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METHOD FOR DETERMINING FLEXURAL PROPERTY CHANGES OF POLYMERIC MATERIALS UPON ACCELERATED AGING IN REFRIGERANT/LUBRICANT MIXTURES

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ABSTRACT

Compatibility of materials with refrigerant/lubricant mixtures is usually determined through accelerated tests in sealed tubes, which require material samples of small dimensions. Such samples do not lend themselves to standard flexural or tensile tests, and very often compatibility assessment has to rely on visual observations and swelling data of polymeric materials in refrigeration systems.

A method for determining flexural property changes of small samples of polymeric materials upon accelerated aging in various refrigerants and or lubricants is described. Results obtained in the compatibility study of different polymers in CFC-12 and HFC- 134a are reported. Linear stress versus strain curves and calculated flexural modulus of materials before and after aging are compared and used to indicate whether a material becomes more flexible (due to absorption of liquid lubricant or refrigerant/lubricant mixture) or less flexible (due to possible extraction of material from the polymeric matrix by the liquid phase). Effects of aging time and aging temperature are also determined.

The described test method of determining flexural property changes provides quantitative measurements which, along with visual observations, linear swelling and changes in hardness, are necessary in the interpretation of compatibility results from sealed tube tests.

INTRODUCTION

Compatibility of materials with refrigerant/lubricant mixtures is usually determined through accelerated tests in sealed tubes [1-3], which require material samples of small dimensions. These samples, typically of 50x6x3 mm (2x0.2x0.1 in.) nominal dimensions, do not lend themselves to standard flexural or tensile tests [4-7]. A method for determining flexural property changes of small samples of polymeric materials, upon accelerated aging in various refrigerants and or lubricants, was developed and used to provide quantitative measurements, which along with visual observations, linear swelling and changes in hardness, are necessary in the interpretation of compatibility results from sealed tube tests.

EXPERIMENTAL PROCEDURES

Samples of polymeric materials were cut to test bar specimens of nominal 50x6x3 mm (2x0.2x0.1 in.) dimensions, weighed and measured, and their flexural properties were determined by the cantilever beam test system, shown in Figure 1. In this system, the sample test bar projected outward beyond a fixed support. Various loads were applied to the extreme free end of the test bar. The maximum deflection or the bar, which occured at the free end, was recorded by a dial micrometer, or read with a cathetometer. The stress S and strain e, sustained by the outermost fibers of the bar, were calculated according to the following equations:

$S = 6 P L / b d^2$ and $e = 3 d y / 2 L^2$, where P is the load, L the distance from the fixed support to the free end of the bar, b the bar width, d the bar thickness, and y the maximum bar deflection. The flexural modulus of elasticity E is given by the slope of the best fit stress versus strain curve through linear regression. After the determination of material properties, the test bars were placed inside clean heavy-wall glass tubes, and lubricant was added. The tubes were evacuated and refrigerant was introduced. The tubes were then sealed and placed in a temperature-controlled oven for aging. At the end of the aging period, the sealed tubes were removed from the oven, inspected for visual changes, cooled to reduce internal pressure, and cut open. The polymeric test bars were removed, cleaned with absorbent paper towel, and their physical and flexural properties were measured.

Four Polyamide materials were tested in accelerated aging at 150°C for 487 hr and 1000 hr in HFC-134a/PAG mixture. Similar tests in CFC-12/mineral oil were conducted to provide a basis for comparison. The test materials included Glass Reinforced Nylon 66 (GRN), Flexible Nylon Alloy (FNA), Plasticized Nylon Copolymers (PNC), and Polyamide 1212 (P12).

RESULTS AND DISCUSSIONS

Material Properties Before Aging

Table 1 is a summary of the material property data before aging. As shown in Figure 2, GRN was the least flexible of all the materials tested and had the highest flexural modulus. The other three materials had similar flexural characteristics and modulus within the same order of magnitude.

