

The effect of liquid gallium on the strengths of stainless steel and thermoplastics

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We have investigated the effect of liquid gallium on type 316L stainless steel (as a candidate for the P - V - T pressure vessel), and four thermoplastics: two semicrystalline (high-density polyethylene and polypropylene) and two amorphous (polystyrene and poly(methyl methacrylate)). Specimens were coated with gallium and held at elevated temperatures and reduced pressure for extended periods. Measurements conducted on the plastics include weight change analyses, tensile tests and particle diffusion analysis using dispersion X-ray spectroscopy. For the stainless steel specimens, tensile and corrosion tests were conducted. Scanning electron microscopy was used to determine the level of corrosion. The results are compared with specimens heat treated identically but without gallium contact. After 3 months, the gallium corroded the surface of the steel to a depth of only 12 μm . No penetration path of the gallium into the steel has been observed. The gallium was also found to cause no change in the mechanical properties of the polymers tested, nor was it found to have caused any weight change in the specimens.

1. Introduction

Environmental mercury contamination has been a major topic of concern for the past two decades. However, despite the environmental concern, mercury is still being used in many applications in medicine and industry, including its use as a pressure medium for pressure–volume–temperature (P - V - T) apparatus. This work began as a search for an alternative to mercury as a confining liquid in P - V - T devices because of our concern with the hazards of mercury. At the time this work started, a P - V - T device to be used mainly for plastics was being developed at Cornell by the Cornell Injection Molding Program (CIMP). That project is now discontinued. However, in the course of our search, liquid gallium became a potential candidate. This paper presents only the results of the various tests conducted on the interaction of liquid gallium with the material for P - V - T vessel [1] and on four randomly selected polymers [2], in order to confirm the suitability of liquid gallium as a potential candidate for P - V - T devices.

Gallium is an odourless grey metal and silvery liquid above 29.78 °C and has a high boiling point of 2403 °C. It has zero vapour pressure and evaporation rate. Its specific gravity is 5.907 (6.09 for liquid). The toxicity of gallium and its compounds as reported by Sax [3] is very low. Table I compares the physical characteristics of both gallium and mercury.

However, there are a few other concerns that need to be addressed. To the best of our knowledge, there is no detailed documentation of the effect of gallium on the physical properties of plastics nor is there extensive literature on its effect on pressure vessels. It is, however, documented that gallium embrittles some metals, notably copper alloys and aluminium alloys [4–7]. These are not the common metals used for P - V - T devices. It was thus imperative that we investigate the effect of liquid gallium on the physical properties of plastics as well as on the material proposed for the P - V - T apparatus, namely, stainless steel. It has been observed that gallium embrittles copper and aluminium alloys [4, 5]. Data on its effects on steels is, however, inconclusive. Rostoker [5] reported no

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TABLE I Comparing physical properties of liquid gallium and mercury

| | Gallium | Mercury |
|---|-----------------------|-------------------------|
| Melting point (°C) | 30 | −39 |
| Boiling point (°C) | 2403 | 357 |
| Density (liquid) | 6.11 at melting point | 13.5 at 293 °K |
| Toxicity | Negligible | Very high |
| Thermal conductivity at 300 °K (W m ^{−1} K ^{−1}) | 40.6 | 8.34 |
| Volumetric coefficient of thermal expansion (K ^{−1}) | 6 × 10 ^{−5} | 18.1 × 10 ^{−5} |

embrittlement of a structural steel, while Tanaka and Fukunaga [8] reported embrittlement of a low-carbon steel. Tanaka and Fukunaga also found that, for gallium-induced embrittlement of a carbon steel, holding the specimen at an elevated temperature before the tensile test has no appreciable effects.

A second concern is that gallium is also known to corrode and penetrate some structural metals [6, 7, 9]. Ponimash *et al.* [9] found evidence that gallium interacts with and penetrates a grade of stainless steel at high temperatures (800 °C), although the path of penetration is not mentioned.

Our efforts have two main objectives. First to determine whether gallium is a suitable replacement for mercury in the hydrostatic chamber used for *P–V–T* measurements. The issue is to find the degree of embrittlement and corrosion that gallium might have on the stainless steel. Whereas mercury is known to be inert to almost all polymer systems [10], no such information is available for gallium. The second objective, then, was to test whether liquid gallium will interact with plastics in such a way as to affect their physical characteristics at elevated temperatures. In particular, we were concerned with the effect of gallium on the mechanical properties of some selected commercial plastics.

The steel walls of the pressure chamber typically experience tensile loads. Since the walls are not subjected to any collisions, we do not consider impact tests relevant. A high number of pressurization and depressurization cycles is not expected, either. Therefore, we limited our studies on the effect of gallium on the mechanical properties of steel and selected thermoplastics to constant-extension-rate tensile tests only. Since liquid-metal-induced embrittlement (LMIE) often starts near the melting point of the embrittler [4], which is 30 °C for gallium [8], we performed most of the tests at room temperature. Tests were also performed at 300 °C for the steel.

