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PHYSICAL AND CHEMICAL REACTIONS OF ISOPRENE AND FLUOREL ELASTOMERS BETWEEN -150° C AND 150° C

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16. Abstract

Differential thermal analysis measurements were made on two elastomers which have been proposed for spacecraft application, isoprene elastomer and a closed-cell Fluorel foam, over a temperature range from -150° C to 150° C at pressures of 100 kN/m^2 and 2 N/m^2. A subzero chemical reaction in both elastomers was indicated on the thermograms and by the generation of an effluent which was identified as water vapor.

A glass transition temperature of -62° C was shown for isoprene elastomer but a definite transition for Fluorel could not be established.

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PHYSICAL AND CHEMICAL REACTIONS OF ISOPRENE AND FLUOREL ELASTOMERS BETWEEN -150° C AND 150° C

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SUMMARY

Experimental studies of isoprene elastomer and a closed-cell Fluorel elastomer which are candidate materials for spacecraft use were made by the differential thermal analysis technique over a temperature range from -150° C to 150° C at a pressure of 100 kN/m^2 and a reduced pressure of approximately 2 N/m^2. The thermograms and pressure measurements showed a subzero reaction in both elastomers which produced water vapor as an effluent.

A glass transition temperature of -62° C was manifested by the isoprene thermograms. However, the glass transition temperature of the Fluorel could not be definitely established by this technique.

INTRODUCTION

Applications of elastomers in spacecraft systems and subsystems and in expandable space structures impose a wide range of temperature on these materials. Within this temperature band, the mechanical behavior of these elastomers can change from high ultimate stress and low ultimate strain at low temperatures to low ultimate stress and high ultimate strain at high temperatures. This change in material properties occurs above the glass transition temperature. While glass transition temperatures have been measured for many pure polymers (e.g., ref. 1), commercial formulations differ from the pure polymer, and polymer preparation also affects this property. Thus, the glass transition temperature of a commercially formulated polymer may vary significantly from that of the pure polymer.

Differential thermal analysis measurements were made to determine glass transition temperatures for two elastomer formulations: isoprene elastomer, which was one of several candidate materials for a flexible window for spacecraft (ref. 2), and a closed-cell Fluorel foam, which is a candidate for use inside manned spacecraft cabins and expandable space structures (ref. 3). Determination of the glass transition temperature is necessary to establish the lowest temperature for deployment of flexible structural elements incorporating these elastomers.

The differential thermal analysis measurements were made over a temperature range from -150° C to 150° C at static pressures of 100 kN/m^2 (1 atm) and approximately 2 N/m^2 (2×10^{-5} atm). The trapped effluent was analyzed with a mass spectrometer.

MATERIALS

Isoprene Elastomer

The polymer specimens were taken from a clear transparent sheet of isoprene elastomer that was supplied as a candidate for a flexible window matrix for spacecraft (ref. 2). The basic polymer was a cis-1,4-polyisoprene which has the same structure as natural rubber. The elastomer of this investigation was compounded of polyisoprene, a cross-linking agent, and an absorber for ultraviolet light, as shown in the following table:

Constituent	Parts by weight
Polyisoprene: $CH_2:CHC(CH_3):CH_2$	100
Cross-linking agent: 2,5-bis(tert-butylperoxy)-2,5-dimethylhexane	1.25
Ultraviolet absorber: 2-hydroxy-4-methoxy-benzophenone	0.6

Closed-Cell Fluorel Foam

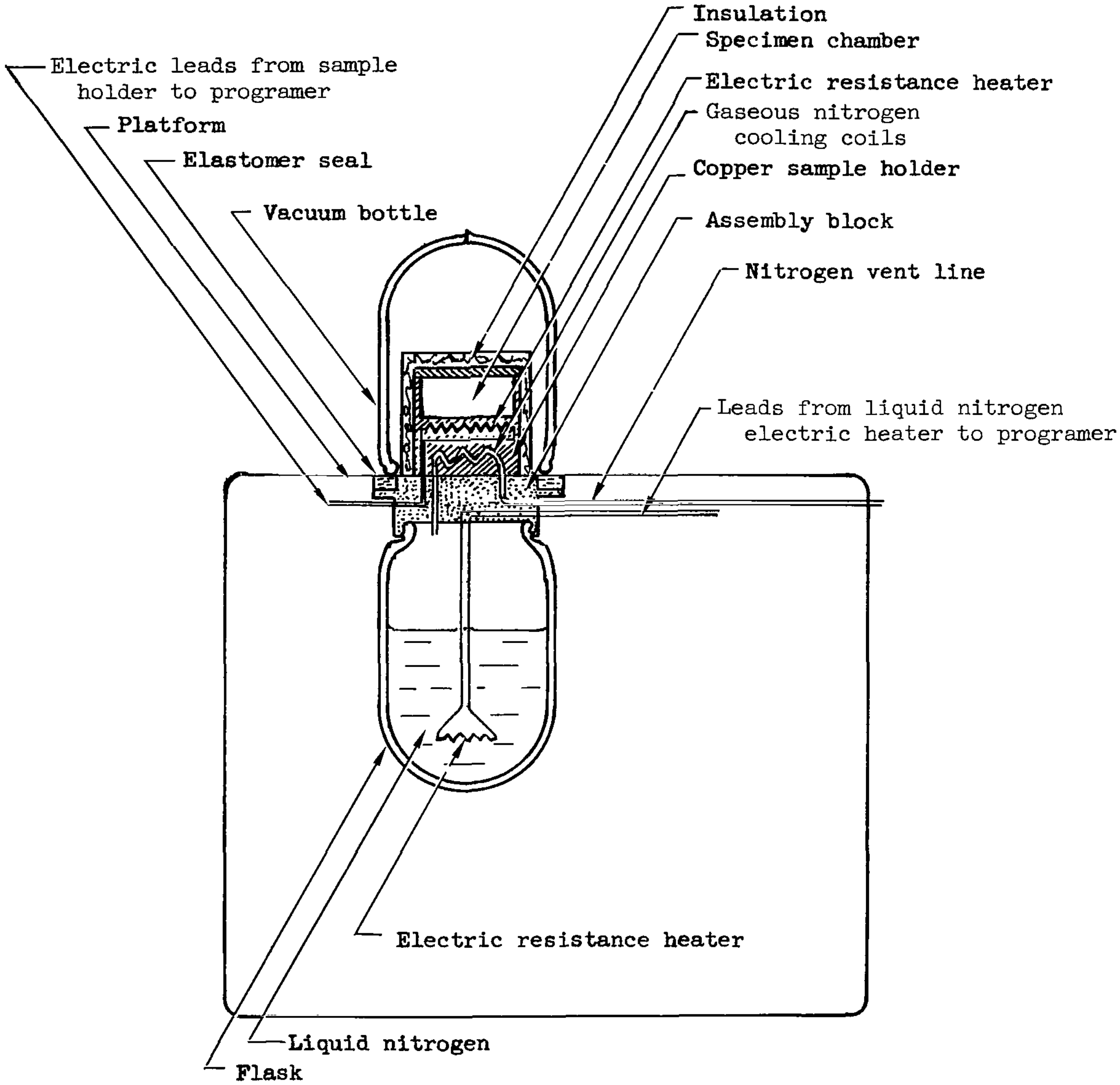
The Fluorel elastomer that was used for the preparation of the closed-cell foam is a copolymer of hexafluoroprene ($CF_2:CFCF_3$) and vinylidene fluoride ($CH_2:CF_2$) which had proprietary compounding to allow foaming and to lower the usable temperature limits. Unpublished data indicate that Fluorel closed-cell foam is nonflammable in 100 percent oxygen at a pressure of 42 kN/m^2, and thus is a candidate for interior use in manned spacecraft. The low-temperature brittle point of the base polymer before compounding is -25° C.