Material Property Changes Due To Aging

Visual observations of changes in test materials or refrigerant/lubricant mixtures after aging, as shown in Table 2, indicated that appreciable swelling and reaction occured in FNA with CFC-12/mineral oil. GRN, PNC and P12 showed various degrees of reactions with either CFC-12/mineral oil or HFC-134a/PAG, as evidenced by cloudiness in the refrigerant/oil mixture or by changes in color of the test samples. The effects of these reactions on other material properties are shown in Table 3 and Figures 3 to 6. The high weight and volume increases shown by FNA in CFC-12/mineral oil, combined with a relatively high decrease in hardness, indicate possible absorption of refrigerant/oil mixture by the polymeric material. PNC became very brittle and broke when aged in CFC-12/mineral oil. In HFC-134a/PAG, this polymer showed a high loss in weight and volume, as well as a small increase in hardness, corresponding to materials extraction from the polymeric matrix by the refrigerant oil/mixture. GRN and P12 registered low to moderate weight, volume and hardness changes in either CFC-12/mineral oil or HFC-134a/PAG.

Changes in Flexural Properties Due To Aging

Figures 3 to 6 are flexural stress versus strain curves of the polymeric materials tested, before and after accelerated aging, and show very clearly the effects of refrigerant/oil mixture and aging time on the materials. A study of these figures indicates that the polymeric materials reacted with the refrigerant/oil mixture at 150°C in three different ways:

1. The reactions resulted in a very small change in flexural property, and there are no significant effects of aging time or refrigerant/oil mixture, such as seen with Glass Reinforced Nylon 66 in Figure 3.

2. The reactions resulted in a more flexible material, such as with Flexible Nylon Alloy. The effects of refrigerant/oil mixture on flexural properties is also clearly indicated in Figure 4, while the effect of aging time is not so marked in this particular case. The polymeric material had absorbed some oil or refrigerant/oil mixture, with resulting increases in weight and volume and decreases in hardness and flexural modulus.

3. The reactions resulted in a stiffer material, as shown in Figures 5 and 6 for Plasticized Nylon Copolymers and Polyamide 1212. With these materials, the effects of refrigerant/oil mixture and aging time were both significant. There was extraction of materials from the polymeric matrix, as evidenced by cloudiness in the liquid phase, resulting in significant losses in weight and volume and increases in hardness and flexural modulus.

Repeatability, Reproducibility, and Accuracy Of The Measured Flexural Modulus

The repeatability and reproducibility of the flexural modulus obtained through the method described are shown in Tables 4 and 5. Repeatability is indicated by deviations from the average value of six individual determinations for the same material (P12), by the same operator using the same equipment on the same day. Reproducibility is indicated by deviations from the average value of three individual determinations for the same material, by three different operators using the same equipment on different days.

The repeatability of the measured flexural modulus was shown to be within +/-9% of the average value, and the reproducibility was within -8% and +5%. Therefore, in the comparison of the flexibility of samples before and after aging, any changes of less than +/-10% were considered insignificant.

The accuracy of the measured modulus may be inferred from a comparison of the measured values of materials before aging with values reported in the literature for materials of the same composition. This comparison, presented in Table 6, showed that the flexural modulus obtained through the method described above were of the same order of magnitude as the literature values [8], measured at 50% RH according to ASTM method D 790. This comparison is however very limited and additional data is needed before a correlation between values obtained through the above method and those obtained through standard ASTM method could be established.

CONCLUSIONS AND RECOMMENDATIONS

A method for determining flexural property changes of small samples of polymeric materials, upon accelerated aging in various refrigerants and or lubricants, was developed and used to provide quantitative measurements, which along with visual observations, linear swelling and changes in hardness, are necessary in the interpretation of compatibility results from sealed tube tests. This method was used primarily as a research control method for accelerated testing and screening of material compatibility. The stress versus strain curves and corresponding flexural modulus were used to compare material samples before and after aging, and the effects of refrigerant/oil mixture as well as aging time and temperature on material flexibility were easily assessed. This method, however is not to be used to obtain design parameters for equipments to be made from the various materials tested, or to establish material specifications.

