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A STUDY OF VARIANT SILICONE RUBBER HEART VALVE POPPETS BY THERMOGRAVIMETRY–DIFFERENTIAL THERMAL ANALYSIS

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ABSTRACT

Thermal analyses were used to assist in the characterization of forty selected silicone elastomer heart valve poppets which have been implanted in humans for time periods varying from 22 to 79 months. Three distinct types of thermograms were obtained which were related to the amount and general type of constituents absorbed by the poppets during implants. These results are analyzed and discussed in terms of other analytical results from solvent extraction, gas chromatographic and thin-layer chromatographic analyses.

INTRODUCTION

Upon exposure to body fluids, silicone rubber heart valve poppets absorb (adsorb) lipids in the form of fatty acids, triglycerides, cholesterol, cholesterol esters and related compounds. The lipid content can attain values of 15–30 wt. % of the total poppet weight. The incidence of functionally variant valves represents approximately 1.5% of the aortic and less than 0.05 percent of the mitral prostheses which have been supplied by one manufacturer[1]. The work summarized in this paper represents an attempt to utilize thermal analytical methods to obtain information concerning the behavior of silicone heart valve poppets which had been exposed to human in vivo conditions for varying periods of time. Specifically, the results reported here are based upon 40 selected poppets which had been implanted for time periods from 22 to 79 months.

EXPERIMENTAL

Simultaneous thermogravimetry (TG) and differential thermal analysis (DTA) were obtained using a Mettler thermoanalyzer. Analyses were made in 8-mm platinum

crucibles on samples weighing approximately 90 mg. The samples were prepared from representative volumes of each poppet by dicing to about 1.5-mm^3 pieces. The heating rate was either 6 or 10°C/min. depending upon the type of information being sought. Both flowing air (5 l/h) and flowing nitrogen (5 l/h) atmospheres were used. Aluminum oxide (Al_2O_3) was used as the reference material for DTA measurements. It was found to be more feasible and more informative to obtain curves in air as opposed to nitrogen.

Data from the thermal analysis curves were compared to those obtained from solvent extraction and subsequent gas chromatographic (GC) and thin-layer chromatographic (TLC) results.

DISCUSSION AND RESULTS

We illustrated in an earlier communication that the bulk polymer in a used poppet had undergone chemical changes as the result of body exposure[2]. The overall physical appearance and feel of the poppet indicated that gross changes had indeed occurred. The hardness and associated mechanical properties had deteriorated to a noticeable degree and the color had changed from opaque white to various shades of yellows and browns. It was established that new silicone rubber heart valve poppets contain several percent of unreacted linear polymer and that after an extended implantation period (in this case 58 months) this material is no longer detectable by our extraction-spectrographic techniques. Preliminary thermal analyses showed that the thermograms from a new and used poppet were significantly different and that the used material lost weight at a much earlier temperature than the new ball. This appeared to be consistent with other analyses which reflected a deterioration of properties. It was found, however, that extracted samples of new and used poppets gave practically identical curves. This suggested that changes in the properties of the

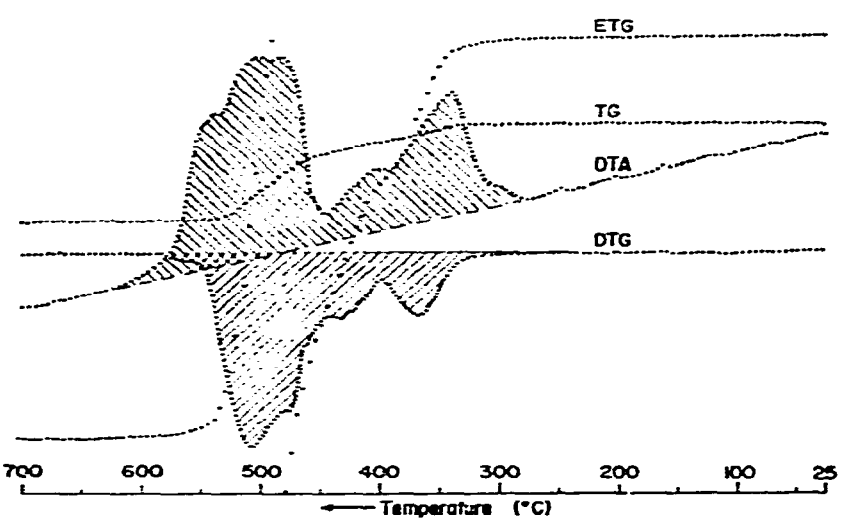

Fig. 1. Thermogram of a new used Type I poppet decomposed in air.