The stainless steel grade tested was type 316L, which typically has good corrosion resistance. Some old data [11] from the 1940s describe stainless steel as having “limited” resistance to attack by liquid gallium at 300 °C. We were interested in more quantitative measurements of the rate of corrosion of type 316L stainless steel because this grade was chosen for the *P–V–T* vessel we referred to in the introduction.

2. Experimental procedure

The source of gallium used in this work was from Johnson Matthey Catalog Company, and was specified as 99.9999% pure gallium ingots.

2.1. Materials and material preparation

2.1.1. Stainless steel specimens

The steel used in the experiments is AISI 316L, obtained from Thyphin Steel Co. It is a low-carbon austenitic chromium–nickel stainless steel. It was cold rolled into 18 gauge sheets, which is 1.27 mm (0.05 in) thick, then solution annealed at 1040 °C until all carbon deposits had dissolved and finally cooled with a forced air quench for 11 s. The resulting material had a grain size designated as ASTM number 8, i.e., an average of 2048 grains mm^{−2}. The average grain diameter is 22 μm.

2.1.2. Preparation and tensile testing of stainless steel specimens

The sheets were cut into strips 127 mm × 25 mm. A hole was drilled in the gripping areas of each strip and screws were used to hold several specimens together during the milling process. The holes later aided in aligning the specimens in the Instron tensile-testing machine used for these measurements. The strips were milled, using a $\frac{1}{8}$ in bit, in groups of five to seven. During the milling process, some of the strips were damaged and discarded. The undamaged specimens were polished with successive grades of sandpaper, ending with a 600 grit paper.

Gallium was applied in a ring around the centre of the gauge region. The ring was about 2 mm thick (Fig. 1). The specimens were then placed in a furnace and kept at 300 °C and low pressure for extended periods, to give the gallium a chance to penetrate into the steel, if it would.

Control specimens were milled and polished in the same manner as the coated specimens. They were also placed in the furnace to give them the same heat treatment as the coated specimens.

The specimens were pulled in uniaxial tension at a constant displacement rate of either 0.25 or 0.5 mm min^{−1}. Tensile tests were conducted at both room temperature (about 23 °C) and at an elevated temperature of 300 °C. A thermostatically controlled furnace was used for the elevated temperatures. The

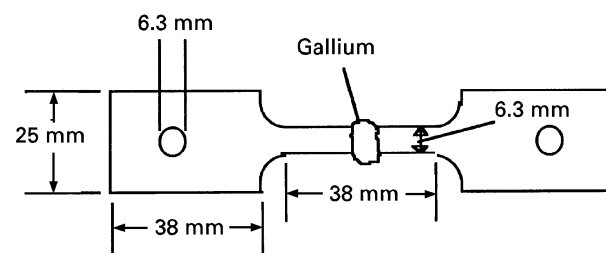


Figure 1 Nominal dimensions of the specimens used for the tensile tests. Specific gauge lengths are shown in Table II.

thermocouple used to measure and control the temperature was placed about 1 in from the centre of the gauge region of the specimen. The furnace controller kept the temperature within $\pm 2^\circ\text{C}$ of the desired value.

The specimens were lightly loaded to about 2000 lbf in⁻² before the grips were tightened, using the holes drilled in each gripping region. This helped to align the rods and specimen properly.

2.1.3. Preparation of the corrosion specimens

The corrosion specimens were strips of stainless steel. The specimens were cleaned with successive grades of sandpaper, ending with a 600 grit paper. Drops of gallium approximately 5 mm in diameter were applied at several places on the strip (Fig. 2a). The specimens were placed in a furnace and kept at 300 °C and low pressure (3 kPa). After different holding times, the specimens were removed from the furnace and the gallium was wiped off with soft tissue. A diamond-edge saw was used to cut the specimens along a cross-section through the area where the gallium had been applied. Since each strip had several droplets attached, several cross-sections were obtained from each strip. These were mounted together and polished with successive grades of sandpaper and polishing solution, ending with a 0.05 μm alumina suspension. The mounted specimens were ultrasonically cleaned and allowed to dry overnight. Penetration or corrosion of the gallium on the steel was examined using scanning electron microscopy (SEM) under both normal imaging and back-scatter imaging conditions.

