Relaxation phenomena of automotive TPEs

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Executive summary

In the automotive industry, the most widely used technique to predict the sealing capacity of gasketing material is based on compression set data which is obtained after short-term aging in air or reference fluids.

This is an indirect measure of sealing capacity and can easily be misleading as a predictor of the sealing performance of gaskets.

Recent increases in service temperature requirements along with the use of SG-grade motor oils have created the need for a better means of measuring the long-term performance of gasket materials.

This paper reports compression stress relaxation measurements on thermoplastic elastomer materials and how these measurements compare with compression set data.

The report also outlines the trends of testing gasket materials within the automotive industry and other sectors.

Historically, the use of thermoplastic elastomers in severe service environments has been limited by TPEs' inherent intrinsic properties.

The "softer" grades of most TPEs possess neither high temperature- nor oil/solvent-resistance to displace the thermoset elastomers that have dominated severe service applications for many years.

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With the development of newer thermoplastic materials and changing perceptions, however, it is evident that some TPEs, thermoplastic vulcanizates and co-polyesters are finding expanding markets in these environments as the press toward TPEs with improved heat- and solvent-resistance continues to result in more resins in the market place which are performance competitive with TSEs.

One of the TSE mainstays has been automotive engine compartment applications, particularly oil and transmission seals—applications "off limits" for conventional TPEs.

Increasing under-the-hood temperatures have driven the upper end of the required performance temperature window to 175° C for certain elastomeric components.

TPEs continue to make inroads into several underhood applications, usually where specification requirements are typically a maximum of only 125° C. At the same time, seals in contact with various fluids at these service temperatures further eliminate a number of TPEs from consideration for use as gaskets, O-rings and fluid-component sealing applications.

Since both temperature and fluid exposure in combination represent particularly difficult challenges for TPE materials in sealing applications, it becomes increasingly important to be able to predict the performance of new resins in both of these environments.

As the industry pursues the manufacture of these improved resins, appropriate performance evaluation tools continue to evolve as well. Historical single-point material property characterization testing, e.g., stress-strain, hardness and flexural properties, is useful when attempting to predict the life expectancy of a part, particularly in severe service. The advent of computer modeling and finite element analysis as applied to thermoplastic parts is particularly useful in identifying localized stress concentration areas, but is less useful when complicating and transient environmental variables are introduced.

For several years now, manufacturers of high performance TSEs, including Dow Corning STI and General Electric Co., as well as automotive manufacturers, most notably Ford Motor Co. and General Motors Corp., have been investigating the use of compression stress-relaxation testing as a means of predicting the service life of TSE seals in simulated service environments[2-5]. While most of this test work has emphasized higher service temperatures (150° C and 175° C), other TSE and TPE polymer manufactures, notably Shell Chemical Co., AES and Zeon Chemicals Inc., have developed an interest in testing for compression stress-relaxation at reduced temperatures (70° C to 125° C).

At the same time, the Society of Automotive Engineers under the auspices of its CARS subcommittee on Long Term Aging, recently issued SAE J2236 which defines the continuous upper temperature limit for elastomeric materials based on long-term aging performance (1,008 hours)[6].

Also forthcoming from Ford and GM are specification performance standards for automotive seals based on compression stress-relaxation testing, which most likely will replace or be added to existing compression set testing requirements (ASTM D 395). ISO/BS compression stress-relaxation standards have been in existence for some time now[7-9].

Defining 'severity'

The term "severe service" as applied to elastomeric materials is commonly associated with hostile temperatures and chemical environments, either singly or more often in combination.

For the manufacturers of TPE components for automotive underhood applications, the term "severity" varies considerably, depending not only on the environmental variables but on the TPE polymer itself. In the family of all TPEs, severity varies considerably.

Consequently, service life prediction for an individual TPE should be made only within near-reasonable temperatures and environments.

Accelerated aging

In 1990, Rapra Technology Ltd.'s R.P. Brown[10] conducted a survey on the status of methods for accelerated durability testing of polymers.

Input from 350 companies worldwide was solicited. Rapra concluded in part that, "... normally single-point (tests) are really only effective as (quality assurance) procedures ..." and that, "... for thermal effects, the only recognized procedure is Arrhenius."

The classic Arrhenius equation,
$(d \ln k)/dt = -(E/t^2)$, can be modified to:
$\log k = (E/2.303R)(1/T) + C$
Where:
k = Specific activation rate
E = Activation energy for the reaction
R = Gas constant per gram molecular weight
T = Absolute temperature in Kelvin
C = Mathematical constant

A straight line is produced when the log of a specific reaction rate is plotted against the reciprocal of absolute temperature since the above equation form is $y = mx + b$.

