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ADHESION FAILURES OF PLASTICS BONDED TO VARIOUS MATERIALS

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Abstract

Plastics are bonded in many applications to a wide variety of materials, including metals, ceramics and the same or other plastics. The adhesive may be the plastic, such as bonding metal to metal. Failure of the adhesive bond may be due to (1) formulation additives migrating into the adhesive bond, (2) extraneous foreign contaminants, (3) environmental conditions such as water and temperature, (4) physical effects of the bonded materials such as coating thickness. Differences in coefficient of thermal expansion, such as metal and plastic, may stress the adhesive bond as temperature changes. Analytical methods to identify the cause of failure involving formulation additives and contaminants are infrared spectroscopy and thermal desorption gas chromatography/mass spectroscopy at and below the surface.

1. Introduction

Many applications require the adhesive bonding of plastic materials of a wide variety of thicknesses and shapes to a substrate, which may be the same or another plastic, metal, etc. The bonding may be by way of an adhesive or primer, i.e., a third material between the plastic and what it is bonded to, or the bond may not involve a separate adhesive. By this broad definition, paints and other coatings are included as well as the bonding of printing on a plastic surface. Also included are applications in which the bonding involves much thicker plastics than thin coatings or prints. In most cases high bond strength is required and failure typically occurs due to too low bond strength resulting in debonding. In some cases, low bond strength is desired, such as easy-open packages, so that high bond strength, making opening difficult, would constitute a failure. In all cases, the nature and condition of the surfaces and the interface are critical factors in achieving good adhesion or, conversely, poor adhesion.

Inadequate bond strength may occur at the time of manufacture or may develop with storage or service time. Compositional factors within the plastic formulation or the adhesive play a major role in achieving proper bonding. For example, adhesives may contain a tackifier to promote adhesion, i.e., an intentional additive. Some additives, such as plasticizers or internal lubricants have the potential to interfere with adhesion by migrating to the surface. Very low content of some additives can have a particularly harmful effect on adhesion, such as silicone oil, or hydrocarbon waxes. In some cases the interfering substance may be an extraneous foreign contaminant, such as a compounding process aid added during compounding or present as a formulation component, or present on a formulation component such as a filler.

Bond failure may be caused by environmental conditions, such as water immersion, humidity level in the air, and too high or too low temperature. If a plastic is bonded to a material with a large difference in coefficient of thermal expansion such as a metal, too high or too low temperature may set up stress/strain conditions at the interface that lead to fracture or separation of the bond. High temperature may enhance migration of an additive in the plastic to the bonded interface and reduce bond strength. Examples are given which illustrate various types of adhesive failure.

Adhesive failure may have product liability consequences. An insurance claim involved glue that was defective and would not seal paper envelopes. Unusable envelopes were returned by dissatisfied customers to the envelope manufacturer who held the glue manufacturer liable for loss of customers and business [1].

2. Experimental methods

While many well-known analytical and test methods may be appropriate for the wide range of types of adhesive failure indicated below, two in particular have been found to be useful in many cases: thermal desorption GC/MS (gas chromatography/mass spectroscopy) [2,3] and infrared spectroscopy in general and micro FTIR (fourier transform infrared spectroscopy) in particular [4]. The University of Connecticut website on GC/MS is at http://www.ims.uconn.edu/~lavigne/gcmslab.html. Using GC/MS, one may take a sample from a surface, such as by scraping with a knife or use of a suitable solvent, and analyze composition relative to that within the bulk of the sample, i.e., below the surface. Materials that migrate and tend to concentrate on the surface can be detected and identified from MS and GC retention time this way. Contaminants from the atmosphere can be identified. Surface versus bulk composition can also be determined by IR comparing surface composition by reflectance IR to bulk composition by transmission. The method is not as informative as GC/MS, however, because there is no separation of compounds. Micro IR can be very useful for identification of contaminants and also allows for obtaining a microphotograph (to about 100X) of what is in the spectrum.

A useful way to determine if a bonding problem is due to material at the surface is to clean the surface either with a solvent that won't attack the polymer such as alcohol or by lightly sanding the surface. If the bond strength is improved significantly after cleaning the surface, then the problem may be due to material at the surface. The offending material may have migrated from the plastic to the surface, or may have been deposited there as a contaminant from the atmosphere or from processing, such as a mold spray to prevent sticking (external lubricant). If the poor bonding recurs with time under controlled storage conditions, then exudation from the formulation is indicated.

3. Types and examples of adhesive failure

3.1 Failures due to polymer formulation

3.1.1 Formulation additives [5]

(1) The bond between plasticized vinyl floor tile and the adhesive on the floor failed causing the floor tiles to become loose. The vinyl contained a phthalate plasticizer and an aliphatic ester plasticizer with the phthalate content higher than the aliphatic content. In the failed tile, the ratio had been reversed unintentionally, i.e., aliphatic plasticizer was present as the larger amount. Because the content exceeded its compatibility in the PVC, some of it migrated to the surface, and weakened the bond to the adhesive. This failure was caused by a production operator error.

