

CASE STUDIES OF ADHESIVE FAILURE OF BONDED PLASTICS

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1. Abstract

Failure of the adhesive bond between plastics and various materials is a common type of failure. Examples are given which illustrate compositional and environmental factors which affect adhesive bond strength of thermoplastic and thermosetting resins. These include additives within the plastic formulation, contaminants at the interface, moisture and water effects, and service temperature. Particularly in cases of migrating additives and of contaminants, thermal desorption gas chromatography/mass spectroscopy provides useful information by comparing the relative content at the surface and within the bulk of the material.

2. 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 "unintentional additive", 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.

3. 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)^{1,2} and infrared spectroscopy in general and micro FTIR (fourier transform infrared spectroscopy) in particular³. 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.

4.0 Categories and Examples of Adhesive Failure

4.1 Failures Due to Chemical Composition of Polymer Formulation Being Bonded

4.1.1 Intentional Additives⁴

(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 decals on to 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.

4.1.2 Unintentional Additives⁴

(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 cracking⁵.

(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.

4.2 Failure Due to Contaminants at the Interface Prior to Bonding

(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 1 and 2 are thermal desorption GC/MS chromatograms of a cured molded phenolic resin part that could not be bonded well to RTV silicone. Figure 1 is for surface scrapings, and Figure 2 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 1 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 Fig 2 for resin below the surface, indicating that the hydrocarbon is a contaminant deposited during storage or handling.

Fig 1 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 (Fig 2). 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 Fig. 2 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 Fig. 1 and 2 are as follows:

GC/MS - Hewlett/Packard 5890II/5971 A fitted with UCONN/IMS direct dynamic thermal desorption device^{1,2}.

Thermal desorption - 4'/300°C; cryofocus.

Sample weight - 0.02 mg (Fig 1); 0.04 mg (Fig 2).

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) 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 sites⁶.

(3) 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. (strippability) 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 (Fig. 3) and micro IR (Fig. 4) revealed the presence of a cellulosic film contaminant in the stearate. The spectrum is for the area in the circle on the contaminant in Fig. 3. 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.

(4) 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 deposit on parts being molded.

4.3 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 (Fig. 5). 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.

4.4 Failures Due to Environmental Effects in Service

(1) 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 cinder-block and loss of adhesion of a bonded baseboard.

(2) Water and moisture are common environmental agents that usually have a deleterious effect on bond strength. If a significant part of bond strength is due to weak physical (Van der Waals) forces between parts being bonded, water may displace them with bonds to water, effectively reducing bond strength. If instead of weak physical bonds, covalent bonds exist between materials being bonded, bond strength is less likely to be reduced significantly by water. An example of such a system is the copolymer of ethylene and vinyl mercapto propionate, analogous to ethylene and vinyl acetate except instead of acetate (COCH₃) the ester group is COCH₂CH₂SH. The SH mercapto group can react with many systems to form a covalent bond including steel and epoxy resin. As a primer, the mercapto ester forms a covalent bridge between parts being bonded. In addition, the flexible polymeric nature of the primer provides resistance to fracture under the influence of different coefficients of thermal expansion.

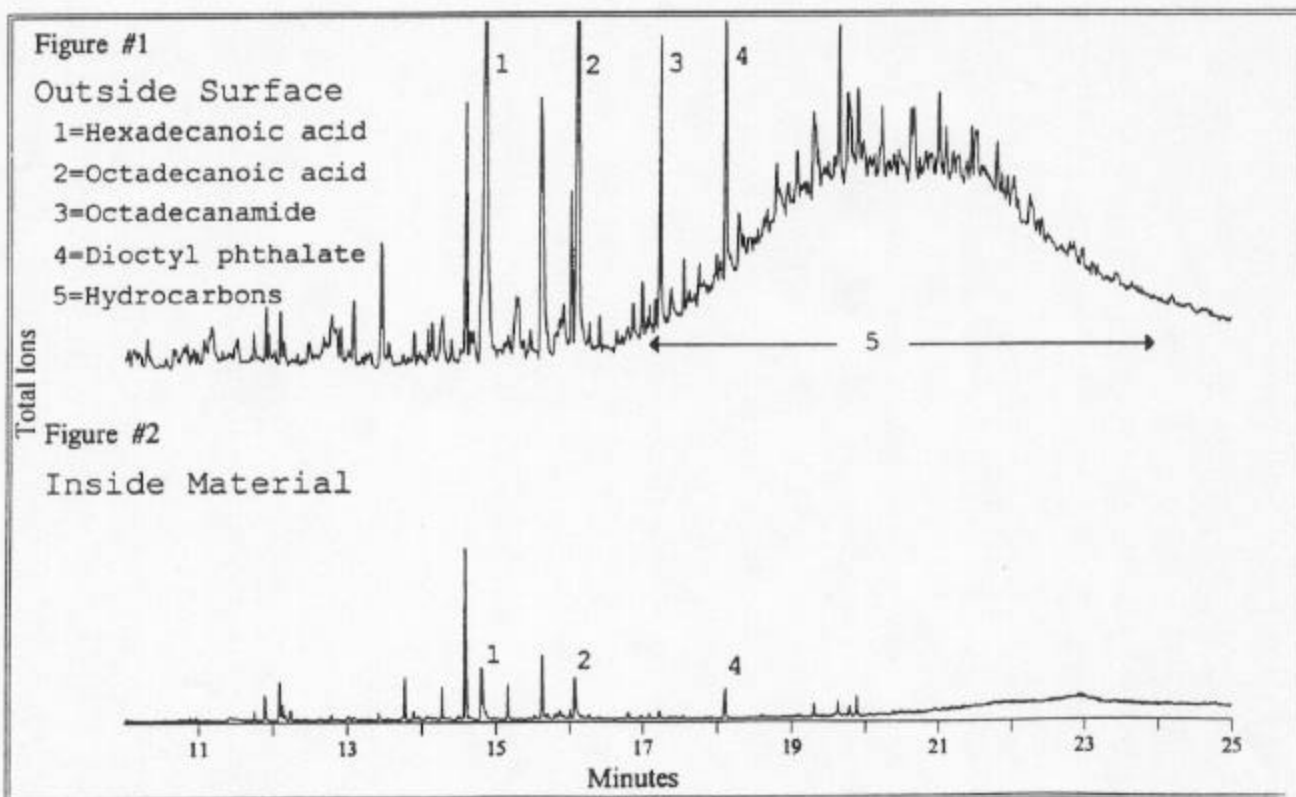
The ethylene mercaptoester copolymer is obtained by reaction of ethylene vinyl alcohol with an appropriate mercapto carboxylic acid.

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.

5. References

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Figures 1,2 - GC/MS chromatogram of outside surface (Fig. 1) and material below the surface (Fig. 2) of phenolic resin part that could not be bonded well to silicone RTV adhesive.