polymer after exposure to body fluids were the result of absorbed materials in the polymer matrix, and that these materials were acting as plasticizers effecting the observed physical changes. Because the previous work was based on only one sample and was intended only to demonstrate the feasibility of thermal techniques as an analytical tool in this area, a detailed study was not attempted. In the present study a sample size of 40 was considered sufficient to attempt a more complete analysis.

Figure 1 shows the complete curve of a new heart valve poppet which had been decomposed in air. The new poppet, in air, is characterized by a weight loss of approximately 9% between 260–410 °C with the bulk of this loss being between 360–410 °C. The apex at 390 °C in the DTG indicates that the cause of the weight loss is probably an independent event which is exothermic; the maximum exotherm occurring at 360 °C. From 410–600 °C the TG profile is characteristic of a multievent oxidative decomposition. This is also evident in the accompanying exotherm.

Three types of curves were observed for used poppets which were decomposed in air. For those poppets containing less than 5% extractables the Type I curves were essentially the same as for the new poppets, except that the TG showed an initial weight loss ($<5\times10^{-5}$ mg/mg sample-°C) starting at about 150–160 °C. The initial weight loss for the original poppet started at 260 °C.

For those poppets containing larger amounts of extractables two other distinct types of curves were obtained. Type II (Fig. 2) shows two distinct DTG apexes, one at 440–450 °C and another at 500–520 °C with an initial weight loss discernable at

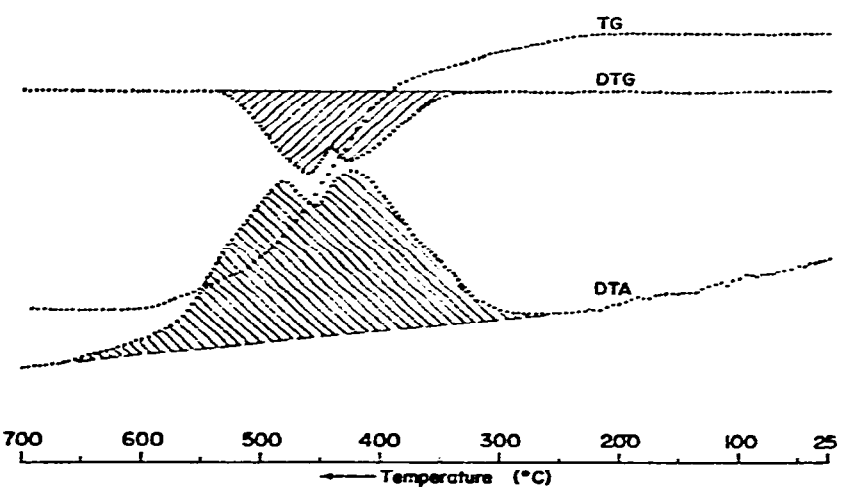

Fig. 2. Thermogram of a used Type II poppet decomposed in air.

150–160 °C. It is of interest to note that the DTG apex and the DTA exotherm seen on the original poppet curve at 390 °C have disappeared and that a new apex and exotherm have appeared at 440–450 °C. The degradation, as evidenced by TG weight loss, is complete at 600 °C which is the same as for the original poppet. The event

taking place at 390°C in the original poppet is accompanied by a definable change in TG slope and the normalized rate of weight loss was 1.4×10^{-3} mg/mg sample-°C. The rate of loss Fig. 3 at 390°C is 5.7×10^{-4} mg/mg sample-°C, or two and one half times less than for the original poppet. The rate of loss at 440–450°C was 3.8×10^{-3} mg/mg sample-°C. At first glance it appeared reasonable that the larger rate of loss could be overshadowed by the smaller rate in the present case if the amount of

