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ABSTRACT

THE EFFECT OF LIQUID GALLIUM ON PLASTICS

As part of a joint effort by Cornell University and NJIT to find a replacement for mercury as a pressuring medium for P-V-T devices, we investigated the effect of liquid gallium on four thermoplastics: two semi-crystalline (high density polyethylene and polypropylene) and two amorphous (polystyrene and polymethylmethacrylate). Test specimens were covered with liquid gallium and held in vacuum oven at temperatures close to their melting points for up to two weeks. Change in weight after treatment with gallium was measured, along with tensile testing and particle analysis using dispersion x-ray spectroscopy. The results are compared with specimens treated under identical conditions but without contact with gallium. The gallium was found to cause no change in the mechanical properties of the polymers tested. Its diffusion into all the polymers was also negligible. These results encourage the use of liquid gallium in place of mercury in various devices.

THE EFFECT OF LIQUID GALLIUM ON PLASTICS

by
Vivek P Dwivedi

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APPROVAL PAGE

THE EFFECT OF LIQUID GALLIUM ON PLASTICS

Vivek P Dwivedi

Dr. Kwabena Albert Narh, Thesis Advisor — Date
Assistant Professor of Mechanical Engineering,
New Jersey Institute of Technology

Dr. Rong-Yaw Chen, Committee Member — Date
Professor of Mechanical Engineering,
New Jersey Institute of Technology

Dr. Zhiming Ji, Committee Member — Date
Assistant Professor of Mechanical Engineering,
New Jersey Institute of Technology

BIOGRAPHICAL SKETCH

Author: Vivek P Dwivedi

Degree: Master of Science in Mechanical Engineering

Date: October 1995

Undergraduate and Graduate Education

- Master of Science in Mechanical Engineering,
  New Jersey Institute of Technology,
  Newark, New Jersey, 1995

- Bachelor of Technology in Mechanical Engineering,
  Regional Engineering College,
  Kurukshetra, India, 1993

Major: Mechanical Engineering

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CHAPTER 1

INTRODUCTION

1.1 Motivation

In order to measure the pressure-volume-temperature (PVT) relations for plastics, a controllable hydrostatic pressure has to be generated at a constant temperature in order to get accurate results. This hydrostatic pressure is best produced with a liquid pressure medium, which should not react with either the tested plastic system nor with the pressure vessel materials at all operating conditions. The stability of a confining fluid is judged primarily by its potential for interaction with the sample, and by its own PVT characteristics.

Currently, there is only one commercial PVT device (GNOMIX PVT Apparatus) in use. It uses mercury as a pressuring medium. Mercury is an almost ideal confining fluid, as it is known to be inert to almost all the polymer systems [11]. It is also widely used for being a liquid metal. It is however a highly toxic substance and costly safety gear has to be provided along with the equipment using mercury. Its vapor pressure at room temperature (25°C) is many times above the Occupational Safety and Health Administration (OSHA) limit [10]. The GNOMIX PVT apparatus requires a very expensive shielding system and filling and emptying is done in a ventilated hood.

A different design version of the PVT apparatus is currently being developed at Cornell University [11, 12, 14], and there is also a search for an alternative pressurizing

medium. The tentative choice is liquid gallium, with low toxicity and much superior thermal characteristics compared with mercury (see table 1.1). Gallium is an odorless gray metal and silvery liquid above 29.78°C and has a high boiling point of 2403°C. It has zero vapor pressure and evaporation rate. Its specific gravity is 5.907 (6.09 for liquid). The toxicity of gallium and its compounds as reported in Sax [10, pp.1793-1794] is very low. Amounts up to 15 mg/Kg of body weight were injected intravenously and were tolerated without harm by laboratory animals. Metallic gallium as well as the nitrate produced no skin injury, and subcutaneous injection of relatively large amounts could be tolerated both by rabbits and rats without evidence of injury [11].

Gallium can thus be considered as a replacement for mercury in the PVT apparatus and also in other equipment where mercury is being used currently although the 29.78°C melting point may appear somewhat restrictive at room temperature.

Table 1.1 A Brief Comparison Between Liquid Gallium and Mercury

	Gallium	**Mercury**
Melting Point	30°C	-39°C
Boiling Point	2403°C	357°C
Density	6.11 at mp.	13.5 at 293°K
Toxicity	negligible	very high
Thermal conductivity at 300°K (W/m/K)	40.6	8.34
Volumetric coefficient of thermal expansion K^{-1}	6×10^{-5}	18.1×10^{-5}

Source: Reference [11]

A recent M. Eng. Project study [12] on liquid gallium shows that this substance does not embrittle stainless steel, which is the pressure vessel material for PVT device, even after prolonged exposure at elevated temperatures, nor does it have any significant effect on any other mechanical property of stainless steel. However no study has been done so far on the effect of gallium on the physical properties of plastics.

1.2 Proposed Study of Effect of Gallium on Plastics

The present project was scheduled as a corollary to the project on stainless steel [12] and was carried out jointly with Cornell University. The main objective was to test if liquid gallium will affect the physical characteristics of a selected plastic systems at elevated temperatures. The experiments on plastics were similar to those carried out on stainless steel [12]. In particular, the effect of gallium on the mechanical properties of selected commercial plastics were carried out. Traces of gallium molecules in the plastics were measured with well developed techniques for the purpose.

1.3 Procedure of Study

Two amorphous and two semi-crystalline plastics were tested. The study was carried out in three steps (refer sections 1.3.1 to 1.3.3). It started with the basic method of weight difference as an initial attempt to assess the extent of gallium diffusion into the polymer. It was used to highlight any serious diffusion interaction between gallium and the polymer. The other two methods were used to obtain more accurate data. Samples for all the three steps were injection molded under the identical conditions. Each test set contained at least two samples, both treated under exactly identical conditions, the only difference being that

one was in contact with gallium (treated specimen) and the other was not (control specimen). For treatment, both time and temperature were variables. The working temperature was varied from low to up to a maximum temperature near the softening point of the polymer. During treatment, samples were kept in a vacuum of 25 inches of mercury.

1.3.1 Weight Test (step 1)

The samples were weighed before and after treatment at elevated temperatures in vacuum to assess any change in weight due to gallium diffusion into the polymer (refer to chapter 4 for details).

1.3.2 Mechanical Testing (step 2)

Tensile testing was carried out to determine any changes in the relevant mechanical properties of the polymer. Mechanical testing was carried out as per ASTM D638 specifications. According to this specification, tensile test specimens should either be machined or injection molded. It was decided to use only those polymers which can be easily injection molded such as high density polyethylene (HDPE), polystyrene (PS), polypropylene (PP) and polymethylmethacrylate (PMMA) since machining leaves rough surfaces which might result in stress concentration at certain points. The temperature of treatment was kept below the melting temperature of the polymer in order to maintain the shape of the treated specimens (refer to chapter 5 for details).

1.3.3 Particle Analysis Using Energy Dispersion X-ray Spectroscopy (step 3)

This method was used to detect if gallium had diffused into the plastic. Samples were examined by energy dispersion x-ray spectroscopy for particle analysis after treatment at elevated temperatures in vacuum (refer to chapter 6 for details).

CHAPTER 2

MATERIALS AND MACHINES

2.1 Liquid Gallium

The gallium used was supplied by Johnson Matthey. Tables 2.1 and 2.2 show the chemical and physical data provided by the supplier.

Table 2.1 Material Identification

Product code	10185
Product name	Gallium Ingot
Chemical family	Metallic element
Molecular formulae	Ga
Ingredients	99.9999% Gallium

Source: Reference [6]

Table 2.2 Physical Data

% volatiles	0
Solubility in water	Insoluble
Specific gravity (H_20 = 1)	5.907 (6.09 for liquid)
Freezing/Melting point	29.78°C
Evaporation Rate (butyl acetate =1)	Essentially zero

Source: Reference [6]

2.2 Plastics

The High Density Polyethylene was supplied by The Dow Chemical Company in granular form. Its Melt Flow Index (MFI) was given as 40 gm/10 minutes. Polystyrene and polypropylene were supplied as tensile test specimens by Mechanical Engineering Department, New Jersey Institute of Technology. Polymethylmethacrylate was supplied as tensile test specimens by Polymer Processing Institute, Stevens Institute of Technology, New Jersey.

2.3 Injection Molding Machine

Plastar TI-90G injection molding machine manufactured by Toyo Machinery & Metal Co., Ltd., Hitachi Group, Japan, with a clamping force of 90 US ton and injection capacity of 9.9 $in.^3$ was used for molding the test specimens satisfying ASTM D638 (type I).