(2) The bond made by silk screen printing on an injection molded part was poor, causing smearing and easy removal by abrasion. The resin contained a mold release agent. The problem was probably due to mold release agent at the surface interfering with adhesion to the plastic. Mold release agents typically are waxy substances that are used to prevent sticking to the mold. On the product surface, however, it may prevent an intended bond from being as strong as it needs to be. When the resin manufacturer reduced the level of mold release agent to the minimum needed for molding purposes, the printing problem was reduced to an acceptable level.

(3) Bonding of thermally transferred printed material (decals) onto sporting equipment with a urethane coating was satisfactory when the urethane coating was deposited from a solution containing volatile organic solvent. Municipal regulations requiring reduction in volatile organic compounds led to a reformulating of the urethane coating. The bond of decals to the new coating was poor, due to additives that were incorporated into the new formulation. It was determined that composition at the surface was the problem by cleaning the surface, leading to good adhesion.

(4) A polymeric adhesive for bonding metals to each other is a two part system in which an initiator is added when the bond is made. Without the initiator the polymer does not develop as needed to effect a good bond. In cases where there was bond failure analysis by thermal desorption GC/MS showed that the initiator had not been added. The method utilizes the exceptional sensitivity of the mass spectrometer and the excellent resolution of the chromatographic method. Using single ion monitoring of the mass spectrometer enhances the detectability by searching only for the largest peak of the compound of interest, the initiator.

The analysis for initiator was done by scraping the surface of unbonded metal, providing 0.1-0.2 mg. sample. Using the University of Connecticut direct dynamic thermal desorption device, the sample was heated at 250°C/2 minutes [2,3]. The volatiles thus generated were carried onto the head of the cryofocused GC column. Programmed heating at 15°C/minute produced the chromatogram of Figure 1. The initiator peak is indicated as a very small peak at a certain retention time (X axis). The next figure 2a shows the mass spectrum of the peak for the initiator. Using single ion monitoring Figure 2b is the chromatogram only for mass 212 species, the major peak of the initiator. The presence of initiator is confirmed by all three ways of utilizing GC/MS: (1) a GC peak at the GC retention time known to be correct from control runs of initiator; (2) the whole mass spectrum of the peak in comparison to that of known initiator; (3) a semi-quantitative measure of initiator content from the peak area of the main 212 peak by SIM (single ion monitoring). In the case shown initiator was present. In others none was detected, and was responsible for adhesive failure of the metal to metal bond. It is also possible that initiator content may be low or poorly dispersed so that bond strength is not as high as it might otherwise be.

In spite of the very small peak for initiator, the resolution and sensitivity of the analytical system make it possible to make positive identification of a compound present at very low level.

3.2 Failures due to extraneous foreign contaminants

(1) Compounding process aids used to facilitate incorporation of additives, such as pigments, into a plastic may be present at the surface of products made therefrom. Zinc stearate is an example of such material. Its waxy nature and limited compatibility in crystalline polymers, in particular, such as polyethylene may reduce or prevent bonding. Applications such as thin films are particularly

vulnerable to this problem. Thermally fused bonds may be weak if the interfering substance prevents good fusion of the plastic layers. Other problems beside adhesion which have been experienced due to compounding process aids at the surface of products include environmental stress cracking [6].

(2) Another version of (1) above is the case of titanium dioxide pigment, which contained a low level of silicone oil as furnished by the pigment supplier. In a case of poor bonding of polyethylene-containing coextruded film, solvent extraction of the film isolated silicone oil, which had originated on the pigment. The company that had purchased the pigment was not aware that it contained silicone oil. While this additive might not cause problems in many products, some applications can not tolerate even small amounts of such interfering substances.

(3) This is a case of debonding within a fused plastic caused by a contaminant [7]. Extruded HDPE polyethylene sheet 3.175 mm thick used to fabricate protective sports equipment experienced delamination when shapes were punched out (see arrow in Figure 3). In the opened areas there were thin pieces of a transparent plastic film contaminant. The contaminant prevented the PE on either side of it from fusing to each other. The PE did not fuse permanently to the contaminant. As a result, it took only the force of the cutting tool to cause separation where contaminant was present along the punched edge.

(4) Cellulosic lint fibers on epoxy-phenolic coating over aluminum led to localized delamination of plasticized vinyl latex coating applied on the lower coating. Both coatings contain liquid additives such as plasticizers, that migrated freely between the two coatings. Where the interface consisted of an uninterrupted tight bond between the coatings, the exchange of plasticizers did not affect adhesion. At contaminant sites, however, plasticizer could not transfer freely across the interface, causing some to be deposited at the interface, lowering the bond strength at the contaminant sites. Micro IR, microphotography and GC/MS showed that plasticizer was present as a tiny pool at delaminated sites [8].

