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Effects of Surface Treatment on Difficult to Bond Plastics

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Abstract

Difficult to bond plastics, such as polyolefins and fluoropolymers, are commonly used in various industries for some of the following reasons: the cost of the materials and their inherent chemical and thermal resistance. It can be challenging for manufacturers to find solutions to join these difficult to bond materials together. This paper will provide background information on difficult to bond materials, review techniques for quantifying the surface energy of a plastic, review the latest solutions for surface modification and introduce innovative adhesive solutions to meet the challenges of bonding these specific substrates.

Introduction

Difficult to bond materials, such as polyolefins, are commonly used in production, since they offer a variety of different benefits to manufacturers. These materials lead to issues when manufacturers need to join these plastics materials during production. This article will review some of the techniques that can be used in the assembly of these difficult to bond materials.

The first step will be to define what exactly is meant by a difficult to bond material. Difficult to bond materials are a classification of materials with low surface energy, smooth glossy surfaces, and poor wet out. These materials are commonly thermoplastics and/ or advanced engineering plastics.

The goal of this paper is to provide some techniques that can be used to improve the adhesion to these difficult to bond plastics. The techniques included are surface treatment modification techniques and innovative adhesive chemistries formulated to bond these materials

Definition of Hard to Bond Plastics

Hard to bond plastics are materials with low surface energies. The surfaces of these plastics are typically smooth and glossy. When a liquid is applied to the surface of a low surface energy plastic the adhesive beads up on the surface rather than forming a sheet of water. The effect of an adhesive forming a sheet of water on the surface is referred to as “wet out.” A surface with a low surface energy, such as a freshly waxed car, shows poor “wet out”, resulting in water beading up on the surface. Some examples of difficult to bond plastics are polyolefins, fluoropolymers, acetal homopolymers, and thermoplastic elastomers. Manufacturers select these plastics due to some of the benefits that they provide to the final assembly. These are typically inexpensive materials with a high toughness, high thermal resistance and superior chemical resistance.

As mentioned above, hard to bond plastics have a low surface energy. The surface energy of a plastic is measured by evaluating the contact angle of the plastic. Figure 1 shows the contact angle measurement for a low surface energy plastic on the left and a high surface energy plastic on the right.

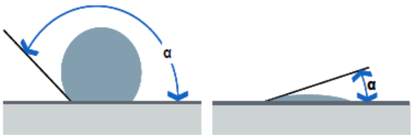

Figure 1. This picture represents the Contact angle of a low surface energy plastic on the left and a high surface energy plastic on the right.

A low surface energy plastic shown on the left side of Figure 1 has a larger contact angle with poor wet out of the surface and poor adhesion. A high surface energy plastic (shown on the right side of Figure 1) has a smaller contact angle, which allows the liquid to spread out more evenly over the surface of the plastic rather than beading up.
There are two main reasons for low surface energy on plastics. The two different causes can be poor cleanliness of the parts and/or low surface activation.

All surfaces have some level of contamination no matter how clean they appear to be. Some common sources of contamination are mold release from the molding process and contamination from operators handling the parts. Contamination prevents the adhesive from coming in contact with the part and decreases the strength of the bonded assembly. One common way to reduce the level of contamination is to clean the part surface with Isopropyl alcohol.

Low surface activation also leads to poor wet out and poor adhesion on parts. There are several techniques that are used to increase the surface activation of a plastic, making it easier to bond. These techniques will be reviewed in the next section.

Surface Modification Techniques

Plasma Treatment
Plasma treatment is used to modify a plastic surface by bombarding a surface with ions of gas. The gas selected for plasma treatment can vary; some of the commonly used gases are Argon, Helium, Nitrogen, or Oxygen. This treatment results in the introduction of amine, carboxyl, hydroxyl, and aldehyde groups on the surface of the plastic. These functional groups increase the surface activation and surface energy of the plastic. The increase in surface energy is shown in Table 1. The increase in surface energy leads to a comparable increase in adhesive wet out and consequently adhesive strength.

Table 1: Effect of Plasma treatment on Surface Energy in dynes/ cm2.
Courtesy of GaSonics International Plasma Corp.

Substrate	Initial Surface Energy	Surface Energy following Plasma
Polyproylene	29	> 73
Polyethylene	31	> 73
PTFE, FEP	22–37	72–73
Polycarbonate	46	> 73
Polysulfone	41	> 73
Silicone	24	> 73

Corona Treatment
Corona treatment exposes the plastic part to an electrical discharge in the presence of air. This process results in the introduction of carbonyl, hydroxyl, hydroperoxide, aldehyde, ether, ester, and carboxylic functionalities. This allows for improved adhesive strength on the surface of the part. This process also modifies the surface by introducing roughness on the surface of the part. This treatment is commonly used on polyolefin based materials. Corona treatment is commonly used on line in a production environment, as it is designed to be implemented in-line in manufacturing. (Henkel Bonding Guide)