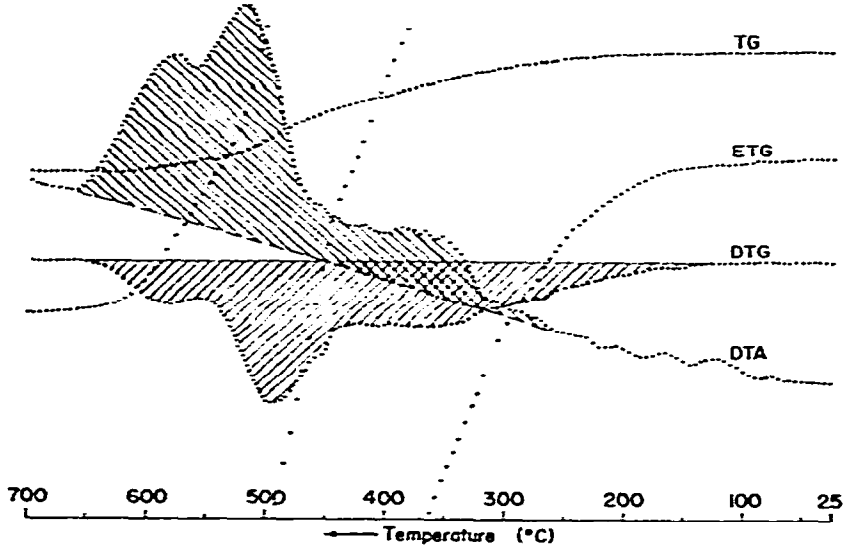

Fig. 3. Thermogram of a used Type III poppet decomposed in air.

absorbed material was large. This was not the case. A more careful examination of the curves showed that the magnitude of TG apexes and the DTA exotherms were essentially the same in Figs. 1 and 2 and that, if the event described at 390°C in the original poppet were still taking place in the Type II used poppet, it should have been evident in both the DTG and DTA curves of Fig. 2. 16 of the 40 poppets studied fell into the Type II category. There appear to be sufficient data to raise several pertinent questions to which we do not have the answers at present. (1) It has been accepted that the cured silicone rubber heart valve poppets can contain up to several percent of unreacted polymer which is no longer detectable after the poppets have been exposed to body fluids for an extended time period. Are there other materials (unreacted polymer which is complexed with fillers which is not solvent extractable, but which can desorb in body fluids, reaction products with the catalyst which can desorb in body fluids, etc.) which are lost due to in vivo exposure? (2) Are there compounds in the poppets which have complexed with components from the body fluids which decompose in a manner similar to the adsorbed lipids? (3) Does the new event seen at 440–450°C represent a selective absorption of materials from the body fluids and is the desorption of one set of species independent of the absorption of another set of species?

Type III curves (Fig. 3) represented 14 of the 40 samples tested. They are

different from Type II in several respects. Both the DTG and the DTA curves were complex and individual events were difficult to distinguish. An initial weight loss was discernable at 150–160 °C in all cases. A small exotherm was distinguishable at 380–400 °C with major exotherms at 520 and 580 °C. The DTG deviations were evident starting at 150–160 °C with a smooth increase until the major polymer decomposition at 520 °C. A new and separate event was found at 580 °C which was complete at 680 °C indicating that the Type III poppets had absorbed or formed a material which decomposed at a higher temperature than the original poppet.

Based upon GC and TLC analyses of extracts from the used poppets, C_{18} fatty acid and cholesterol were selected for thermal studies. Both of these materials were known to contain impurities so as to represent principal body fluid components. Figure 4 shows the curve for stearic acid in air. The broad melting range, the DTG, and the principal DTA curves are characteristic of the impure acids. The weight loss began at about the same point as the absorbed material in the used poppet. Another distinct exotherm and DTG apex were observed at about 500 °C. This event could be the result of a small amount of triglycerides present in the initial fatty acids, or if unsaturated chains containing some conjugated double bonds were present, there is always the possibility that Diels–Alder products could have been formed during the heating. It is important to note that all activity was complete at a temperature (560 °C) lower than that required to decompose a used poppet (680 °C).