(5) A cellulosic contaminant contained in zinc stearate was also at fault when the stearate was used to reduce bond strength between the outer jacket and the carbon black-containing insulation shield over insulation in an electrical power cable. The stearate is applied as a fine powder before the jacket is extruded over the cable. Without it, the polymers in the jacket and in the insulation shield would fuse together. The purpose of the stearate, and of another coating applied to the insulation shield, is to permit easy removal of the jacket (stripability) when connections are made in service. At some locations the bond was too strong, so that the jacket could not be stripped off readily. Microphotography and micro IR revealed the presence of a cellulosic film contaminant in the stearate. Where the contaminant was at the interface between jacket and the rest of the cable, the stearate was absent and so could not control adhesion as intended.

(6) In this case silicone oil prevented thermal bonding of a blister pack for a medical product. Silicone oil was used elsewhere in the operation but it was thought that it would not be present at the surfaces to be bonded. The polymeric layers for bonding on the perimeter of the package bonded only partially, leaving some portions of the approximately 6.35 mm wide bonded seam unbonded. When the incomplete bonding occurred, silicone oil was suspected. It was detected by infrared spectroscopy/attenuated total reflectance (IR/ATR), a reflectance method that probes to about 1-2 micron depth of a surface. The amount of contaminant present is often so little that sophisticated methods are needed to detect it. In this case spectra were obtained of suspect surface, of normal clean surface, and the difference spectrum. The latter revealed silicone oil in the suspect area; the match to the IR spectrum of known silicone oil was good. Figure 4 is for the surface containing silicone oil; Figure 5 is for normal surface. Figure 6 is for the subtraction of normal surface from suspect surface. Figure 6 also shows the match to known silicone oil. Identification of contaminants is useful in narrowing down the sources. For silicone oil, it is also possible to do thermal desorption GC/MS, which can further help to define the grade of silicone oil. See section (7) below.

(7) This example is like the previous one involving surfaces that won't bond due to contamination with silicone oil. The complaint was that the adhesive would not wet the surfaces to be bonded, consequently would not bond. The surface of suspect surface area was scraped giving about 0.1 mg sample. Analysis was by thermal desorption GC/MS. A control satisfactory area was used as reference. Figure 7 is the chromatogram of the scraping of the suspect area. Several cyclic silicone oligomers were found. For confirmation the chromatogram was searched for ion mass 73, a major one for dimethylsiloxanes (Figure 8). Each peak corresponds to a different component of silicone oil.

(8) In this case the adhesive broke away from the fiberglass cleanly. Contamination was suspected. Thermal desorption GC/MS of fiberglass was done at the surface and from the inner core of the material. Figure 9 is the GC chromatogram of surface scraping, which revealed the presence of the fatty acids – tetradecanoic, hexadecanoic and octadecanoic (C_{14}, C_{16}, C_{18}). They are absent in the inner material (Figure 10). These fatty acids generally denote stearic acid, a natural material containing oligomeric fatty acids. In polymer technology the fatty acids are often present as a metal salt, like calcium or zinc stearate. The stearates are common mold release agents.

Being incompatible with polymers in general, they migrate to the surface. Detection of the fatty acids is because the stearates contain some uncombined fatty acids. Failure was due to the waxy nature of the stearate and fatty acids interfering with bonding, acting as contaminants.

(9) Two part silicone polymers that are mixed, applied and allowed to react and crosslink contain a platinum catalyst that causes the vinyl ($-CH=CH_2$) portion of one of the two parts to polymerize. Polymerization may be prevented by compounds that "poison" the catalyst, i.e., render it ineffective [9]. Examples are (1) sulfur compounds (mercaptans, sulfates, sulfides, thiols) and rubbers vulcanized with sulfur will inhibit polymerization. (2) Nitrogen compounds (amides, amines, nitriles and tin compounds).

The presence of a poison may not be known and should be suspected if silicone does not react as expected.

3.3 Failures due to environmental effects in assembly or in service

(1) Injection molded phenolic resin parts bonded to polypropylene via silicone RTV adhesive (room temperature vulcanizable) experienced variable bond strength to the RTV. A major factor in the quality of the bond was contaminants that deposited on the phenolic parts during storage in the open factory environment prior to bonding. GC/MS readily identified hydrocarbon oil type deposits that came from sources such as the exhaust of vehicles that were driven in the plant. Adhesion was improved greatly by preventing such contamination of the parts during storage.