2.1.4. Thermoplastics used

Transport properties such as diffusion coefficient and permeability are strongly dependent on the degree of

crystallinity of semicrystalline plastics. The crystalline component is, for most polymers, impermeable to most small and large molecules. For this reason, we decided to conduct our experiments on both semicrystalline and amorphous polymers in order to assess the effect of interaction of gallium, if any, with some common plastics. The choice of the particular thermoplastics was dictated more by the availability of the material in our laboratory. Four injection-moulding-grade thermoplastics, two amorphous and two semicrystalline, were used for our studies. These were high-density polyethylene (HDPE), polypropylene (PP), general-purpose polystyrene (PS) and poly(methyl methacrylate) (PMMA). These materials were obtained from different resin suppliers.

2.1.5. Preparation of thermoplastic specimens

Three different measurements were conducted in order to assess the effect of gallium on the plastics. These were weight tests, tensile tests and SEM particle analysis, all requiring slightly different specimen preparation protocol, described below. All specimens were injection moulded.

The Plastar TI-90G injection-moulding machine manufactured by Toyo Machinery & Metal Co., with a clamping force of 90 US tons and injection capacity of 9.9 in³, was used for moulding the test specimens, all satisfying ASTM D638 (type I) requirements. The HDPE, PP and PS specimens were all moulded using this machine, in the plastics processing laboratory at New Jersey Institute of Technology (NJIT). The PMMA specimens were injection moulded at the Polymer Processing Institute (PPI) at Hoboken. Samples for weight tests, and energy-dispersive X-ray spectroscopy (EDXS) measurements were prepared by cutting portions from the injection-moulded specimens, measuring approximately 0.6 mm \times 0.6 mm \times 2.5 mm. Samples for all the tests were treated under identical thermal conditions as far as possible. As in the case with stainless steel, a drop of liquid gallium was placed on the surface of the specimen in a ring of about 2 mm thick. They were then placed in a temperature-controlled vacuum oven. In order to minimize thermo-oxidative degradation, all the specimens were heated under vacuum. Furthermore, in order to isolate the effect of gallium from other spurious effects, a control specimen of identical dimensions but without gallium on top was also placed in the oven. The treatment temperatures ranged from 75 to 95 °C, depending on the glass transition and melting temperature of the polymer. As an additional precaution to minimize thermooxidative effects, the specimens were removed only after cooling to room temperature. The exposure time for 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 flow of 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 visible discolouration on the specimen surface that was in contact with gallium.

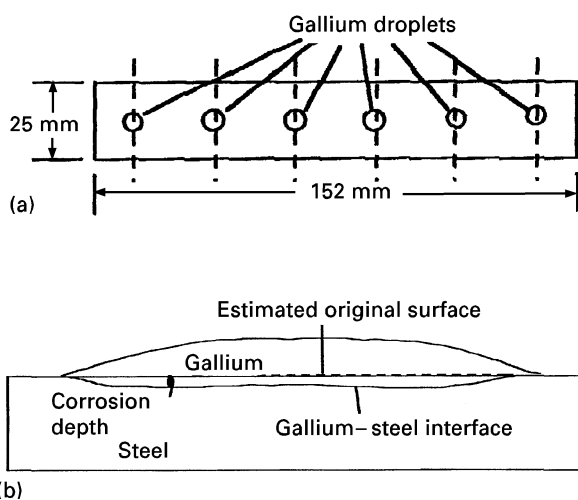


Figure 2 The specimens used for corrosion measurements. (a) The strips with gallium droplets. (b) A gallium droplet on a steel specimen. The corrosion depth is the distance between the observed gallium-steel boundary and the estimated original surface of the steel. The original surface is estimated by extending and connecting the surface from areas where gallium was not applied.

The exposure time and temperature were the variables for the very first polymer tested, which was HDPE. 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 the stepwise increase in temperature and exposure time in the oven. The only additional treatment required was deposition of a thin layer of gold on the specimens for the X-ray spectroscopy, to make them conducting.

2.2. Weight tests

Any interaction between liquid gallium and the polymer can be expected to increase the weight of polymer if there is large enough diffusion of the gallium molecules into the plastic. 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 from other factors, the change in weight of the test samples treated with gallium were compared with that of the control specimen. All specimens were weighted before and after the heat treatment described in the preceding sections, using a microbalance.

2.3. Tensile tests

Tensile tests were conducted at a fixed testing speed of 5 mm min^{-1} to determine the effect of exposure of polymer systems to gallium at elevated temperatures on the tensile strength, Young's modulus, percentage elongation at yield and percentage elongation at break. Measurements were made at room temperature (about 23°C).

2.4. Scanning electron microscopy particle analysis

2.4.1. Theory of X-ray operation

A SEM particle analysis utilizes the technique of EDXS. The technique exploits the fact that each element always exhibits a definite family of energies that can serve as a fingerprint for that element. So EDXS 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} line (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.

The specimens for EDXS analysis were coated with a thin layer of gold to make them conducting. The analyses were carried out under standard SEM conditions. In particular, all the analyses were conducted in the specimen chamber under vacuum.

