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NEW POLYMERS TO PROTECT SPACE VEHICLES

by

H.F. Mark, F.R. Eirich and J. Fock

Final Report No. PIBMRI 1385-67

for

U.S. Army Research Office - Durham

Contract No. DA-31-124-ARO-D-278,

October 1967

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ABSTRACT

The synthesis and the characterization of new polymeric systems to be used as protective coatings for space vehicles is described. Particular emphasis is placed on ablators which have low irradiation and particle emissivity under the conditions of typical reentry of a space vehicle into the atmosphere.

Crosslinking by ionizing radiation in carbon black filled Kel-F and Teflon has been established by mechanical and thermoanalytical methods. Polyaromatic systems such as polyphenylene, methylated poly-phenylene, poly-benzyl poly-p-xylylene, furthermore phenolic resins and a styrene-divinyl benzene copolymer have been synthesized and investigated by thermogravimetric analysis. In addition Pluton impregnated with poly-vinyl fluoride or crosslinked polystyrene has been investigated. As a fourth approach towards new ablative materials the synthesis of aromatic fluorocarbon and silicon type ladder polymers was initiated.

The research on carbon-filled Teflon indicates a considerable improvement in heat shielding with polymeric ablators in terms of better mechanical properties and lower weight-to-heat dissipation ratios.

NEW POLYMERS TO PROTECT SPACE VEHICLES

I. Introduction

Work was undertaken partly to make a thermal-physical, and spectroscopic study of ablating polymers with a view to comparing the relative suitabilities as cooling surfaces of high speed bodies in the atmosphere, and secondly to synthesize and screen a number of new polymeric materials which might be likely candidates for improved ablative coatings.

Earlier studies by many agencies have indicated that any suitable ablative agent must fulfill certain basic conditions which can be clearly related to the required mode of functioning. To quote some of the principal required properties, the material must have a fairly high melting point, either a high viscosity after melting, or a melting point above the decomposition temperature so that charring will occur, a high heat capacity, low heat conductivity, a high energy of dissociation, and a high emissivity while in situ and a low emissivity of the ablated gases. Some high energy inorganic materials, mostly ceramics, come close to many of these specifications. Organic materials do inasmuch as they produce a mechanically strong char and require the breakage of strong CH or CF bonds. Polar polymers are in general not very suitable because they produce too many highly emissive fragments on their decomposition. This study therefore concentrated partly on the synthesis of high melting aromatic polymers, but also partly on the following special projection.

Polytetrafluoroethylene, commonly called teflon, was for some time recognized as having potential in the above respects except that its melting point is rather low and that it has a high rate of thermal decomposition. It appears to us very likely that a filled teflon resin could overcome these objections provided a suitable filler could be found which would raise the melting point and which would anchor thermal decomposition products by interacting with them. A substantial portion of work under this contract has gone into exploring this possibility which looks very promising indeed. The following discussion of results and method will pertain to these two areas while the conclusion will report on status and prospects.

II. Discussion

1. Investigation of Effects of γ - Irradiation on Carbon Black Filled Fluoro Carbon Polymers

a. Kel-F - Carbon Black

As first example for the crosslinking of fluorine-carbon polymers by ionizing irradiation in the presence of carbon black Kel-F Elastomer was chosen. This polymer turned out to be more appropriate to get an estimation of the problems involved in the preparation and characterization of samples than Teflon.

Kel-F Elastomer is a copolymer of trifluorochloroethylene and vinylidene fluoride. Carbon black CX 87 and Spheron (Cabot Corp.) was added to the elastomer after a curing agent (Diak I) had been thoroughly incorporated at 125°C. on a rubber mill. The source of irradiation was γ -radiation emitting Co^{60} with a dose rate of 95000 r/h. The integral dose was $2-70 \cdot 10^6$ r. The structural transformations in the irradiated elastomer were estimated by changes of the solubility, by the percentage of swelling, the elastic modulus and the tensile strength.

Irradiation of Kel-F in presence of carbon black produces predominantly a network which is demonstrated by the loss of swelling-ability and by a sharp change of the physico-mechanical properties.

First the swelling properties of Kel-F in acetone in dependence of the dose were measured. The results are shown in Figure 1.

The crosslinking process is evident and shows a linear dependence on dose (Fig. 1). The influence of oxygen appears not to be large in the presence of carbon black CX 87, which contains about 3% oxygen, although it is known that the structural changes of pure Kel-F elastomer on irradiation in air are considerably higher than in the absence of oxygen. This fact may be due to the formation of C-O Polymer and C-OO Polymer-bonds. The same result was observed by the increase of the elastic modulus in dependence on dose (Fig. 2). The activity of the two fillers in irradiation could be explained by the formation of considerable quantities of chemical bonds between filler surface and copolymer. This is confirmed by the sharp increase of the equilibrium modulus and of the tensile strength, which

is more pronounced in the presence of XC 87 than in that of Spheron (Fig. 3 and 4).

It is known that the activity of fillers in the case of chemical vulcanization is determined also by the nature of their physical surface. Thus the two fillers in quantities corresponding to an equivalent surface were introduced. In Figure 5 are given the data of maximum swelling of the vulcanization depending on the absorbed energy. The equal slope of the straight lines in a dose range of $10 - 20 \times 10^6$ r points out that unexpectedly in the case of the Kel-F elastomer the physical nature of the surface does not influence the rate of vulcanization.

Finally Figure 6 shows the dependence of the strength of the fluorine copolymer upon the quantity of filler. As anticipated, the strength of the elastomer increases much more in the presence of CX 87 than in the presence of Spheron.

Although the oxygen containing CX 87 black exhibits better properties in respect to the mechanical features, the investigations of the thermal behavior of the reinforced elastomers is yet incomplete, but it is expected that, as a consequence of the more readily interchanging -O- or -O-O bonds on CX 87, Spheron filled Kel-F could perform better at higher temperature.

b. Teflon - Carbon Black

The unusual high thermal stability of Teflon is contrary to its often reported sensitivity to radiation. It could be demonstrated that bond-rupture in the course of irradiation is not unusually predominant compared with other systems; however, due to the fact that for good mechanical strength teflon must have a molecular weight higher than 10^6 only few carbon-backbone-scissions cause serious declines in mechanical properties.

By ESR studies it is also known that radicals in an irradiated Teflon react with oxygen to form peroxy-type radicals. Furthermore, the thermal decomposition of Teflon is accelerated by the presence of oxygen. It could be shown that the exclusion of oxygen showing the irradiation of virgin, and especially of carbon black containing Teflon, gives a different dependence of the mechanical strength on γ -dose.

Microspecimens of different mixtures of carbon black and Teflon, resp. virgin Teflon with 1/8" thickness, were obtained from molding sheets whose preparation was described in the last letter report.* The specimens were sealed in Pyrex ampoules after evacuation of 10^{-5} mm Hg. and irradiated with different doses (range 0 - 2.5×10^7 r) with a dose-rate of 3×10^5 r/h. Tensile strength measurements were done on an Instron Testing equipment.

The results shown in Figs. 7, 8, 9, and 10** indicate.

1. Teflon is relatively resistant to irradiation by γ -rays, when treated in vacuo. It was reported that Teflon irradiated in the presence of oxygen loses its tensile strength almost completely already at a dose of about $5-6 \times 10^6$ r. Also, the initial decrease in strength from irradiation in vacuo could be explained by the influence of oxygen released from container walls and traces in the samples. It is known e. g. that irradiation releases gases from glass. It is believed, that in case of virgin Teflon crosslinking takes place.

2. The addition of oxygen free carbon black (Spheron) prevents a decrease of tensile strength. (Fig. 7, 8). Only small decreases occur at low doses which become less significant at higher Spheron concentrations. This small decrease should again be due to traces of oxygen. Qualitatively, there appears to be an increase in stiffness, in as much as percentage of elongation of the material decreases with dose. This fact, and the low effect of irradiation on tensile strength, indicate that crosslinking processes have occurred, not only due to the formation and combination of: $mCF_2 - \overset{F}{C} CF_2 m$ radicals, but also by formation of bonds between polymer and carbon black. There is no explanation for the slight increase of tensile strength at low doses for the 25% Spheron/Teflon mixture. It has to be shown by more extended experiments in how far irradiation can cause an increase in tensile strength and where the maxima with respect to dose and carbon black are located.

* Fourth Quarterly Letter Report for the period ending 30 June 1965.

** Fig. 8 and 10 were drawn for better demonstration of the influence of the different molding procedures for virgin and carbon black containing Teflon on the mechanical properties.

3. Teflon reinforced with XC 72 (Fig. 9, 10) carbon black behaves differently on irradiation apparently due to its content of oxygen (3%). The addition of 5% XC 72 increases the tensile strength by about 25%. On the other hand, the effect of radiation is strikingly detrimental, especially at low doses, where the presence of the adsorbed oxygen leads to a rapid deterioration of the polymer by the formation of peroxy type radicals. After a dose of about $5 - 10^6$ r a stabilization, probably caused by competing crosslinking processes, occurs. The dependence of the tensile strength is again decreased with increasing carbon black content (Fig. 10). There is no explanation yet for the low tensile strength of the 25% XC 72 Teflon mixture.

