

A DMTA study of the fuel resistance of elastomers¹

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Abstract

One of the major factors that determines the useful lifetime of a polymeric material is the chemical resistance of the polymer to its environment. Knowledge of the chemical resistance of gasket materials to their environment is critical as their failure leads to downtime for the system and increased maintenance costs, as well as fire and safety hazards. In this paper, the results of a dynamic mechanical thermal analysis (DMTA) study of the chemical resistance of several elastomeric materials to naval distillate fuel and aviation turbine fuel are reported. The changes in weight, hardness, mechanical properties and glass transition temperature T_g are used to assess the effect of fuel exposure on the properties of the elastomers.

INTRODUCTION

A knowledge of how a polymer will perform in a chemical environment is important for several reasons. If the polymer is attacked by the environment, the performance of the material in service will be adversely affected. Degradation of the performance of the polymer may lead to premature failure of the material, result in increased downtime for the system, and necessitate costly maintenance procedures. In systems where flammable liquids are used, the failure of a gasket or O-ring can pose a significant fire and safety hazard.

The chemical resistance of a polymer to a particular fluid is related to the interaction between the polymer and the fluid. The interaction is dependent on both the structure of the polymer and the nature of the fluid [1, 2]. The chemical resistance can vary from excellent, where there is little or no interaction between the polymer and the fluid, to poor, where the fluid dissolves or degrades the polymer completely. Between these two

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extremes, exposure of the polymer to the fluid can cause the polymer to swell, reduce the modulus and tensile strength of the polymer, and leach additives from the polymer.

The chemical resistance of a polymer to a fluid can be assessed in several ways. Weight gain–immersion time studies [1, 3, 4], changes in properties such as hardness and tensile strength, volume change [2], and changes in the dynamic properties of the polymer as a function of temperature using techniques such as dynamic mechanical thermal analysis (DMTA) have been used to assess the effect of fluids on the properties of polymeric materials. Changes in properties such as modulus and the glass transition temperature T_g [5] have been related to the weight of the fluid absorbed by the polymer. Absorbed fluids act to plasticize a polymer, leading to a reduction in hardness, modulus, and T_g . Swelling of a polymer in contact with a fluid reduces chain entanglements and interchain interactions [3] and affects the properties of the polymer under load.

In this paper, the results of a study of the resistance of several elastomers to 3-GP-11 naval distillate fuel and JP-5 aviation turbine fuel are reported. Weight gain, hardness and T_g of the elastomers exposed to these fluids are discussed with reference to their chemical resistance.

EXPERIMENTAL APPROACH

Materials

The structure of the elastomers used in this study, namely, Buna N rubber, a white nitrile rubber (Snowden Rubber, 60 Durometer), a black nitrile rubber (Snowden Rubber, 60 Durometer), an ethylene-propylene-diene-based rubber (EPDM), a chlorosulfonated polyethylene-based elastomer (Hypalon), and butyl rubber are shown in Fig. 1. The Buna N, white nitrile and black nitrile rubbers were all poly(acrylonitrile-butadiene) rubbers.

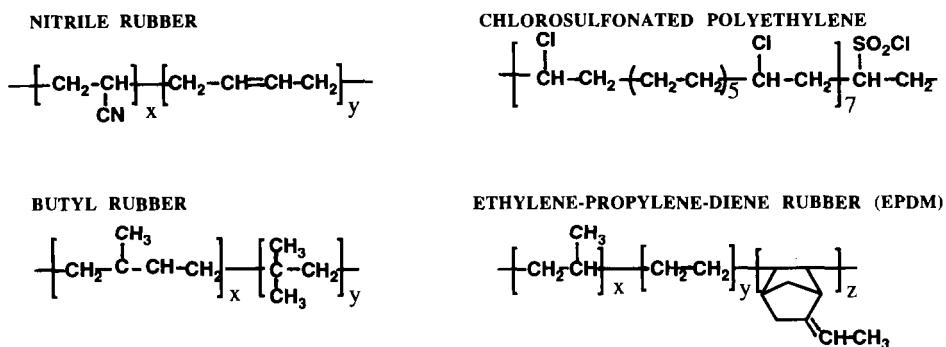


Fig. 1. Structure of the rubbers used in this study.