2.4 Vacuum Oven

The vacuum oven used was supplied by National Appliance Company (Model 5851) with a maximum working limit of 30 inches mercury of vacuum. The vacuum pump for a 24" × 24" AAA thermoformer with a capacity of 30 inches of mercury (vacuum), was used.

The temperature control dial of the oven, which read from 1 to 10, was calibrated to directly read the temperature of the oven using a digital thermometer. The dial setting was read after 24 hour equilibrium. Table 2.1 shows the calibration data, with figure 3.1

showing the corresponding plot. The straight line is the best fit to the data points. The data for the graph in figure 2.1 were recorded after one our equilibrium.

Table 2.1 Calibration Data

Knob Reading	Thermocouple Reading (°C)
2	54.5
3	71.3
4	90.0
5	101.8
6	119.8
8	140.1

2.5 Energy Dispersion x-ray Spectroscopy System

An energy dispersion x-ray spectroscopy, System 5000, was used for x-ray microanalysis. Its hardware include an electron microscope using HNU system's Si (Li) detector, system 5000 spectrometer and an AT compatible personal computer.

2.6 Miscellaneous

A digital thermometer with a J-type thermocouple supplied by Omega was used to measure the oven temperature. A microbalance (Mettler AE 240) of an accuracy of 0.0001 gm was used for weight measurements.

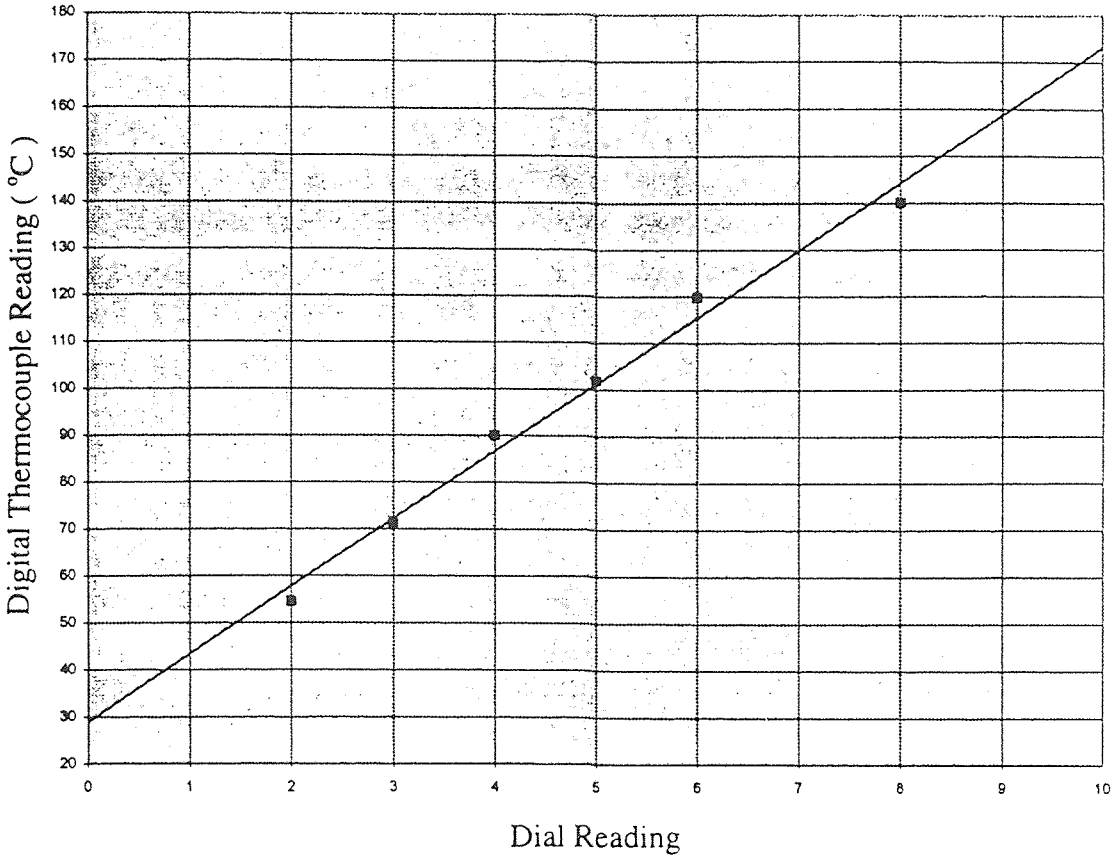

Figure 2.1 Calibration Curve

CHAPTER 3

WEIGHT TEST

3.1 Introduction

Any serious diffusion interaction between liquid gallium and the polymer can be expected to increase the weight of polymer. However a change in weight can only provide an indication of possible interaction as weight changes could also be due to other factors such as moisture loss. Thus an increase in weight of a relatively high magnitude can be taken as an indication of possible strong interaction with gallium. To isolate the effect of gallium, the change in weight of test samples treated with gallium were compared with a control specimen.

3.2 Specimen Preparation and Testing for High Density Polyethylene

Injection molded high density polyethylene specimens (refer to chapter 5 and section 1.3 for more details) were cut into a square sheet of approximately $^1/_2$ in. $\times$ $^1/_2$ in. $\times$ $^1/_{10}$ in. size. A drop of liquid gallium was placed on the surface of the specimen which was placed in the oven with the smeared surface up. Samples for weight tests, tensile tests and energy dispersion x-ray spectroscopy measurements were prepared simultaneously so that they could be treated under identical conditions as far as possible. To minimize thermo-oxidative effects, the specimen was removed only after cooling to room temperature. The exposure time of a specimen in the oven was calculated to the nearest hour. After treatment, the gallium was gently wiped off the specimen with soft cotton under constant

treatment, the gallium was gently wiped off the specimen with soft cotton under constant flow of lukewarm water. This was repeated three to four times to ensure that there was no trace of gallium left. After washing, the specimens were allowed to dry. There was no obvious discoloration on the specimen surface which was in contact with gallium.

3.3 Results and Discussion

Tables 3.1 to 3.6 show the results of weight tests for high density polyethylene specimens treated under different conditions for both the control and treated specimens.

Table 3.1 Weight Test - 65°C for 10 hours.

Specimen Number	Weight Before Treatment (gm)	Weight After Treatment (gm)	Gallium Contact	% Reduction in Weight
1	0.2979	0.2979	yes	0
2	0.2656	0.2656	yes	0
3	0.2419	0.2419	yes	0
4	0.2891	0.2891	no	0
5	0.2472	0.2470	no	0.0809
6	0.2483	0.2481	no	0.0805

Average % reduction in weight for treated specimens = 0

Average % reduction in weight for control specimens ≅ 0.054

Table 3.2 Weight Test - 65°C for 165 hours

Specimen Number	Weight Before Treatment (gm)	Weight After Treatment (gm)	Gallium Contact	% Reduction in Weight
7	1.2165	1.2157	yes	0.0658
8	1.2310	1.2303	yes	0.0569
9	1.1997	1.1989	yes	0.0667
10	1.4602	1.4592	no	0.0685
11	1.2586	1.2586	no	0.0477
12	1.1884	1.1878	no	0.0505

Average % reduction in weight for treated specimens ≅ 0.063

Average % reduction in weight for control specimens ≅ 0.055

Table 3.3 Weight Test - 95°C for 10 hours.

Specimen Number	Weight Before Treatment (gm)	Weight After Treatment (gm)	Gallium Contact	% Reduction in Weight
13	0.2673	0.2670	yes	0.1122
14	0.2295	0.2295	yes	0
15	0.2567	0.2567	yes	0
16	0.2424	0.2414	no	0
17	0.2029	0.2027	no	0.0986
18	0.2609	0.2609	no	0

Average % reduction in weight for treated specimens = 0.037411

Average % reduction in weight for control specimens ≅ 0.033

Table 3.4 Weight Test - 95°C for 165 hours.

Specimen Number	Weight Before Treatment (gm)	Weight After Treatment (gm)	Gallium Contact	% Reduction in Weight
19	0.8413	0.8400	yes	0.1545
20	0.6614	0.6602	yes	0.1814
21	0.8029	0.8014	yes	0.1868
22	0.9187	0.9171	no	0.1742
23	0.7495	0.7480	no	0.2001
24	0.7259	0.7246	no	0.2066

Average % reduction in weight for treated specimens ≅ 0.174

Average % reduction in weight for control specimens ≅ 0.194

Table 3.5 Weight Test - 95°C for 370 hours.