TEST EQUIPMENT

Differential Thermal Analysis System

Sketches of the subzero differential thermal analysis (DTA) test apparatus used in the investigation are presented in figure 1. The temperature difference between the test and reference specimens is indicated by the electric potential across the two iron-constantan ring thermocouples which were connected in series. These thermocouples are located in a copper sample holder which is heated or cooled to produce the temperature changes in the specimens. The temperature within the sample holder is measured by an iron-constantan reference thermocouple.

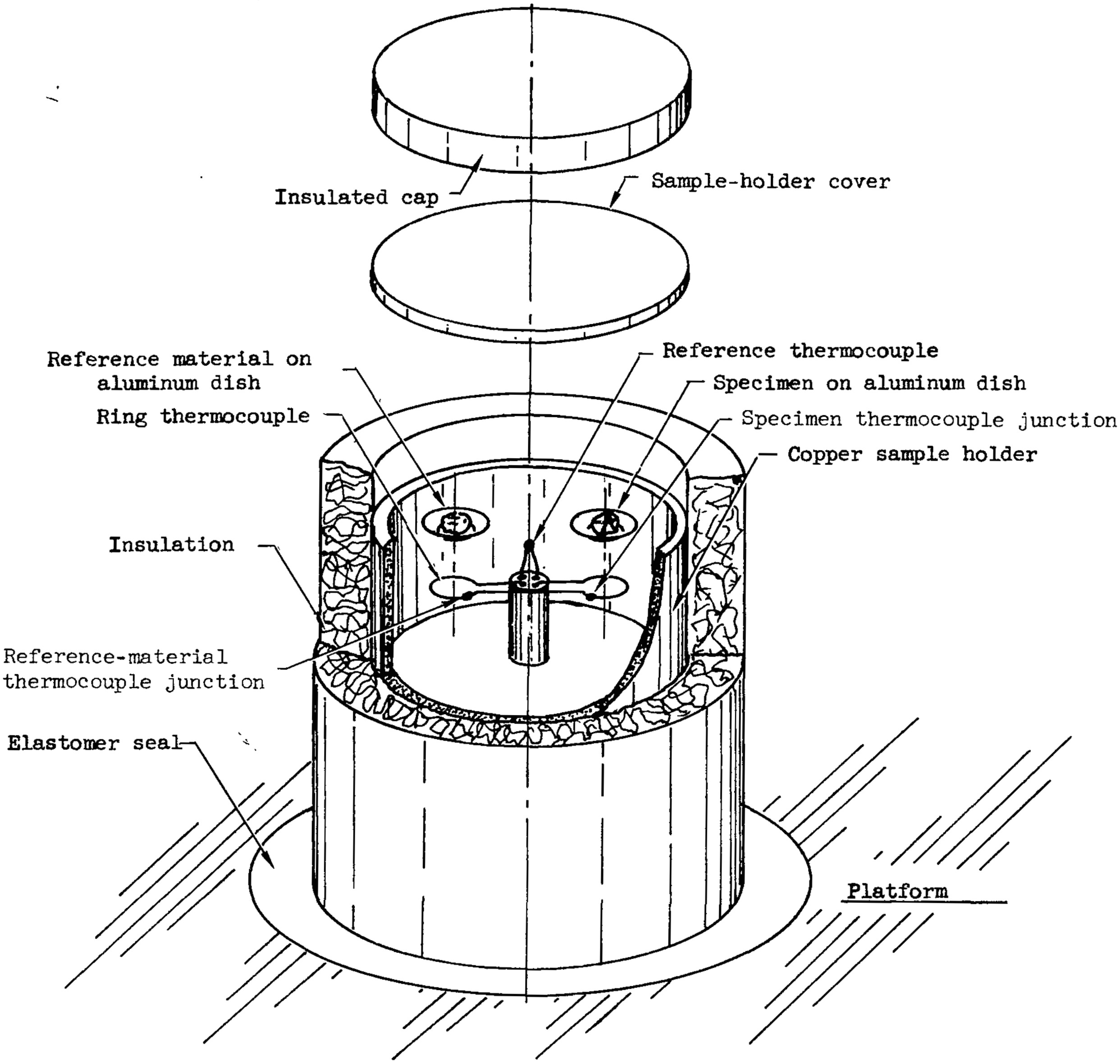
The elements of the subzero DTA system are a furnace platform, a furnace programer, a furnace controller, a dc amplifier, a derivative computer, x-y recorders, and a mechanical vacuum pump. The operating ranges are -150° to 150° C and -150° to 300° C. A liquid nitrogen (LN_2) flask which is suspended beneath the furnace platform



(a) Diagram of subzero DTA test apparatus.

Figure 1.- Subzero differential thermal analysis equipment.

supplies the coolant to reduce the sample-holder temperatures. The coolant, gaseous nitrogen, is produced by electrically heating the LN_2 to the boiling point. To increase the sample-holder temperature above approximately -50° C, electric resistance heaters inside the sample holder are used. The sample holder is enclosed by the furnace platform and a vacuum bottle. The enclosure is connected to a vacuum system (fig. 2) which has a nominal capability of attaining a pressure of 1.33 N/m^2. In addition, DTA tests may be made at ambient pressures.



(b) Sample holder and thermocouple arrangement.

Figure 1.- Concluded.

The full-scale recorder range is 10 mV, which corresponds to a 19.05-cm vertical displacement of the recorder pen. For these tests the potential difference between the specimen and reference-material thermocouples gives a temperature-difference scale of 0.1109 °C/cm at -125° C, 0.0839 °C/cm at 0° C, and 0.0765 °C/cm at 125° C.