ACKNOWLEDGEMENTS

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Table 1 : Physical Data of Test Materials Before Aging

Property	Test Material			
	Glass Reinforced	Flexible Alloy	Plasticized Copolymer	Polyamide 1212
Density, g/cc (lb/ft^3)	1.36 (84.90)	1.00 (63.43)	1.11 (69.30)	1.03 (64.30)
Shore Durometer (D-hardness)	91.5	93.5	93.3	93.1
Flexural Modulus MPa (psi)	6217 (901,700)	250 (36,300)	298 (43,200)	374 (54,200)

Table 2 : Visual Observations After Aging

Material (1)	Refrig./ Lubricant	Aging Time,hr	Liquid Appearance	Solid Bar Appearance
GRN	CFC-12/ mineral oil	487	Extremely light cloudiness	No visible change
		1000	Liquid appeared clear	Color became darker
	HFC-134a/ PAG	487	Very light tan cloudiness	No visible change
		1000	Very light tan cloudiness	No visible change
FNA	CFC-12/	487	White cloudiness	No visible change
	mineral oil	1000	White cloudiness	Bar swollen and split lengthwise
	HFC-134a	487	Extremely cloudy	No visible change
	PAG	1000	White cloudiness	No visible change
PNC	CFC-12/	487	Light cloudiness	Color became darker
	mineral oil	1000	Light cloudiness	Color became darker
	HFC-134a/	487	Clear	Color change
	PAG	1000	Clear	Color change
P12	CFC-12/	487	Very cloudy	No visible change
	mineral oil	1000	Very cloudy	No visible change
	HFC-134a/	487	Extremely cloudy	No visible change
	PAG	1000	Extremely cloudy	No visible change

(1) GRN=Glass Reinforced Nylon; FNA=Flexible Nylon Alloy; PNC=Plasticized Nylon Copolymers; P12=Polyamide 1212

Table 3 : Physical Property Changes Due To Aging

Material (1)	Refrig./ Lubricant	Aging Time,hr	Property Changes, % Weight	Volume	Hardness	Flexural Modulus
GRN	CFC-12/	487	1.0	1.0	0	-4.1
	mineral oil	1000	1.7	0.8	4.4	-13.1
	HFC-134a/	487	0.9	0.0	4.8	-1.4
	PAG	1000	0.5	2.5	4.5	-6.9
FNA	CFC-12/	487	43.0	53.8	-9.9	-71.9
	mineral oil	1000	43.5	62.1	-8.5	-77.7
	HFC-134a/	487	4.6	0.8	-0.5	12.8
	PAG	1000	4.9	3.9	-0.3	13.7
PNC	CFC-12/	487	Bar broken			
	mineral oil	1000	Bar broken			
	HFC-134a/	487	-11.8	-9.9	0.5	68.4
	PAG	1000	-11.3	-6.2	2.8	68.1
P12	CFC-12/	487	2.8	0.7	2.0	20.3
	mineral oil	1000	2.7	3.0	2.9	10.8
	HFC-134a/	487	-0.4	-2.8	-2.2	58.4
	PAG	1000	-0.7	2.8	0.6	34.9

(1) GRN=Glass Reinforced Nylon; FNA=Flexible Nylon Alloy; PNC=Plasticized Nylon Copolymers; P12=Polyamide 1212

Table 4 : Repeatability of Flexural Modulus Measurements
(Material : Polyamide 1212)

Operator	Measurement	Flexural Modulus, MPa(psi)	Deviation from Average, %
1	1	376 (54,500)	0.5
1	2	404 (58,600)	8.0
1	3	375 (54,400)	0.3
1	4	360 (52,200)	-3.7
1	5	359 (52,100)	-4.0
1	6	369 (53,500)	-1.3
Average		374 (54,200)	
2	1	430 (62,400)	3.4
2	2	380 (55,100)	-8.7
2	3	437 (63,400)	5.0
Average		416 (60,300)	

Table 5 : Reproducibility of Flexural Modulus Measurements
(Material : Polyamide 1212)

Operator	Flexural Modulus, MPa(psi)	Deviation from Average, %
1	374 (54,200)	-7.7
2	416 (60,300)	2.7
3	426 (61,800)	5.2
	405 (58,700)	

Table 6 : Accuracy of Flexural Modulus Measurements

Material	Measured Flexural Modulus, MPa(psi)	Published Data(1) MPa
Glass Reinforced Nylon	6217 (901,700)	6205
Flexible Nylon Alloy	250 (36,300)	270
Plasticized Nylon Copolymers	298 (43,200)	207

(1) Design Handbook for DuPont Engineering Plastics - Module II - Publication E-42267 (Measured at 50% RH according to ASTM method D 790).