Figures 11 and 12 are thermal desorption GC/MS chromatograms of a cured molded phenolic resin part that could not be bonded well to RTV silicone. Figure 11 is for surface scrapings, and Figure 12 is for resin below the surface. Note that the sample weight used for analysis is only 0.02-0.04 mg, which indicates the extraordinary sensitivity of GC/MS. Figure 11 indicates the presence at the surface of a hydrocarbon contaminant with a broad range of composition and molecular weight (peak 5). This material is absent from Figure 12 for resin below the surface, indicating that the hydrocarbon is a contaminant deposited during storage or handling.

Figure 11 also indicates several sharp peaks originating in metal stearate and stearic acid in the formulations. These are mold release agents that naturally migrate to the surface. Their content within the bulk of the resin is much lower (Figure 12). One of the peaks at the surface is octadecanamide (peak 3), which is not part of the formulation. It is formed during curing by the reaction of ammonia, released during curing by hexa (hexamethylene tetramine) and octadecanoic acid (stearic acid). The amide has lower compatibility with phenolic resin than the corresponding acid, so that there is concern about the effect of the amide on adhesion. Analysis of the uncured resin showed the absence of the amide, confirming that it was formed during cure.

In Figure 12 the relative content of the fatty acids and amide is much lower than at the surface, so that low adhesion to RTV may be due, in part, to their presence. In this case, however, the high content of hydrocarbon contaminant is the major reason for low adhesion. Nevertheless, it is well to be aware of materials in the formulation that could, under some circumstances, adversely affect adhesion.

Experimental conditions for the thermal desorption GC/MS used in Figures 11 and 12 are as follows:

GC/MS - Hewlett/Packard 5890/5971 A fitted with UCONN/IMS direct dynamic thermal desorption device [2,3].
Thermal desorption - 4'/300°C; cryofocus.
Sample weight - 0.02 mg (Figure 11); 0.04 mg (Figure 12).
GC column - 100% methyl silicone, 12 m x 0.2 mm ID, 0.33 μ film thickness.
Temperature program - 35 to 300°C at 15°/min.
MS - 10 to 400 atomic mass units, 1.8 scans per second.

(2) Adhesion problems have occurred in which the composition of the part being molded and the molding conditions were not at fault. Other molding operations in the same room, in which an external lubricant was sprayed on a mold, caused some lubricant spray to be carried in the air over to other machines and deposited on parts being molded.

(3) Too high or too low temperature is a critical factor that can cause failure of bonded systems, particularly for systems with different coefficients of thermal expansion bonded to each other. A liquid nitrogen dispensing station at a location not originally expected to be used for that purpose experienced peeling of paint on nearby cinderblock and loss of adhesion of a bonded baseboard.

(4) Water and moisture are common environmental agents that usually have a deleterious effect on bond strength. However, water is not necessarily always harmful to adhesion. Paper/resin laminates on top of desks and library furniture, of the common "Formica" type, failed in adhesion in dry climates but not in moist climates. The laminates were bonded with EVA latex type adhesives (ethylene vinyl acetate). The bottom of the laminate which is in contact with adhesive is phenolic resin impregnated Kraft paper. Experiments in controlled temperature and humidity environments confirmed that for good adhesion

adequate moisture in the air is required. Apparently water provided a necessary bridge of the hydrogen bond type between adhesive and the resin impregnated paper. In the absence of adequate water, there was no significant physical bond between the two parts and the laminate could be removed easily.

3.4 Failures due to physical effects of materials being bonded

(1) Alkyd resin clear coating on tennis racquets had low adhesion in some areas and was satisfactory at others. A claim was brought against the resin supplier. The critical property that differed between well bonded and poorly bonded coating was the coating thickness. Above a certain thickness adhesion was poor. This illustrates a general characteristic of many bonded systems, i.e., shrinkage forces at an interface between dissimilar materials will reduce bond strength more the greater the thickness of the coating.

(2) Continuous embossed floor tile consisting of three layers of different composition tends to warp. The top layer is a clear polyurethane wear layer, over a foamed plasticized vinyl layer, under which is a largely inorganic backing sheet. The curvature imparted by having been in a roll is retained somewhat. The warping is particularly bad at the end or edge of an area. The adhesive may not be strong enough to resist warping force, causing lifting along edges. In some cases, the only way to keep the floor covering in place is to mechanically prevent it from lifting, as with a baseboard.

4. Metal/polymer adhesion problems

There are many applications in which a metal and a polymer formulation are bonded to each other. The bond strength, whether intentionally low or high, is important to the application.

(1) A polymeric electrical insulation was covered with a thin layer of copper wrap, over which was a plasticized PVC (polyvinylchloride) jacket. In service the jacket shrank to an unacceptably high extent. Contacts were left unprotected by the jacket. The jacket was tested for percent shrinkage by heating at about 150°C for several minutes until no further shrinkage occurred. The percent shrinkage was over 20%, which is high. After extrusion, the PVC was probably cooled too rapidly so that orientation was frozen in. It would relax gradually in service above room temperature. The bond of PVC to copper was very low and there was little frictional force or mechanical interlocking to prevent easy sliding of the PVC along the copper sheet. The difference in coefficient of thermal expansion of copper and PVC also contributed to the two materials separating with the PVC shrinking.

