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Failure analysis and quality control of automotive elastomeric seals by thermal analytical techniques

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Abstract

Integral parts of any automotive fluid system are the seals. Elastomers are used in automotive applications for their resilience and rebound attributes. These elastomeric parts are flexible, impervious to hostile engine environments, including hot-stressed additized motor oils. There are a number of standard tests for tensile quality and elongation of rubber seals and parts. Most standard rubber tests are based on quasi-real world conditions.

Thermal analysis can be used to evaluate rubber seals and parts for composition by thermogravimetric analysis (TGA). Dynamic mechanical analysis (DMA), thermomechanical analysis (TMA) and differential scanning calorimetry (DSC) can ascertain mechanical strength and the glass transition temperature, T_g. TGA/differential thermal (DTA), DSC and pressure DSC can evaluate the oxidative stability of seals. Results of a TMA and TGA quality control test differentiated pass and fail elastomeric seals and parts. Characterization of several failed seals revealed the source of some unique field problems.

Keywords: Thermomechanical analysis; Thermogravimetric analysis; Elastomers

1. Introduction

The elastomers studied represent high profile automotive seal and gasket type polymer [1]. These rubber products are capable of being formed under load, but must maintain their highly elastic properties. Traditional seals, for example, a nitrile elastomer or a fluoroelastomer, can degrade while in contact with hot lubricant oils by cross-linking through their unsaturated chemical bonds or by thermal degradation.

MacPherson and Conary studied elastomer compatibility with gear lubricants in immersion tests [2]. They observed that additive chemistry effected the average percent change in tensile strength for 144 h: +21% for the fluoroelastomers and −3% for nitrile rubber seals. They demonstrated that elastomeric seals when subjected to immersion tests in gear oils are susceptible to gear oil chemistry. Various gear oil additives give rise to differing degrees of degradation in nitrile, polyacrylate and fluoroelastomer seals. The repeatability of immersion tests was deficient, and they recommended multiple tests be run on any given oil. They also noted that polyacrylate elastomers are superior to either a fluoroelastomer or nitrile with those gear oils selected for testing. Further, they reported that good compatibility with oil with any one supply of polyacrylate elastomer does not mean that compatibility will be observed with all seals of this type used in the field.

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The seals studied by TMA and TGA were nitrile rubber or fluoroelastomer, Viton®. The nitrile rubber seal chemically degrade by becoming harder, loose tensile strength and crack under load. Elastomeric compatibility with engine oils is a current and active domestic and European specification for fluoroelastomers, acrylics, silicone and nitrile rubber seals. Maximum variation after a seven day immersion test are recorded for hardness, percent change in tensile strength, percent change in elongation at rupture and percent change in volume [2,3].

Thermal techniques are useful in evaluating new and used rubber seals and parts, understanding field failure problems and determining the polymer quality and identity [4–6]. Thermal Analysis, TMA and TGA are used to determine physical properties that can establish quality assurance and distinguish a product from competitors.

An objective of this study is to develop a TGA and TMA quality control and failure analysis protocol. The composition of the rubber part can be semi-quantitatively determined by TGA. The type polymer can be identified by the assigned glass transition temperature and either gas chromatography–mass spectrometry or FT Infrared Spectroscopy. The protocol must include a precision and bias statement. A scheme to analyze a failed part must include evaluation of its thermal and mechanical properties. Establishing the proximate cause of a field failure aids the internal or external customer and improves the process.

2. Experimental procedures

A Seiko-Haake RTG 220 thermogravimetric analyzer coupled with a differential thermal analyzer; TGA/DTA was used for the thermal (in nitrogen) and oxidation (in air) studies. The experimental conditions are as follows: 10 mg sample mass, 250 ml/min-air-flow rate, 10°C/min ramp rate, maximum temperature was 900°C and the sample containers were platinum pans.

A Seiko-Haake thermal mechanical analyzer was used to assign the glass transition temperature, T_g. The TMA conditions were cool to -80°C, heat to 50°C at 10°C/min under a 5 mg load.

A TAI modulated DSC was used to assign the T_g in the reversing heat flow mode. The MTDSC conditions were to cool to -80°C, isothermal 5 min, modulation ± 0.30°C/min, period 60 s, ramp at 2.0°C/min to 20°C.