TABLE 1

The thickness (l), initial hardness (H_i), maximum percentage weight gain (Wt_{\max}), percent weight gain after 240 h exposure (Wt_{240}), final hardness (H_f), and diffusion coefficients (D) for rubber samples following exposure to 3-GP-11 naval distillate fuel

Rubber	l/mm	H_i	Wt_{\max} in % (h)	Wt_{240} in %	H_f	$D/\text{cm}^2 \text{ s}^{-1}$
Buna N	3.2	62	25.11 (264)	25.11	31	3.07×10^{-8}
Black nitrile	3.2	65	24.38 (216)	24.22	31	3.74×10^{-8}
White nitrile	2.9	65	25.80 (504)	25.39	47	4.88×10^{-8}
Hypalon	3.3	63	35.73 (504)	30.00	34	1.71×10^{-8}
EPDM	6.8	62	68.90 (334)	68.29	36	1.56×10^{-7}
Butyl	1.8	55	213.17 (504)	211.07	28	

Circular coupons, 47 mm in diameter, were used for the diffusion study. The thickness of the samples, which varied from 1.8 mm for the butyl rubber sample to 6.8 mm for the EPDM rubber sample, are listed in Tables 1 and 2.

Naval distillate fuel (CGSB 3-GP-11Mb) [6] and JP-5 aviation turbine fuel (CGSB 3-GP-24Mb, Nato Code F44) [7] were used as received from the stores system CFB Halifax. The specification for naval distillate fuel requires that the maximum temperature for 90% recovery of the sample in a distillation is 360°C, that the fuel have a minimum flash point of 60°C and a pour point of at least -6°C. The specification for aviation turbine fuel requires that 10% of the sample be recovered in a distillation by 205°C and that the final boiling point be 290°C maximum. This fuel can contain a maximum of 25% aromatics and 5% olefins by weight and has a minimum flash point of 60°C.

To monitor the uptake of either fuel by the elastomers, the elastomers

TABLE 2

The thickness (l), initial hardness (H_i), maximum percentage weight gain (Wt_{\max}), percent weight gain after 240 h exposure (Wt_{240}), final hardness (H_f), and diffusion coefficients (D) for six rubber samples following exposure to JP-5 aviation turbine fuel

Rubber	l/mm	H_i	Wt_{\max} in % (h)	Wt_{240} in %	H_f	$D/\text{cm}^2 \text{ s}^{-1}$
Buna N	3.2	62	20.41 (72)	17.90	31	9.81×10^{-8}
Black nitrile	3.1	65	19.65 (54)	17.12	34	1.05×10^{-7}
White nitrile	3.0	65	21.46 (504)	21.32	44	1.14×10^{-7}
Hypalon	3.3	63	30.64 (264)	30.64	30	4.01×10^{-8}
EPDM	6.8	62	71.05 (168)	70.50	35	3.85×10^{-7}
Butyl	1.6	55	179.08 (504)	177.61	36	

were immersed in the fluid, removed periodically, wiped dry and weighed. The weight per cent absorbed fluid ($M_{\%AF}$), of either 3-GP-11 or JP-5, was calculated using eqn. (1), where M_i is the initial weight of the sample and M_t is the weight of the sample after immersion in the fluid for a given period of time

$$M_{\%AF} = [(M_t - M_i)/M_i] \times 100\% \quad (1)$$

The weight of the sample at equilibrium or infinite time M_{inf} was taken as the point in the weight gain versus time plot where no further weight gain was observed.

Hardness measurements on the elastomers were made with a Shore Type 'A' Durometer hardness tester. The reported hardness was the average of at least five measurements. Dynamic mechanical thermal analysis of the elastomers was carried out on a Du Pont model 983 dynamic mechanical analyzer in the resonance mode using a heating rate of 3 K min⁻¹. The storage modulus E' , loss modulus E'' and $\tan \delta$ were measured between 153 and 313 K. A Du Pont model LNCA II liquid nitrogen accessory was used for the DMTA runs at sub-ambient temperatures.