Specimen Number	Weight Before Treatment (gm)	Weight After Treatment (gm)	Gallium Contact	% Reduction in Weight
25	08236	08209	yes	0.3278
26	0.7831	07805	yes	0.3320
27	0.6925	06903	yes	0.3177
28	0.9614	09582	no	0.3329
29	0.7958	0.7930	no	0.3519
30	0.6873	0.6851	no	0.3201

Average % reduction in weight for treated specimen ≅ 0.326

Average % reduction in weight for control specimen ≅ 0.326

Almost all specimens showed a weight decrease except a few in tables 3.1 and 3.3 which did not show any change. After comparing the average % decrease in weight it becomes apparent that the weight decrease was both time and temperatures dependent.

In tables 3.1 and 3.4, treated specimens showed a higher % reduction in weight compared to the control specimens. On the other hand, the results in tables 3.2 and 3.3 show a lower % reduction compared to the control specimens. In table 3.5, treated specimens and control specimens showed equal % reduction in weight.

3.4 Conclusion

No increase in weight of the treated specimens was observed. The decrease in weight is most probably due to the reduction of moisture in the specimen when kept at high temperature for long periods under vacuum.

There is small variation in the rate of moisture loss from sample to sample but this is large enough to offset any effect of gallium diffusion. Hence gallium diffusion in high density polyethylene, if any, is very small and could not be measured by weight test. These results together with the fact that particle analysis was planned to be anyway carried out to confirm the weight tests or to detect any small amount of gallium present which could not be measured by weight test led to the decision to skip weight test for rest of the polymer systems.

CHAPTER 4

TENSILE TEST

4.1 Mechanical Properties

A tensile test is one of the most widely used mechanical property tests. Tensile tests were conducted to determine the effect of exposure of polymer systems to gallium at elevated temperatures on the tensile strength, Young's modulus, % elongation at yield and % elongation at break. A test specimen of standard ASTM geometry (ASTM D638, type I, see figure 4.1 for dimensions) was used, which allowed quantitative comparison of data from materials treated under different conditions. The Instron tensile testing machine was used for the mechanical property measurements.

4.2 Specimen Preparation

High density polyethylene, polypropylene and polystyrene specimens were injection molded using the 90 ton clamping force Toyo injection molding machine described previously equipped with test specimen mold. Polymethylmethcylate specimens were injection molded at Stevens Institute of Technology.

During the molding process, initial specimens were discarded so that the machine is purged of any other plastic, dust or rust, etc. Specimens with obvious flaws like abnormal flow pattern were discarded. ASTM standard test method for Tensile Properties of plastics, ASTM D638 was followed throughout. The type I specimen is preferred [13,

sec.6.1] when sufficient material having a thickness of 0.28 in. (7 mm) or less is available, and this was used for tensile testing.

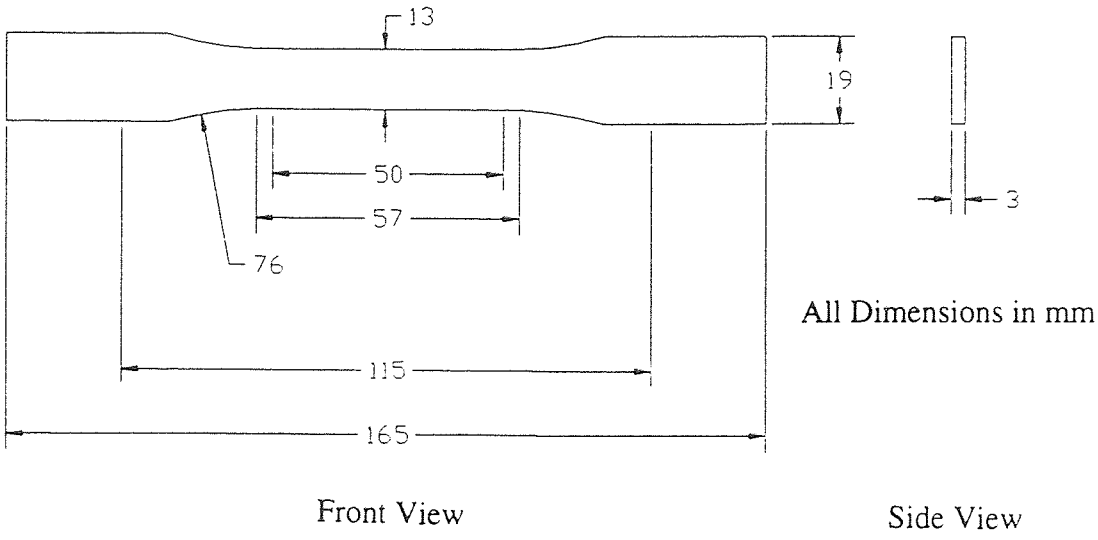

Figure 4.1 Tensile Test Specimen as per D638

A drop of gallium was applied to the center of the gauge region. Measurement temperatures were below the softening or melting points of the specimens. This ensures that the specimens do not loose their shape after the heat treatment. Table 4.1 shows glass transition temperature (T_g) and melting temperature (T_m) of all the polymer systems tested along with the maximum temperature to which they were exposed.

Table 4.1 Glass Transition, Melting and Maximum Exposure Temperatures.

Plastic	Glass Transition Temperature (T_g)	Melting Temperature (T_m)	Maximum Temperature Limit
HDPE	-125°C to -33°C	110°C to 140°C	95°C
PP	-10°C to -20°C	176°C	75°C
PS	100°C	240°C	75°C
PMMA	90°C to 105°C	160°C	95°C

Time and temperatures were the variables for the very first polymer tested which was high density polyethylene. Experience gained from its results, which suggested no interaction between high density polyethylene and gallium, led to the decision of exposing the rest of the polymers to the most extreme treatment conditions instead of gradually increasing temperature and time of exposure.

4.3 Testing

An Instron tensile testing machine with a constant rate-of-crosshead-movement and with fixed and moving members carrying one grip each was used. The grips were self aligning, that is, they were attached to the fixed and moving member, respectively in such a manner that they move freely into alignment as soon as any load is applied, so that the long axis of the test specimen will coincide with the direction of the applied pull load along the center line of the grip assembly. The specimen was aligned as perfectly as possible with the direction of pull so that no rotary motion that may induce slippage occurs in the grips. A testing speed of 5 mm/min ($\cong$ 2 in./min.) was selected for the cross-head movement. This was found to be the optimum speed for clearly observing characteristics of stress strain curve which was the concern of the measurement [13, section 9.2]. Measurements were made at room temperature ($\cong 23^{\circ}C$).

4.4 Results and Discussion

4.4.1 High Density Polyethylene

Stress-strain curves for both test and control specimens, after treatment are shown in figures 4.2 to 4.5. The mechanical properties of the specimen including tensile strength, Young's modulus, % elongation at yield and % elongation at break calculated from these curves and are shown in tables 4.2 to 4.5.