Similar insulation and jacket were also in a different configuration without a metal sheet between the two. In this case the PVC was in direct contact with the insulation. In service the jacket did not shrink away from the insulation. While there was not strong adhesion between the jacket and insulation, there was enough frictional force between the two to prevent the jacket from shrinking back. The lesson is that a polymeric formulation is not likely to bond sufficiently to a smooth metal layer to prevent shrinkback of the polymer. Also, in extruded applications of polymer/metal materials, the polymer should be processed or annealed to minimize shrinkage with heat.

(2) Polymeric electrical insulation extruded over a twisted array of several individual conductor strands usually bonds well enough that the polymer and conductor do not separate in service. The mechanical interlocking of polymer in the folds and valleys of the twisted conductor strands contributes to the adhesive bond.

When the conductor is a single strand with a smooth surface, the bond between polymer and conductor lacks the mechanical interlocking of the twisted multiconductor strand case. Separation of conductor and polymer is more likely.

(3) Traces of contaminants such as oil on metal conductors onto which polymeric electrical insulation is to be extruded, can cause low and variable adhesion of metal to polymer. One way to eliminate contaminants that are volatile or combustible is to pass the conductor prior to extrusion through a flame. Oil is commonly present on metal such as electrical conductor strands because it is needed to lubricate the movement of metal over processing lines. Its removal is important to assure an adequate adhesive bond of metal conductor to extruded insulation.

(4) Figure 13 shows the plastic handle of an umbrella to which a metal ring was bonded at one end. The plastic is injection molded impact grade polystyrene. The metal ring became unbonded with normal handling and use of the umbrella. Adhesion of metal to plastic tends to be poor partly because of the difference in coefficient of thermal expansion of metal and plastic. The result is stress and loosening of the bond. When the temperature falls well below room temperature, the plastic shrinks more than the metal, which will tend to loosen the adhesive bond.

(5) In this case polycarbonate is bonded to lead with epoxy resin. The system is also immersed in hydrocarbon oil in an electrical power supply. The bond must be resistant to separation of PC and lead, and the whole system must be resistant to hydrocarbon oil. Evaluation of two epoxy resins gave satisfactory results in oil for one and not for the other. PC and lead have different coefficients of thermal expansion: 29×10^{-6} in/in/°C for lead and 68×10^{-6} for PC. As temperature changes and lead and PC ex-

pand at different rates, a stress is placed on the adhesive. If it is flexible, it will adjust itself to the stress caused by the differential expansion. The epoxy resin that did not fail had a lower glass transition temperature T_g by differential scanning calorimetry (DSC) than the other, below room temperature, thus contributing to bond retention.

References

1. M. Ezrin, *Plastics Failure Guide – Cause and Prevention*, Hanser, 319 (1996).
2. M. Ezrin and G. Lavigne, *Society of Plastics Engineers Annual Technical Conference Proceedings*, 2230 (1991).
3. M. Ezrin and G. Lavigne, *Society of Plastics Engineers Annual Technical Conference Proceedings*, 1717 (1992).
4. M. Ezrin and G. Lavigne, *Society of Plastics Engineers Annual Technical Conference Proceedings*, 3302 (1994).
5. M. Ezrin, *Society of Plastics Engineers Annual Technical Conference Proceedings*, 1492 (1988).
6. M. Ezrin, *Society of Plastics Engineers Annual Technical Conference Proceedings*, 1478 (1990).
7. M. Ezrin, *Plastics Failure Guide – Cause and Prevention*, Hanser, 30 (1996).
8. M. Ezrin and G. Lavigne, *Society of Plastics Engineers Annual Technical Conference Proceedings*, 3302 (1994).
9. Gelest, *Reactive Silicones*, Gelest, Inc., 42 (1997).

Keywords: adhesion failure, plastics failure, metal/plastics failure, infrared spectroscopy, gas chromatography/mass spectroscopy, adhesion failure due to contaminants, adhesion failure due to formulation additives, adhesion failure due to environmental effects.