Figure 1: Cantilever Beam Test System

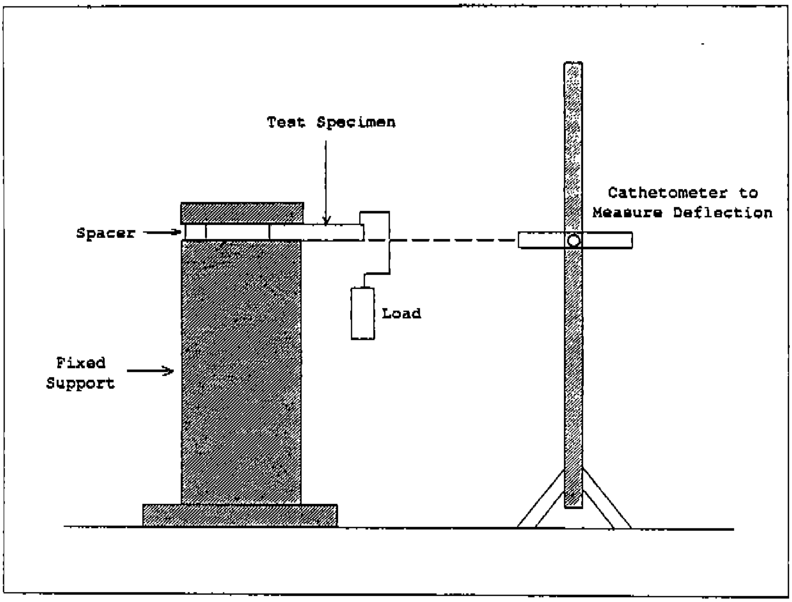

Figure 2: Stress Versus Strain Curves of Materials Before Aging

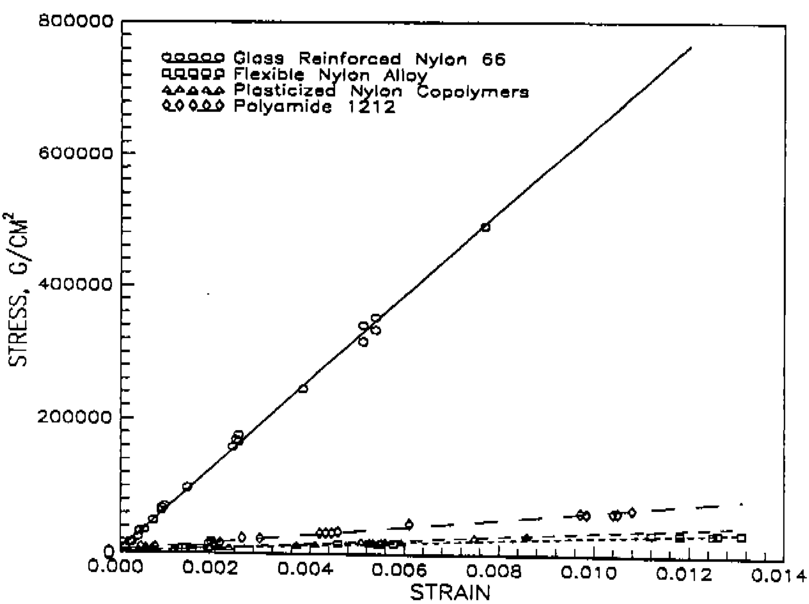

Figure 3: Stress Versus Strain Curves of Glass Reinforced Nylon
(No significant effects of refrigerant/oil mixture and aging time)