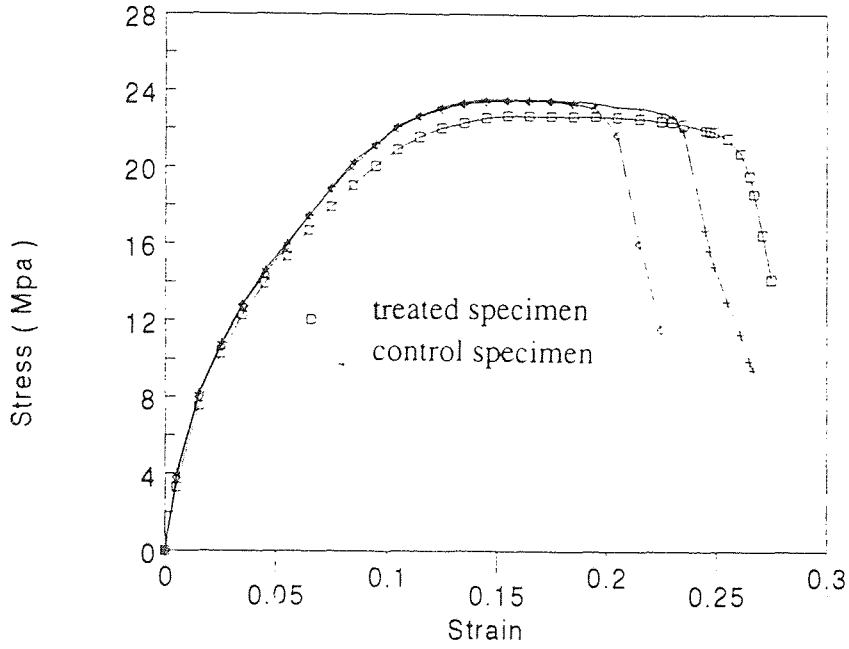

Figure 4.2 Tensile Test - 65°C for 10 hours

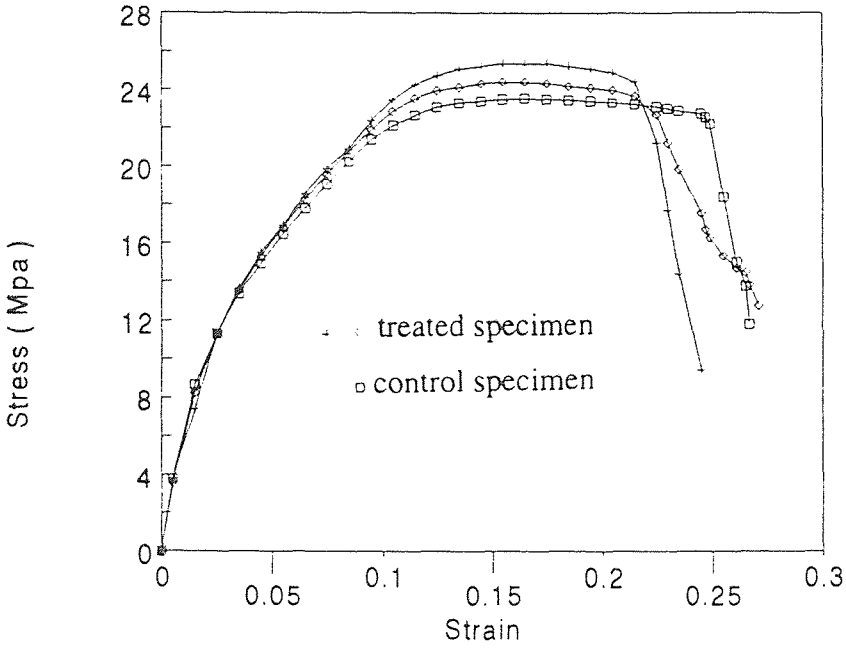

Figure 4.3 Tensile Test -95°C for 10 hours

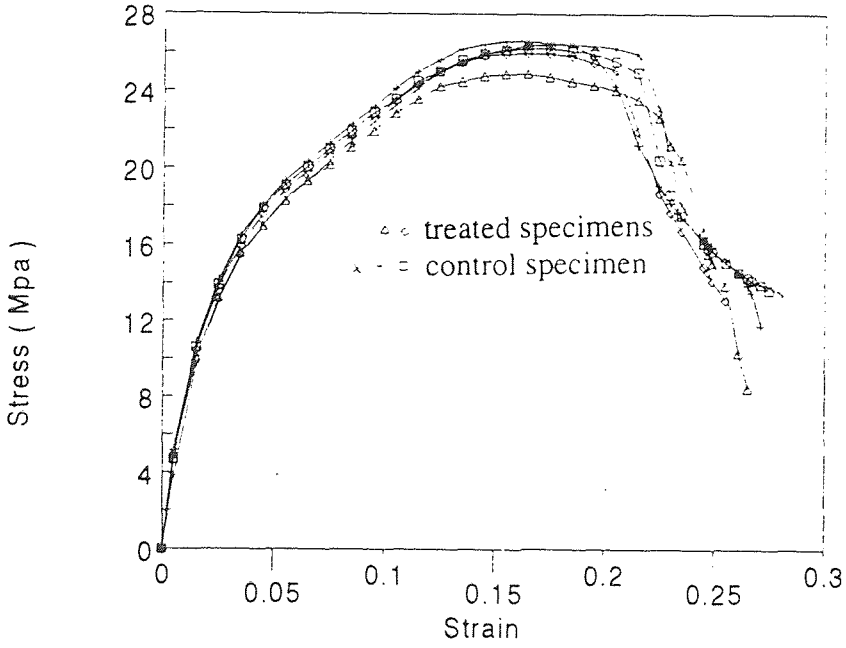

Figure 4.4 Tensile Test -95°C for 165 hours

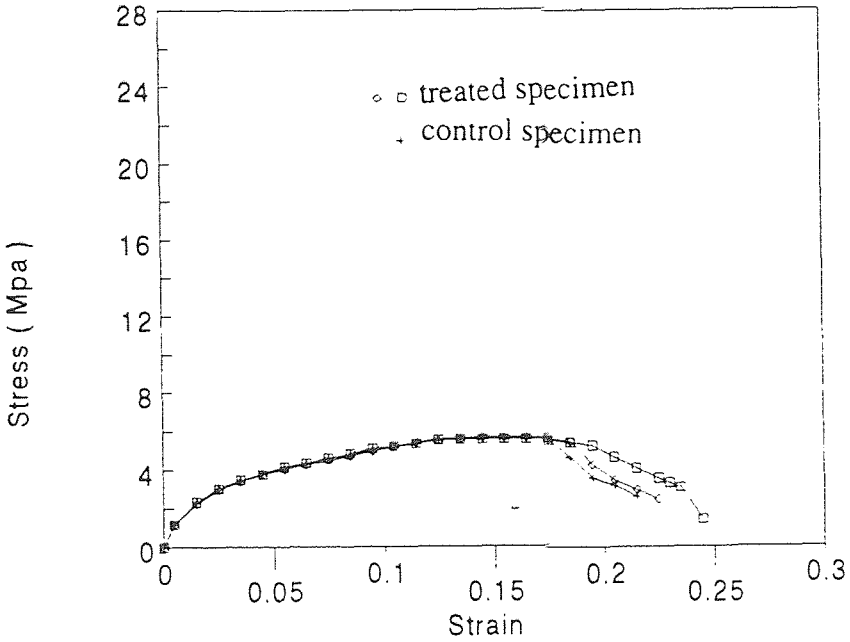

Figure 4.5 Tensile Test -95°C for 370 hours

Table 4.2 Mechanical Properties - 65°C for 10 hours.

Specimen Number	Gallium Contact	Failed at the Location of Gallium?	Tensile Strength (Mpa)	Young's Modulas (Mpa)	% Elongation at Yield	% Elongation at Break
1	yes	no	23.181	389.226	32.4	57.2
2	yes	no	23.950	392.765	30.6	46.2
3	no	N/A	24.046	389.226	30.4	54.6
Average			23.726	390.406	31.1	52.7

Table 4.3 Mechanical Properties - 95°C for 10 hours.

Specimen Number	Gallium Contact	Failed at Location of Gallium?	Tensile Strength (Mpa)	Young's Modulas (Mpa)	% Elongation at Yield	% Elongation at Break
4	yes	no	25.874	353.842	31.2	49.6
5	yes	no	24.816	353.842	30.8	56.8
6	no	N/A	24.046	442.303	32.6	55.0
Average			24.912	383.329	31.5	53.8

Table 4.4 Mechanical Properties - 95°C for 165 hours.

Specimen Number	Gallium Contact	Failed at Location of Gallium?	Tensile Strength (Mpa)	Young's Modulas (Mpa)	% Elongation at Yield	% Elongation at Break
7	yes	no	26.451	613.326	31.4	52.8
8	yes	no	25.393	483.584	31.4	54.0
9	no	N/A	26.691	471.789	32.2	56.8
10	no	N/A	27.172	495.379	31.6	55.6
11	no	N/A	26.932	436.405	34.8	58.4
Average			26.528	500.097	32.3	55.5

Table 4.5 Mechanical Properties - 95°C for 370 hours.

Specimen Number	Gallium Contact	Failed at Location of Gallium?	Tensile Strength (Mpa)	Young's Modulas (Mpa)	% Elongation at Yield	% Elongation at Break
12	yes	no	5.567	96.717	28.0	50.2
13	yes	no	5.567	94.358	30.0	46.4

Table 4.5 Mechanical Properties - 95°C for 370 hours (continued).

14	no	N/A	5.662	96.717	28.6	44.6
Average			5.599	95.931	28.9	47.1

None of the test specimen failed at the location treated with gallium. In fact, failure occurred at locations very far from the region of gallium application. The average tensile strength of all specimens kept at 95°C for 370 hours decreased by approximately 76%, elongation at break decreased by approximately 12%, elastic modulus decreased by approximately 75% and elongation at yield decreased by 7% as compared to specimen kept at 65°C for 10 hours. This is due, presumably, due to secondary crystallization.

In tables 4.2, 4.4 and 4.5, the tensile strength of treated specimen was found to be lower than the control specimen except in table 4.3 where it was higher. In tables 4.3 and 4.5, the Young's modulus of the treated specimen was found to be lower than the control specimen. On the other hand, these trends are reversed in tables 4.2 and 4.4. Tables 4.3 and 4.4, show that the % elongation at yield of treated specimen was lower than the control specimen. These results are reversed in tables 4.2 and 4.5. Finally, tables 4.2, 4.3 and 4.4 show that the % elongation at break of treated specimen was lower than control specimen. This trend was reversed in table 4.5. In summary, the results of tables 4.2 to 4.5 show no consistency which can be attributed to the interaction of the plastics with gallium.