It has been empirically demonstrated that many reactions double or triple their rates for every 10° C. As a result of both empirical observation and the

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Fig. 1. Compression stress relaxation test jig.

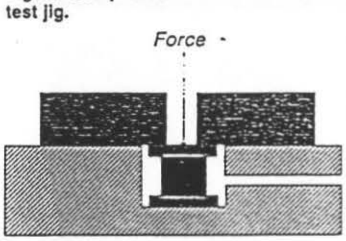

Fig. 2.

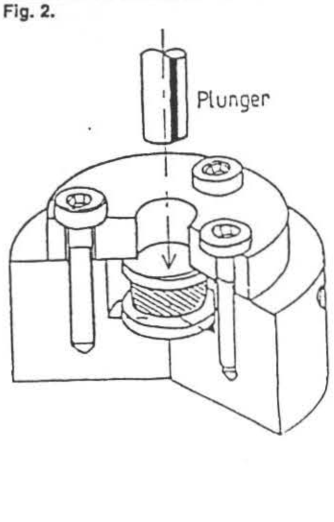

Fig. 3. Sealing force decay.

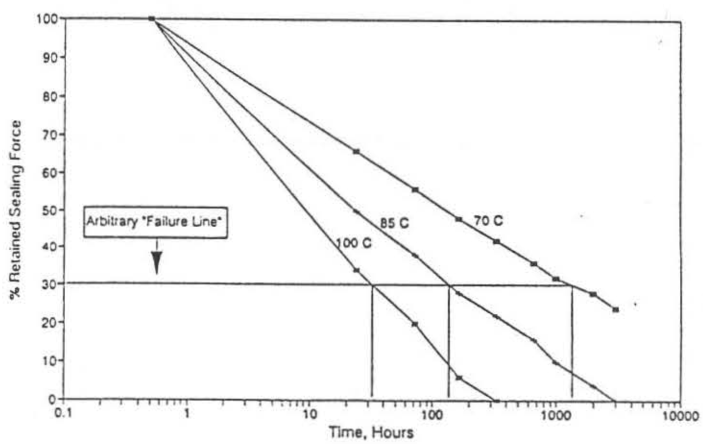

Fig. 4. Percent of retained sealing force.

Time Hours	70°C TPE #1	70°C TPE #2	85°C TPE #1	85°C TPE #2	100°C TPE #1	100°C TPE #2
0.5	100.0	100.0	100.0	100.0	100.0	100.0
22	42.0	49.9	26.0	35.3	14.0	27.6
72	37.1	43.7	20.4	30.9	13.2	27.1
166	31.4	37.6	19.5	28.6	0.0	26.1
336	29.4	33.6	18.0	25.9	0.0	24.5
666	27.3	31.5	17.8	25.2	0.0	23.6
1000	25.2	31.8	13.9	24.5	0.0	21.8
2000	25.4	31.8	0.0	23.8	0.0	16.8
3000	25.6	33.2	0.0	22.9	0.0	11.7

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above linearity, if one carefully chooses a meaningful property that relates to service life, it's possible to predict performance at extrapolated temperatures based on observed results at several actual temperatures. This technique has been used successfully for many years when dealing with thermoset elastomers in severe environments[11-12].

Gasketing life expectancy

The automotive industry has focused on the percent of retained sealing force as a function of time as the multipoint parameter for useful service life prediction: When sealing force has decayed to 2.5 percent of the original sealing force, the seal is considered to have failed.

The stress decay of polymer components under constant compressive strain is known as compression stress-relaxation. The test measures the sealing force exerted by a seal or O-ring under compression between two plates (See Fig. 1). It provides definite information for the prediction of service life by measuring the sealing force decay of a sample as a function of time, temperature and environment.

The ARDL test apparatus used for the compression relaxation measurements is the ISO 3384 Wykeham Farrance device. This device measures the counter force exerted by a specimen maintained at a constant strain between two stainless steel plates inside the compression jig.

The instrument has a variety of jigs for accommodating test pieces or O-rings up to 100 mm outer diameter. Various service environments such as liquid, gas, or a mixture of liquid and gas can be introduced into the stainless steel compression jig and maintained during aging and testing. A typical cross-section view of the compression jig is shown in Fig. 2.