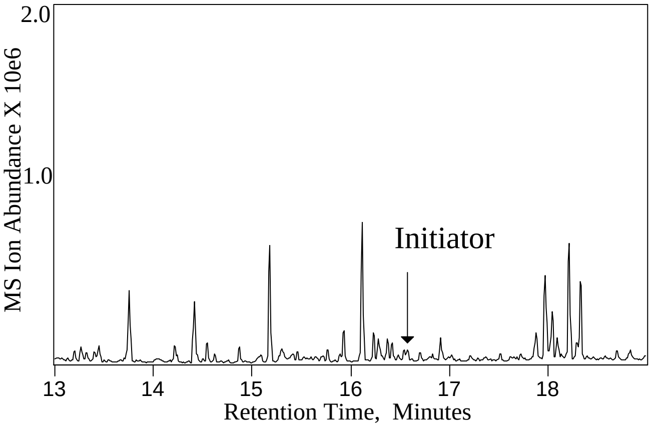

Figure 1. Thermal desorption GC/MS of surface to detect initiator

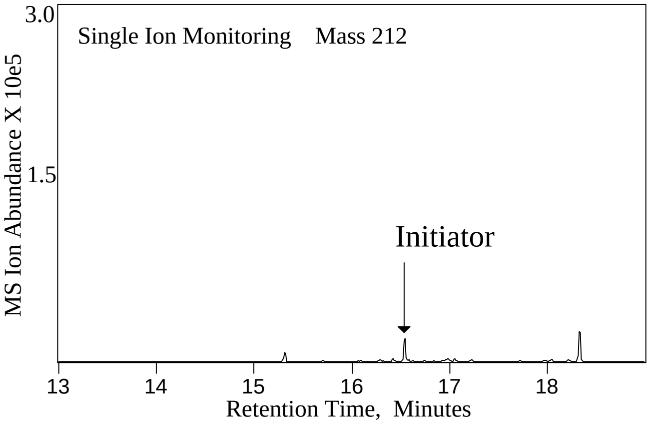

Figure 2b. GC/MS of Figure 1 with single ion monitoring of ion mass 212.

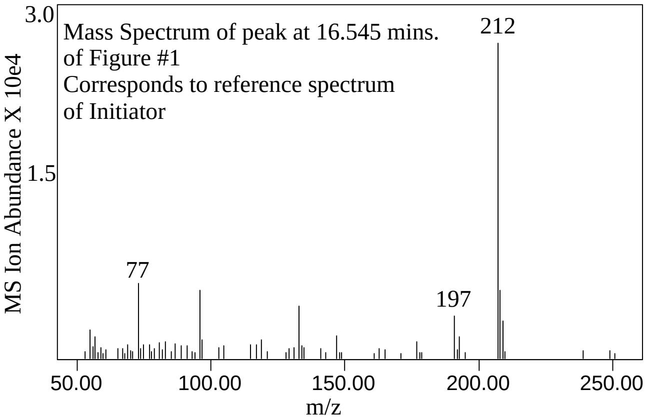

Figure 2a. Mass spectrum of GC peak to identify initiator.

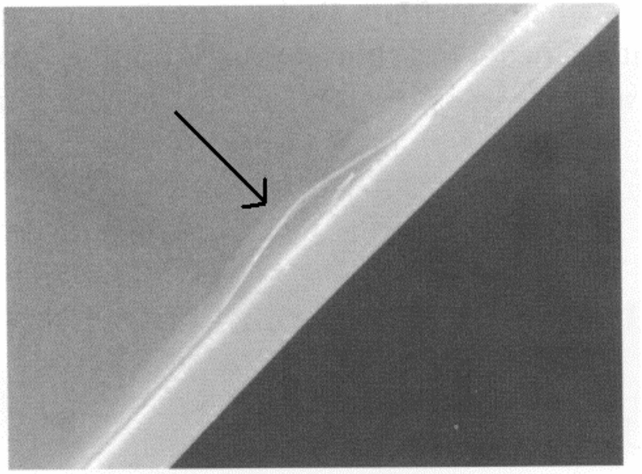

Figure 3. Polyethylene sheet delaminated at contaminant site (arrow) by punching to size (Ref. 1, p. 30).

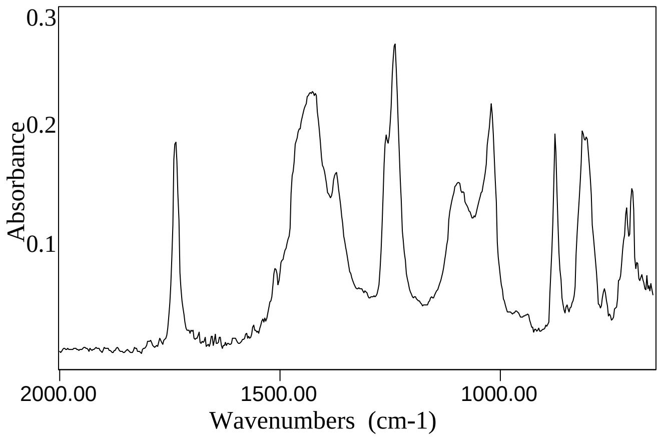

Figure 4. Infrared spectrum of surface to detect silicone oil.