2. Synthesis and Thermoanalytical Investigations of Thermostable Polymers

a. Polyphenylene

This polymer was synthesized by treatment of benzene (1 mol), with CuCl_2 (0.5 mol) and water (1 ml) at 40°C for 1 hour. The reaction mixture was then added to water and filtered. After treatment with 10% HCl, the product was treated with boiling NaOH until the filtrate was colorless and the polymer was washed repeatedly with distilled water. It resulted in a light brown solid, which was insoluble and infusible.

The polymer was heated in vacuo with a heating rate of about $5^\circ\text{C}/\text{min}$. The weights (W) were registered as functions of temperature (W_0 = original weight of the sample). Figure 11 shows the W/W_0 vs. temperature curve which exhibits some tendency to stabilization, probably indicative for carbonization during pyrolysis.

Although these polymers cannot be used as resins; they may be applied as reinforcing agents, for example in the case of silicones or fluoride-containing polymers.

b. Methylated polyphenylenes

By the introduction of CH_3 - groups into the phenylene chains one can reach higher solubility of the polymer and higher molecular weights. The preparation of these polymers was effected by condensation of 4, 4' Diiodo-3, 3' -Dimethyl-Diphenyl, with Ullman-Copper in dry α -Methyl-naphthalin at 240°C for 16 hours under nitrogen. The dark sticky tar was extracted with anisole, filtrated and the solvent vaporized. Yield was

approximately 80%. The intrinsic viscosity of the product in benzene at 20°C was about 1.0. The polymer was fractionated into three parts by precipitating it from the solution in benzene with methanol.

	<u>Softening point °C</u>	<u>Intrinsic viscosity</u>
Fraction 1	290 - 310	2.4
" 2	230 - 245	1.1
" 3	110 - 140	-

The thermal behaviour is not yet investigated. The main disadvantage in preparing these polymers is that one gets the monomer from o-nitrotoluene via o-toluidin only in very low yields.

Experiments to get methylsubstituted polyphenylenes from 3, 3' - dimethyl - diphenyl with AlCl_3 - CuCl_2 - water gave oily products with intrinsic viscosities around 0.02.

c. Polybenzyl

By heating benzylchloride at 100° in the presence of FeO as catalyst under nitrogen polybenzyl was prepared. After removing the residual monomer the polymer was dissolved in benzene and filtered. By adding an aceton-methanol mixture to the solution the polymer was precipitated. It has a softening point of 73 - 81°C; its molecular weight was determined by the cryoscopic method to be about 5000.

Heating in vacuo with a heating rate of approximately 5° C/min. gave the results shown in (Fig. 11).

d. Poly-p-xylylene

This polymer was obtained by decomposition of p-methylbenzyl-trimethylammonium-bromide in 50% NaOH by refluxing under nitrogen for 5 hr. (The ammonium salt was prepared in 80% yield by quaternization of p-methyl-benzyl-bromide with triethylamine.) The reaction mixture was poured into water, the resulting polymer filtered and extracted with boiling ethanol. The polymer was washed with ether and dried under vacuum. Approximately 60% yield. $\eta_{sp} = 1.21$ was determined at 305°C with a concentration of 0.5% in benzoyl-benzoate. The polymer starts to soften at 220°-250°C and subsequently melts at 410 - 420°C. This is

followed by rapid thermal degradation. Poly-p-xylylene can be passed to thin films at 350° which are tough, clear and drawable. We plan to impregnate pluton with poly-p-xylylene.

Pyrolysis of the polymer was studied in vacuo; it was found that there was no pronounced difference in the behaviour of poly-p-xylylene and poly-benzyl. The high thermal stability of the two polymers may be explained on the ground of a high degree of resonance along the chains (Fig. 11).

3. Impregnation of Pluton with Several Polymers and Thermoanalytical Analysis

a. Phenolic Resins

Sample Phenolic I was prepared in the presence of Ca(OH)_2 as catalyst by heating the mixture of formaldehyde and phenol at 65°C for 5 hr. at pH = 9.0. After cooling to 20°C CO_2 was added to the solution until a pH of 6.0 was reached. CaCO_3 was filtered off, and water and the excess of phenol evaporated in vacuo. The resin was then cured by heating for 15 min. at 94°C, then for 15 min. at 101°C and at last for 30 min. at 127°. The product - a B-stage Resole - was dissolved in ethanol to a 60% solution. Pluton fabric was soaked with the solution and dried in an oven at 90°C; 12 layers of the impregnated fabric were pressed for 3 hours at 150°C. The resin-pickup of the fabric was about 35%.

Sample Phenolic II (Reichhold Ptyophen 50/2) was used to impregnate Pluton fabric in the same manner.

The thermal behaviour of powdered samples of phenolic I and II was tested by a thermogravimetric balance of the Mettler Company, Switzerland in the temperature range from 20° to 1600°C under atmospheric pressure of air with a heating rate of 25°/min. This is shown in Fig. 12.

Stabilization seems to occur between 600 - 1200°C indicated by the fact that the weight loss in this range is only 20%; charring of the polymer may be the main process at this stage. It was found that the residue at 1200° consists almost entirely of carbon. The main difference between Phenolic I and II is in the temperature range under 500° where Phenolic II turns out to be more stable. The thermal stability of the phenolic Pluton appears to be higher than that of Pluton alone. There is still a residue of 25% in the case of Phenolic II, whereas the Pluton has almost disappeared.

On the other hand the smaller oxygen content in the Pluton reinforced sample is evident.

b. Styrene-divinylbenzene copolymer

A 55% solution of divinylbenzene in ethylstyrene was mixed with 10% polystyrene and 0.2% AIN as an initiator. Pluton was soaked with this mixture. 12 layers of the impregnated fabric were pressed for 18 hrs. by a laboratory press at 150°. The resin pickup turned out to be 26%.

The sample was heated in the Mettler Thermogravimetric balance in the temperature range from 20 to 1600° under atmospheric pressure of air with a heating rate of 25°/min. This is also shown in Fig. 12.

There was a certain stabilization observed beginning at about 600°C, which is similar to that of the phenolic resin. But generally this material turned out to be less stable than the latter, for example at 1000°C one has only 25% as a residue while the phenolic shows a value of 53%.

An approach to a higher thermal resistance is intended by preoxidizing the polydivinylbenzene to form a dense network, leaving approximately the 8 fold residue compared with the uncured polymer. Figure 13 shows an example of a differential thermal analysis curve made from Pluton fabric calculated for both the original weight of the material subjected to DTA and the weight at temperature t. These measurements will be valuable for calculating the thermodynamical properties of our samples later on. The Mettler equipment allows to plot DTA and TGA curves simultaneously.

c. Polyvinylidene fluoride

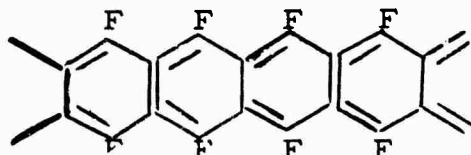
This polymer from the Minnesota Mining and Manufacturing Corp. was dissolved in dimethyl formamide (25%) to impregnate a piece of Pluton fabric. After evaporation of the solvent, the sample was pressed to a black sheet in a laboratory press at 350°C. Although the press form was covered carefully with silicone grease there was a very firm adhesion of the polymer to the metal surface, which may be explained by a partial thermal decomposition of the polymer yielding hydrogen fluoride. One part of the pressed sample was irradiated with a dose of approximately 12 Mrad. Although no quantitative measurements were made, the tensile strength of the material seems to be increased in a pronounced manner.

The thermal behaviour has not yet been measured.

4. Synthesis of New Ladder Polymers

a. Aromatic Fluoro-carbon polymers

The preparation of the fluoro-carbon polymer with the expected structure



was first tried via 1, 4-difluoro-3-iodobutene-1. 2-fluoro-1, 1, 2-tribromoethane has been prepared from tetrabromoethane and mercuric fluoride. Debromination of the tribromo compound gave cis- and trans-1-bromo-2-fluoroethylene in high yield. The substituted ethylene was heated with KI in a glass tube at 200° to yield 1-fluoro-2-iodoethylene. The latter was devoted to a reaction with vinyl fluoride and 1, 4-difluoro-3-iodobutene-1 was obtained. Unfortunately, the approach to get a 1, 2-polymerization with a radical catalyst at high temperature failed due to the removal of the Iodo-group, which consequently gave a black and insoluble black tar.