3. Results and discussion

TMA and TGA evaluated automotive clutch seals, see Tables 1 and 2. The rubber seals were submitted with a limited knowledge of the polymer type or composition. The polymer T_g was assigned by evaluating the TMA thermal curve. The T_g was taken as the extrapolated onset temperature in the dimensional change (y-axis) versus the sample temperature (x-axis). There appeared to be at least three to four type polymers characterized by TMA. Type I had a T_g at -32°C, Type II at T_g at -10°C, Type III, two T_g values at -71 and -32°C and Type IV, which could also be related to a Type II polymer, had a T_g at -10 and -78°C. The coefficient of linear expansion measured before the transition the T_g aided in identifying the various seals and parts. The original engine manufacturer (OEM) reported that there was only one polymer type for this application. However, there appears to be at least two different seals differentiated by TMA. Compositional analysis of the clutch seals confirmed the presence of two distinct seal types by TGA, see Table 2. Type II had higher decomposition temperatures, a higher polymer content and a lower weight percent carbon black than Type III. The polymer types were also clearly distinguished by TGA, based on the polymer's decomposition temperature and composition.

A set of clutch seals (Type III) leaked in a field taxi fleet car at 32,000 miles. Polymer Types II and III were not specifically associated with a leaking seal. Another fleet car had seals that exhibited no leaking at 25,000 miles and the seals were identified as being Types I, II or III. The mechanical properties and composition were not apparently related to the failed leaking seals. This implies that the failure may be related to the clutch hardware or seal surface cracking not detected by TMA or TGA.

A series of Viton® and Nitrile o-rings and a Rulon® bearing in a semi-passive shock absorber were evaluated by TMA, T_g and coefficient of linear expansion (COE), see Table 3. The Viton® T_g was -14°C with

Table 1
Thermal and mechanical properties of automotive clutch seals[a]

Clutch seals				TMA-T_g polymer type	Glass transition temperature (°C)			Coefficient of linear expansion (1/°C)		
Description		Problem			T_{g1}	T_{g2}	T_{g3}	COE1	COE2	COE3
1. Outer	Old	Unused	A	I		−32.1			46.8	134
2. Inner	Old	Unused	A	I		−32.4			48.2	121
3. Inner	New	Unused	A	I		−29.8			51.5	31.4
4. Front	New	Unused	A	II			−10.6		35.9	Penetration
5. Taxi fleet	32,089[b]		B	I		−29.3			57.3	88.6
6. Taxi fleet	32,089[b]		B	II			−9.6		36.5	Penetration
7. Taxi fleet	32,089[b]	Leaked	B	III	−69.6	−32.2		40.6	46.4	78.2
8. Taxi fleet	32,089[b]	Leaked	B	III	−69.9	−31.8		51.1	42.6	101
9. Fleet test	26,708[b]	No leaks	C	III	−74.4	−34.2		41.9	49.1	95.6
10. Fleet test	26,708[b]	No leaks	C	IV=II	−75.6		−10.2	36.2	48.2	38.1
11. Fleet test	26,708[b]	No leaks	C	I		−34.3			54.2	108
12. Fleet test	25,384[b]	No leaks	C	III	−70.6	−30.9		8.55	54.5	97.6
13. Fleet test	25,384[b]	No leaks	C	III	−71.9	−32.6		44.1	36.4	111
14. Fleet test	25,384[b]	No leaks	C	IV=II	−80.1		−10.4	39.2		5.38
15. Fleet test	25,384[b]	No leaks	C	III	−63.8	−33.8		33.9	31.9	25.3
16. Fleet test	25,384[b]	No leaks	C	III	−68.5	−33.2		36.8	50.3	71.1

[a] TMA-T_g polymer type=based on T_g values and COE's; $T_{g1}=T_g$ in the temperature range below −60°C; $T_{g2}=T_g$ in the temperature range of −60 to −20°C; $T_{g3}=T_g$ in the temperature range above −20°C; COE1=coefficent of linear expansion below T_{g1} ($\times 10^{-6}$); COE2=coefficent of linear expansion below T_{g2} ($\times 10^{-6}$); COE3=coefticent of linear expansion above 40°C ($\times 10^{-6}$).

[b] Indicates mileage.