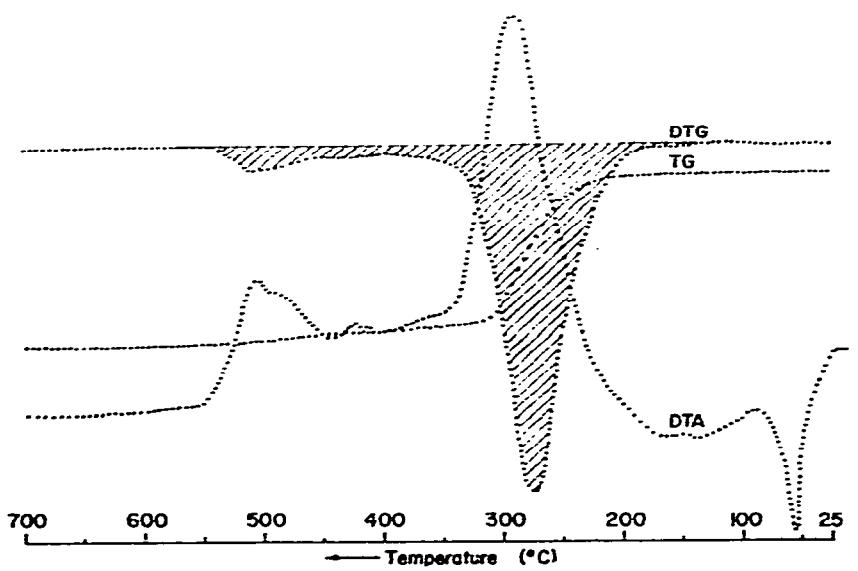

Fig. 4. Stearic acid decomposed in air.

Figure 5 shows the curve obtained for the impure cholesterol in air. This compound is characterized by a melting point in the 130–135 °C range with weight loss beginning at 200 °C. There are one major and two minor exotherms with accompanying DTG responses. It is important to note that all activity is complete at about

680°C, the same temperature as observed in the decomposition of the used poppet, and that the final DTA and DTG responses are also the same as observed for the Type III poppets. Further, the thermal studies, along with other analytical data, clearly indicated relatively large amounts of cholesterol or cholesterol-like products in 14 cases. TLC analyses were used to separate the absorbed materials into lipid classes. While TLC gave some evidence of cholesterol, the results were not entirely conclusive because of streaking. Additional analytical work is being done as the result of the thermal studies.

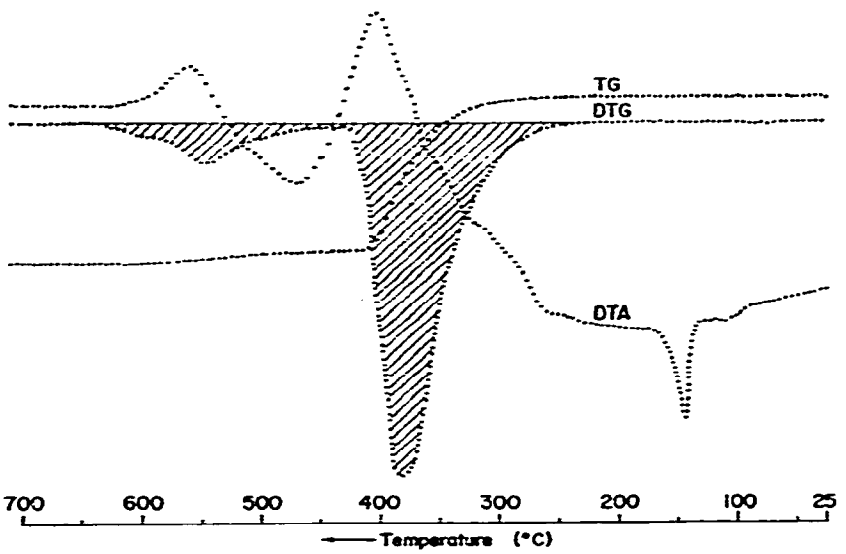

Fig. 5. Cholesterol decomposed in air.

In comparing Figs. 4 and 5 with Figs. 2 and 3 it is apparent that the endothermic DTA responses associated with the melting of the C_{18} acid and the cholesterol are not present, as such, in the used poppet curves. Products found in the used poppets are present as plasticized solids which are syrup-like in nature. These products appear to be compatible with each other and with the silicone rubber, resulting, at least, in partial solubility of the combined components. Any residual endothermic responses would be expected to be small when the entire mass of poppet plus absorbed material is considered.