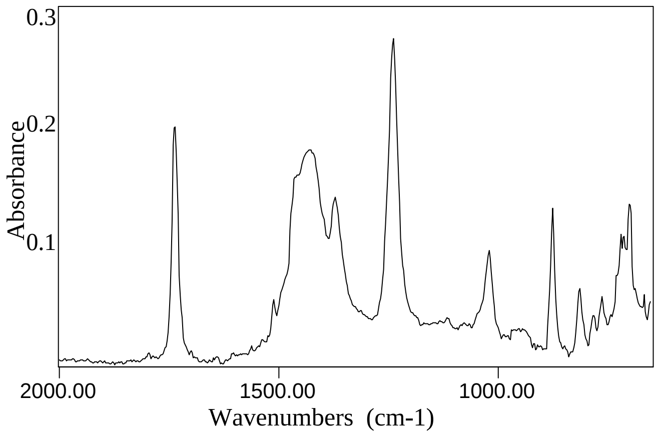

Figure 5. Infrared spectrum of normal surface without silicone oil.

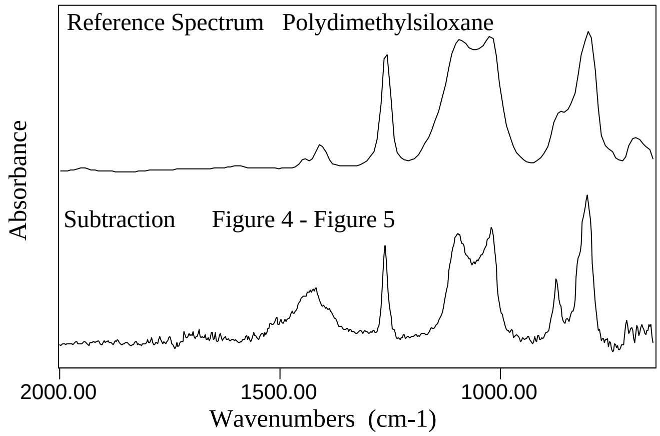

Figure 6. Subtraction of normal surface spectrum (Fig. 5) from suspect surface (Fig. 4) (lower curve); reference spectrum of silicone oil (upper curve).

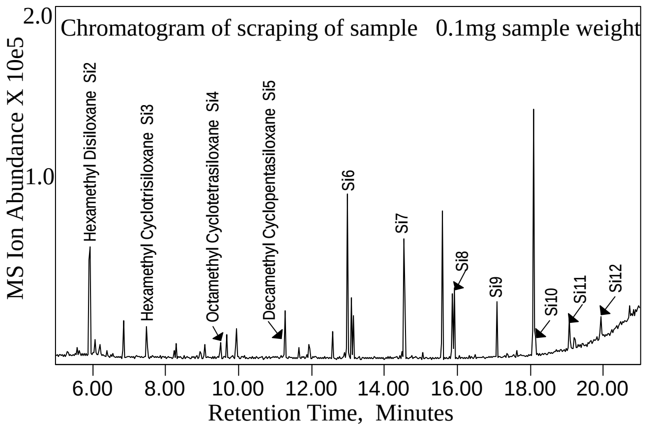

Figure 7. Thermal desorption GC/MS of scraping of suspect area to detect silicone oil.

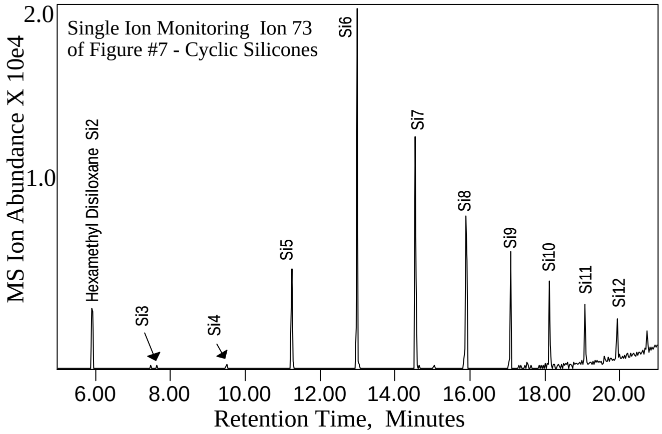

Figure 8. Single ion monitoring of ion mass 73 of Figure 7.

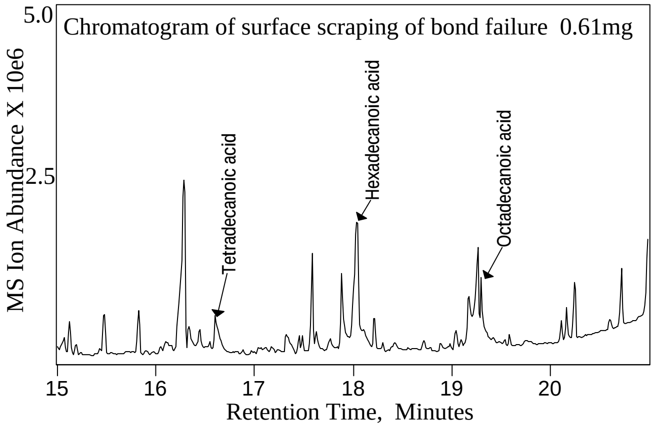

Figure 9. Thermal desorption GC/MS of surface scraping of fiberglass that would not bond to adhesive.