EXPERIMENTAL

1. Preparation of 2-fluoro-1, 1, 2-tribromoethane

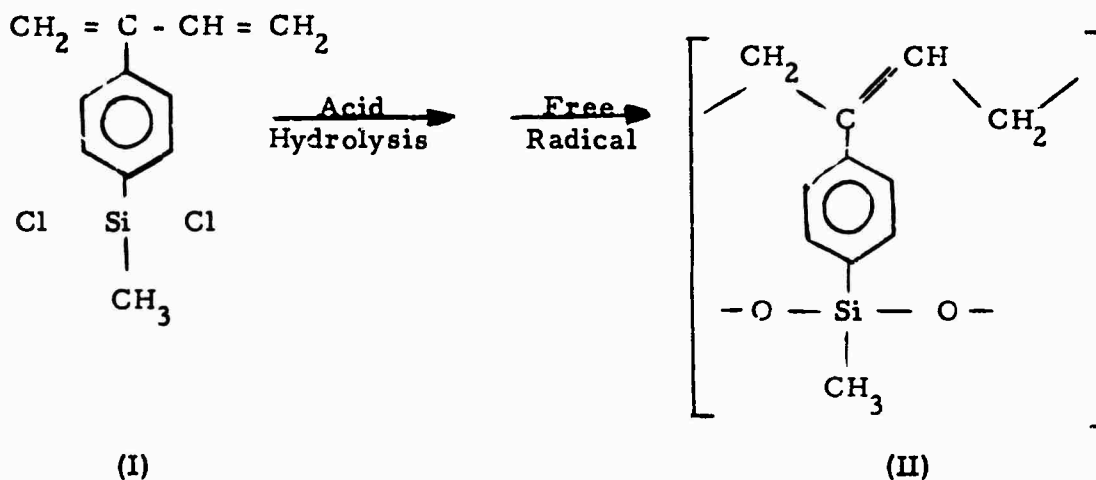
Mercuric fluoride 113.5g (0.478 mole) was slowly added over a period of 3 hours to 541g. (1.57 mole) of tetrabromoethane heated to 120°C in a monel three-necked metal flask fitted with a metal stirrer, a glass reflux condenser and an addition bottle for adding the mercuric fluoride. After the addition the mixture was slowly heated to 155° for two more hours using an oil bath. The reaction mixture was allowed to cool to room temperature and anhydrous ether was added to wash out the contents of the flask into a beaker. The solid inorganic material was filtered off and the ether was removed by vacuum distillation. The product was again filtered and fractional distillation of the material gave 80.3g (58% yield) of the desired product B. p. 77°/30 mm. 5g. of 2, 2 difluoro-1, 1-dibromoethane B. p. 29/30 mm was collected as a forerun. 396g. of tetrabromoethane was recovered.

2. Preparation of cis and trans - 1 bromo-2 fluoroethane

To 70 g. of zinc powder suspended in 100 ml. of freshly distilled ethanol (distilled from radium) heated to 60 - 64° was added 80 g. (0.28 mol) of 2-fluoro-1, 1, 2 tribromoethane at such a rate that gentle reflux occurred. The addition was slowly at first, rapid toward the end. The product was collected as it distilled through a 6 inch column and condensed with a dry-ice distillation head. Collect product boiling over a range of 22-40°C. Redistillation gave 33 g. of product (94%) B.p. 20 - 39.5°C (Lit. 94% of cis - trans mixture; Trans 20°, cis 39.5°. Vapor phase chromatography using a Perkin-Elmer silver nitrate packed column at room temperature showed the presence of two peaks.

a. Siloxane carbon ladder polymer

The second ladder polymer now under investigation is expected to have the following structure:



For its preparation the corresponding difunctional monomer dichloro-di-(p-2-butadienyl phenyl)-silane is planned to be hydrolyzed first without affecting the butadienyl-function to yield the siloxane-backbone (-Si-O-Si-linkage). Free radical polymerization of the butadiene group would yield the other backbone needed to form the desired ladder polymer.

The proposed method for obtaining the monomer involves the preparation of 2-(p-bromo phenyl) butadiene as an intermediate step. The Grignard reagent of this compound could be prepared by reacting it with magnesium

in either tetrahydrofuran or ethylether. By adding the Grignard reagent to the THF or ether solution of SiCl_4 , the desired dichloro-di-(p-2-butadienyl phenyl) silane would be obtained with trichloro-p-2-butadienyl-silane as a probable by-product.

The preparation of 2-(p-bromo phenyl) butadiene is not described in the literature. The initial attempt at its preparation involved the reaction of p-bromoacetophenone with vinyl-magnesium-chloride in tetrahydrofuran to yield expectedly a mixture of the alcohol (3-p-bromo phenyl butene-1ol-3) and the diene. Distillation of the mixture from anhydrous KHSO_4 would yield the diene. Actually, it turned out, that after several attempts under different reaction conditions, only about 1% of the desired diene was obtained on distillation, the remaining material was undistillable. It is presumed that an aldolization of the p-bromoacetophenone caused by the Grignard reagent has occurred.

Another attempt at the preparation of 2-p-bromo-phenyl-butadiene involved converting methyl-vinylketone to methyl-vinyl-p-bromophenylcarbinol with p-bromophenyl magnesium bromide and then dehydrate the carbinol to the desired butadiene. This two-step sequence was particularly attractive since it appeared readily adaptable to the preparation of a number of derivations of butadiene which would be required in a later investigation. When the mono-Grignard reagent of p-dibromobenzene was reacted with the mentioned ketone in ether at 0°C ., the expected methylvinyl-p-bromophenyl carbinol was obtained in very low yield. The other product was 4-(p-bromophenyl)-butanone-2, also obtained in very low yield. The rest was undistillable and accounted for the bulk of the reaction material. In tetrahydrofuran as a solvent only 4-(p-bromophenyl)-butanone-2 was collected in a low yield together with a large quantity of undistillable material. Now the reaction was modified by using p-bromochlorobenzene instead of p-dibromobenzene to get the mono-Grignard-reagent more easily than the di-Grignard compound in the case of di-bromobenzene. When p-chlorophenyl-magnesium bromide was reacted with methylvinylketone in refluxing ether, the distillable products obtained in low yields were: 4-p-chlorophenyl-butadiene, some 1-p-chlorophenyl-butadiene and some methylvinyl-p-chlorophenyl carbinol. Again the bulk of the material was undistillable. The IR spectrum

of the fractions obtained were almost identical to the IR's of the fraction obtained using the p-bromophenyl magnesium bromide as the Grignard reagent. Several attempts to isolate the major component in the undistillable material met with failure. It is well known that under certain conditions Grignard reagents react with α, β -unsaturated carbonyl compound yielding a ketone in a 1,4-addition. This would account for the preparation of the substituted 2-butanone. In a recent paper Bornstein and Nunes suggested that the greater steric bulk of the cyclic Grignard reagent is primarily responsible for the aldolization of hindered carbonyl group compounds instead of addition to the carbonyl group. Using this argument and the enolization and aldolization of ketones by Grignard reagents, it is now believed that once the substituted ketone forms, it undergoes aldolcondensation in the presence of the remaining Grignard reagent. This theory is currently under investigation. Experimental details along with results and conclusions will appear in future reports when definite conclusions have been established.

The next attempt at the preparation of 2-p-bromophenyl butadiene involves the dehydrobromination of 2-p-bromophenyl 2,3-dibromobutane using NaOC_2H_5 in ethanol. 2-p-bromophenyl-2,3-dibromobutane was prepared by bromination of the new compound 2-p-bromophenyl-2-butane which was obtained in good yield from the reaction of methyl magnesium iodide with p-bromopropiophenone in ether. p-bromopropiophenone was prepared by a Friedel-Craft reaction of bromobenzene, propionyl chloride and AlCl_3 in CS_2 . The dehydro-bromination is now under investigation.

EXPERIMENTAL

1. Preparation of p-Bromopropiophenone

In a 5 l. round bottomed, three-necked flask fitted with a mechanical stirrer, separating funnel, and a reflux condenser, is placed 392 g. (2.5 moles) of bromobenzene in 1 liter of dry carbon disulfide. To this is added 750 g. (5.6 moles) of anhydrous aluminum chloride. The mixture is heated until gentle refluxing starts, and then 186 g. (2.0 moles) of propionyl chloride (B. p. 77-78°) is added slowly through the dropping funnel. The time of addition is about one hour. Gentle refluxing should be continued throughout the time of addition of the acid chloride and for one hour afterwards.

The carbon disulfide is distilled under reduced pressure without removing the flask from the steam bath. After the removal of the solvent (about 800-900 ml.), the reaction mixture is allowed to cool somewhat; but while it is still warm, it is poured slowly with stirring over ice to which hydrochloric acid has been added. The volume is now about 6 liters. Each 3 l. portion is extracted three times with 400, 200, and 200 cc. portions of ether. The extracts are combined and washed twice with 200 cc. of water, once with 300 cc. of 10% sodium hydroxide solution and twice more with water (200 cc. portions).

The extract is dried overnight with 60 g. of anhydrous magnesium sulfate and filtered. The ether is removed by distillation at reduced pressure. After a forerun of bromobenzene, p-bromopropiophenone 324.2 g (76% yield) is distilled at $96^{\circ}/0.35$ mm. which solidifies on standing m. p. $45 - 46^{\circ}\text{C}$. (Lit. 137-140/2 mm, 58%, m. p. $45 - 46^{\circ}\text{C}$).

2. Reaction of p-bromopropiophenone with methyl magnesium iodide. Formation of 2-(p-bromophenyl)-butene-2 and 2-(p-bromophenyl)-butanol-2.