A typical sealing force decay graph of a TPE gasket is shown in Fig. 3. These curves were obtained at 25-percent constant compressive strain at three accelerated aging temperatures (70° C, 85° C and 100° C). In this example, the specimens were aged until an arbitrary "failure point" for retained sealing force is reached, i.e., when the sealing force decays to 25 percent of the original unaged sealing force. Sealing force readings may be found in Fig. 4.

Fig. 5 is the Arrhenius service life plot from data obtained from the three decay plots from Fig. 3. The abscissa is the reciprocal of the absolute temperature, but for convenience, the equivalent Celsius temperature is shown.

Compare the single-point compression set data on the two TPEs (Fig. 6) with the multipoint compression stress-relaxation curves (See Figs. 7,8 and 9). Note that TPE #2 does not totally degrade at 100° C, but that TPE #1 does. This data partially explains original equipment manufacturers' preference for the stress-relaxation data.

Besides elevated temperature testing, the environment during compression stress-relaxation also can be varied to obtain data at low temperatures and/or in corrosive, oxidative or fluid environments. An example of multi-media predicted service life curves from a recent TSE study is shown in Fig. 10.

Compression stress-relaxation testing is now underway at ARDL on a variety of elastomeric seals in several "severe" environments for 1,008-hour agings. The results of a previous study were given in Denver at the ACS Rubber Division meeting in May 1993.

Predictive testing

Data to date has shown two particu-

Fig. 5. Arrhenius service life prediction.

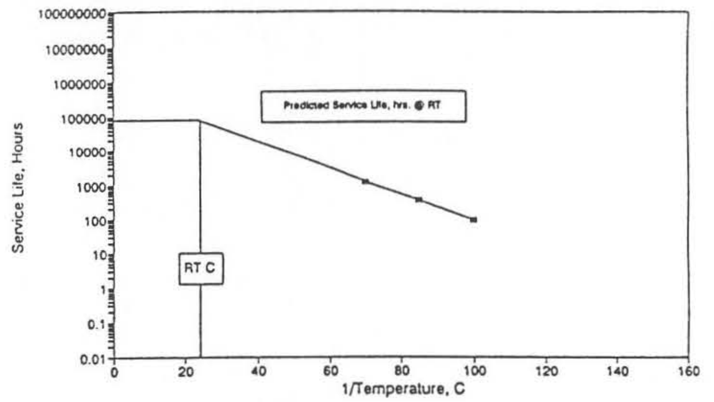


Fig. 6. Compression set (ASTM D-395).

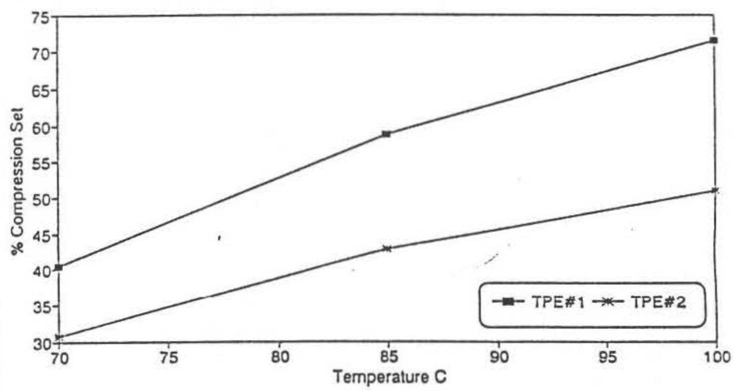


Fig. 7. Compression stress relaxation at 70° C.

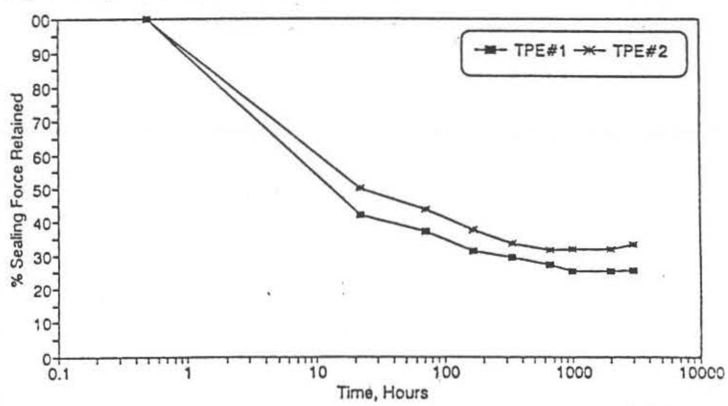
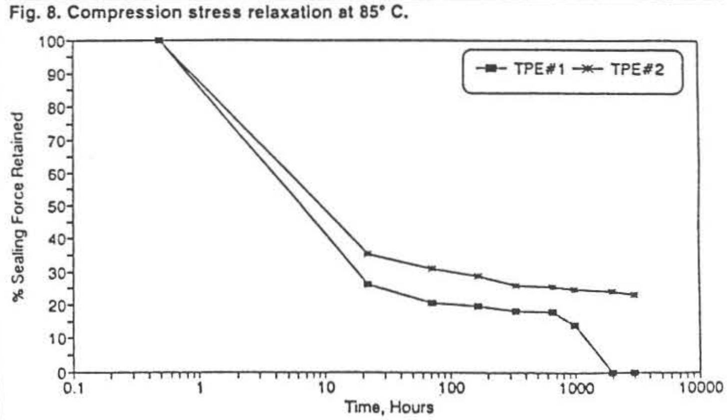