Elastomer composition

The % extractable, % ash and the elemental composition of the ash of the six elastomers used in this study are listed in Table 3. The % extractable was determined from the difference in the weight of samples of elastomers before and after refluxing in toluene for 3 h. Analysis of the extractables indicated that phthalic acid-based esters were the major extractables from all of the elastomers. However, there was a considerable difference in the weight of material extracted from the six elastomers, varying from 5.5% extractables from the Buna N rubber to 27% extractables from the EPDM rubber. There was also a significant difference

TABLE 3

The % extractables, % ash and elemental composition of the six elastomers

Rubber	% Extractable	% Ash	Ash constituents
Buna N	5.5	40.3	Ca, Al, Si, Zn, Ba
Black nitrile	11.7	40.9	Ca, Al, Si, Zn, Ba
White nitrile	17.4	45.8	Si, Al, Ti, Ca
Hypalon	11.5	32.9	Si, Al, Ca
EPDM	27.0	9.1	Ca, Zn, S
Butyl	11.3	3.6	Zn, Mg

in the % extractables from the three butadiene-acrylonitrile-based rubbers, ranging from 5.5% from the Buna N to greater than 17% from the white nitrile rubber.

The % ash (non-combustibles) from the samples was determined by comparing the weight of the residue of the sample after heating at 1073 K in air for 3 h to the original weight of the sample. The % ash varied from less than 4% for the butyl rubber sample to greater than 45% for the white nitrile rubber sample. The % ash and the elemental composition of the Buna N and black nitrile rubbers were similar but varied from those for the white nitrile rubber. The similarity in the % ash and elemental composition of the ash of the Buna N and black nitrile rubbers is indicative of the similarity of the formulations of these two rubbers. However, the elemental composition of the white nitrile rubber differed from the other acrylonitrile-butadiene rubbers. This indicated that the fillers used in the white nitrile rubber were different from those used in the Buna N and black nitrile rubbers, i.e., aluminum silicate in the white nitrile rubber, and calcium aluminum silicate and barium sulfate in the Buna N and black nitrile rubbers. The presence of titanium in the ash of the white nitrile rubber indicated that titanium dioxide was used to give the white nitrile rubber its color.

RESULTS AND DISCUSSION

The percentage weight gain following immersion for 240 h and the equilibrium weight gain of the elastomers in naval distillate fuel and aviation turbine fuel are listed in Tables 1 and 2 respectively. The percentage weight gains of the Buna N, black nitrile and white nitrile rubbers are approximately 25% in 3-GP-11, while the Hypalon, EPDM and butyl rubbers gained approximately 35%, 68%, and 211% respectively. Similar results were observed from the rubbers following exposure to JP-5. That is, the acrylonitrile-butadiene rubbers showed the smallest weight gain following exposure to JP-5 (17%–20%), while the Hypalon, EPDM, and butyl rubber samples absorbed approximately 35%, 71%, and 171% JP-5.

For a particular rubber, the maximum percentage weight gain was lower for the rubber immersed in JP-5 than for the same rubber immersed in 3-GP-11Mb, although for the Buna N, black nitrile, Hypalon, and EPDM rubbers the time to maximum weight gain was shorter in JP-5 than in 3-GP-11. This is related to both the differences in the molecular weights (boiling points) and the structure of the constituents of the fuels. The rate of uptake of hydrocarbons by an elastomer has been found to depend on the molecular weight (boiling point) of the hydrocarbon in an analogous series, the rate increasing as the molecular weight of the hydrocarbon was decreased [8], and on the structure of the hydrocarbon [1]. As JP-5 is

composed of lower molecular weight paraffinic hydrocarbons than 3-GP-11 and also contains approximately 25% aromatic hydrocarbons, the faster rate of weight gain by the rubbers immersed in JP-5 can be attributed to these factors.