Methyl magnesium iodide was prepared from 8.88 g. (0.37 mole) of magnesium and 46.8 g. (0.33 mole) of methyl iodide in 200 ml. of ether. The Grignard reagent was filtered through a coarse fritted tube into a 250 ml addition funnel where it was added over a period of 1 hour to 64.3 g. (0.30 mole) of p-bromopropiophenone in 250 ml of ether in a nitrogen-atmosphere. The ether was rapidly refluxing during the addition once for one hour afterwards. The resulting mixture was decomposed with 50cc of hydrochloric acid in 500 g. of ice. The ether layer was removed and the aqueous phase was extracted twice with 40 ml portions of ether. The combined ethereal extracts were washed with water, dried over anhydrous sodium sulfate, and concentrated under reduced pressure to give a dark yellow residue. Fractional distillation gave 36.4 g. (57.5%) of the alkene B. p. $37 - 40^{\circ}/0.075$ mm and 18.3 g. (27%) of the alcohol B. p. $74 - 76^{\circ}/0.28$ mm.

Vapor phase chromatography using a Perkin-Elmer silicone grease packed column at 230° showed the presence of 3 major peaks for each of the fractions. This procedure is going to be repeated and analytical samples for analysis will be obtained.

3. Reaction of 2-(p-bromophenyl)-butene-2 with bromine.

To 2-(p-bromophenyl)-butene-2 28.9 g. (0.137 mole) dissolved in 30 ml of anhydrous carbon tetrachloride kept at -10° was added over a period of one hour bromine 7.3 cc. (0.14 mole) such that the reaction temperature was maintained at -10° to -5° . A slight excess of bromine was added. The resulting mixture was vacuum distilled to remove all of the low boiling components leaving a clear light yellow viscous oil. An IR - spectrum of the crude material showed the absence of double bond characteristic.

III. Conclusions

During this phase of the work, the synthesis and thermal analytical investigations of new stable polymers as proposed and as briefly discussed again in the present introduction, occupied the major effort. Three new polymers were synthesized of which polybenzyl appears sufficiently promising to merit further study.

In a parallel investigation a new fluorinated aromatic ladder polymer was prepared and that of a second containing siloxane was attempted. Work on both of these materials, which are promising with regard to their structures but offer great difficulties in their preparation, is to be continued.

In addition work has gone forward on the impregnation of the highly heat resistant carbonized Pluton fabric with phenolic, crosslinked styrene and fluorinated polymers. This composite structure corresponds exactly to the line of present thinking that a non-fusible grid containing highly energy absorbing, high melting polymers should come close to ideal ablative materials. Though we have not yet carried out all measurements data to date do in fact look highly promising.

The same is true for our attempts in studying and preparing various types of carbon black filled teflon, attempts which will be seen should lead indeed to structures very similar to those of the impregnated Pluton. It was indeed found that the carbon black reduces the thermal decomposition of teflon, though only if the black as well as the surrounding atmosphere were free of oxygen. The former can of course be obtained by a suitable

choice of black and the latter would be true under usage conditions. We consider therefore these findings as highly significant and a major effort to elaborate them will be made during the following contract year.

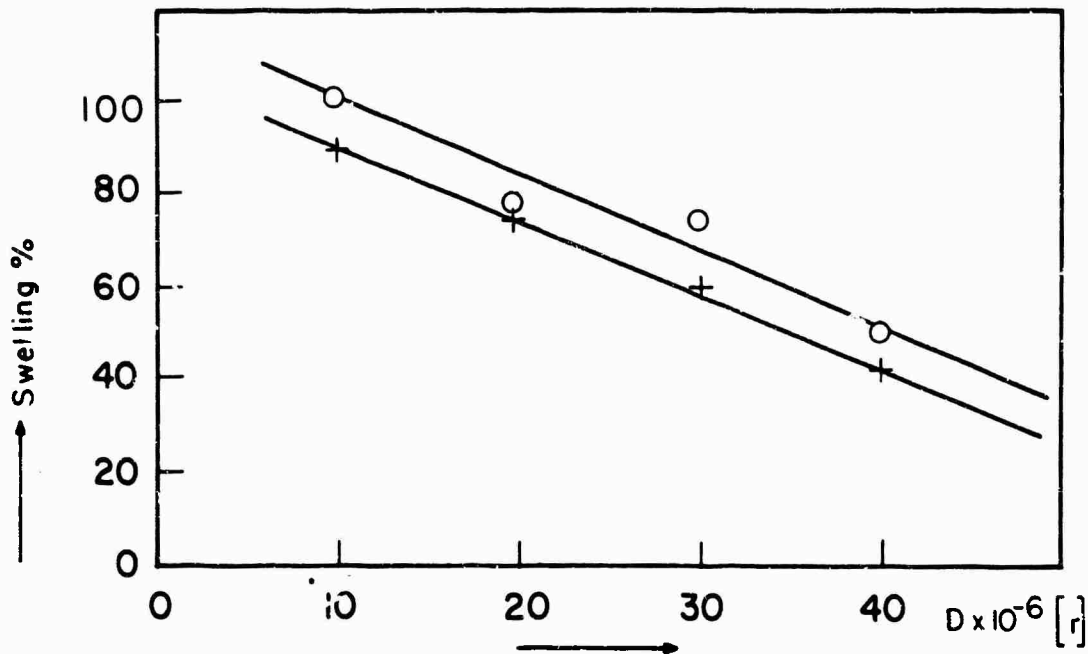


Fig. 1 Influence of γ - radiation on the swelling properties of Kel-F-Elastomer in the presence of CX87 carbon black (○ in air, + in a vacuum)

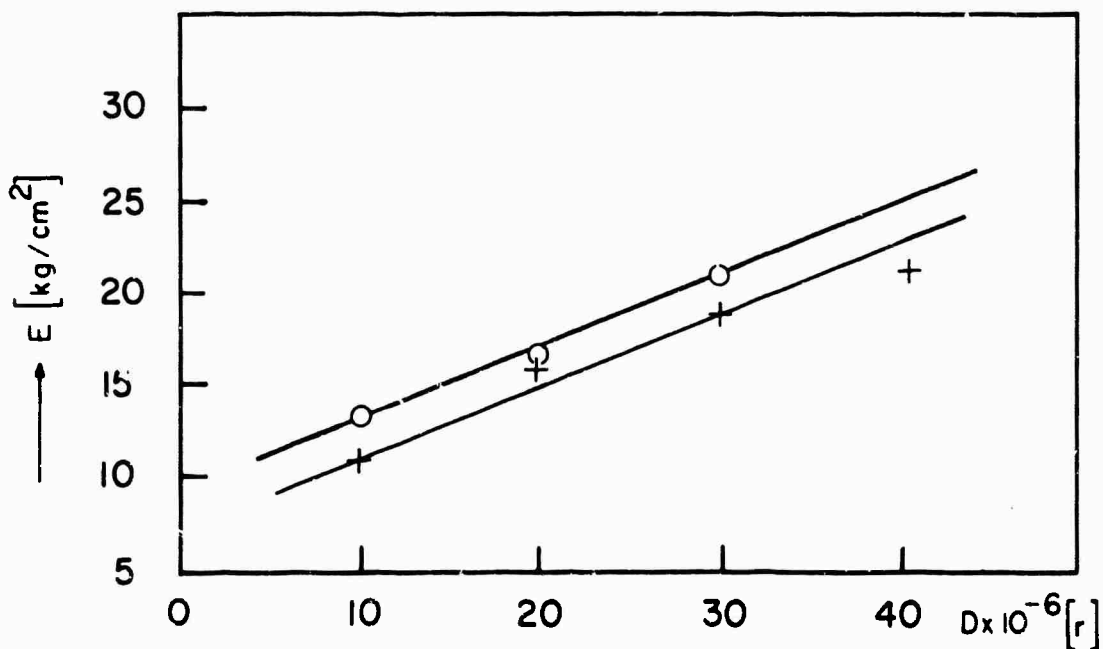


Fig. 2 Influence of γ - radiation on the elastic modulus of Kel-F-elastomer in the presence of carbon black CX87. (○ in air, + in vacuum)