Fig. 8. Compression stress relaxation at 85° C.



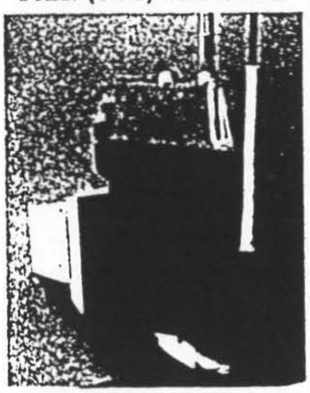


Fig. 9. Compression stress relaxation at 100° C.

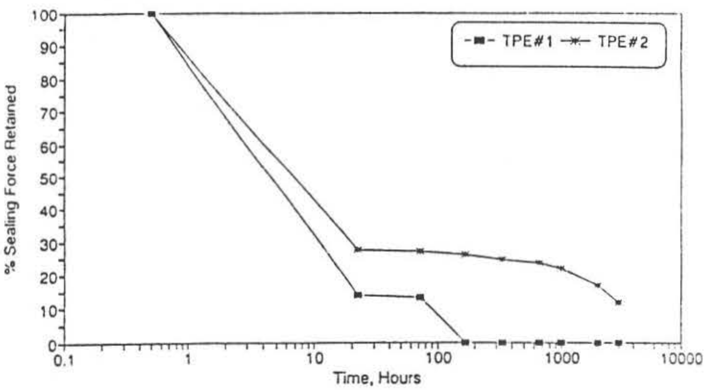
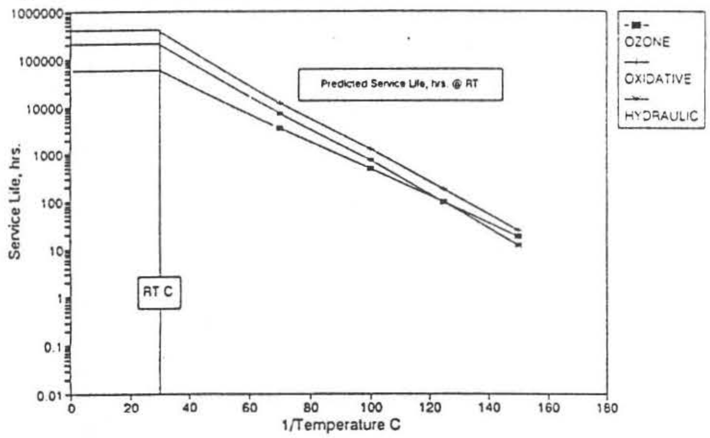


Fig. 10. Service life in severe environments.



lar benefits from a TPE perspective:

- behavioral characteristics of thermoplastics under constant compressive strain; and
- the concept of maximum service temperature for TPE seals.

The thermoplastic behavior short term is consistent with compression set results obtained after short duration; thereafter the retained sealing force plateaus in contrast to TSE materials which show progressive deterioration.

As expected, TPEs are more temperature-sensitive than TSE materials, with a tendency to degrade beyond certain temperature limits. While this is a characteristic of thermoplastic material, it can be used to establish the continuous upper temperature for a given material application, particularly when tested in the proper media.

Summary

Compression stress-relaxation is the testing methodology currently being used to assess performance and predict the service life of thermoset elastomeric seals in severe environments, and will most likely replace the single-point compression set test on automotive material specifications.

As thermoplastic elastomer materials are developed for more severe-service applications, this testing methodology can be used to predict service life for TPE seals. It also can be used for comparative testing against TPE controls or other TSEs already being used in a particular application.

The life prediction methodology is soundly based on continuous multipoint stress-relaxation coupled with classical Arrhenius aging. Screening TPE materials utilizing this approach yields insight into long-term performance in severe environments.

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