DIFFUSION COEFFICIENTS

The relationship between the fractional weight gain of a sample (M_t/M_{inf}) exposed to a fluid and the diffusion coefficient D of the fluid in the sample with planar geometry is given by eqn. (2), where l is the sample thickness and t is the time of immersion of the sample in the fluid [9, 10].

$$M_t/M_{inf} = 4(Dt/\pi l^2)^{1/2} \quad (2)$$

For a material that exhibits Fickian absorption behavior, the plot of M_t/M_{inf} versus $t^{1/2}/l$ is linear for fractional weight gains of up to 0.5 and then becomes concave with respect to the x -axis [11]. The value of D for the polymer–fluid system can be calculated from the slope of the linear portion of the plot of M_t/M_{inf} versus $t^{1/2}/l$.

Plots of M_t/M_{inf} versus $t^{1/2}/l$ for black nitrile and Buna N rubbers in 3-GP-11 and JP-5 are shown in Figs. 2 and 3. Similar plots were made from the other rubbers and the diffusion coefficients of both 3-GP-11 and JP-5 were calculated from the slopes of the plots for fractional weight gains up to 0.5. The diffusion coefficients are listed in Tables 1 and 2. The plots of M_t/M_{inf} versus $t^{1/2}/l$ for the butyl rubber samples in 3-GP-11 and JP-5 were sigmoidal in shape for M_t/M_{inf} values up to 0.5 and could not be used to calculate diffusion coefficients. The sigmoidal shape of these plots indicates that the diffusion of 3-GP-11 and JP-5 in butyl rubber deviated significantly from Fickian diffusion behavior.

The diffusion coefficients for 3-GP-11 increased in the order Hypalon <

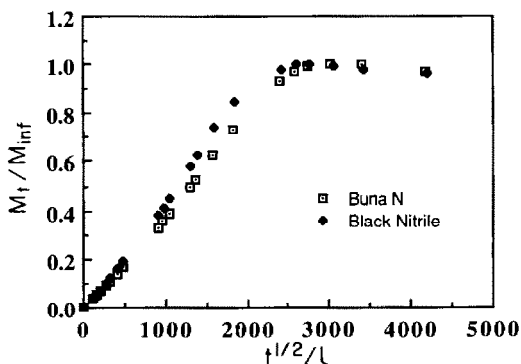


Fig. 2. Plot of fractional weight gain (M_t/M_{inf}) of samples of Buna N and black nitrile rubbers immersed in 3-GP-11 against $t^{1/2}/l$, where t is immersion time (s) and l is the sample thickness (mm).

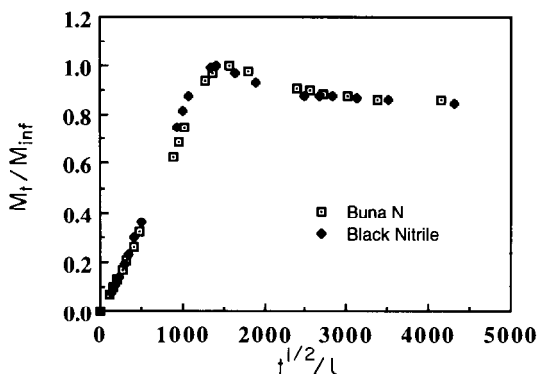


Fig. 3. Plot of fractional weight gain (M_t/M_{int}) of samples of Buna N and black nitrile rubbers immersed in JP-5 against $t^{1/2}/l$, where t is immersion time (s) and l is the sample thickness (mm).

BunaN < black nitrile < white nitrile < EPDM from $1.71 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ for Hypalon to $15.6 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ for EPDM. The diffusion coefficients for JP-5 in these elastomers increased in the same order; however, the diffusion coefficients were larger in JP-5 than in 3-GP-11, e.g., $3.07 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ for 3-GP-11 in Buna N versus $9.81 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ for JP-5 in Buna N.

As was observed for the rate of weight gain for the elastomers exposed to either JP-5 or 3-GP-11, the diffusion coefficients of 3-GP-11 and JP-5 in the elastomers were found to differ. That is, the diffusion coefficient for JP-5 in a particular elastomer was higher than that for 3-GP-11. As JP-5 contains lower molecular weight hydrocarbons and a higher percentage of aromatic hydrocarbons than 3-GP-11, the difference in the diffusion coefficients can be attributed to the difference in the composition of the fuels. These results are consistent with those of Harogoppad and Aminabhavi [3] who found that the diffusion coefficients of *n*-alkanes in polychloroprene rubber, EPDM rubber, and acrylonitrile-butadiene rubber decreased as the molecular weight of the alkane was increased. In addition, the diffusion coefficients have been found to depend on the structure of the hydrocarbon, aromatic hydrocarbons interacting differently with the rubbers than aliphatic hydrocarbons with similar molecular weights and boiling points [1].