3. Results and discussion

3.1. The tensile tests: stainless steel

Table II compiles the conditions under which the tests were run and the resulting yield strength, tensile strength and ductility. Table III summarizes the results illustrated in the Table II.

The shapes of the stress-strain curves of the gallium-coated specimens and of the control specimens at 300°C were very similar. As seen from Table II, several of the specimens coated with gallium did not fail at the location where the gallium had been applied (N/A indicates no contact with gallium). Therefore, it appears that gallium does not embrittle the steel at this temperature, regardless of the time spent in the furnace. The samples that spent the longest time in the furnace remained ductile. In fact, two of the samples that did not break at the coated region had spent the most time in the furnace.

At room temperature the results lead to a different conclusion. All the gallium-coated specimens are closely grouped near 60% ductility, while the control specimens reached 67% ductility. This suggests that gallium may have some embrittling effects on the steel at room temperature.

Specimens G6 and G7 were made in the same group and experienced the same holding time in the furnace. Although the strain rates differed, their stress-strain curves are nearly identical, as are the curves for the two control specimens. The conclusion is that changing the extension rate from 0.25 to 0.5 mm min^{-1} has no significant effects on the ductility of the steel, either coated or uncoated.

On the other hand, changing the holding time appears to have an effect in room-temperature tests, although this must be qualified. There are only two samples held for 95 days and one for 60 days. The difference in ductility is small (it is quite possible that the embrittling effect of the gallium does not depend on the time spent in the furnace before the tensile tests).

Tentatively, we find a correlation between the holding time and the degree of embrittlement. The three specimens that had been held in the furnace for about 60 days, (G9, T5 and T6) showed nearly identical trends, except that the gallium-coated specimen was less ductile. Meanwhile, the longer-treated specimens (G6 and G7) experienced a greater reduction in both strength and ductility. The decrease in ductility is, therefore, attributable to the effects of the gallium. The two samples that had been in the furnace the longest experienced the most decrease. It appears, however, that the degree of embrittlement in room-temperature

TABLE II The conditions and results of the tensile tests

| Sample number | Area (mm ²) | Length (mm) | Yield strength (MPa) | Tensile strength (MPa) | Elongation (%) | T (°C) | Velocity (mm min ⁻¹) | Time in furnace (days) | Failed at location of gallium ? |
|---------------|-------------------------|-------------|----------------------|------------------------|----------------|--------|----------------------------------|------------------------|---------------------------------|
| G2 | 6.4 | 37.6 | 195 | 432 | 33 | 300 | 0.25 | 95 | Yes |
| G3 | 6.3 | 38.1 | 198 | 439 | 33 | 300 | 0.25 | 95 | No |
| G4 | 6.3 | 36.3 | 203 | 437 | 39 | 300 | 0.25 | 95 | No |
| G5 | 6.3 | 36.8 | 198 | 439 | 35 | 300 | 0.25 | 95 | Yes |
| G8 | 6.1 | 37.3 | 191 | 449 | 33 | 300 | 0.25 | 60 | Yes |
| G11 | 6.3 | 33.0 | 202 | 437 | 38 | 300 | 0.25 | 21 | No |
| T1 | 7.6 | 38.6 | 199 | 436 | 36 | 300 | 0.25 | 88 | N/A |
| T2 | 7.5 | 39.1 | 189 | 438 | 36 | 300 | 0.25 | 88 | N/A |
| T4 | 7.4 | 39.6 | 194 | 448 | 37 | 300 | 0.01 | 88 | N/A |
| T7 | 6.3 | 35.3 | 262 | 460 | 32 | 300 | 0.02 | 60 | N/A |
| G6 | 6.3 | 35.6 | 259 | 596 | 60 | Room | 0.50 | 95 | Yes |
| G7 | 6.3 | 35.8 | 262 | 598 | 60 | Room | 0.01 | 95 | Yes |
| G9 | 5.7 | 35.3 | 257 | 625 | 63 | Room | 0.02 | 60 | No |
| T5 | 7.2 | 39.9 | 271 | 622 | 67 | Room | 0.01 | 60 | N/A |
| T6 | 6.0 | 36.1 | 255 | 622 | 67 | Room | 0.02 | 60 | N/A |

TABLE III The movement of the interface region between gallium and steel for different periods in a furnace at 300 °C

| Specimen number | Time in furnace (days) | Apparent movement of interface (µm) |
|-----------------|------------------------|-------------------------------------|
| 1 | 95 | 12, 10.5, 9.5, 9.5 |
| 2 | 95 | 12, 10, 9.5, 9.0 |
| 3 | 60 | 10, 8.0, 7.5, 7.5 |
| 4 | 10 | 0, 0, 0, 0 |

tests depends weakly on the previous heat treatment at an elevated temperature.