Vacuum System and Gas-Sampling Arrangement

A schematic diagram of the vacuum and gas-collection system is shown in figure 2. The manifold represented in this figure is common to all elements of the thermal analysis system although only the subzero system lines are drawn in this sketch. Tubing of 14.7-mm diameter is used to connect the manifold and the subzero instrument to the collection loop. All hardware in the collection loop is of stainless steel. Quick-disconnect fittings are employed to facilitate the removal of the 500-cm^3 sample bottle after collection of the desired effluent gas. In normal operation, the effluent gas is pumped through the sample bottle. Samples of the gas were collected by closing the bottle shutoff valves and opening the bypass valves.

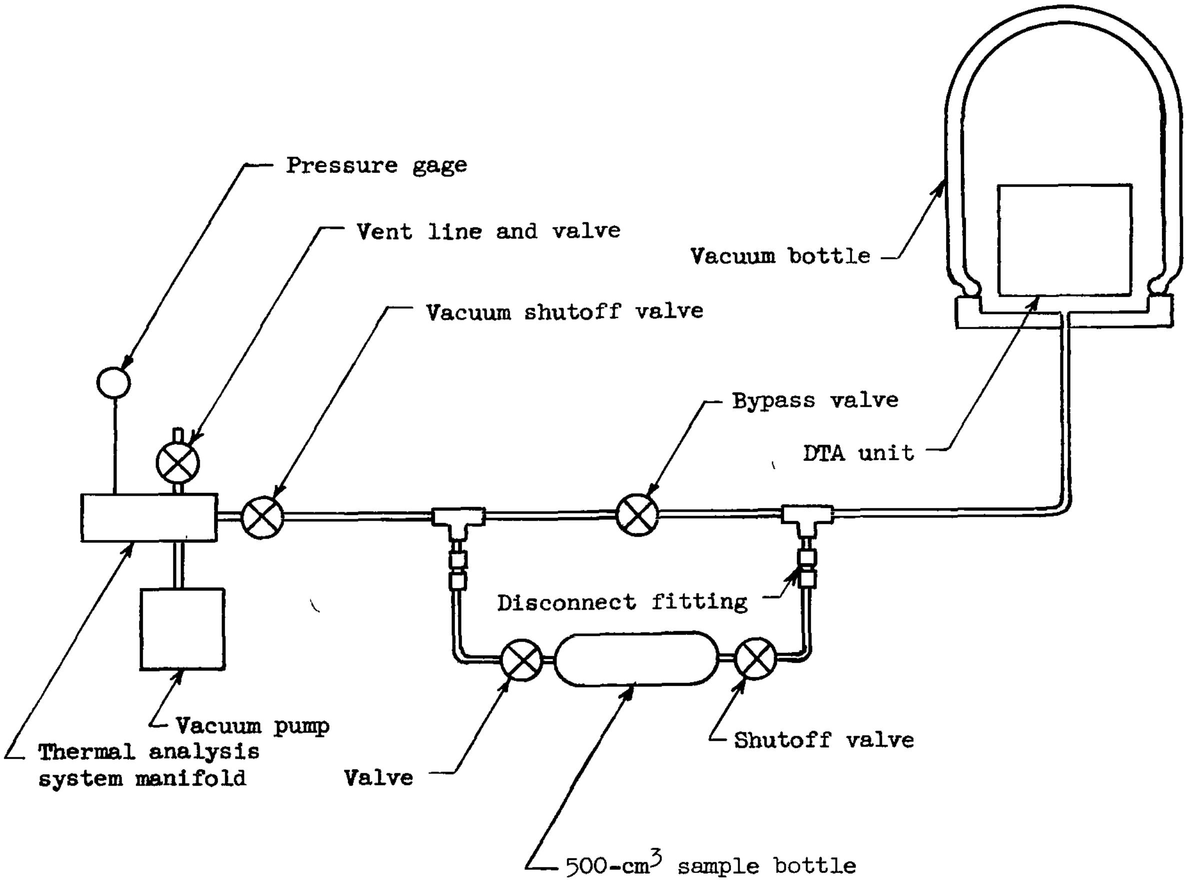


Figure 2.- Schematic diagram of vacuum system and gas-sample collector.

Mass Spectrometer

A time-of-flight mass spectrometer was used to identify the effluent gas. A quick-disconnect fitting was installed on the mass spectrometer gas-injection system to couple the sample container to the instrument. Mass data were visually observed on an oscilloscope, and a direct-recording oscillograph produced the spectrogram.

TESTS AND MEASUREMENTS

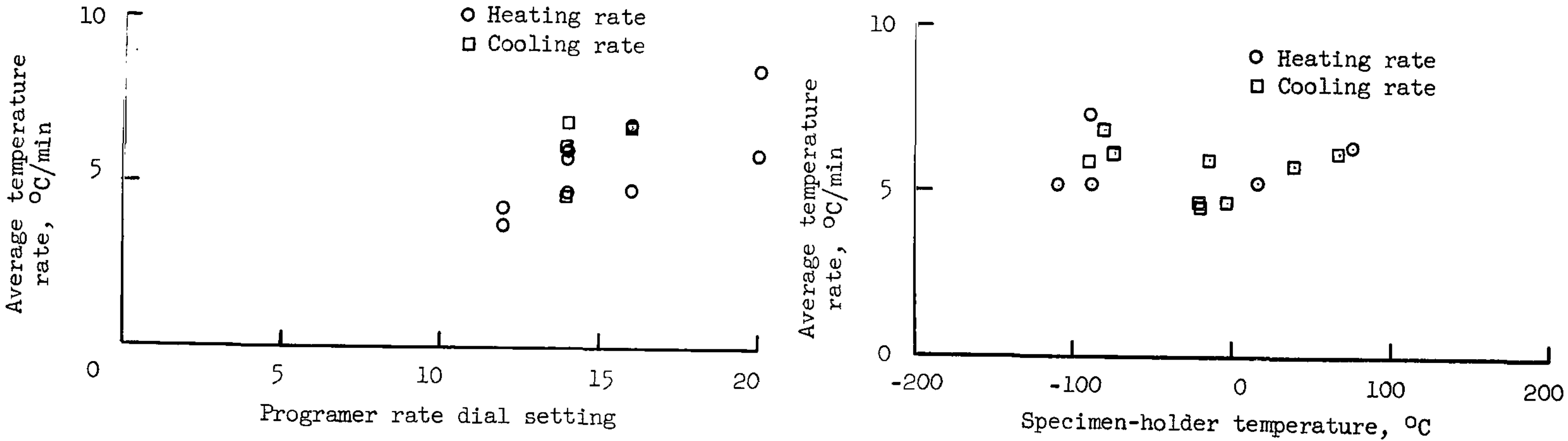
Programer Rate Calibration

To determine the furnace programer rate and its effect on thermograms, tests were made by using aluminum pans on each ring of the ring thermocouple. The instrument was placed in the cooling mode to decrease the sample-holder temperature from ambient to the instrument's low value of -150° C and then switched to the heating mode to increase the sample-holder temperature. Several features are evident on these thermograms which must be kept in mind during analysis of specimen data. These features are vertical displacements on the thermograms which occur after the start of the test run, after the change from the cooling mode to the heating mode, and after the change from a passive heat input to an electric heater between -100° C and -50° C during the heating phase.