SHORE A HARDNESS

The Shore A Durometer hardness of the six elastomers before and after exposure to 3-GP-11 and JP-5 are listed in Tables 1 and 2. The hardness of all of the samples decreased following exposure to either fuel.

The initial hardness of the elastomers and their hardnesses following

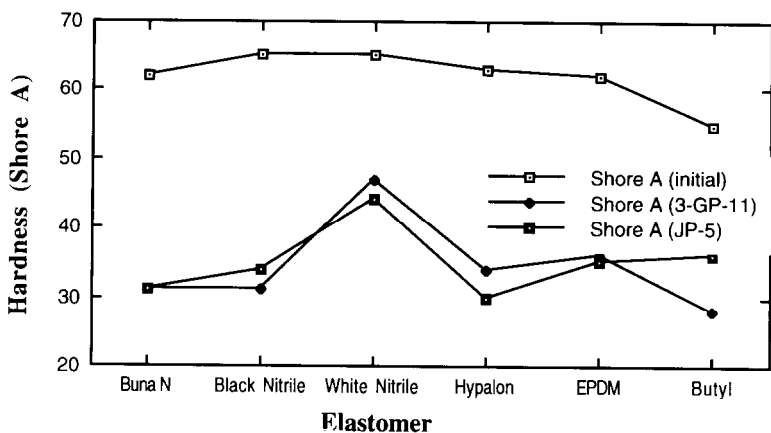


Fig. 4. Shore A hardnesses of six elastomers before and after exposure to 3-GP-11 and JP-5 fuels.

exposure to either 3-GP-11 or JP-5 are plotted in Fig. 4. The change in hardness of the white nitrile rubber was much smaller ($\approx 30\%$) than for the other elastomers ($\approx 40\%–50\%$); however, the changes in hardness of a particular elastomer were similar for exposure to either 3-GP-11 or JP-5 fuel.

DYNAMIC MECHANICAL THERMAL ANALYSIS

DMTA of the six rubbers was carried out to determine the effect of absorbed fuel on the dynamic mechanical properties (and T_g) of these rubbers. Figures 5 and 6 show plots of $\tan \delta$ versus temperature for Buna N

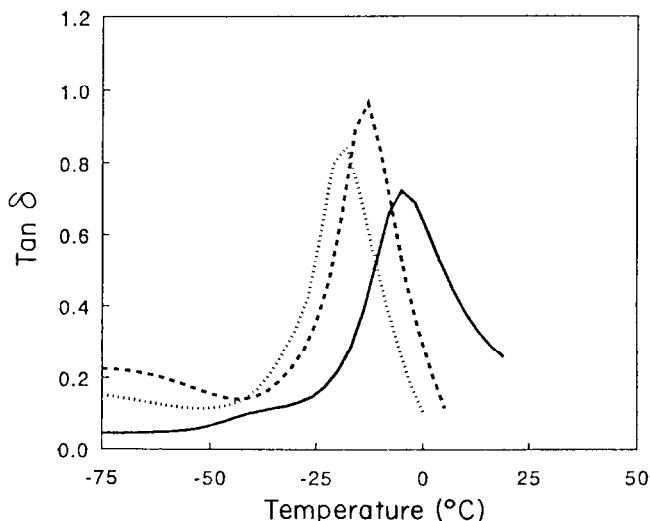


Fig. 5. Plot of $\tan \delta$ versus temperature for samples of Buna N rubber, as received (—), following exposure to 3-GP-11 (---), and following exposure to JP-5 (···).