4.3.2 Polypropylene

Stress-strain curves for both test and control specimens, after treatment are shown in figures 4.6 to 4.7. The mechanical properties of the specimen including tensile strength, Young's modulus, % elongation at yield and % elongation at break calculated from these curves are shown in table 4.6.

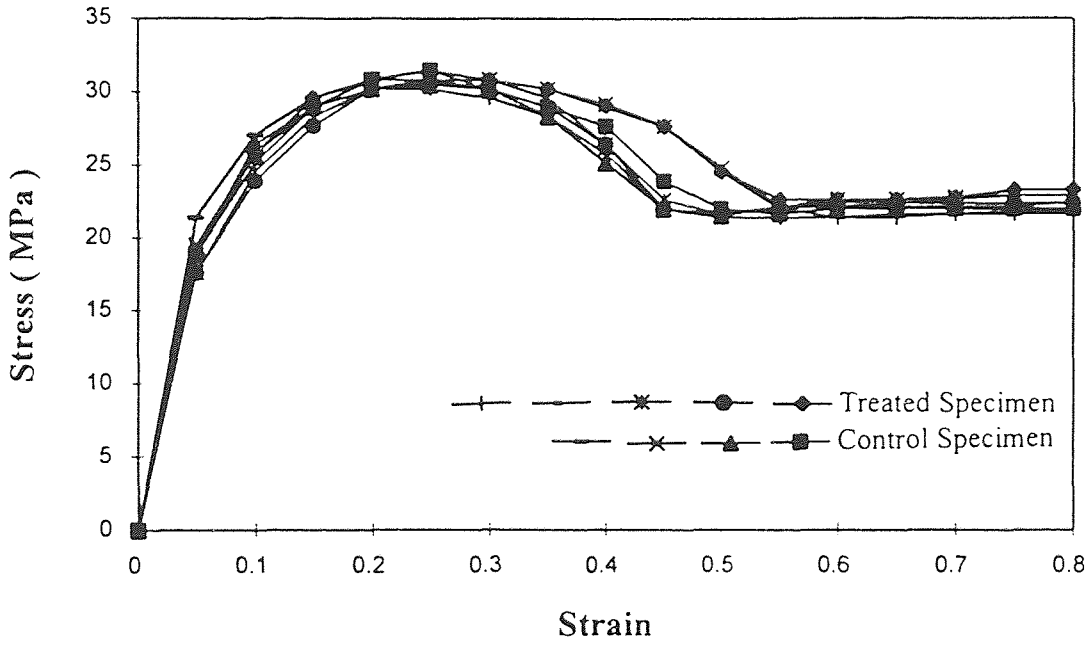

Figure 4.6 Tensile Test (PP)-75°C for 370 hours

Table 4.6 Mechanical Properties - 75°C for 370 hours.

Sample Number	Gallium Contact	Yielding Started at Location of gallium?	Tensile strength (Mpa)	Young's Modulus (Mpa)	% Elongation at Yield
1	yes	no	23.890	1533.928	29
2	no	N/A	22.125	1374.127	28
3	no	N/A	22.380	1469.993	27

Table 4.6 Mechanical Properties - 75°C for 370 hours (continued).

4	no	N/A	22.880	3834.785	27
5	yes	N/A	22.880	1406.083	28
6	yes	yes	22.380	1406.083	28
7	yes	no	21.625	2940.011	27
8	yes	no	21.752	1278.262	27
9	no	N/A	22.007	2556.523	27
Average			22.435	1977.755	27.555

Only one out of five specimens failed at the location of gallium application. From table 4.6, treated specimen do not show abnormal behavior as compared to control specimen.

4.3.3 Polystyrene

Stress-strain curves for both test and control specimens, after treatment are shown in figures 4.8. The mechanical properties of the specimen including tensile strength, Young's modulus, % elongation at yield and % elongation at break calculated from these curves and are shown in table 4.7.

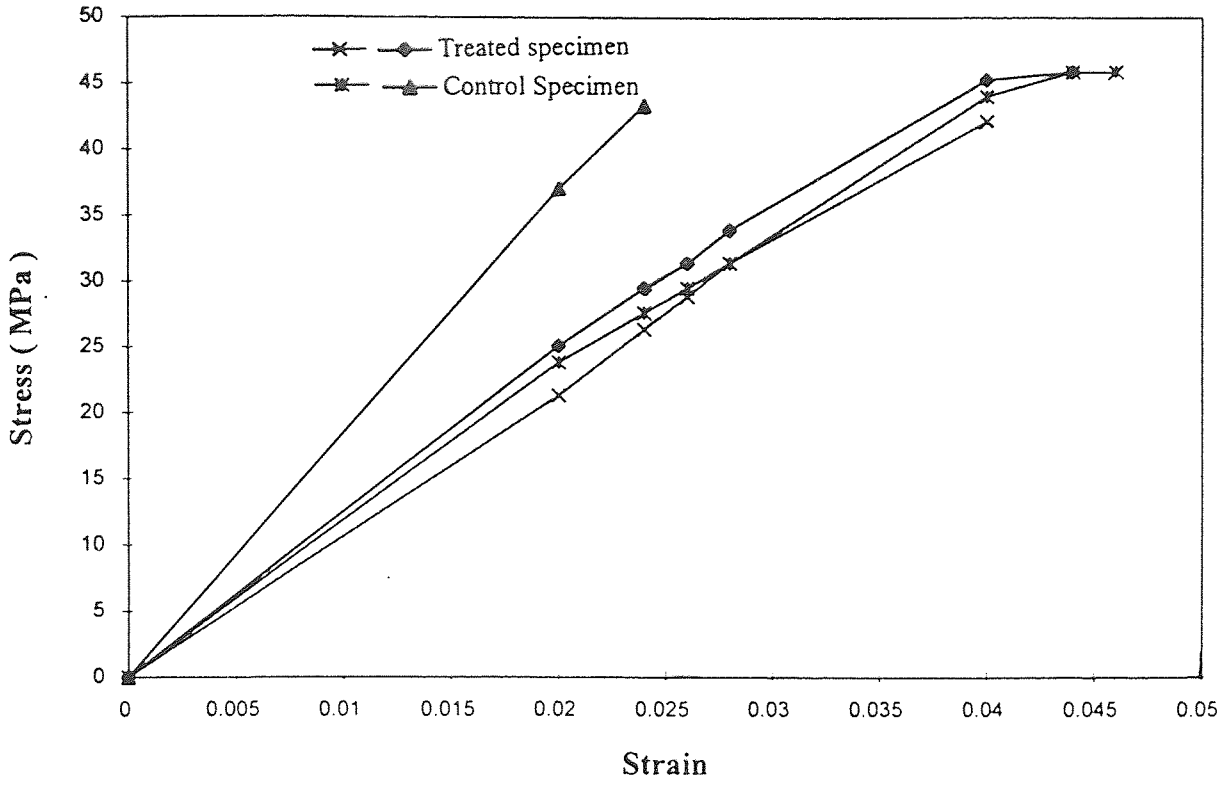

Figure 4.7 Tensile Test (PS)-75°C for 370 hours

Table 4.7 Mechanical Properties - 65°C for 370 hours.

Sample Number	Gallium Contact	Failed at Location of gallium?	Tensile strength (Mpa)	Young's Modulas (Mpa)	% Elongation at Yield
1	no	N/A	45.897	1342.172	11
2	yes	no	27.028	1195.183	6.5
3	no	N/A	42.121	1342.172	10
4	yes	yes	45.897	1182.396	10.5
Average			40.864	1408.645	8.9

Only one out of three specimens failed at the location of gallium application. From table 4.7, treated specimen do not show abnormal behavior as compared to control specimens.

4.3.4 Polymethylmethacrylate

Stress-strain curves for both test and control specimens, after treatment are shown in figures 4.9 to 4.10. The mechanical properties of the specimen including tensile strength, Young's modulus, and % elongation at break calculated from these curves and are shown in table 4.8.