An attempt was made to determine the amount of absorbed lipids in the different specimens through the thermograms obtained in air. Values agreeing within 2% (on an absolute basis) with solvent extraction values were obtained by subtracting the weight loss (after total thermal degradation) of an extracted original poppet from the total weight loss of the used poppets. This method is obvious in those cases where the poppets being compared contain the same amount and kinds of filler, but not in other cases. The curves were examined to determine if an empirical relation existed which would allow the estimation of the quantity of absorbed lipids.

For those samples which did not exhibit the distinctive apex at 390°C a relationship was established which allowed the estimation of the amount of absorbed materials. For Type II poppets (which showed a definite apex at 440°C) the weight loss corresponding to this apex was divided by the total sample weight in order to compute the percent of extractable material. For Type III poppets (where the apex was not distinct) the weight loss at 440°C was divided by the total sample weight and the percent of extractable material computed on this basis. Table 1 shows that these methods of estimation are reasonable. Based upon curves from the original poppets

TABLE 1

COMPARISON OF % ABSORBED LIPIDS BY SOLVENT EXTRACTION AND BY THERMOGRAVIMETRY

Sample identification	*Implantation time (months)*	*% Solvent extractable*	*% Absorbed by TG*	*Type curve*
AM-69	34	20.4	21.2	II
AM-70	23	20.6	18.6	II
AM-71	28	23.5	24.4	III
AM-72	22	28.5	27.1	II
AM-73	27	22.3	23.7	II
AM-75	35	21.5	22.3	III
AM-76	34	15.8	16.5	II
AM-78	34	2.8	5.7	I
AM-79	30	15.5	16.2	III
AM-81	38	24.5	29.2	III
AM-82	37½	40.7	41.7	III
AM-83	30	18.6	19.3	III
AM-84	50	30.6	29.8	II
AM-85	48½	28.4	21.3	III
AM-86	48	18.0	18.5	III
AM-87	53	17.8	18.1	II
AM-88	60	35.3	19.2	III
AM-89	45	4.4	6.7	I
AM-90	69	30.5	28.6	II
AM-91	59	23.3	25.3	II
AM-92	54	20.4	22.0	III
AM-93	69	5.4	5.3	I
AM-94	53	12.0	13 9	II
AM-95	76	3.7	5.1	I
AM-96	79	6.8	6.8	II
AM-97	65	12.1	13.4	II
AM-99	72	29.2	36.3	III
CM-01	60	17.7	19.3	III
CM-03	32	21.0	23.5	III
CM-04	67	7.5	6.0	I
CM-05	32	21.5	26.3	III
CM-06	30	24.4	23.3	—
CM-07	50	24.9	24.6	II
CM-08	77	4.0	5.6	II
CM-09	78	11.8	19.2	II
CM-10	—	2.6	4.0	I

and those of the 40 used poppets it was shown that the bulk of the absorbed material has reacted and diffused from the sample.

Results are also reported for thermal studies obtained in a dry nitrogen atmosphere. The new poppet in nitrogen (Fig. 6) started to decompose at about the same temperature as in air. However, the rate of weight loss was slower and was not