Table 2
Compositional analysis and decomposition properties of clutch seals by TGA[a]

Clutch seals				TMA-T_g polymer type	Thermogravimetric analysis						
Description		Problem			Decomposition temperature (°C)			$T_{e1}-T_{o1}$	Compositional analysis		
					T_{o1}	T_{e1}	T_{o2}		w%1	w%2	Residue
1. Outer	Old	Unused	A	I	439	491	688	52	54.3	40.8	4.9
2. Inner	Old	Unused	A	I	436	495	687	59	53.7	41.3	5.0
3. Inner	New	Unused	A	I	437	496	689	59	54.4	41.2	4.4
4. Front	New	Unused	A	II	495	539	691	44	78.7	13.7	7.6
5. Taxi fleet	32,089[b]		B	I	433	493	668	60	51.3	40.8	7.9
6. Taxi fleet	32,089[b]		B	II	496	537	703	41	71.8	18.5	9.7
7. Taxi fleet	32,089[b]	Leaked	B	III	432	493	678	61	51.7	42.8	5.5
8. Taxi fleet	32,089[b]	Leaked	B	III	432	493	676	61	52.7	41.8	5.5
9. Fleet test	26,708[b]	No leaks	C	III	428	495	680	67	52.3	42.4	5.3
10. Fleet test	26,708[b]	No leaks	C	IV=II	497	538	681	41	70.6	18.7	10.7
11. Fleet test	26,708[b]	No leaks	C	I	428	495	687	67	52.1	42.7	5.2
12. Fleet test	25,384[b]	No leaks	C	III	426	497	686	71	52.9	40.6	6.5
13. Fleet test	25,384[b]	No leaks	C	III	428	495	684	67	52.4	42.6	5.0
14. Fleet test	25,384[b]	No leaks	C	IV=II	497	537	695	40	69.6	19.1	11.3
15. Fleet test	25,384[b]	No leaks	C	III	425	495	684	70	50.9	40.9	8.2
16. Fleet test	25,384[b]	No leaks	C	III	429	495	688	66	52.5	41.8	5.7

[a] T_{o1}: extrapolated onset temperature of polymer mass loss; T_{e1}: end temperature for polymer mass loss; T_{o2}: onset temperature for carbon-filler mass loss; w%1: wt.% elastomer in nitrogen; w%2: wt.% carbon black=carbon+air; residue: wt.% residue at 900°C in air.

[b] Indicates mileage.

Table 3
Thermal and mechanical properties of automotive seals and polymers[a]

Seals				Color	Glass transition temperature, T_{g1} (°C)	Coefficient of linear expansion (1/°C)	
Polymer		Pass/fail	Status			COE1	COE2
1. Viton	c		New	Black	−15.5	48.9	220
2. Viton	d		New	Brown	−14.6	38.8	214
3. Viton	q		New		−12.5	43.4	261
4. Viton	l	Passed	Used	Brown	−12.5	48.2	248
5. Viton	n	Passed	Used	Brown	−15.6	32.5	228
Average pass					−14.1	42.4	235
6. Nitrile	o		New		−27.4	39.9	146
7. Nitrile	g	Failed	Used	Brown	−13.2[b]	25.4[b]	235[b]
8. Nitrile	i	Passed	Used		−26.8	41.1	144
Average pass					−27.1	40.5	145
9. Rulon	p		New		25.2	74.3	Contraction
10. Rulon	j	Passed	Used		28.6	66.1	Contraction
Average pass					26.9	70.2	

[a] T_{g1}: T_g of the polymer, °C; COE1: coefficient of linear expansion below T_{g1} ($\times 10^{-6}$); COE2: coefficient of linear expansion above T_{g1} ($\times 10^{-6}$).

[b] These values are not included while taking the average.

Table 4
Compositional analysis and decomposition properties of Viton seals by TGA[a]

Seals				Color	Thermogravimetric analysis						
Description		Status	Pass/fail		Decomposition temperature (°C)			$T_{e1}-T_{o1}$	Compositional analysis		
					T_{o1}	T_{e1}	T_{o2}		w%1	w%2	Residue
1. Viton	c	New		Black	435	488	670	53	54.3	40.9	4.8
2. Viton	k	Used	Passed	Black	433	487	671	54	53.1	43.7	3.2
Average					434	488	670	54	53.7	42.3	4.1
3. Viton	d	New		Brown	467	507	635	40	60.9	5.6	33.5
4. Viton	q	New		Brown	468	506	635	38	60.8	5.7	33.5
5. Viton	l	Used	Passed	Brown	467	506	635	39	61.5	4.7	33.8
6. Viton	n	Used	Passed	Brown	471	505	635	34	60.4	5.7	33.9
7. Viton	h	Used	Passed	Brown	469	506	635	37	60.7	6.1	33.2
8. Viton	g	Used	Passed	Brown	468	506	637	38	60.9	5.5	33.6
9. Viton	m	Used	Passed	Brown	470	505	635	35	60.6	5.5	33.9
Average					469	506	635	37	60.8	5.5	33.7