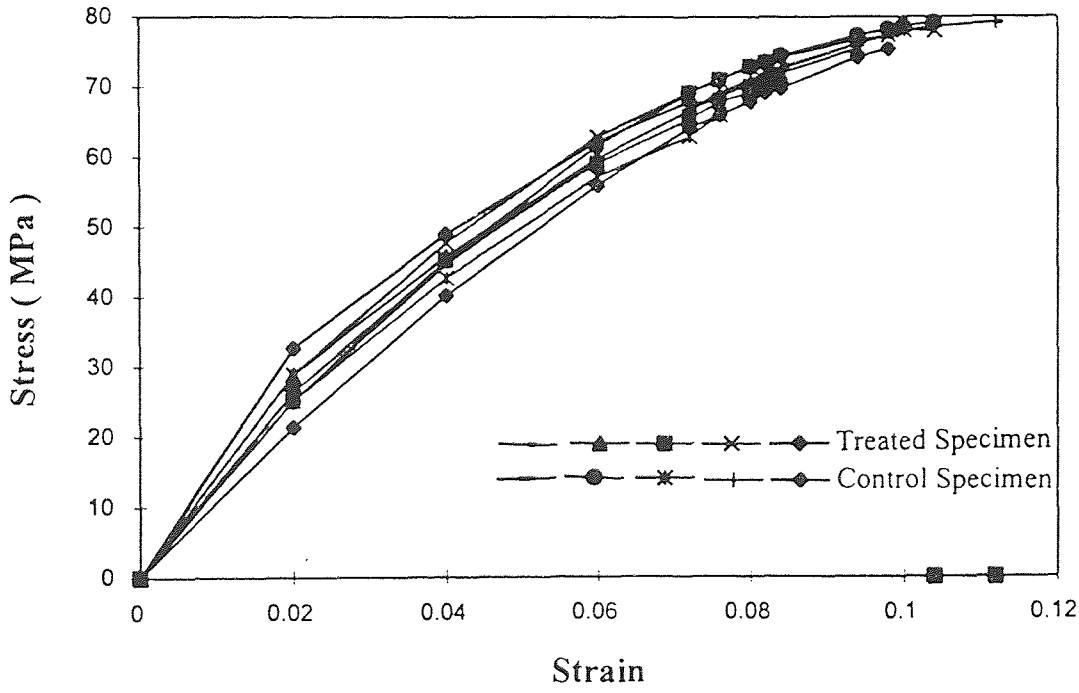

Figure 4.8 Tensile Test (PMMA)-95°C for 370 hours

Table 4.8 Mechanical Properties - 95°C for 370 hours.

Sample Number	Gallium Contact	Failed at Location of gallium?	Tensile strength (Mpa)	Young's Modulas (Mpa)	% Elongation at Break
1	no	N/A	75.435	3115.766	9.8
2	yes	no	70.414	3675.008	8.4
3	yes	yes	75.435	3275.542	9.4
4	yes	no	77.956	3595.120	10.6
5	no	N/A	66.011	3355.430	7.6
6	no	N/A	79.211	2157.082	10.4
7	no	no	79.211	3275.542	10.6
8	yes	N/A	79.211	3195.654	11.4
9	no	N/A	70.414	3275.542	8.4
10	yes	no	67.894	6391.308	7.4
Average			74.119	3331.199	9.4

Only one out of three specimens failed at the location of gallium application. From table 4.8, treated specimen do not show abnormal behavior as compared to control specimens.

4.5 Conclusion

The fact that very few specimens failed at the region exposed to gallium coupled with the fact that the values of mechanical properties obtained fall within the scatter range expected for the properties tested indicate that there is no effect of gallium on the physical properties of the polymers.

CHAPTER 5

PARTICLE ANALYSIS

5.1 Theory of x-ray Operation

The x-ray spectroscopy exploits the fact that each element always exhibits a definite family of energies that can serve as a fingerprint for that element. So energy dispersion x-ray spectroscopy is used to determine the elements present in the sample under investigation. The x-rays are generated by means of an accelerated electron beam that strikes the sample material, each electron acquires an amount of energy equal to the accelerating potential. If this energy exceeds the K_{ab} (absorption-edge energy for the K shell) of the sample materials, there is a high probability that it will interact with an atom of the sample and generate either K_a or K_b x-ray. Or it may strike an electron in the L shell of the sample atom and cause the generation of an L-series x-ray. There can also be multiple elastic collisions and deflections with successive loss of fractions of the total kinetic energy of the electron in the beam so that a wide spectrum of energies is radiated.

If the sample contains a variety of known or unknown elements, the electron beam will cause a fluorescence of the elements if the beam energy exceeds the K_{ab}, L_{ab}, or M_{ab} of the element.

5.2 Specimens Preparation

After tensile test , treated and control specimens for x-ray spectroscopy were prepared made by cutting small pieces from the treated and gallium free portions of the specimens. These were coated with gold to make them conducting in order to use the energy dispersion x-ray spectroscope (EDX). They were then put into the vacuum chamber of the EDX one at a time and particle analysis was carried out for the worst affected specimens and at one location for the control specimen kept at 65°C for 10 hours.

5.3 Results and Discussion

Printouts of the energy dispersion spectra are shown in figures 5.1 - 5.5. The presence of any element is determined by the presence of the corresponding energy peaks. The quantity of various elements present could be assessed by comparing the height of their corresponding energy peaks. For any element to be present, all corresponding energy peaks should be present with a substantial height. The printouts indicate the places where the peaks of gallium, gold, etc. should be present whether or not elements are actually present. The spectra also show the presence of silicon, iron and nickel due, presumably, to the holder of the specimens. It can be seen from figures 5.2 to 5.5 that the heights of gallium energy peaks are very low even for the worst affected. As expected the spectra in figure 5.1 shows the absence of gallium for the control HDPE specimen, indicating that there was no contamination of gallium on this sample.

HNU X-Ray System 5000
Spectrum Ploting Program
Printout V3.000

Energy Range: 0 - 20 KeV 10 eV/ch Hi Res
Preset: off
Real Time: 595.84 Sec. Live Time: 406.16 Sec.
30% Deadtime 11480 Counts/Second

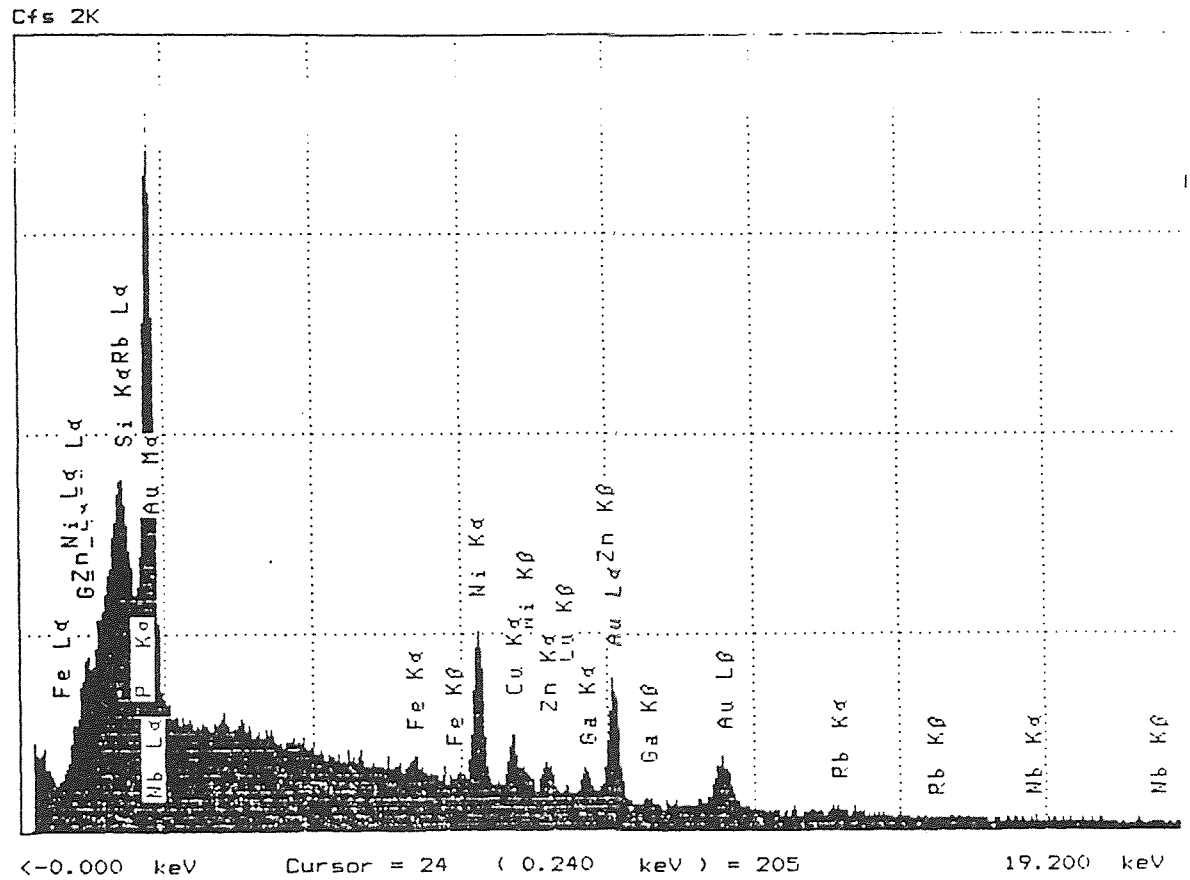

Figure 5.1 EDX - High Density Polyethylene at 95°C for 370 hours with Gallium

HNU X-Ray System 5000
Spectrum Ploting Program
Printout V3.000

Energy Range: 0 - 20 KeV 10 eV/ch Hi Res
Preset: off
Real Time: 235.90 Sec. Live Time: 160.91 Sec.
35% Deadtime 13515 Counts/Second