When embrittlement occurred, the shapes of the stress-strain curves did not change apart from being shortened. Tanaka and Fukunaga reported a 48% decrease in elongation at failure and a 23% decrease in tensile strength for gallium-coated specimens in comparison with uncoated specimens. The degree of embrittlement that we have found for the type 316L stainless steel is much less and is not enough to affect the tensile strength.

As was noted earlier, LMIE usually occurs first at a temperature just above the melting point of the embrittler, and at a higher temperature ductility returns. Tanaka and Fukunaga also noted that there is an optimum temperature for embrittlement. With this in mind, it seems likely that room temperature falls within the “ductility trough”, the temperature region where embrittlement occurs, while 300 °C is above this region.

Changing the strain rate at room temperature had no apparent effect on the degree of embrittlement or on the ductility of the steel. It has been noted that increasing the strain rate increases the optimum temperature for embrittlement [9]. It may be speculated that, at higher strain rates, 300 °C might fall in the embrittlement region. Also, no effect of the holding time in the furnace on the degree of embrittlement was observed at 300 °C, although there is a weak correlation between the heat treatment and the room-temperature ductility.

3.2. The corrosion experiments

SEM images were taken from the cross-sections cut through the regions where the gallium droplets had been applied (Fig. 2). In order to determine the position of the original surface of the steel, photographs were taken of the interface between the gallium-coated and gallium-free surface. The region under a droplet, showing the original surface and the penetration of the gallium, is illustrated in Fig. 2b.

Higher magnifications show no evidence of gallium penetration into the steel region along a preferred path, or any reaction or compounds formed at the interface.

Table III illustrates the shift of the interface between the gallium and steel for the different specimens. For each specimen, measurements were taken at four cross-sections. Table III shows that there was no apparent (less than 0.1 µm observed) movement of the interface up to 10 days, but for longer times there was evidence of gallium penetration.

Type 316 stainless steel is rated to have “excellent” corrosion resistance against mercury, even at 300 °C [12]. This is defined as penetration of less than 2×10^{-3} in (50 µm) per year. If we project the results for gallium over a span of 12 months, assuming a constant rate of corrosion at the highest value, i.e., 12 µm in about three months, we note that type 316L stainless steel also has “excellent” resistance to gallium. Experiments by Ponimash *et al.* suggest gallium forms a penetration layer that acts as a barrier to further diffusion in another type of stainless steel. This raises the possibility of increasing the corrosion resistance of the steel to gallium using a short isothermal anneal.

3.3. Results for weight tests

Almost all the specimens showed a weight decrease except a few which did not show any change at all. Upon comparing the average percentage decrease in weight, it became apparent that the weight decrease was both time and temperature dependent, indicating

that these might be due to loss of moisture. For example, gallium-treated specimens stored at 65 and 95 °C for 165 h showed a higher percentage reduction in weight than did the control specimens. On the other hand, specimens stored at 95 °C for 370 h both treated and control all show approximately equal percentage reductions in weight. It appears, therefore, that the reduction in weight has no correlation with the treatment of the samples.

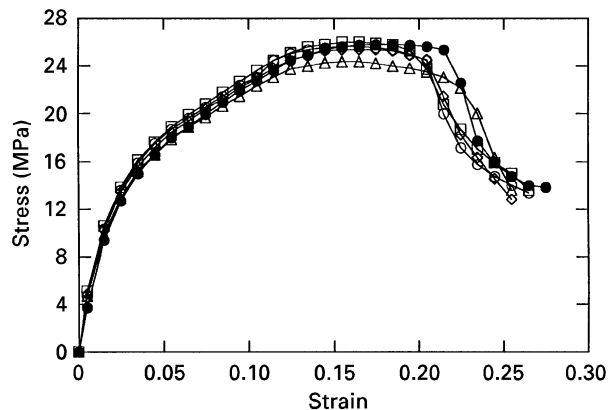


Figure 3 Stress–strain curves for HDPE, where t_i denotes treated specimen i ($i = 1, 2, 3, \dots$) and c_i denotes control specimen i ($i = 1, 2, 3, \dots$). (\square), c_1 ; (\circ), t_1 ; (\diamond), c_2 ; (Δ), t_2 ; (\bullet), c_3 .

3.4. Tensile test results for four thermoplastics

Stress–strain curves for both test and control HDPE specimens, kept under vacuum at 95 °C for 165 h are shown in Fig. 3. The mechanical property data extracted from plots such as those in Fig. 3, for all the storage temperatures and times, are summarized in Table IV. These data include tensile strength, Young’s modulus, percentage elongation at yield and percentage elongation at break.