During each of the rate calibration runs, timing marks were manually noted on each thermogram. An approximate temperature rate was obtained by dividing the temperature difference by the corresponding time interval. Figure 3(a) presents some measured values for the calibration thermograms. The equipment manufacturer's recommended rate for the subzero DTA was 5 $^{\circ}$C/min, and these data indicate that a setting of 14 should be used. Figure 3(b) presents some average rates of temperature change at various specimen-holder temperatures for this setting. However, as shown in figure 4, which was plotted from data of reference 4, the indicated rate of change of temperature with electrical potential of the iron-constantan thermocouple increases almost 50 percent from temperatures near 0° C to near -150° C. This accounts for the high values of programer rate at the lower temperatures. The estimated average rate, 5.75 $^{\circ}$C/min, will be used hereinafter.

Sample-Holder Temperatures

In order to determine the relation between the sample-holder temperature as measured by the reference thermocouple and the temperature of the specimen, a series of calibration-grade chemicals were run in the subzero DTA system. The test procedure for both liquids and solids involved a decrease in temperature to -150° C followed by an increase in temperature beyond the melting point. Since supercooling of the liquid below



(a) Variation of temperature rate with programer setting.

(b) Variation of temperature rate with temperature at a rate setting of 14.

Figure 3.- Measured temperature rates for calibration thermograms.

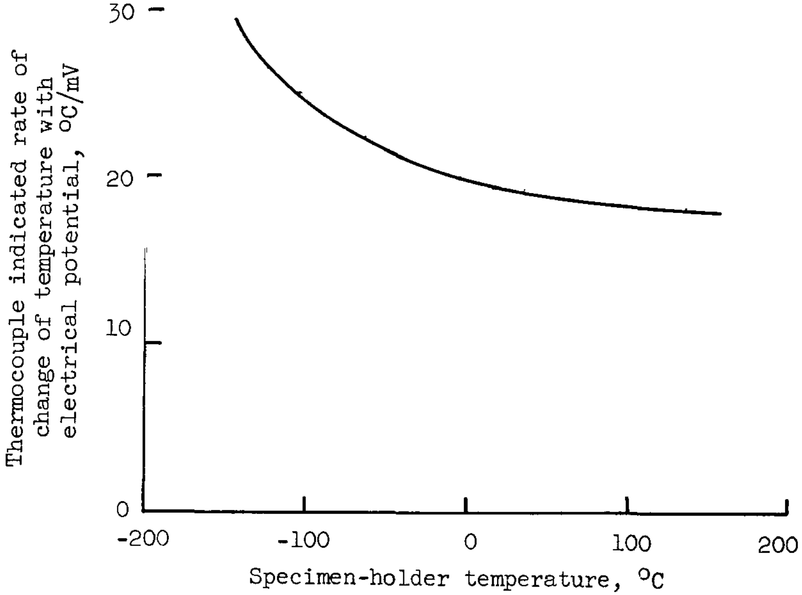


Figure 4.- Characteristics of the iron-constantan thermocouple.

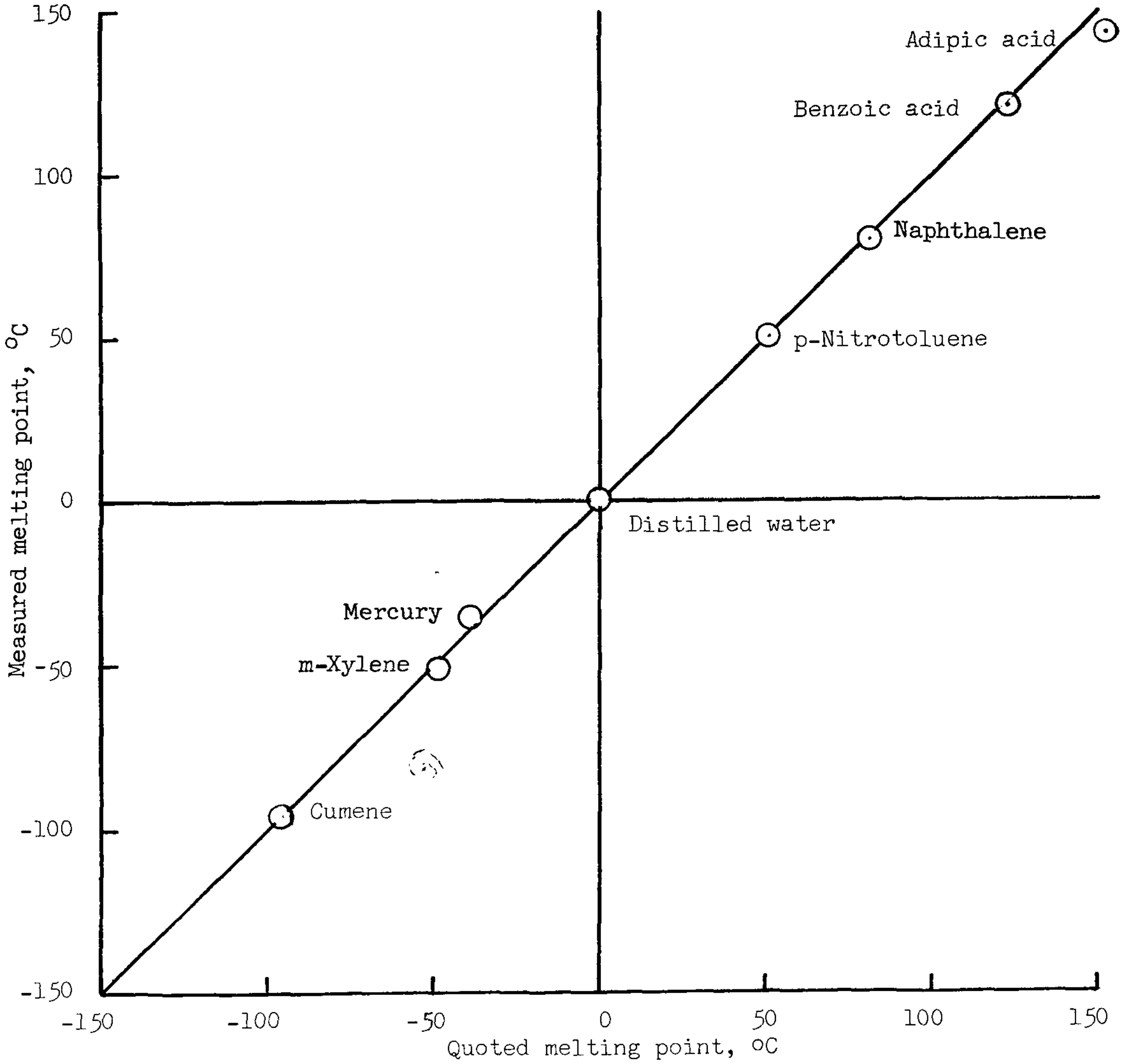


Figure 5.- Comparison of melting points as determined by DTA with the melting points for calibration-grade chemicals.