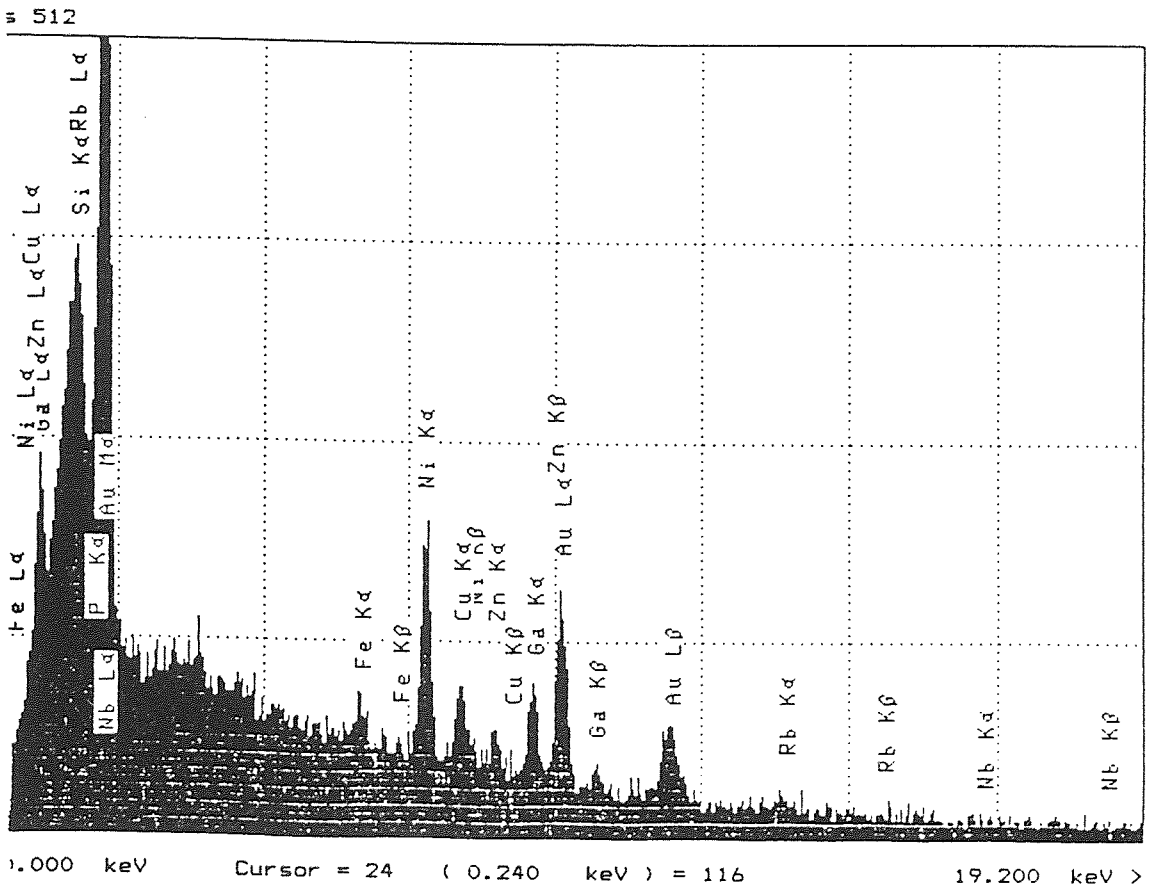

Figure 5.2 EDX - Polypropylene at 75°C for 370 hours with Gallium

HNU X-Ray System 5000
Spectrum Ploting Program
Printout V3.000

Energy Range: 0 - 20 KeV 10 eV/ch Hi Res
Preset: off
Real Time: 941.61 Sec. Live Time: 637.58 Sec.
37% Deadtime 14936 Counts/Second

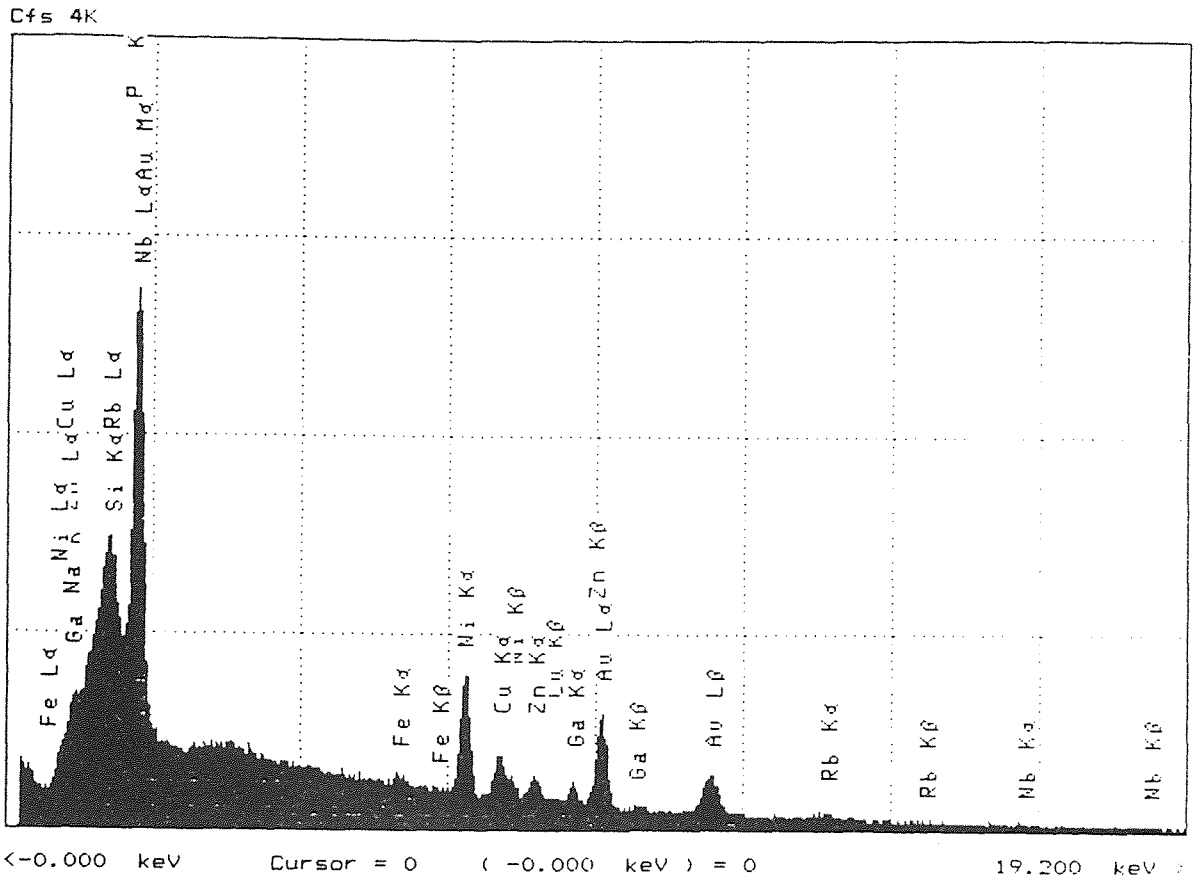

Figure 5.3 EDX - Polystyrene at 75°C for 370 hours with Gallium

HNU X-Ray System 5000
Spectrum Ploting Program
Printout V3.000

Energy Range: 0 - 20 KeV 10 eV/ch Hi Res
Preset: off
Real Time: 689.22 Sec. Live Time: 534.80 Sec.
21% Deadtime 11268 Counts/Second