To summarize the results of the stress–strain curves in Fig. 3, we found that none of the test specimens failed at the location treated with gallium. In fact, failure occurred at locations very far from the region of gallium application. As far as the stress–strain curves are concerned, the shapes are qualitatively identical for all storage temperatures and times, indicating there was no dramatic effect from the contact with gallium. From Table IV, we have determined that the average tensile strength of all specimens kept at 95 °C for 370 h (the longest storage time) decreased by approximately 76%, elongation at break decreased by approximately 12%, elastic modulus decreased by approximately 75% and elongation at yield decreased by 7% compared with specimens kept at 65 °C for 10 h. This is due, presumably, to secondary crystallization.

TABLE IV Mechanical properties of PE annealed at 65 °C for 10 h

| Specimen number | T (°C) | Time in oven (h) | Gallium contact | Failed at the location of gallium? | Tensile strength (MPa) | Young’s modulus (MPa) | Elongation at yield (%) | Elongation at break (%) |
|-----------------|----------|------------------|-----------------|------------------------------------|------------------------|-----------------------|-------------------------|-------------------------|
| 1 | 65 | 10 | Yes | No | 23.181 | 389.226 | 32.4 | 57.2 |
| 2 | 65 | 10 | Yes | No | 23.950 | 392.765 | 30.6 | 46.2 |
| 3 | 65 | 10 | No | N/A | 24.046 | 389.226 | 30.4 | 54.6 |
| 4 | 95 | 10 | Yes | No | 25.874 | 353.842 | 31.2 | 49.6 |
| 5 | 95 | 10 | Yes | No | 24.816 | 353.842 | 30.8 | 56.8 |
| 6 | 95 | 10 | No | N/A | 24.046 | 442.303 | 32.6 | 55.0 |
| 7 | 95 | 165 | Yes | No | 26.451 | 613.326 | 31.4 | 52.8 |
| 8 | 95 | 165 | Yes | No | 25.393 | 483.584 | 31.4 | 54.0 |
| 9 | 95 | 165 | No | N/A | 26.691 | 471.789 | 32.2 | 56.8 |
| 10 | 95 | 165 | No | N/A | 27.172 | 495.379 | 31.6 | 55.6 |
| 11 | 95 | 165 | No | N/A | 26.932 | 436.405 | 34.8 | 58.4 |
| 12 | 95 | 370 | Yes | No | 5.567 | 96.717 | 28.0 | 50.2 |
| 13 | 95 | 370 | Yes | No | 5.567 | 94.358 | 30.0 | 46.4 |
| 14 | 95 | 370 | No | N/A | 5.662 | 96.717 | 28.6 | 44.6 |

TABLE V Mechanical properties of PP annealed at 75 °C for 370 h

| Specimen number | T (°C) | Time in oven (h) | Gallium contact | Failed at the location of gallium? | Tensile strength (MPa) | Young’s modulus (MPa) | Elongation at yield (%) |
|-----------------|----------|------------------|-----------------|------------------------------------|------------------------|-----------------------|-------------------------|
| 1 | 75 | 370 | Yes | No | 23.890 | 1533.928 | 29 |
| 2 | 75 | 370 | No | N/A | 22.125 | 1374.127 | 28 |
| 3 | 75 | 370 | No | N/A | 22.380 | 1469.993 | 27 |
| 4 | 75 | 370 | No | N/A | 22.880 | 3834.785 | 27 |
| 5 | 75 | 370 | Yes | N/A | 22.880 | 1406.083 | 28 |
| 6 | 75 | 370 | Yes | Yes | 22.380 | 1406.083 | 28 |
| 7 | 75 | 370 | Yes | No | 21.625 | 2940.011 | 27 |
| 8 | 75 | 370 | Yes | No | 21.752 | 1278.262 | 27 |
| 9 | 75 | 370 | No | N/A | 22.007 | 2556.523 | 27 |

TABLE VI Mechanical properties of PS annealed at 65 °C for 370 h

| Specimen number | T (°C) | Time in oven (h) | Gallium contact | Failed at the location of gallium? | Tensile strength (MPa) | Young's modulus (MPa) | Elongation at yield (%) |
|-----------------|----------|------------------|-----------------|------------------------------------|------------------------|-----------------------|-------------------------|
| 1 | 65 | 370 | No | N/A | 45.897 | 1342.172 | 11 |
| 2 | 65 | 370 | Yes | No | 27.028 | 1195.183 | 6.5 |
| 3 | 65 | 370 | No | N/A | 42.121 | 1342.172 | 10 |
| 4 | 65 | 370 | Yes | Yes | 45.897 | 1182.396 | 10.5 |