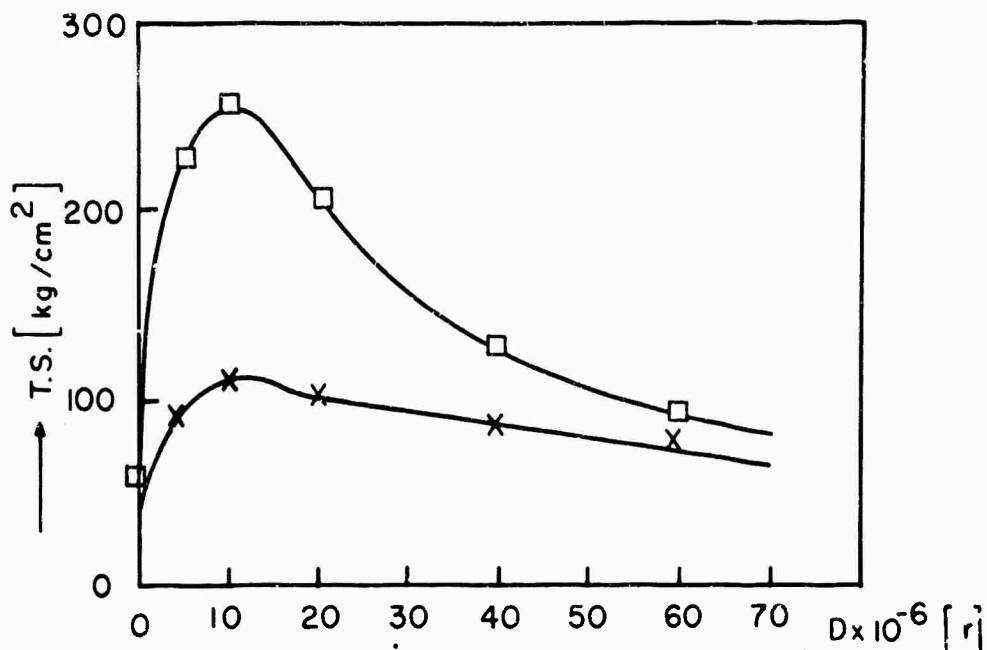


Fig. 3 Influence of γ - radiation on the tensile strength of Kel-F-elastomer filled with CX 87 - black (\square) and spheron (X).

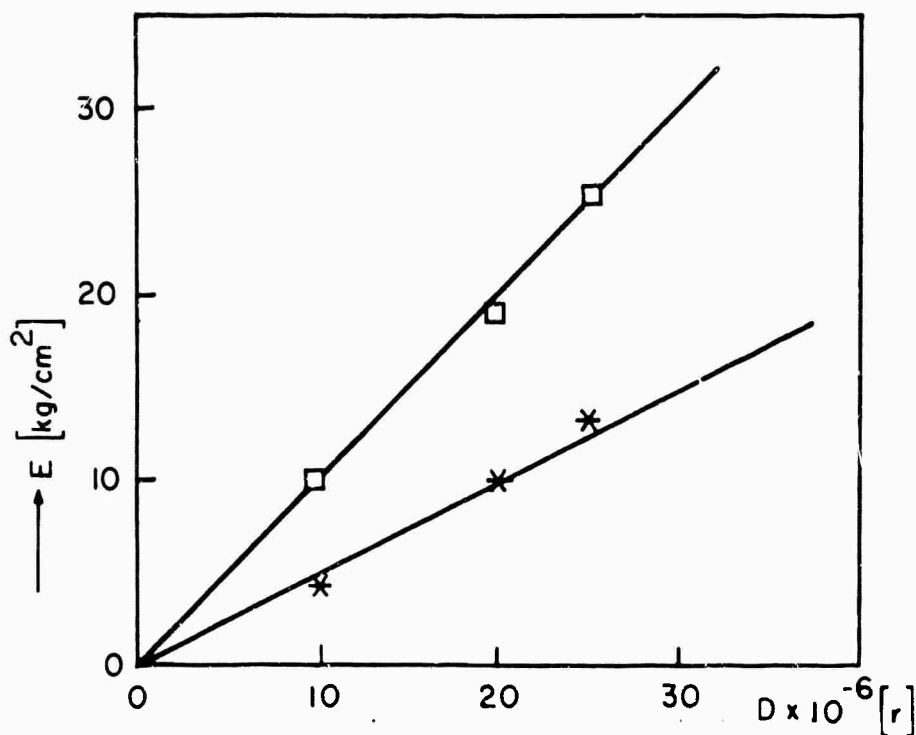


Fig. 4 Influence of γ - radiation on the equilibrium modulus of Kel-F-elastomer filled with CX 87 - black (\square) and spheron (X).

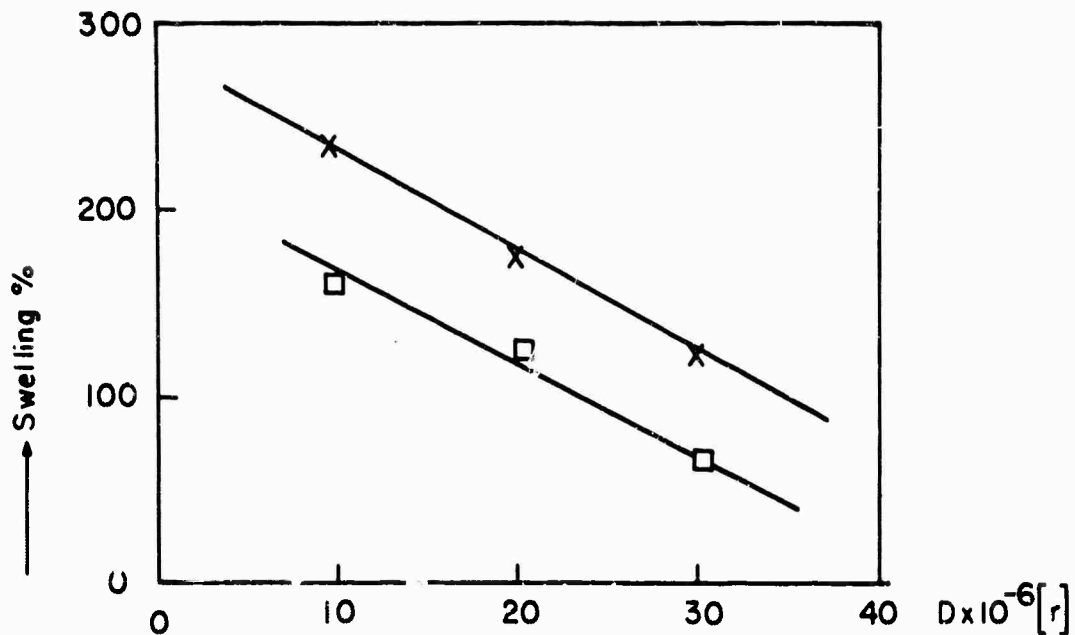


Fig. 5 Dependence of swelling properties of Kel-F-elastomers filled with a CX 87 - black (□) a spheron (X) corresponding to an equivalent surface.

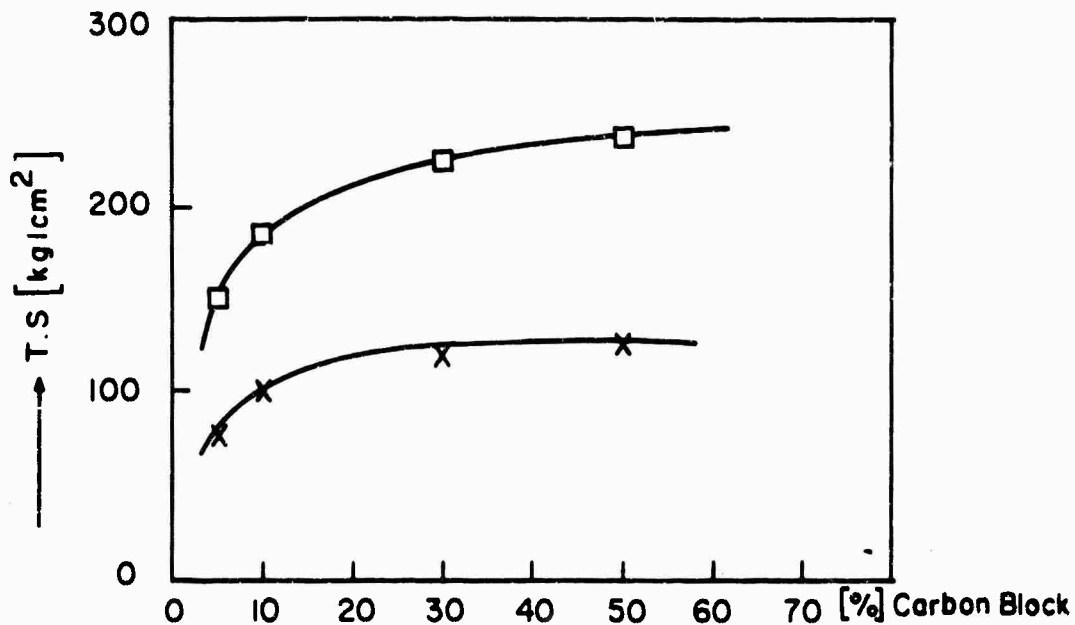


Fig. 6 Dependence of the tensile strength of Kel-F-elastomer on the amount of added carbon black CX 87 (□) and spheron (X) at a dose of 20×10^6 [r]