the freezing point was observed, the melting point was taken as the calibration point. The melting point was taken at the intersection of the average slope of the thermogram before melting and the initial slope during the melt thermogram. The data are shown in figure 5 and indicate that good temperature correlation occurs in the sample holder.

Thermal Analysis Measurements

DTA measurements were made on a 0.0039-mg specimen of isoprene elastomer at a pressure of 100 kN/m^2 over a range from -150° C to 100° C. To examine the material behavior at low pressure, another 0.0039-mg isoprene elastomer specimen was put into the sample holder and the system was pumped down to a pressure of 2 N/m^2. Then DTA measurements were made from -150° C to 100° C. The pressures of the manifold were recorded by the operator during the test. These procedures were duplicated with 0.0088-mg specimens of closed-cell Fluorel foam over a range from -150° C to 150° C.

In order to determine whether volatile residues were present in the materials, test specimens of the elastomers were preconditioned for 24 hours by exposure to air at either (1) ambient laboratory pressure and a temperature of 75° C, (2) reduced pressure of 1 mN/m^2 and a temperature of 22° C, or (3) reduced pressure of 1 mN/m^2 and a temperature of 75° C. These preconditioned specimens were tested in the DTA equipment at a pressure of 2 N/m^2.

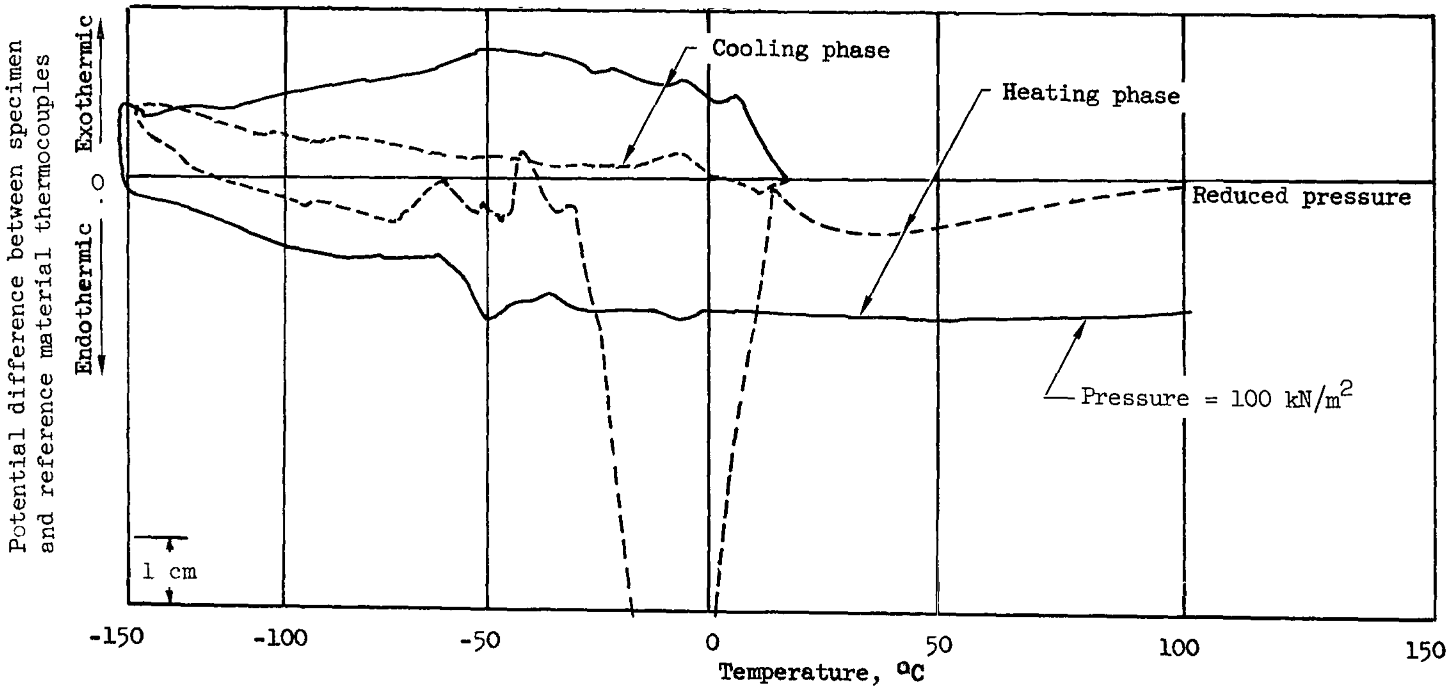
Effluent-Gas Identification

During the thermal analysis measurements of the polymers, samples of the effluent gas were trapped in the sample bottle. Gas samples were taken during the reactions when the manifold pressure gage indicated approach to a pressure peak and at 100° C. In each case the sample bottle was disconnected from the DTA vacuum system and attached to the injection system of the time-of-flight mass spectrometer. After a short pumpdown of the lines to reduce the quantity of enclosed air, the gas-bottle shutoff valve was opened and the effluent gas was injected into the spectrometer.