TABLE VII Mechanical properties of PMMA annealed at 95 °C for 370 h

| Specimen number | T (°C) | Time in oven (h) | Gallium contact | Failed at the location of gallium? | Tensile strength (MPa) | Young's modulus (MPa) | Elongation at break (%) |
|-----------------|----------|------------------|-----------------|------------------------------------|------------------------|-----------------------|-------------------------|
| 1 | 95 | 370 | No | N/A | 75.435 | 3115.766 | 9.8 |
| 2 | 95 | 370 | Yes | No | 70.414 | 3675.008 | 8.4 |
| 3 | 95 | 370 | Yes | Yes | 75.435 | 3275.542 | 9.4 |
| 4 | 95 | 370 | Yes | No | 77.956 | 3595.120 | 10.6 |
| 5 | 95 | 370 | No | N/A | 66.011 | 3355.430 | 7.6 |
| 6 | 95 | 370 | No | N/A | 79.211 | 2157.082 | 10.4 |
| 7 | 95 | 370 | No | No | 79.211 | 3275.542 | 10.6 |
| 8 | 95 | 370 | Yes | N/A | 79.211 | 3195.654 | 11.4 |
| 9 | 95 | 370 | No | N/A | 70.414 | 3275.542 | 8.4 |
| 10 | 95 | 370 | Yes | No | 67.894 | 6391.308 | 7.4 |

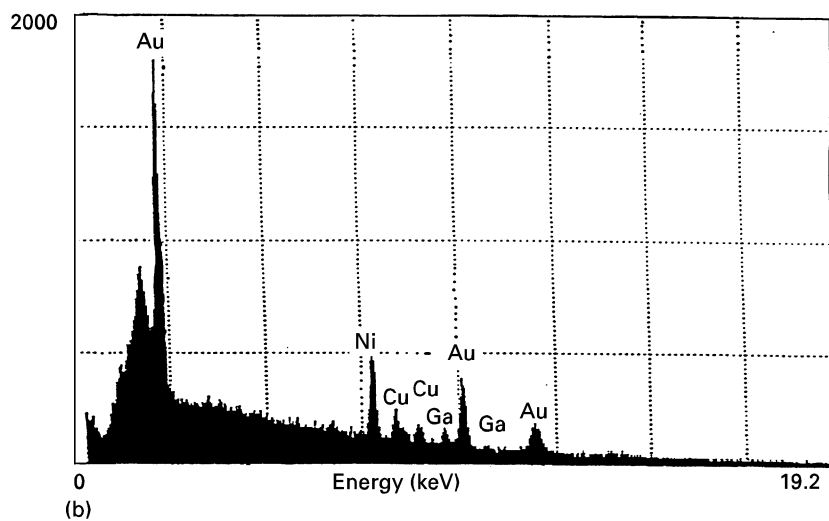
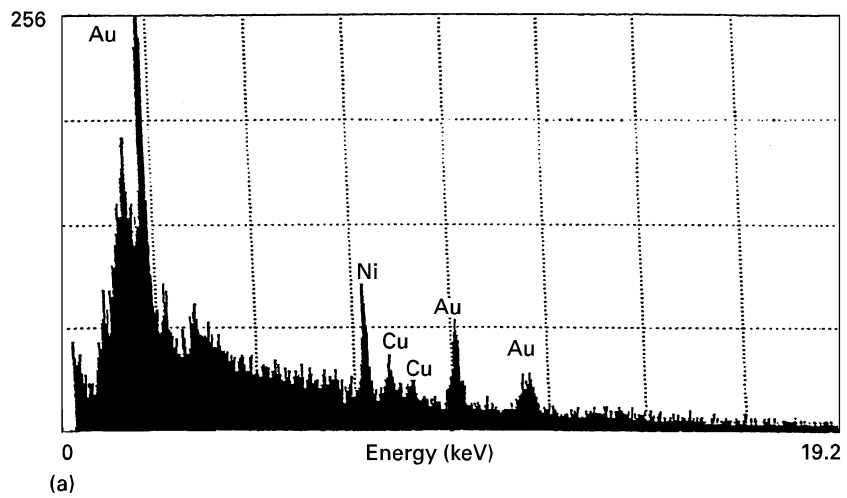