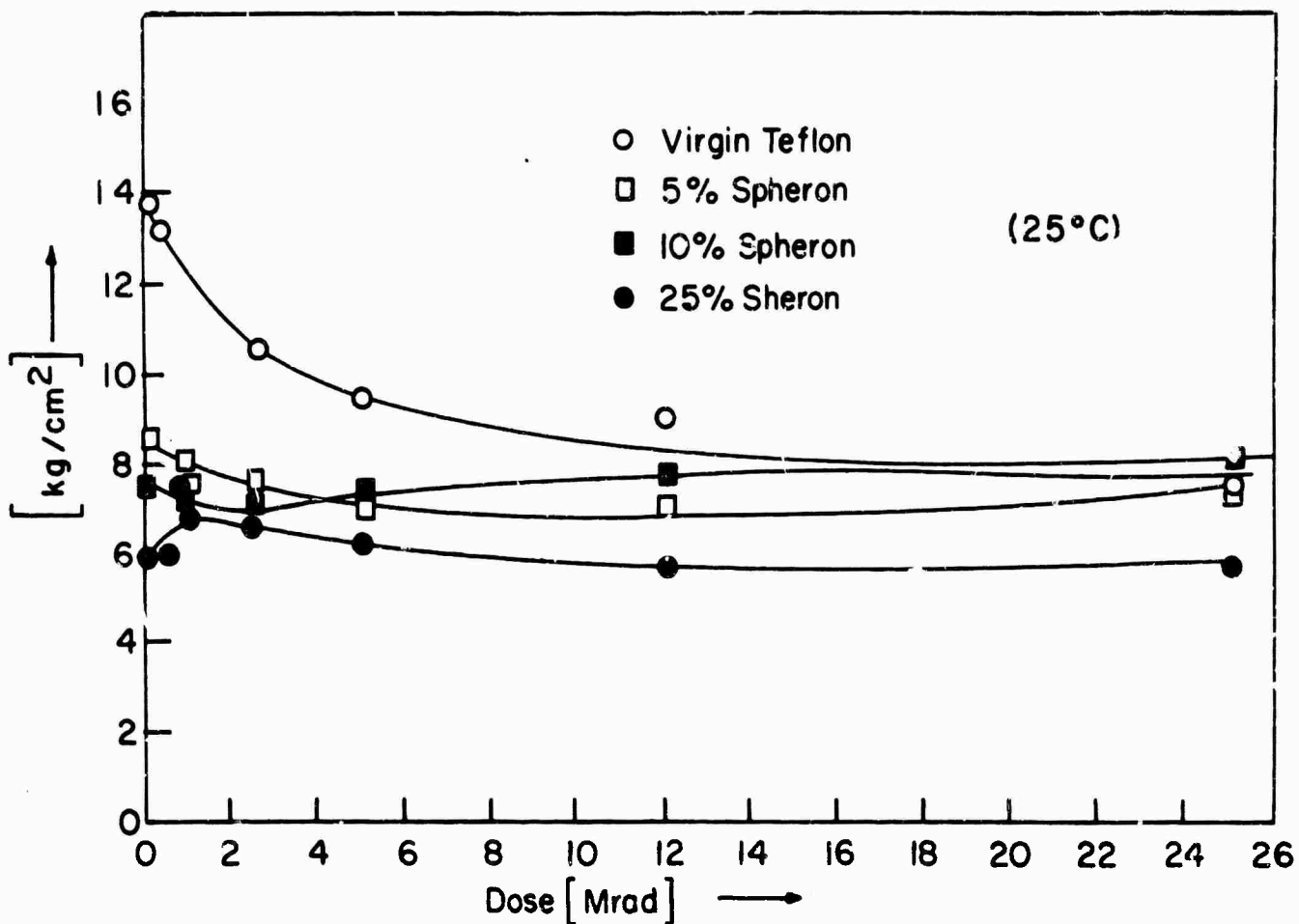


Fig. 7 Dependence of tensile strength for Teflon filled with Spheron (O_2 -free) on the γ - Co^{60} -dose.

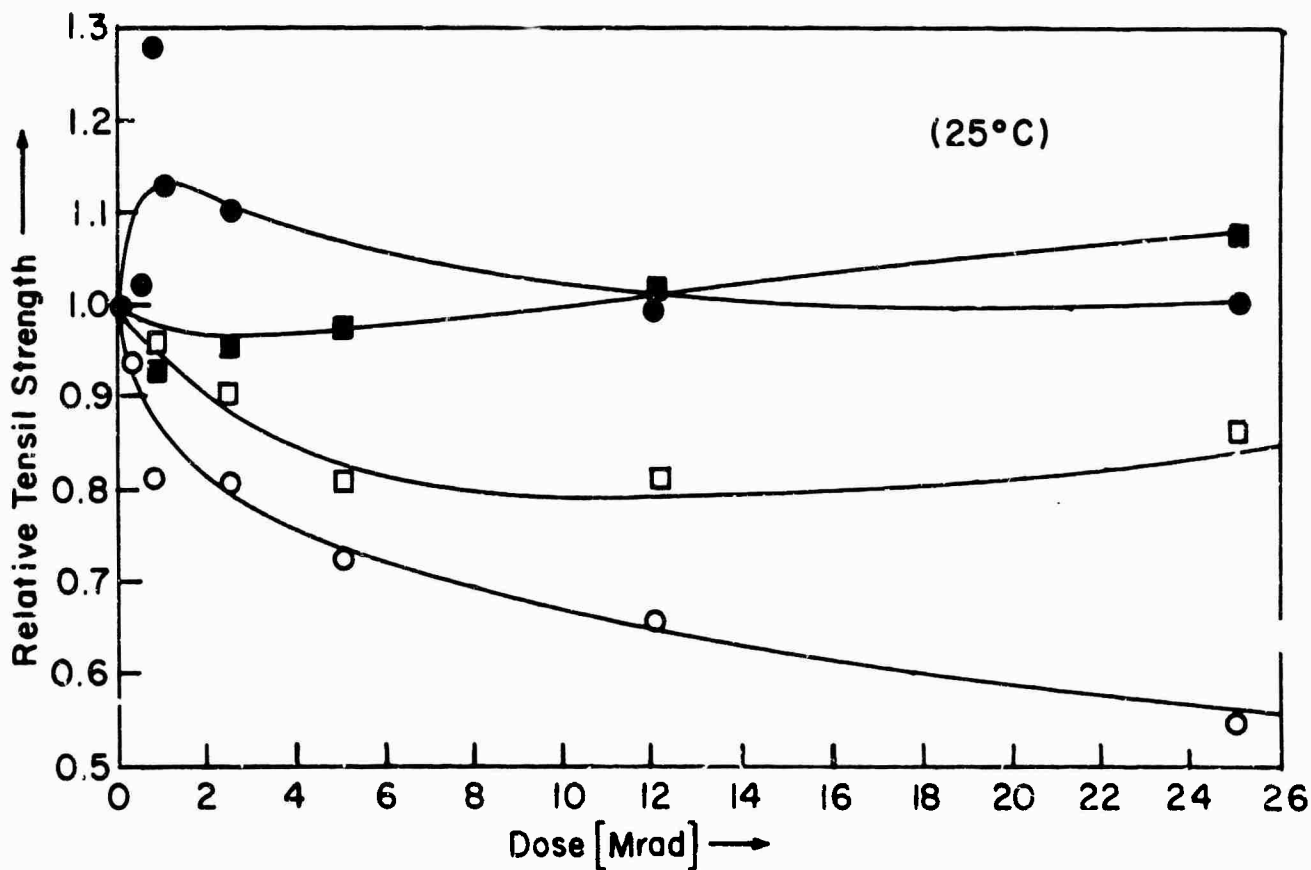


Fig. 8 Dependence of relative tensile strength for Teflon filled with Spheron (O_2 -free) on the γ - Co^{60} -dose.