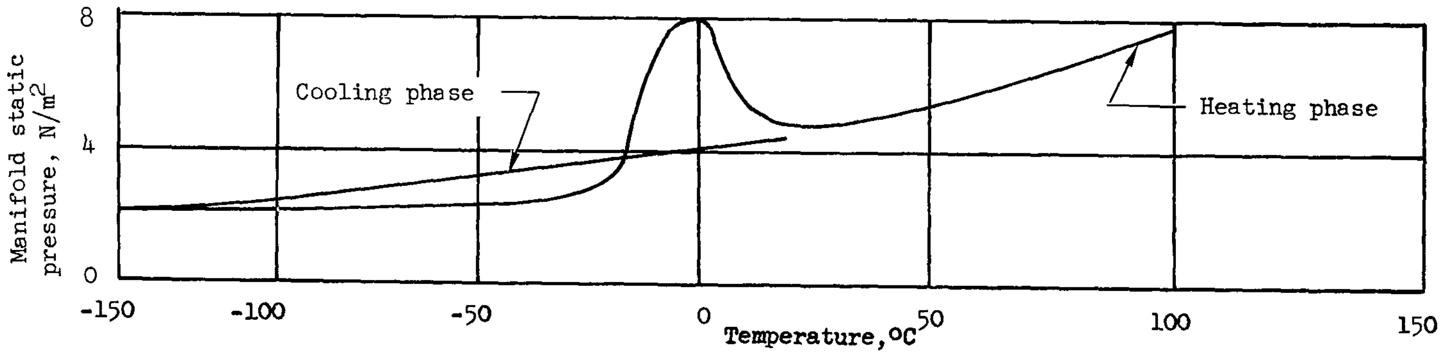
RESULTS AND DISCUSSION

Thermogram Characteristics

The DTA thermograms of isoprene elastomer and closed-cell Fluorel foam, figures 6 and 7, respectively, indicate changes in molecular segment mobility over a temperature range between -130° C and 15° C. Within this temperature range, transition phases occur which change the mechanical behavior of the polymer from that of a rubber to that of a glassy material. The generally accepted divisions of polymer physical behavior (ref. 1) are (1) the glassy state, (2) the leathery state, (3) the rubbery state, and (4) the viscous state. In the range between -130° C and 15° C, several transitions between the states of molecular or molecular chain segment activity are expected and are in fact shown on the thermograms. The thermogram of isoprene made at a pressure of 100 kN/m^2 shows a correspondence between the heating and cooling phases which indicates a reversible process. At the temperature rates used to produce the thermograms, the heating phase appeared to give better definition of the polymer state changes than the cooling phase. This result can be attributed to different values of the molecular partition functions during heating and cooling changes or to a phenomenon comparable to the supercooling of water.

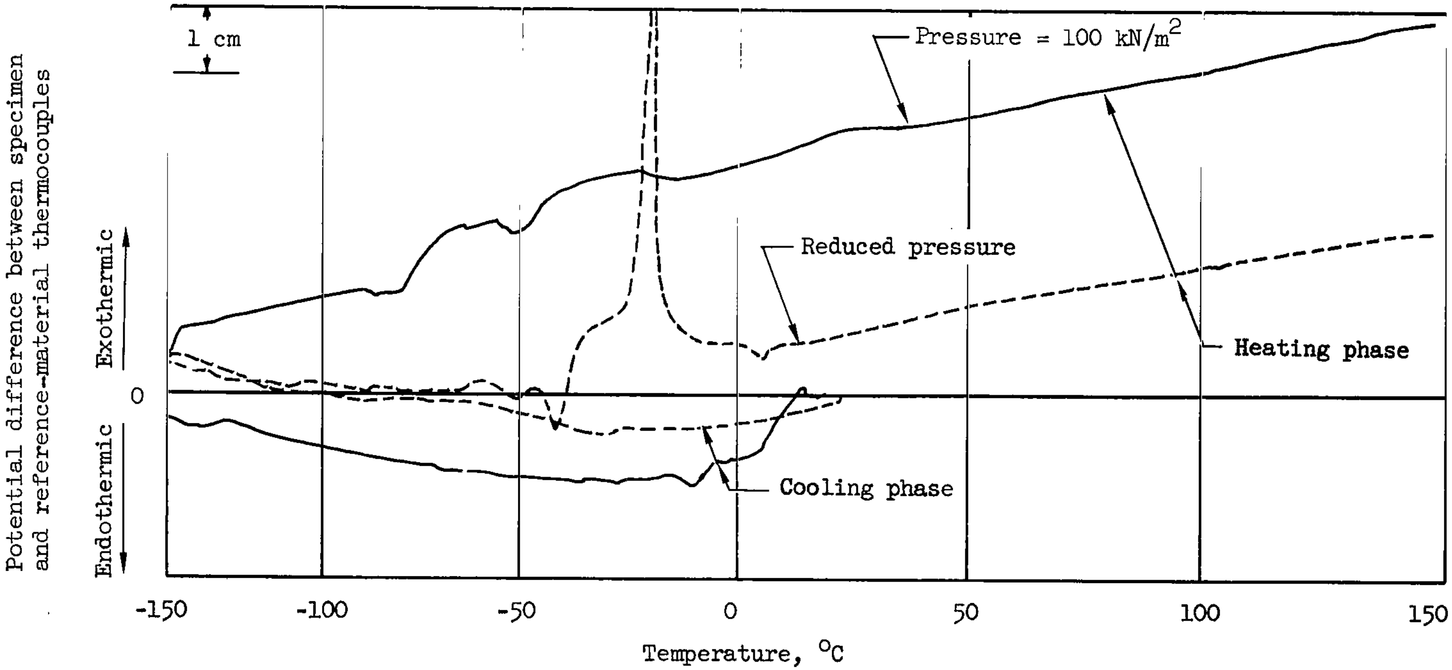


(a) Thermograms of 0.0039-mg specimens of isoprene elastomer. Reference material is alumina.

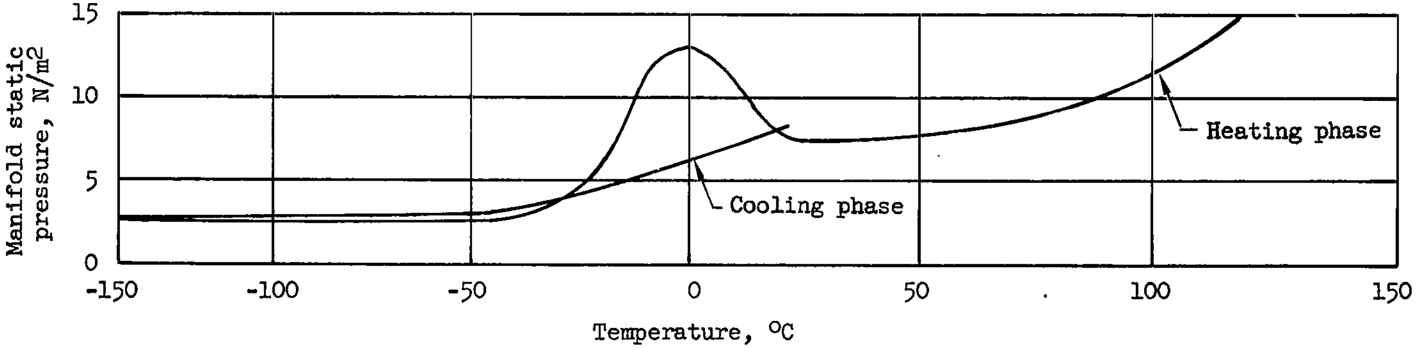


(b) Variation of pressure during the thermal cycle.

