS). Using chemical ionization GCMS, the M+1 peaks were obtained for each of the structures shown in Figure 1. Extracted materials were then used for the development of the HPLC assay to quantitate PET/PBT degradation products.

***HPLC Assay.*** PET degradation products were quantitated using a Waters 600E HPLC system equipped with a Waters 700 WISP autosampler and a HP ChemStation data acquisition system. The stationary phase employed was a $C_{18}$ column (250 mm x 4.6 mm, 5 mm Microsorb-MV; Rainen Instrument Co.). Mobile phases used were (A) 0.5% acetic acid in water and (B) 0.5% acetic acid in acetonitrile. A non-linear (Waters Curve 4) gradient [A to B (35 min.); B held for 5 min., B to A (30 min.)] was used to effect separations. Chromatograms were obtained using a 1 mL/min. flow rate (25 °C) and UV detection via HP Series 1100 diode array detector ($\lambda$ = 230 nm). Using these conditions, a calibration curve was generated for the trimer isolated using the chloroform extraction procedure. In all cases, the HPLC of lubricants before thermal stressing were obtained as the control run. In addition, the chromatograms of lubricants heated in the absence of polymer were also obtained.

***Incubation Studies.*** In one series of experiments, PET and PBT materials were incubated in lubricants of equivalent viscosity but different chemical structure. In a second set of studies, the effect of decreasing POE viscosity on oligomer degradation was the primary focus. Concentration of polymer immersed in each lubricant ranged from 5-10 wt.% for all thermal studies. After incubation at 75 to 180 °C for periods of 1 to 16 weeks, fluid TANs were obtained and PET embrittlement assessed. In addition, the HPLC assay described above was used to quantitate oligomer content. An absolute quantitation of cyclic trimer (mg/mL lubricant) was made after thermal stressing of each lubricant sample which contained 5-

10 wt% PET. In addition, the area percents of cyclic trimer as well as the total percent of oligomer degradation products were measured.

***Compressor Life Tests.***

***a.) ISO 15 POE/R-134a Compressor Tests.*** ISO 15 lubricants were tested in small appliance reciprocating compressors for 2000 hrs. using a high temperature life test. Suction and discharge pressures corresponding to saturation temperatures of -10 °C (1.0 bar) and 55 °C (14 bar), respectively, were maintained while winding temperatures were held at 150 ± 5 °C. Average winding temperatures were kept constant by carefully maintaining ambient temperature at 130 °C throughout the course of the test.

***b.) ISO 7 POE/R-134a Compressor Tests.*** ISO 7 lubricants were subjected to 2000 hr. life tests using small reciprocating compressors (115V/60 Hz). Test conditions included: suction pressure, 1.4 bar ($T_{evap}$ = -5 °C); discharge pressure, 20.5 bar ($T_{cond}$ = 70 °C); winding temperatures were maintained at either 135 ± 5 °C or 150 ± 5 °C.

## RESULTS AND DISCUSSION

***ISO 10 POE Extraction of PET Trimer from Several Different PET Sources (Figure 2).*** Four different PET materials currently used in compressor manufacture were heated in the presence of two different ISO 10 esters at 160 °C for 1 to 3 weeks. After 1 week, the linear ester extracts a greater amount of trimer from the PET film relative to the α-branched ISO 10 POE. At 3 weeks incubation, the differences between the two esters becomes more pronounced.

Relative to the α-Br ester, the linear ester extracts higher levels of PET trimer from three of the four PET films tested. Interestingly, one of the PET film samples appears more susceptible to degradation by the α-Br ester at the 3 wk. time period. In short, at temperatures above 150 °C, significant levels of PET adulteration are seen in the presence of both types of ISO 10 ester lubricant.

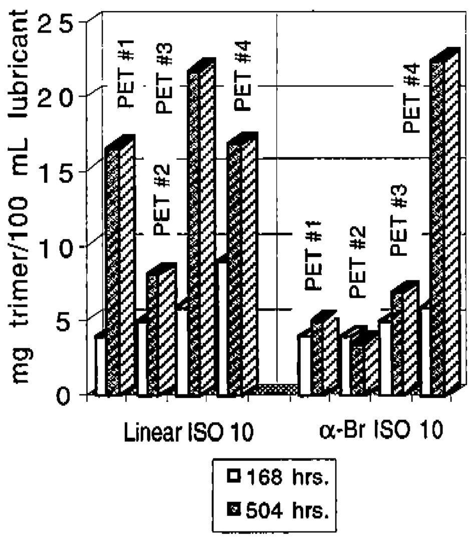



**Figure 2. Extraction of PET Trimer From Several Slot Liner Materials by ISO 10 POEs (160 °C, 1 and 3 wks.)**

***Relationship Between POE Viscosity and Oligomer Extraction (Table 1; Figure 3).*** HPLC analyses of samples incubated at 160°C for 5 weeks clearly illustrate the inverse relationship between viscosity and PET film degradation. That is, as the viscosity of the lubricant decreases, the extent of PET degradation increases sharply. This