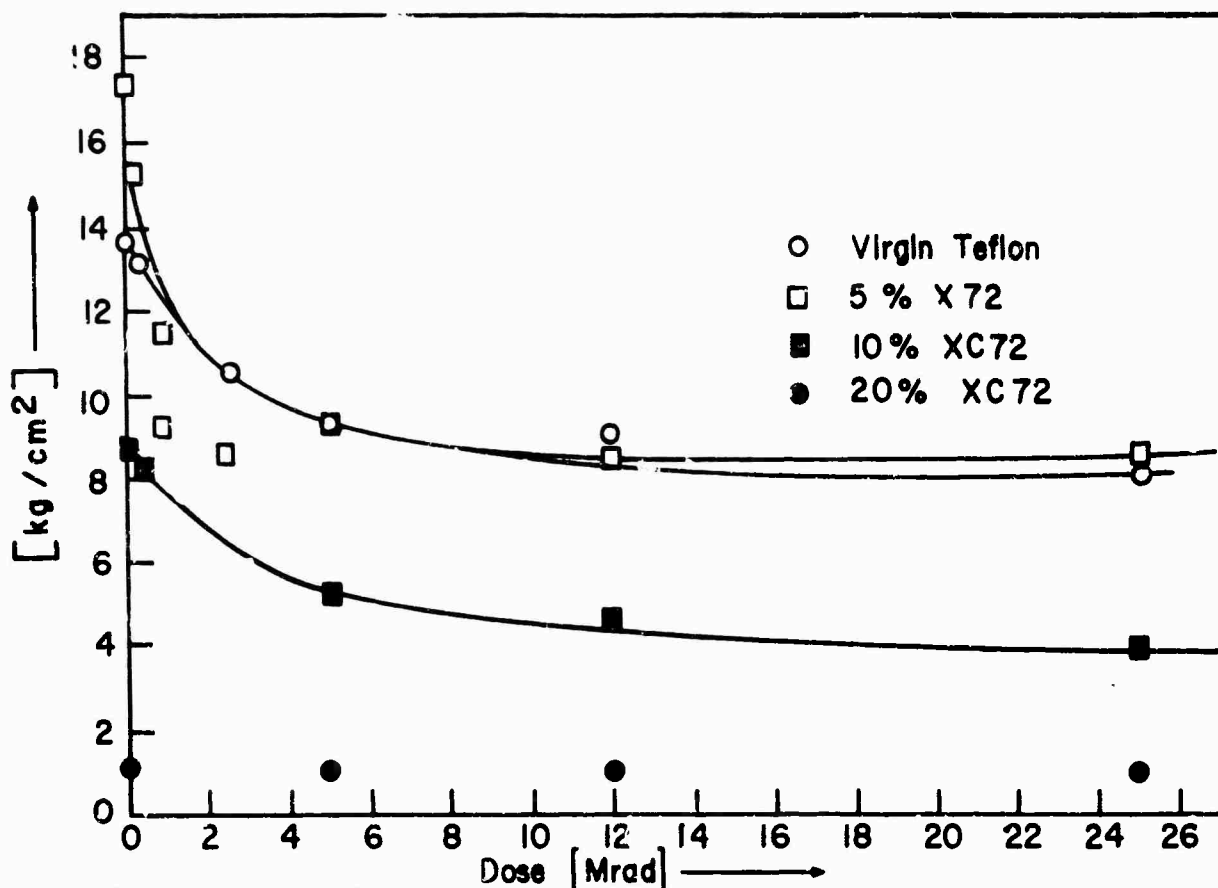


Fig. 9 - Dependence of the tensile strength for Teflon filled with XC72(3% oxygen) on the γ -Co⁶⁰-dose

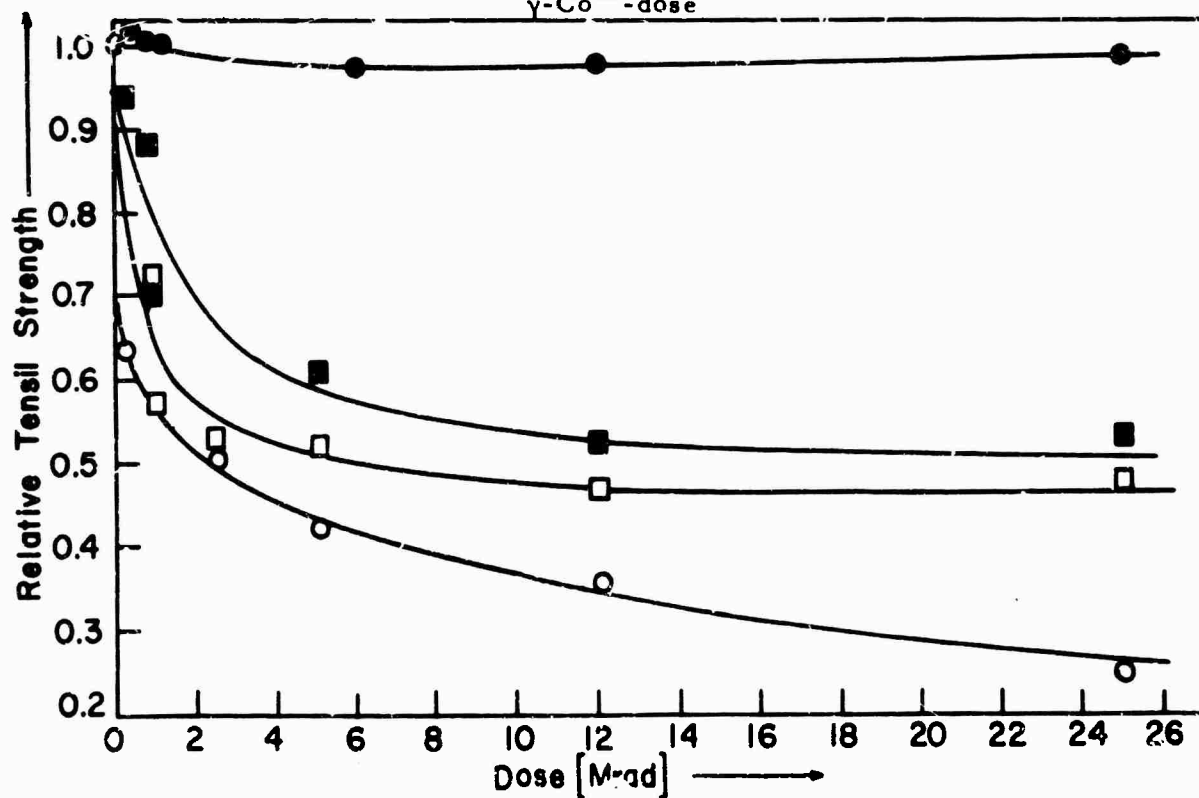


Fig. 10 - Dependence of the relative tensile strength for Teflon filled with XC72 (3% oxygen) on the γ -Co⁶⁰-dose

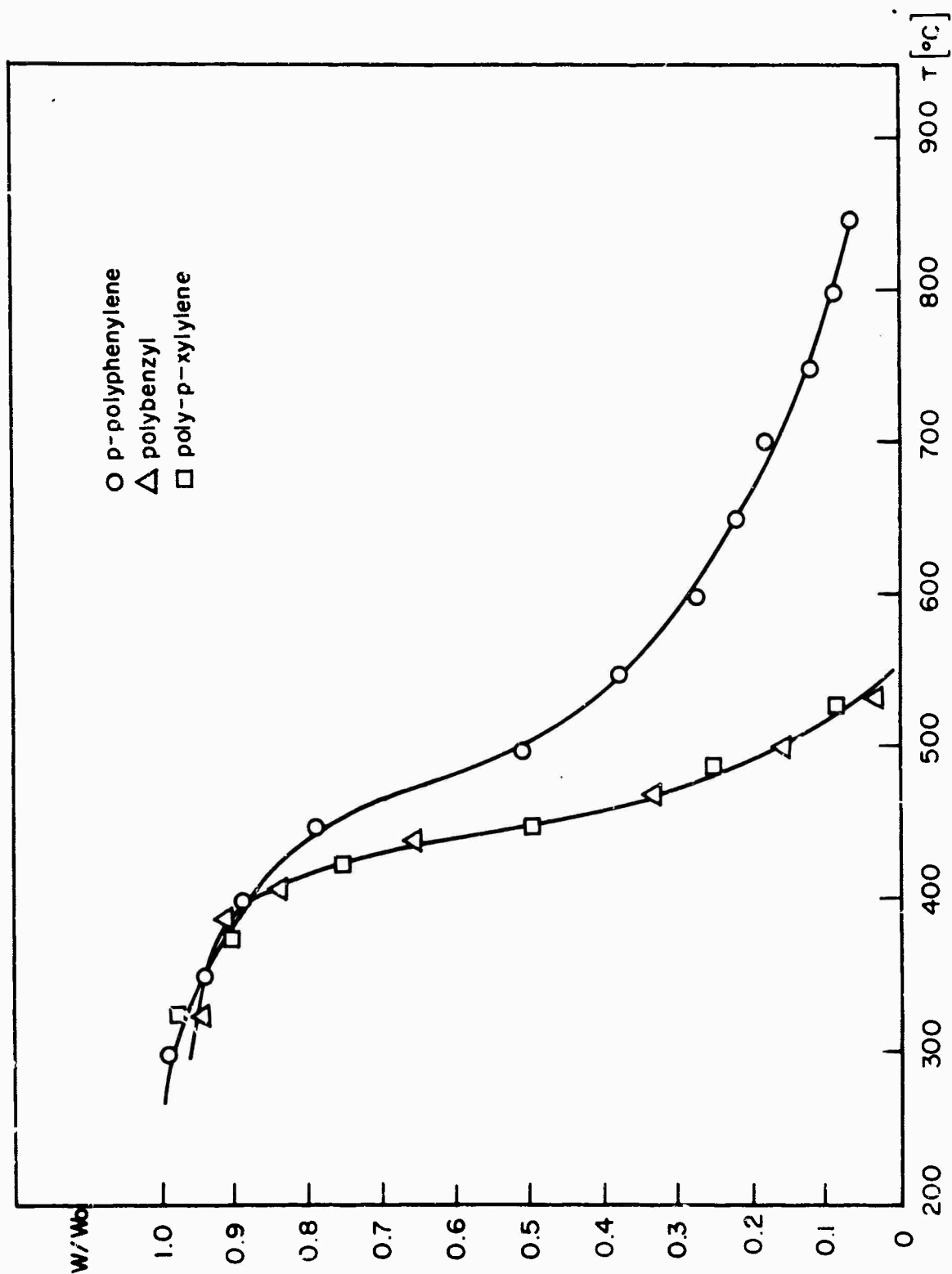


Fig. 11 TGA - diagram for p-polyphenylene, polybenzyl and poly-p-xylylene in vacuo