[a] T_{o1}: extrapolated onset temperature of polymer mass loss; T_{e1}: end temperature for polymer mass loss; T_{o2}: onset temperature for carbon-filler mass loss; w%1: wt.% elastomer in nitrogen; w%2: wt.% carbon black=carbon+air; residue=wt.% residue at 900°C in air.

two COE values, above and below the T_g, respectively, 42 (glass phase) and 235 (rubber phase)$\times10^{-6}$ mm/mm/°C. The nitrile rubber T_g was -27°C and the two COE values were 40 (glass phase) and 145 (rubber phase)$\times10^{-6}$ mm/mm/°C. A failed seal, either a nitrile rubber or a mislabeled seal [7], had a significantly higher T_g at -13°C and a lower COE (glass phase) at 25×10^{-6} mm/mm/°C. The failed seal's mechanical properties suggest a harder, cross-linked rubber [6].

A series of Viton® seals were characterized by TGA, decomposition temperatures and composition, see Table 4. There was a difference between the 'black' and 'brown' seals. The carbon content of the 'black' seals was 42 wt.%, while the brown seal's 'apparent carbon black' or ash was 5.5 wt.%. This studied clearly showed that the TGA method was precise and reliable.

A failed automotive silicone rubber seal had some very unusual physical properties. The reverse mode MTDSC T_g, the inflection temperature of the T_g sigmoid shaped curve, was -46°C. It was as very weak transition. TGA revealed that only 6.5% of the 'seal' were polymeric. The remainder was apparently inorganic. The latter was confirmed by wide-angle X-ray diffraction where the major component was silicon dioxide (SiO_2). This rubber seal was exposed to high temperatures, confirmed by investigation into where and how the seal failed.

4. Conclusions

There is a good correlation between the TMA and TGA test results for a series of clutch rubber seals. The OEM was informed that several elastomers were being used in the clutch seal, and they were apparently different polymer types. TMA and TGA of the bulk elastomer did not differentiate the failed leaking seal from the good performing seal. A failed nitrile rubber seal apparently cross-linked and become harder with a lower coefficient of linear expansion. TGA can identify the decomposition temperatures and composition of polymeric seals. This method was also found to be precise.

The source of a failed silicone rubber was over heating. MTDSC-T_g and X-ray methods, structural examination, aided in this failure analysis.

The TMA and TGA procedures cited in this study are used in a routine manner for quality assurance of seal materials. ASTM standard test methods are the basis for the failure analysis and quality control protocols: ASTM E-1545, 'Test Method for the Assignment of the Glass Transition Temperature by TMA'

[8]; ASTM E-0831, 'Test Method for Linear Expansion of Solid Materials by TMA' [9]; and ASTM E-1131, 'Test Method for Compositional Analysis by TGA' [10].

References

[1] W.C. Wake, Analysis of Rubber and Rubber-like Polymers, Wiley, New York, 1969.

[2] I. MacPherson, G. Conary, Elastomer Compatibility with Gear Lubricants Part 1: Immersion Testing, STLE Preprint No. 94-AM-5C-1, 1994.

[3] Ready Reference for Lubricant and Fuel Performance, Lubrizol, Wickliffe, OH 44092, 1996.

[4] A. Sircar, Elastomers, in: E.A. Turi (Ed.), Thermal Characterization of Polymeric Materials, 2nd Edition, Academic Press, New York, 1997, pp. 888–1300.

[5] R. Rush, Evaluation of ethylene-propylene rubber o-rings for incoming quality control, Thermochim. Acta. 192 (1991) 171–190.

[6] A. Riga, Quality Control of Rubber Products-Tg by DSC and TMA, ACS Northeast Ohio Rubber Group Reprints, Cleveland, OH 2–7, 1973.

[7] Barbara Fabricant, Zeon Chemicals, Louisville, KY, September, 1998, private communication.

[8] ASTM E-1545, 14.02, Annual Book of ASTM Standards, West Conshohocken, PA, 1998, pp. 937–940.

[9] ASTM E-0831, 14.02, Annual Book of ASTM Standards, West Conshohocken, PA, 1998, pp. 504–508.

[10] ASTM E-1131, 14.02, Annual Book of ASTM Standards, West Conshohocken, PA, 1998, pp. 635–639.