**Table 1. HPLC Quantitation of PET Degradation Products (ISO 5 to ISO 46 POE Lubricants, 5 wks., 160 °C)**

| POE Vis @ 40 °C | PET degradation products Area% | PET Trimer Area% | PET Trimer mg/mL |
|---|---|---|---|
| 5 | 82.5 | 5.4 | 0.08 |
| 7 | 78.2 | 2.5 | 0.08 |
| 7.5 | 49.8 | 4.8 | 0.12 |
| 10 | 44.3 | 7.6 | 0.10 |
| 15 | 34.0 | 10.3 | 0.15 |
| 19 | 32.7 | 11.1 | 0.08 |
| 46 | 23.5 | 4.1 | 0.08 |

is particularly true for lubricant having a viscosity lower than 10 cSt @ 40 °C. The extent of PET degradation has been ascertained using the total area% of new products found in the lubricant and not based solely on the PET trimer content.

Supplementary work in our laboratory (results not presented) has indicated that the cyclic trimer species can undergo further hydrolysis and ring-opening transformations, making it necessary to quantitate total degradation products.

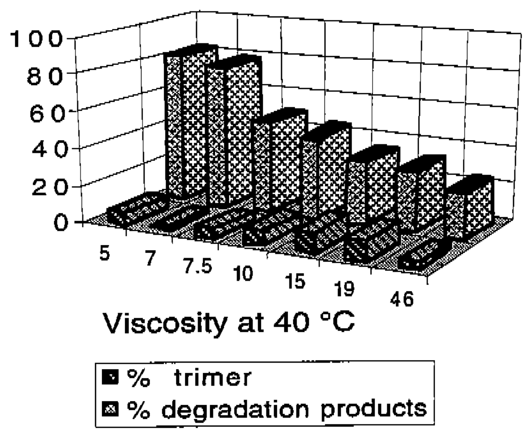



**Figure 3. Effect of POE Viscosity on Extraction of Low Molecular Weight PET Components.**

Esters heated in the absence of PET do not exhibit any of the peaks attributed to PET decomposition. Ester lubricants of interest in this study ranged from 5 to 46 cSt at 40°C.

***Oligomer Degradation During Compressor Life Testing with ISO 15 POEs (Figure 4).*** Upon completion of 2000 hr. life testing with ISO 15 POEs, thorough assessments of the insulating materials were made. Results indicate that the thin PET sheet which covers the exposed parts of the windings were brittle and required only moderate pressure to fracture. In addition, the PET liner used for the stator slots were similarly embrittled. While the average temperature of the motor windings throughout the course of the test was 151.6 °C, at no time during the run did the average temperature exceed 154.5 °C. Local regions of deterioriation were observed as holes in the slot liner films. These results appear to indicate that winding temperatures measured during life testing may not be a true represention of the actual temperatures which can exist at local regions within the motor assembly.

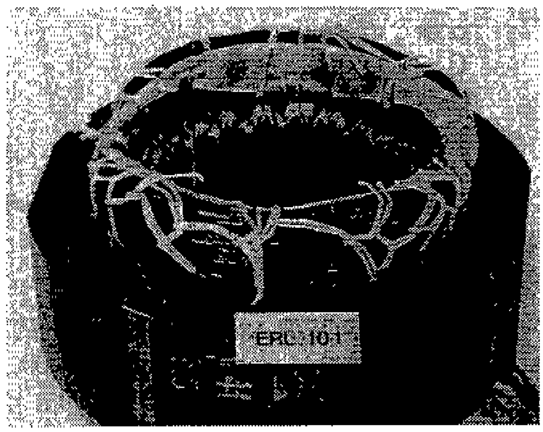
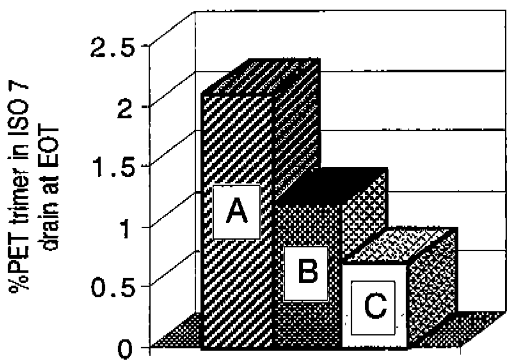


**Figure 4. Photograph of Motor Windings and Insulation Materials after Compressor Testing with ISO 15 Lubricant.**

***Oligomer Degradation During Compressor Testing with ISO 7 POEs (Figure 5).*** Compressor life testing with ISO 7 POE/R-134a resulted in varying degrees of PET/PBT embrittlement with several lubricants which contained antioxidant as the sole additive. The results in Figure 5 show %PET trimer found in each lubricant after completion of the life tests.