Figure 6.- Pressure and thermal measurements for isoprene elastomer.



(a) Thermograms of 0.0088-mg specimens of closed-cell Fluorel foam. Reference material is aluminum.



(b) Variation of pressure during the thermal cycle.

Figure 7.- Pressure and thermal measurements for closed-cell Fluorel foam.

Polymer Molecular State

The temperature range of this study spans the crystallization regime and the glass transition region of these two polymers. At the glass transition, chain segments of polymer molecules participate as units in the general kinetic agitation. This produces a difference in polymer specific heats between the different regions of energy absorption. Changes in slope and displacements that are associated with transition changes are shown and discussed in references 5 to 8. An analysis in reference 5 shows that the differential temperature curve plotted against surface temperature should be sigmoidal in shape. A graphical method of analysis was used herein to determine inflection and displacement temperatures, whereby the slope of the differential temperature on the thermogram is approximated with straight lines. Figure 8 presents the thermogram of isoprene elastomer with the straight-line approximations and shows the glass transition temperature to be -62° C for both heating and cooling cycles. From four separate tests with approximately the same specimen weight, the arithmetic mean of the glass transition temperature was -60.5° C for the heating cycle and -63.8° C for the cooling cycle, with mean deviations of 1.9° C and 1.5° C, respectively. This compares with a value of -75° C for natural rubber from reference 1. However, an additive used in the formulation of the isoprene induces a higher degree of cross-linking, which raises the transition temperature.

The location of a glass transition temperature for the closed-cell Fluorel foam is shown in figure 9. This value, 0° C, contrasts with a measured brittle point for the polymer of -25° C and a nominal usable lower temperature limit of -54° C from unpublished data. Reference 1 states that block and graft copolymers may have two transition temperatures, one close to the value of glass transition for each polymer. The measured value in this report corresponds to a higher temperature transition point. There are possible transition points at approximately -50° C and -79° C shown on the heating phase of the thermogram that are not obvious on the thermogram during the cooling phase.

Low-Temperature Reaction Phenomena

An unexpected result of the thermal analysis measurements reported herein was the observation of a first-order thermal reaction which occurred during the heating cycle for both elastomers at reduced pressure. Figures 6 and 7 for isoprene elastomer and closed-cell Fluorel foam show this peak and also the increase in manifold static pressure that accompanies it. The gas samples collected at -10° C and 100° C from isoprene elastomer and at -30° C from closed-cell Fluorel foam were all composed of O_2, N_2, large amounts of H_2O, and traces of CO_2. The sample collected at 100° C from closed-cell Fluorel foam differed in that it contained a moderate amount of CO_2.

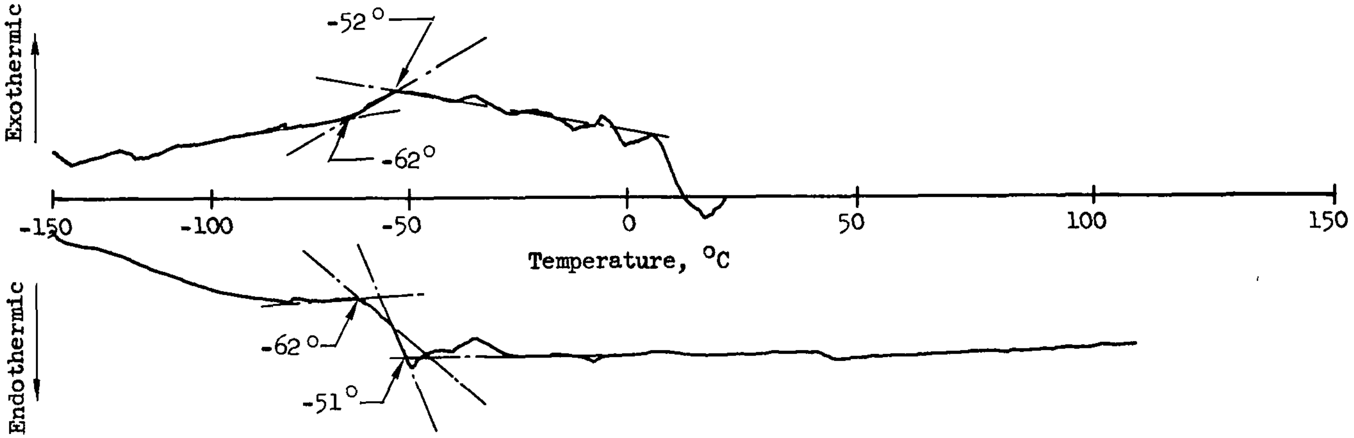


Figure 8.- Graphical analysis of DTA thermogram of 0.0039-mg specimen of isoprene elastomer. Reference material is alumina.

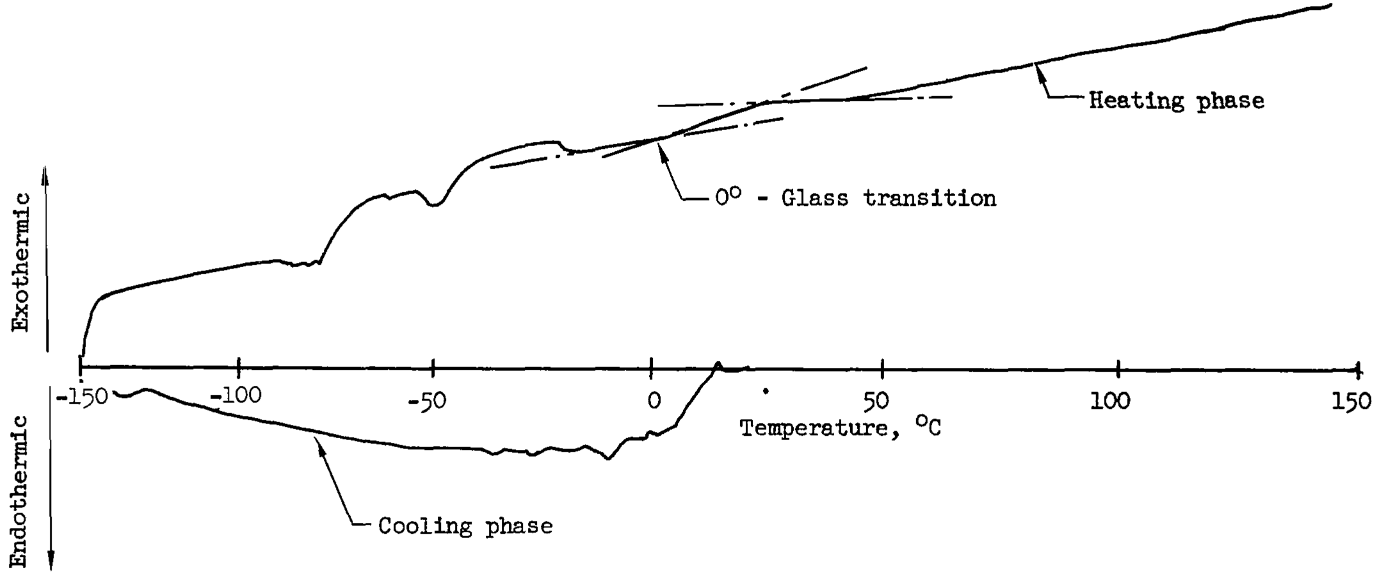


Figure 9.- Glass transition determination for 0.0088-mg specimen of closed-cell Fluorel foam. Reference material is aluminum.