Figure 4(a), (b) Continued

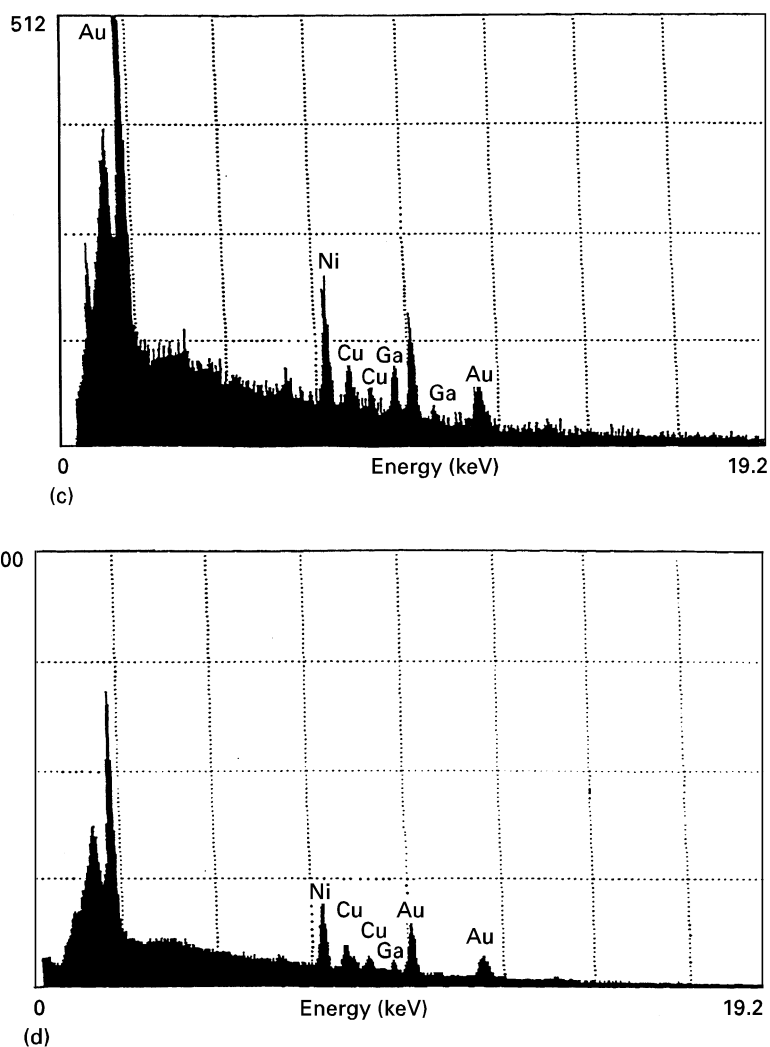


Figure 4 Energy-dispersive X-ray spectra for (a) HDPE stored at 65 °C for 10 h without gallium, (b) HDPE stored at 95 °C for 370 h, in contact with gallium, (c) PP stored at 75 °C for 370 h, in contact with gallium, and (d) PS stored at 75 °C for 370 h, in contact with gallium.

A closer examination of the results in Table IV shows that the mechanical properties of the treated and controlled specimens display a complex pattern which cannot be attributable to the presence of gallium. For instance, whereas some of the treated specimens possess mechanical properties which are lower than the control specimens for some storage temperatures and times, others show the opposite trend. In summary, the results of Table IV show no consistent trend which can be attributed to the interaction of the plastics with gallium.

Stress-strain curves for both treated and control specimens, for PP, PS and PMMA, after storage at the specified temperatures and times were qualitatively similar to those in Fig. 3. Tables V–VII summarize the mechanical properties of the specimens obtained from the stress-strain curves for the three polymers. From these tables, it is again clear that treated specimens do not show any abnormal behaviour when compared with the control specimens, thus confirming the results for PE.

3.5. X-ray spectroscopy results

We now turn our attention to the X-ray spectroscopy results. The print-outs of the energy-dispersive spectra

are shown in Fig. 4. As explained previously, the presence of any element is deduced from 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 print-outs identify the energy bands of the various elements, gallium, gold, etc., whether or not these elements are actually present. The spectra also show the presence of silicon, iron and nickel with substantial energy heights. This is due, presumably, to the specimens holder. It can be seen from Fig. 4b–d that the heights of gallium energy peaks are very low even for the samples that experienced the longest exposure time, and the highest temperature. The results for PMMA is similar to Fig. 4a which shows absence of gallium. Fig. 4a was obtained from the control HDPE specimen, indicating that there was no contamination of gallium on this sample.

4. Conclusions

While gallium does not embrittle type 316 stainless steel when tensile tests were conducted at 300 °C, tests at room temperature show that it does cause a small

decrease in ductility. The decrease in ductility at room temperature appears to depend on the holding time at the elevated storage temperature, of 300 °C, reaching 10% after storage for a few months. The observation that no embrittlement occurred at 300 °C suggests this temperature is above the region in which gallium embrittles steel. At room temperature, changing the strain rate from 5 to 2.5 mm min⁻¹ did not affect the degree of embrittlement.

There is no evidence gallium forms a compound with steel at temperatures of about 300 °C; however, it does corrode the steel surface. Corrosion of about 10 µm was observed after 3 months in a furnace.

Parallel tests on four thermoplastics, including weight tests, tensile tests and EDXS analysis did not show any evidence of adverse interaction of gallium with the plastics even when the latter were stored in contact with gallium for several days, at temperatures close to their softening or melting points. This conclusion was arrived at after test results of gallium-treated specimens were compared with control specimens stored under identical thermal conditions but without contact with gallium. The gallium was found to cause no change in the mechanical properties of the polymers tested, nor did the weight tests show any increase in weight resulting from the possible diffusion of gallium molecules into the plastics.

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