At an average winding temperature of 150 °C, extraction of the PET trimer occurred to the greatest extent with a linear ISO 7 blend which contained an ISO 5 blend component. A single ester ISO 7 fluid showed ~50% less trimer content then the blended lubricant. The α-Br ISO 7, on the other hand, resulted in the lowest amount of PET trimer found in any of the three compressor drains.

**However, quantitation of the trimer alone does not yield an accurate account of polymer interaction with lubricants.** While the α-Br ISO 7 exhibited the least amount of trimer, the total amount of oligomer found in this drain was higher than that of the linear formulations. This suggests that α-Br ISO 7 might interact to a greater degree with polymers such as PBT (cluster assembly) than the linear esters. This α-Br/PBT interaction is supported by the observation that the PBT cluster assembly had undergone severe embrittlement during this test. Even at average winding temperatures in the range of 120-140 °C, film embrittlement is observed upon completion of compressor life tests. Once again the results imply that average winding temperatures do not accurately represent the true conditions within the compressor. In effect, none of these ISO 7 lubricants give desirable performance with respect to materials compatibility.




A: linear ISO 7 Blend
B: linear ISO 7
C: α-branched ISO 7

**Figure 5. Effect of ISO 7 POE Structure on PET Trimer Extraction.**

***Interaction of PET with PVEs.*** Incubation of PET in PVE fluids containing 2000 ppm water results in severe oligomer extraction and PET embrittlement after 7 days at 130 °C. We have determined that the water saturation level of PVEs lies in the range of 7000-8000 ppm, therefore 2000 ppm is approximately one-fourth the saturation level. Under these conditions, the PVE fluids behave like ISO 7 POE lubricants (dry, 160 °C, 5 wks.) with respect to PET decomposition.

**Table 2. HPLC Quantitation of PET Degradation Products in PVE Fluids. (1 wk., 130 °C, 2000 ppm $H_2O$)**

| PVE Vis @ 40 °C | PET degradation products Area% | PET Trimer Area% | mg/mL |
|---|---|---|---|
| 32 | 65.8 | 11.9 | 0.20 |
| 68 | 65.2 | 16.7 | 0.19 |

## CONCLUSIONS

• PET films undergo rapid embrittlement in the presence of low viscosity lubricants at temperatures in excess of 150 °C. Based on sealed tube experiments, the critical temperature at which rapid PET degradation occurs lies in the range of 150-160 °C. The attainment of such temperatures is not uncommon during compressor life testing.

• The embrittlement of polymer components such as PET and PBT appears to correlate with the extraction of low molecular weight oligomers such as the cyclic trimer (PET) and dimeric (PBT) species shown in Figure 1. These low molecular weight oligomers are then further transformed upon interaction with nucleophilic species (water, alcohols, etc.) present in the compressor system. In some cases, the reaction of the dissolved PET trimer in this manner can result in the formation of insoluble deposits. In addition, the dissolved PET and PBT oligomers from embrittled insulating films can also contribute to deposits in capillary expansion devices [8,9].

• Different sources or modifications of PET do not eliminate problems of PET embrittlement in the presence of low viscosity esters.

• In studying PET interactions, quantitation of trimer alone is insufficient to describe the extent of polymer alteration, total oligomer content must be measured.

• Low viscosity POEs typically show greater extraction of oligomeric materials and more embrittlement of insulation materials, relative to their high viscosity counterparts.

• Alternatives to POEs, such as PVEs, also interact with PET films and are particularly prone to degrade PET when the PVE is wet.

• While low viscosity lubricants have been effectively used in small hermetic compressors, it is important to maintain an awareness of the potential interactions of lubricants with motor insulation materials.

## ACKNOWLEDGEMENTS

The authors would like to express sincere thanks to Ken Wagner for the careful observations made during the extended thermal incubation studies and to Greg Lentz for his technical expertise in conducting the HPLC assays.

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