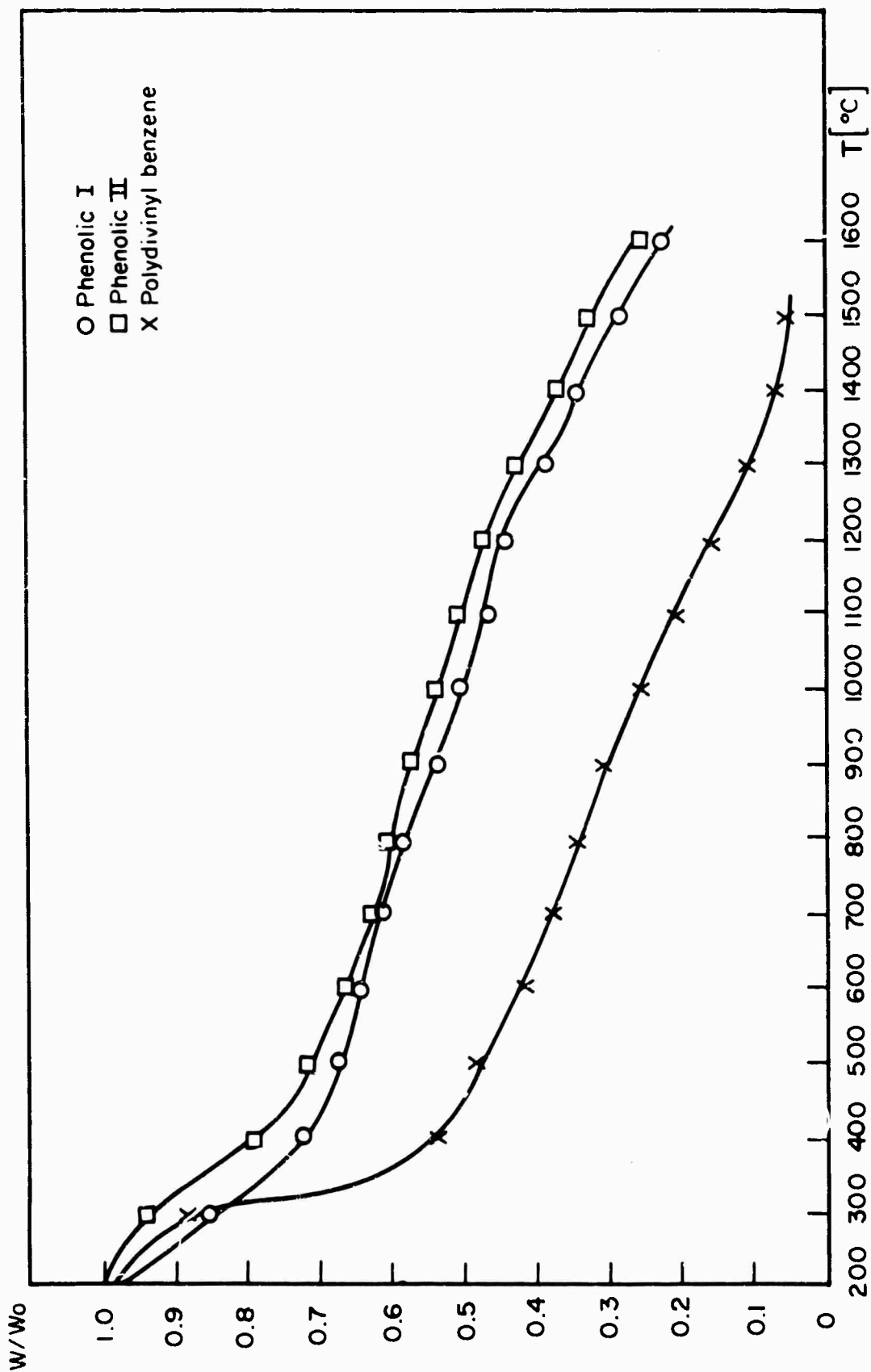


Fig. 12 TGA - diagrams for phenolic I, phenolic II and polydivinyl benzene under atmosphere pressure of air

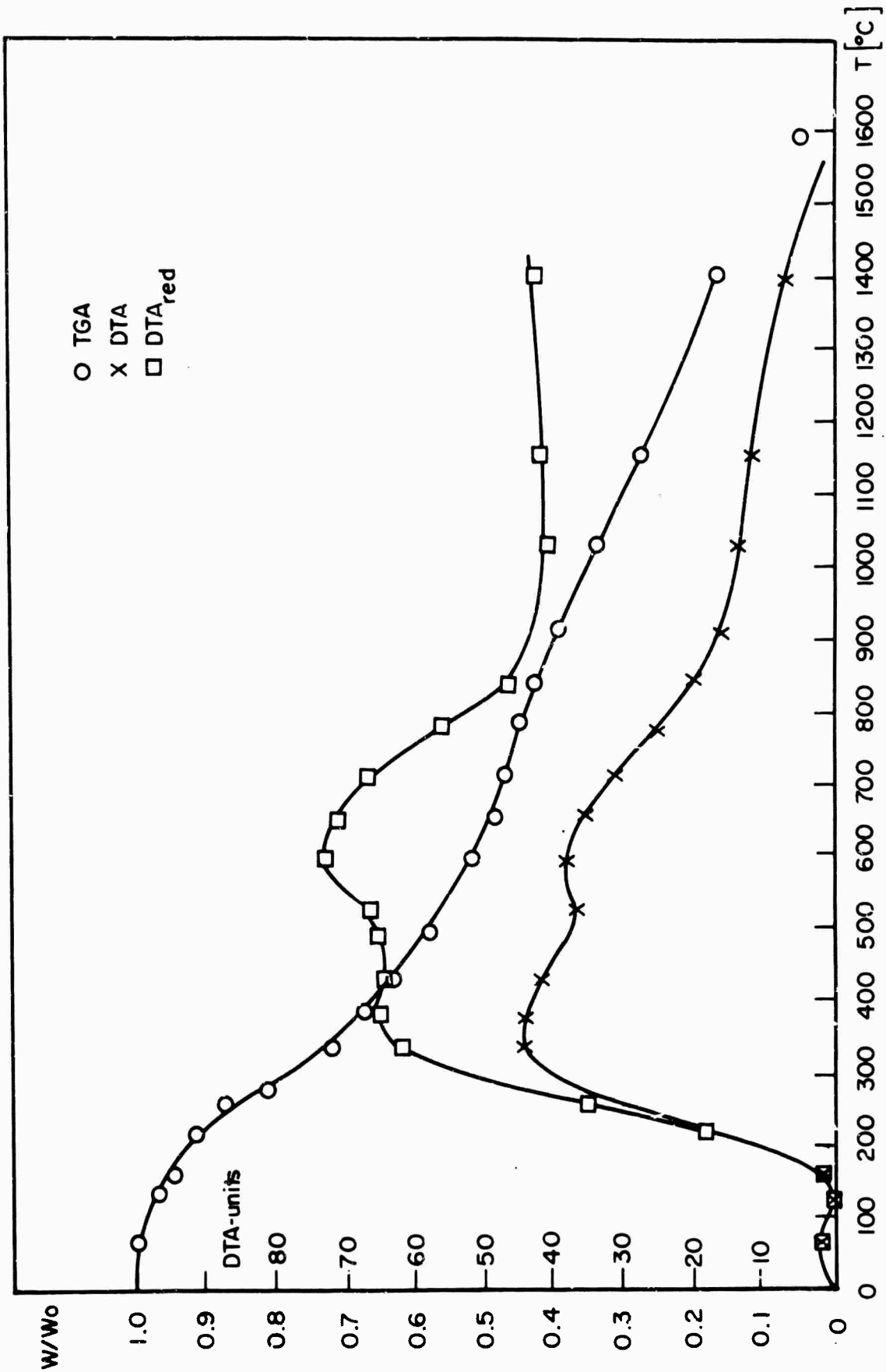


Fig. 13 TGA, DTA and DTA red - Diagrams for Pluton - fabric under atmospheric pressure of air

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13. ABSTRACT

The synthesis and the characterization of new polymeric systems to be used as protective coatings for space vehicles is described. Particular emphasis is placed on ablators which have low irradiation and particle emissivity under the conditions of typical reentry of a space vehicle into the atmosphere.

Crosslinking by ionizing radiation in carbon black filled Kel-F and Teflon has been established by mechanical and thermoanalytical methods. Polyaromatic systems such as polyphenylene, methylated poly-phenylene, poly benzyl poly-p-xylylene, furthermore phenolic resins and a styrene-divinyl benzene copolymer have been synthesized and investigated by thermogravimetric analysis. In addition Pluton impregnated with polyvinyl fluoride or crosslinked polystyrene has been investigated. As a fourth approach towards new ablative materials, the synthesis of aromatic fluorocarbon and silicon type ladder polymers was initiated.

The research on carbon-filled Teflon indicates a considerable improvement in heat shielding with polymeric ablators in terms of better mechanical properties and lower weight-to-heat dissipation ratios.

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