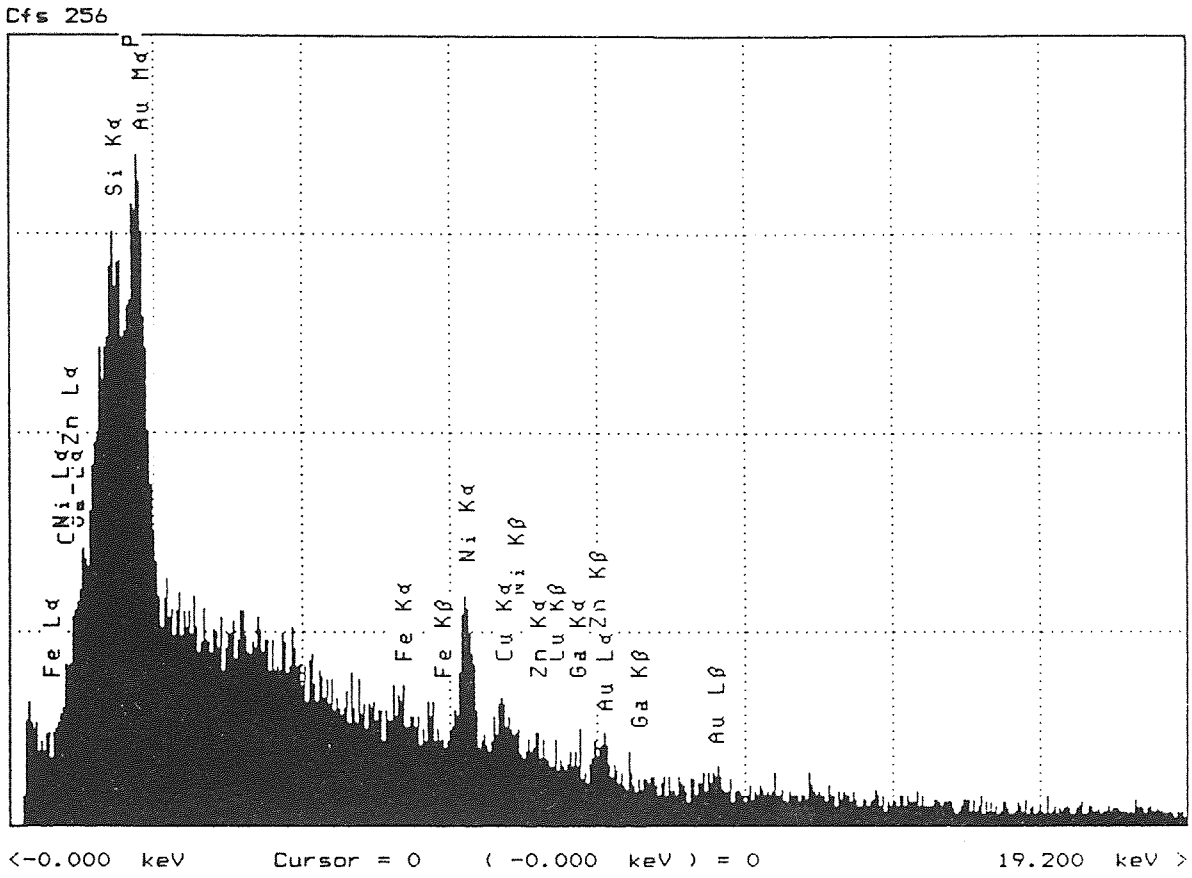

Figure 5.4 EDX - Polymethylmethacrylate at 95°C for 370 hours with Gallium

HNU X-Ray System 5000
Spectrum Ploting Program
Printout V3.000

Energy Range: 0 - 20 KeV 10 eV/ch Hi Res
Preset: off
Real Time: 218.38 Sec. Live Time: 162.29 Sec.
26% Deadtime 11244 Counts/Second

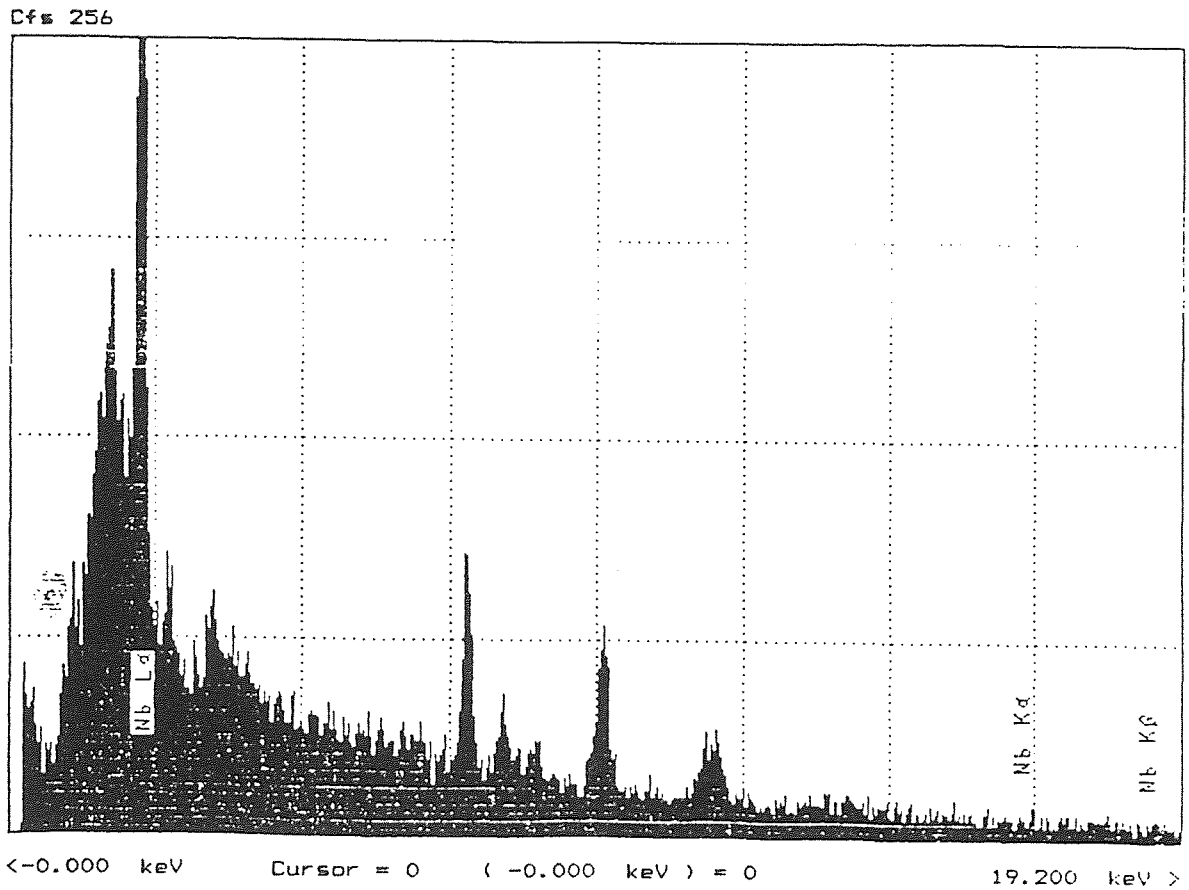

Figure 5.5 EDX - High Density Polyethylene at 65°C for 10 hours without Gallium

6.4 Conclusion

The energy spectra shows very small peaks of energy associated with gallium, indicating very low concentration of gallium in the polymer even after treatment at severe conditions. Consequently, it is concluded that gallium does not diffuse much into plastics even at high temperature for prolonged exposure.

CHAPTER 6

SUMMARY OF PROGRESS

6.1 Summary of Progress

Four polymer systems were tested for this study: high density polyethylene, polypropylene, polystyrene and polymethylmethacrylate.

Weight tests of high density polyethylene lead to the conclusion that there is a small variation in the rate of moisture loss from sample to sample and this is large enough to offset any effect of gallium diffusion. Consequently, the diffusion of gallium into the polymer, if any, is very small and could not be measured by weight test.

The next step after weight tests was mechanical property test. Mechanical properties tested include tensile strength, elongation at break, elongation at yield and elastic modulus. The fact that only a few specimens failed at the region exposed to gallium together with the fact that the values of mechanical properties obtained fall within the scatter range expected for the properties tested shows that there is no effect of gallium on the physical properties of the polymer.

The third step was particle analysis using energy dispersion x-ray spectroscopy for traces of gallium in the polymers. The energy spectra show very small peaks of energy associated with gallium, indicating very low concentration of gallium in the polymers, even after the latter were exposed to liquid gallium at high temperatures for long hours.

Consequently, it is concluded that gallium does not diffuse much into polymers even at the extreme conditions of temperature and time.

The results of the three tests lead to the conclusion that gallium does not interact with the polymers and it is a strong competitor for mercury for a lot of equipment currently using mercury including GNOMIX PVT apparatus. These results could be generalized for all the polymers since test were carried out on both amorphous and crystalline polymers.

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