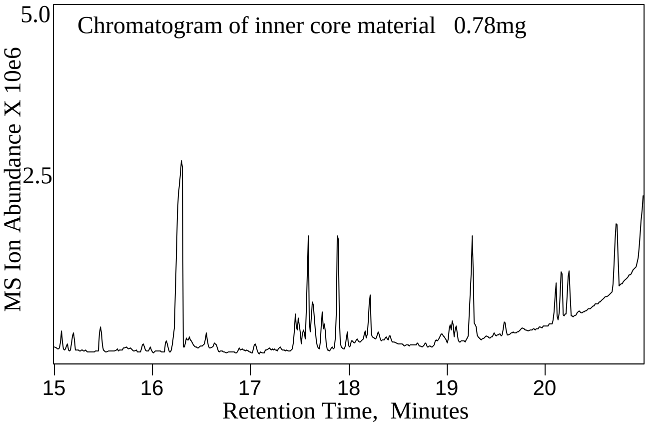

Figure 10. Same as Figure 9 for inner fiberglass material.

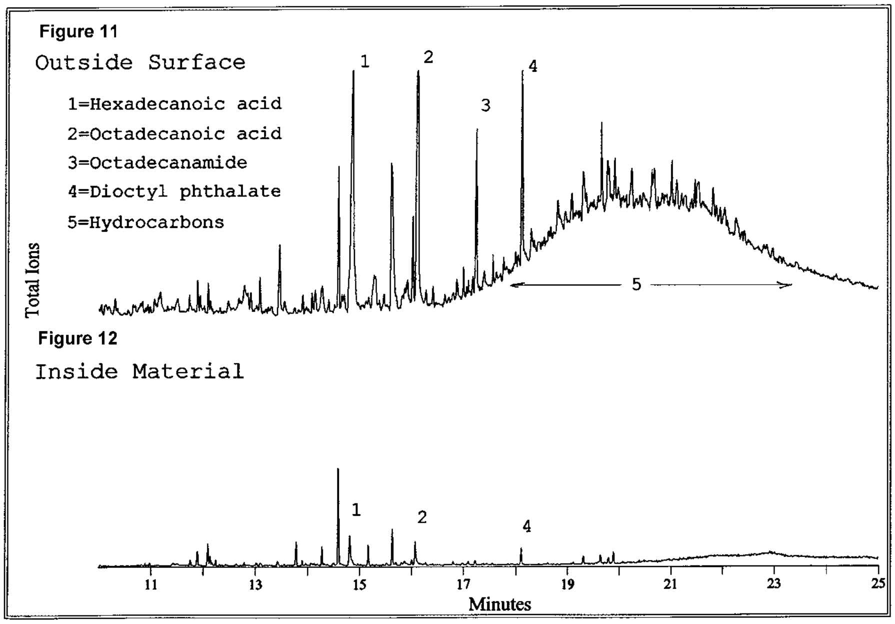

Figure 11. Thermal desorption GC/MS of surface of molded phenolic resin that would not bond to RTV silicone adhesive.
Figure 12. Same as Figure 11 for inner material below the surface.

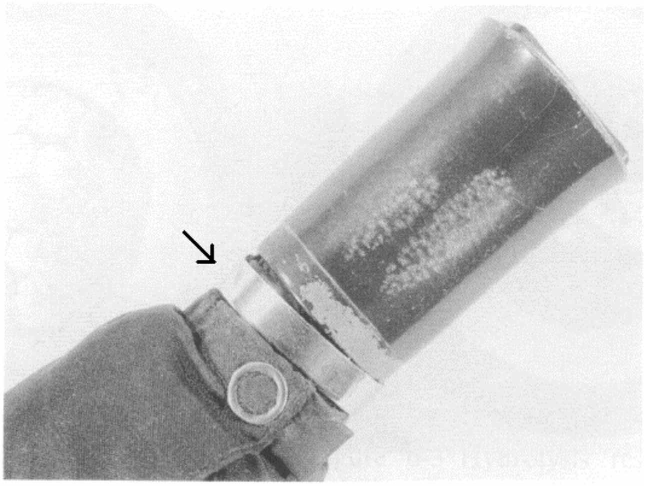

Figure 13. Debonded metal ring (arrow) on injection molded impact grade polystyrene umbrella handle that had been in service (Ref. 1, p. 164).