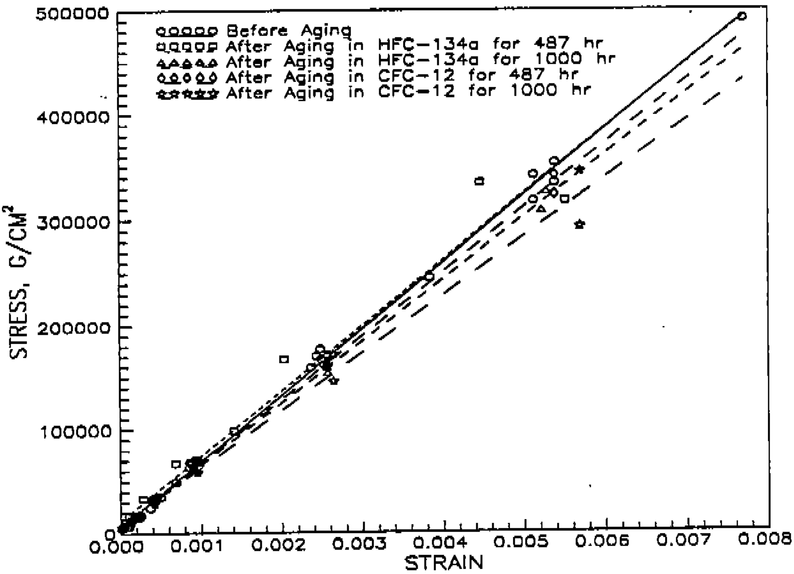

Figure 4: Stress Versus Strain Curves of Flexible Nylon Alloy
(Effect of refrigerant/oil mixture - increased flexibility on aging)

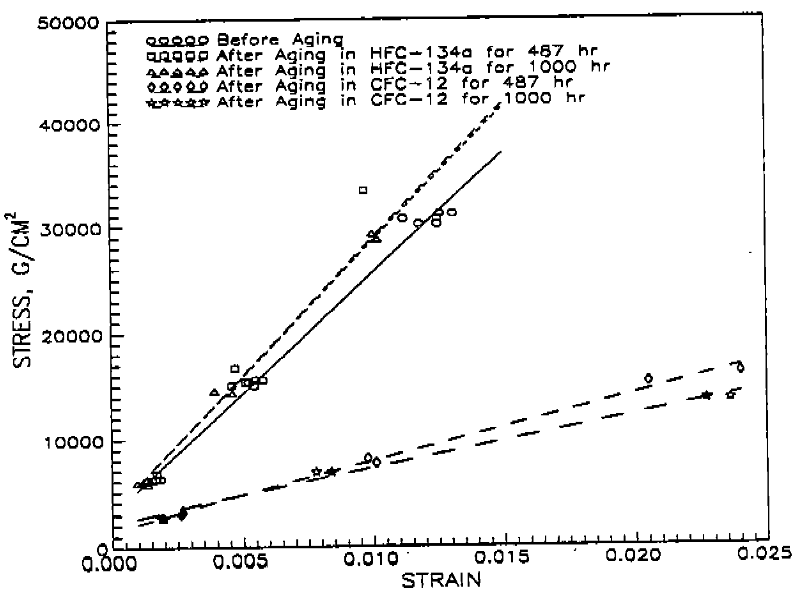

Figure 5: Stress Versus Strain Curves of Plasticized Nylon Copolymers
(Effect of refrigerant/oil mixture - Decreased flexibility on aging)

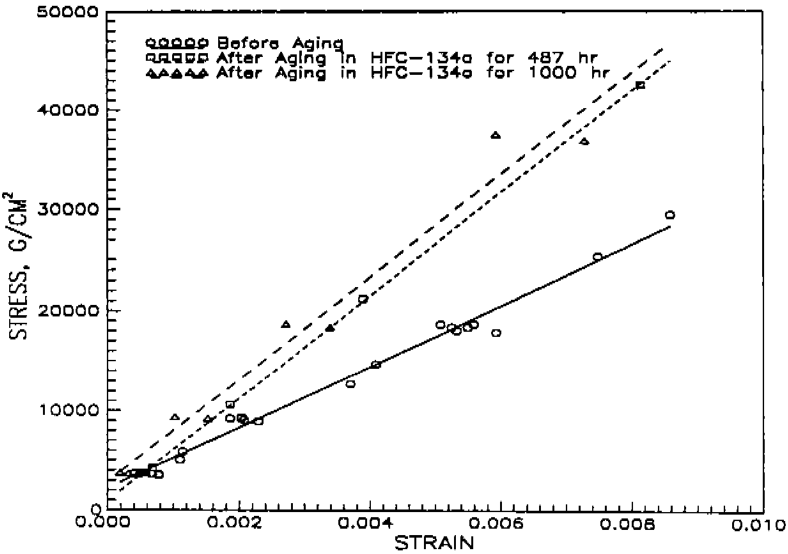

Figure 6: Stress Versus Strain Curves of Polyamide 1212
(Effects of refrigerant/oil mixture and aging time)