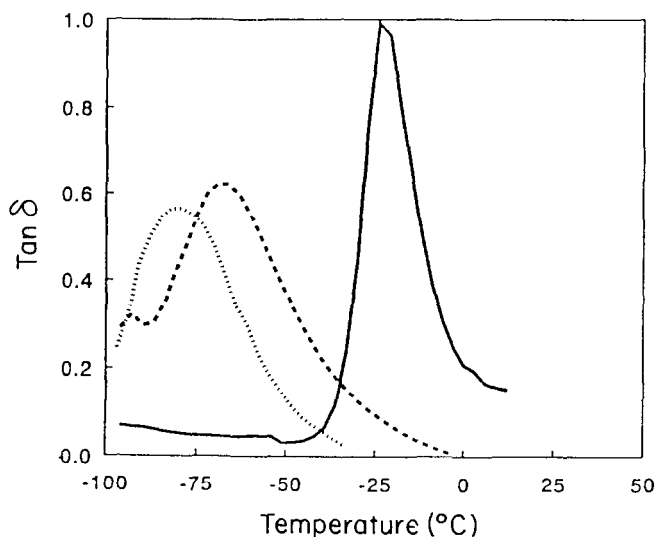


Fig. 6. Plot of $\tan \delta$ versus temperature for samples of EPDM rubber, as received (—), following exposure to 3-GP-11 (---), and following exposure to JP-5 (···).

rubber and EPDM rubber before immersion, and after immersion in 3-GP-11 and in JP-5. The temperatures of the maxima of plots of $\tan \delta$ against temperature for the six rubbers before and after immersion in 3-GP-11 and JP-5 are listed in Table 4. The percentage weight of absorbed fuel for each of the rubbers is listed in Tables 1 and 2.

In all instances, the fuel immersion caused a shift to lower temperature of the maximum in plots of both $\tan \delta$ and E'' versus temperature. These results are consistent with the plasticization of the rubbers by the absorbed fuel and are indicative of changes in the mechanical properties of the

TABLE 4

Temperature of the maximum of $\tan \delta$ for the six rubbers before and after exposure to 3-GP-11 and JP-5

Rubber	Temperature (K) of $\tan \delta$ maximum		
	Unexposed	After exposure	
		3-GP-11	JP-5
Buna N	268.6	259.0	253.9
Black nitrile	271.4	262.2	256.2
White nitrile	265.0	261.8	257.3
Hypalon	271.9	257.2	256.9
EPDM	250.3	205.2	192.2
Butyl	244.8	200.1	<183

rubbers. The depression in the temperature maximum of either $\tan \delta$ or E'' following immersion in either 3-GP-11 or JP-5 varied considerably for the six rubbers. For instance, the temperature of the maximum in $\tan \delta$ of the black nitrile rubber decreased by approximately 9 K following exposure to 3-GP-11, while the temperature of the maximum in $\tan \delta$ for the EPDM and butyl rubber samples decreased by approximately 45 K following exposure to the same fuel.

A plot of the change in the temperature of the maximum in $\tan \delta$ (ΔT) against percent weight gain is shown in Fig. 7. The depression in $\tan \delta$ maximum temperature was found to correlate roughly with the percent weight gain of the fuels by the elastomers. Absorption of a particular weight percent of JP-5 by a particular elastomer caused a greater depression in the temperature maximum of $\tan \delta$ than did absorption of a similar weight percent of 3-GP-11. This could be the result of at least two factors. It has been proposed [5] that the depression of the T_g caused by the absorption of a plasticizer correlates better with the number of moles of absorbed plasticizer than with the weight of absorbed plasticizer. Because JP-5 contains lower molecular weight hydrocarbons than 3-GP-11, absorption of equivalent weights of the two fuels by an elastomer would correspond to absorption of a larger number of moles of lower molecular weight constituents of JP-5. JP-5 also contains approximately 25% aromatics and absorption of a given weight of these compounds might be expected to have a different effect on an elastomer than aliphatic hydrocarbons.