Quantitative values of the mass spectrometer peaks were not obtained, but the O_2 and N_2 peaks were in the approximate ratio of 1:4, as was expected since there was residual air in the system. The ratio of CO_2 to the residual air for both samples of effluent from isoprene elastomer and the low-temperature sample from the closed-cell Fluorel foam was slightly larger than that for atmospheric air. The ratio of CO_2 to the residual air for the sample collected at 100° C from the closed-cell foam was more than three times that present in atmospheric air. The detection of carbon dioxide in the effluent gas is probably due to permeation of the gas from the interior of the cells to the sample-holder chamber, since material permeability is a direct function of the temperature.

The water-vapor peak was several times greater than the N_2 peak, a fact that tends to eliminate residual air as the source. Minor endothermic peaks on the heating cycle at a pressure of 100 kN/m^2 and the corresponding exothermic peaks on the cooling cycle are smaller representations of the water-vapor peak. Figure 10 relates thermal events and measured pressure for isoprene elastomer and water-vapor pressure over ice from

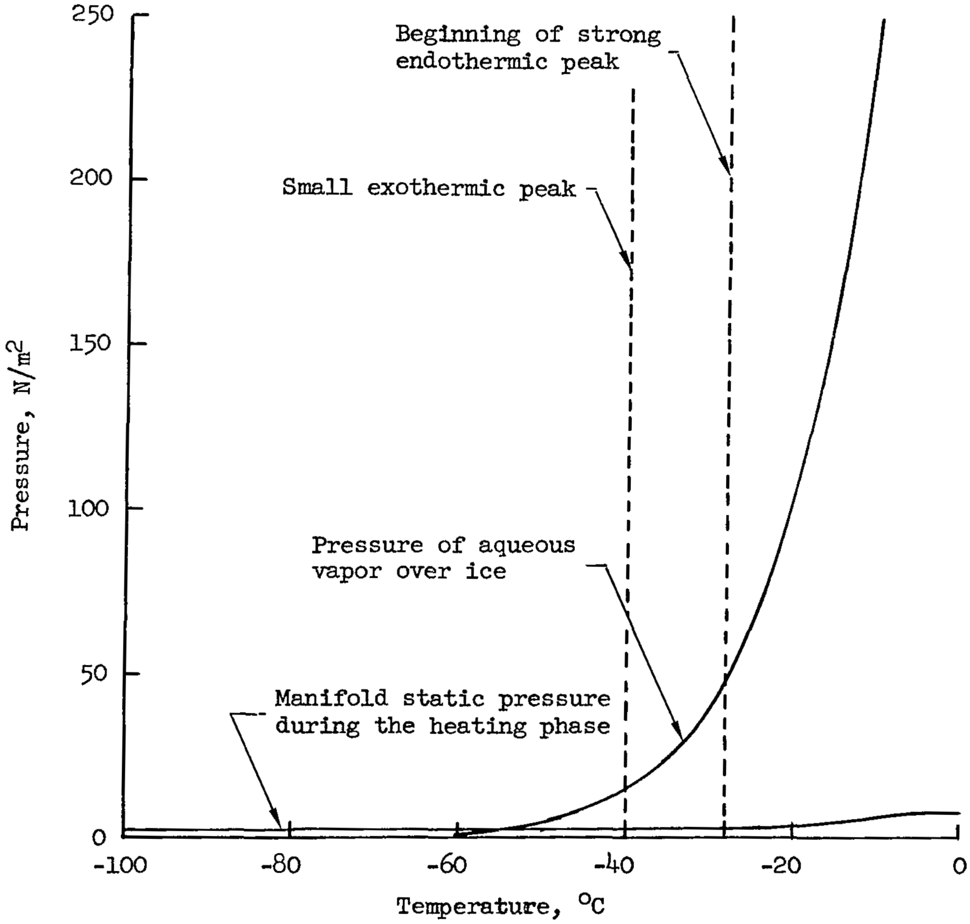


Figure 10.- Relationship of thermal events and pressure for isoprene elastomer.

reference 4. When the lag in manifold pressure is taken into consideration, the large endothermic peak for isoprene elastomer is seen to be related to the vaporization of water.

Potential sources for the water are interior free water from either absorption or the residue of polymer processing, chemically bound water from the catalyst and chain-termination hydrogen and hydroxyl ions, and water physically bound by Van der Waals' force. Experimental evidence in favor of the physically or chemically bound water is found in the weak exothermic peak at -40° C for isoprene elastomer. When the thermograms and manifold pressures of isoprene after preconditioning at 75° C and a pressure of 1 mN/m^2 for 24 hours were compared with thermograms and pressures of corresponding unconditioned specimens, a similarity was noted. This would appear to reduce the possibility that the specimens contained interior free water.

The thermogram for closed-cell Fluorel foam (fig. 7(a)) shows an exothermic peak with the apex at -20° C. For this polymer, it appears that a chemical reaction must exist. Since the reaction is exothermic, it probably is related to chain extension and cross-linking, with the formation of water from hydrogen and hydroxyl ions.

CONCLUDING REMARKS

Differential thermal analysis measurements were made at a pressure of 100 kN/m^2 and at a reduced pressure of approximately 2 N/m^2 for isoprene elastomer at temperatures from -150° C to 100° C and a closed-cell Fluorel foam at temperatures from -150° C to 150° C.

The glass transition temperature of the isoprene elastomer was found to be -62° C, as compared with a glass transition temperature of -75° C for natural rubber. The low-pressure thermograms showed the presence of a subzero reaction that produced water as an effluent vapor for both isoprene elastomer and closed-cell Fluorel foam. It is recommended that further critical investigations of this phenomenon be conducted before application of these elastomers for external use in proximity to instruments on spacecraft.

Langley Research Center,
National Aeronautics and Space Administration,
Hampton, Va., October 31, 1970.

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