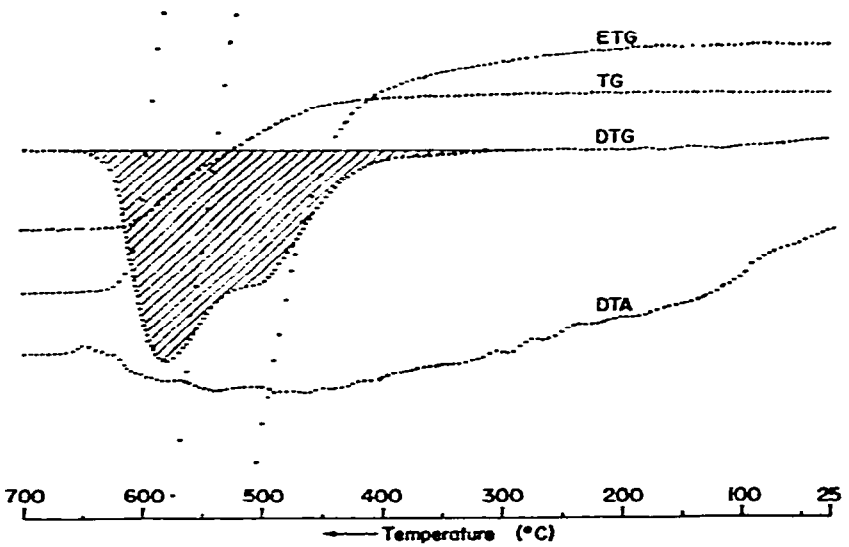

Fig. 6. Thermogram of a new poppet decomposed in nitrogen.

essentially complete until the temperature was higher than 700 °C. A small weight loss was perceptible at 900 °C. Both the DTG and the DTA curves began at about the same temperatures as in air but extended over a longer time–temperature range corresponding to the TG. It is interesting to note that the TG apex seen in Fig. 1 is not evident as such in Fig. 4, even at a higher temperature. The question must be raised again as to whether or not the new poppets contain a species which is subject to oxidation at a lower temperature than for the bulk of the poppet. Further, is this same material, which was not solvent extractable, subject to loss or conversion as the result of in vivo exposure? Evidence to date (by IR, GPC) indicates that the only extractable material from the new poppets is a low molecular fraction of the initial unreacted linear polymer.

Figure 7 shows a typical curve for used poppets which have been decomposed in nitrogen. It is essentially the same as for the new poppet in nitrogen except that the decomposition of the absorbed material began at a lower temperature and was not yet complete at 900 °C. Because of the long decomposition times, the triple pump down-purge procedure required for nitrogen, and the incomplete decomposition at 900 °C, curves obtained in air were found to be more feasible and more informative than for samples run in an inert gas.

At 440 °C a small part of the silicone polymer has also degraded which coinci-

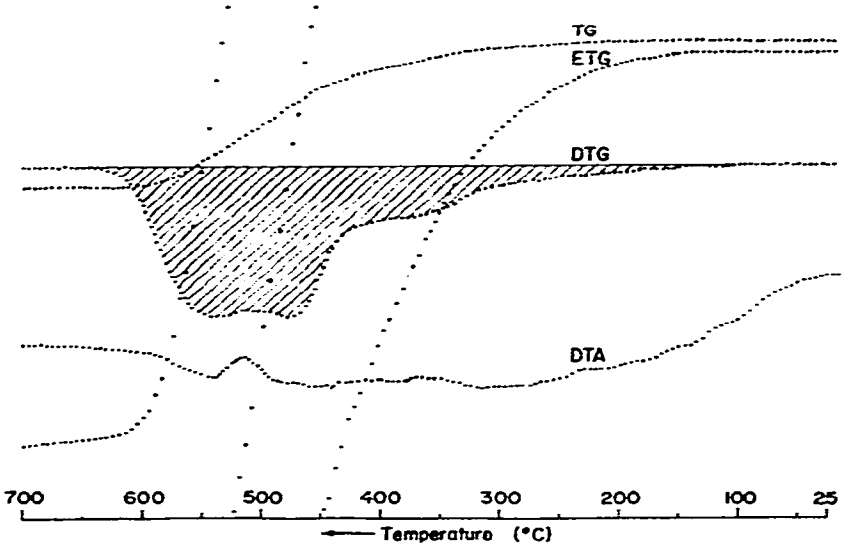

Fig. 7. Thermogram of a used poppet decomposed in nitrogen.

dentally is essentially the same mass as the absorbed materials remaining in the poppets. This point was verified through the solvent extraction data. For those samples which showed a well defined TG apex at 390°C the percent of absorbed material was usually small (3–7%). The weight loss at 390°C was divided by the total sample weight to obtain the amount of absorbed materials.

CONCLUSIONS

Thermal studies have proven useful, in conjunction with other tests, in evaluating silicone heart valve poppets. This information serves in this laboratory to force a more critical evaluation of what is absorbed and which components originally present in the poppet are lost or converted during implantation.

ACKNOWLEDGMENT

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