The results from the DMTA analysis of the rubbers before and after immersion in either 3-GP-11 or JP-5 reflect the relative resistance of the rubbers to these fluids. That is, the depression of the temperature of $\tan \delta$ or E'' of the acrylonitrile-butadiene rubbers, which are reported to have good resistance to fuels, is much smaller than the depression for the

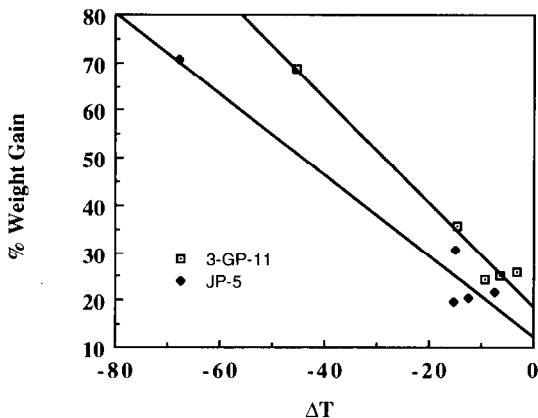


Fig. 7. Plot of the temperature difference of the maximum in a plot of $\tan \delta$ versus T (ΔT) versus percent weight gain of rubber samples immersed in either 3-GP-11 or JP-5.

EPDM and butyl rubbers, which are reported to have poor resistance to fuels. The effect of the absorption of these fuels on the T_g of the Hypalon rubber is intermediate between the acrylonitrile rubbers and the butyl and EPDM rubber samples, and this is consistent with the reported resistance of these elastomers to hydrocarbon-based fluids.

Immersion of a rubber in a fluid may also result in the leaching of additives such as plasticizers from the rubber. Loss of plasticizer can lead to an increase in the T_g of the rubber and a concomitant decrease in the low temperature properties of the rubber. Examination of the plots of fractional weight gain of the Buna N and black nitrile rubbers immersed in JP-5 against the square root of immersion time shown in Fig. 3 indicate that the samples reached a maximum weight and then started to lose weight. Gas chromatography/mass spectrometric analysis of a sample of JP-5 used as the immersion fluid indicated that dioctyl phthalate plasticizer was being leached from these rubbers.

To determine what effect the loss of plasticizer would have on the properties of elastomers, samples were exposed to JP-5 fluid, dried to constant weight and the maximum in $\tan \delta$ determined. The temperature of the maximum in the plot of $\tan \delta$ versus temperature for a sample of white nitrile rubber immersed in JP-5 and “dried”, increased from 265 to 279 K. A similar analysis of a sample of black nitrile rubber resulted in an increase in the maximum of the temperature of approximately 5 K. Analysis of the JP-5 used as the immersion fluid for these elastomers indicated that phthalate-based plasticizers were being leached from the elastomers by the fuel.

For an elastomer that has good resistance to exposure to a particular environment, leaching of an additive from the elastomer can be of concern in applications where the exposure is intermittent. If the elastomer has time to “dry-out”, then it will have properties different from those of an unexposed sample. That is, the T_g and modulus of the elastomer will increase. The increase in the T_g of the elastomer can cause the elastomer to become brittle and adversely affect the ability of the elastomer to perform as designed in low temperature applications. This may lead to premature failure of the elastomer.

CONCLUSIONS

The weight gain, hardness change, and change in the temperature of the maximum in a plot of $\tan \delta$ versus temperature for six elastomers exposed to 3-GP-11 and JP-5 have been determined. The weight gain of the elastomers varies significantly but correlates with the reported chemical resistance of the elastomers to hydrocarbon-based fluids. Hardness changes of the elastomers were similar, with the exception of the white nitrile sample, and therefore are not a good indicator of chemical resistance.

DMTA can be used to assess the chemical resistance of elastomeric materials to 3-GP-11 and JP-5. The decrease in the temperature of the maximum of the plot of $\tan \delta$ versus T (ΔT) after exposure to these fuels correlates roughly with the weight gain of the elastomers and, therefore, to the chemical resistance of the rubbers.

The results of this study indicate that the nitrile-based rubbers have better chemical resistance to 3-GP-11 and JP-5 than the other elastomers. However, leaching of additives, such as plasticizers, affect the “in-service” properties of these elastomers. To fully assess the effect of exposure on an elastomer, DMTA should be carried out on a rubber after immersion to determine if exposure has caused a change in the properties of the elastomers. Such changes may be critical in low temperature applications or in applications where fuel exposure is intermittent.

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