Primer
A primer is a basic chemical species applied to a surface through a solvent carrier. Once applied, the solvent is to allow a certain amount of time for the solvent in the primer to flash off. After the solvent evaporates, the active species of the primer is then left behind on the surface. This active species is a multifunctional reactive group, one reactive site reacts with the surface and the second site reacts with the adhesive. The overall effect of the primer is to increase the strength of the bonded assemblies. Figure 2 shows the effect of primer on adhesive overall strength. (Henkel Bonding Guide)

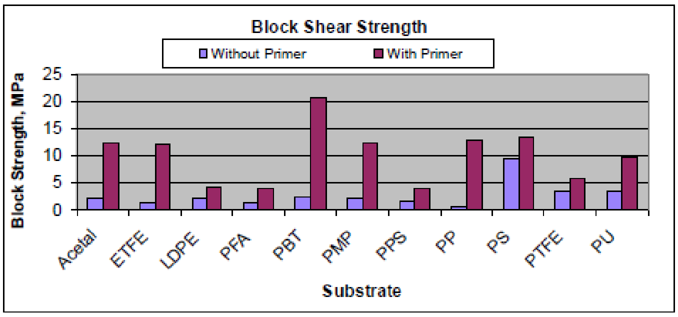

Figure 2: Effect of Cyanoacrylate primer on various substrates.

Flame Treatment
Flame treatment is accomplished by briefly exposing the surface of the parts to a flame. This treatment accomplishes an increase in surface energy by introducing hydroxyl, carbonyl, carboxyl, and amide functional groups. Flame treatment is most commonly used on polyolefin, polyacetal, and polyethylene terephthalate plastics. (Henkel Bonding Guide)

Experimental Procedure
A study was performed to explore the effects of blown ion plasma, variable chemistry plasma, flame treatment, and primer on polyethylene and polytetrafluoroethylene plastic substrates. The adhesives included in this evaluation were cyanoacrylate, epoxy, light cure acrylic, and urethane chemistry. In this study, the substrates were exposed to the designated surface treatment method and then bonded within 24 hours. The treated plastic lap shear substrates were bonded with a 1" overlap and the adhesive was allowed to fully cure. The assemblies were then pull tested in a shear mode to determine the adhesive shear strength with and without treatment and the effect of each treatment on the adhesive shear strength. A new structural acrylic adhesive formulated to bond low surface energy plastics was also tested without any surface treatment and compared to a standard epoxy and standard polyurethane adhesive (Table 4).

Materials

The two substrates tested in this evaluation are polyethylene and Polytetrafluoroethylene (PTFE). Both of these substrates are difficult to bond low surface energy plastics with very low activation.

Results and Discussion

Polytetrafluoroethylene

Table 2 shows the adhesive shear strength achieved with the blown ion plasma, the variable chemistry plasma, flame treatment and the cyanoacrylate primer. Of the treatments tested, the most effective surface treatment for bonding PTFE is the cyanoacrylate adhesive with the cyanoacrylate primer. The primer increases the adhesive strength from 0.19MPa in the control to 0.93MPa with primer.

Table 2: Effect of surface treatment on PTFE.

	Cyanoacrylate	Light Cure Acrylic	Epoxy	Urethane
Surface Treatment	Average Strength [MPa]	Average Strength [MPa]	Average Strength [MPa]	Average Strength [MPa]
Control	0.19	0.29	0.22	0.03
Blown Ion Plasma	0.04	0.29	0.25	0.09
Variable Chemistry Plasma	0.02	0.24	0.22	0.07
Flame Treatment	0.05	0.23	0.30	0.06
Cyanoacrylate Primer	0.93			

Polyethylene

Table 3 shows the effect of blown ion plasma, variable chemistry plasma, flame treatment and cyanoacrylate primer on polyethylene. All of the treatments are effective in increasing the adhesive shear strength of the polyethylene plastic. It is important to select the surface treatment that is most compatible with the adhesive being used, since certain surface treatments work better with certain adhesives. For example if a polyethylene assembly is being bonded with a cyanoacrylate, the best surface treatment is the cyanoacrylate primer. If an epoxy is being used on a different assembly, the blown ion plasma treatment is a better choice.

Table 3: Effect of surface treatment on Polyethylene

	Cyanoacrylate	Light Cure Acrylic	Epoxy	Urethane
Surface Treatment	Average Strength [MPa]	Average Strength [MPa]	Average Strength [MPa]	Average Strength [MPa]
Control	0.15	0.59	0.48	0.40
Blown Ion Plasma	1.5	2.2	4.3	2.8
Variable Chemistry Plasma	0.94	1.1	1.5	2.4
Flame Treatment	1.4	2.2	2.5	2.4
Cyanoacrylate Primer	2.9			

Henkel has developed a new structural adhesive formulation, Loctite 3035, that is developed specifically to improve adhesive strength to polyolefin substrates. The adhesive is formulated to get superior strength as compared to other adhesives without the use of primers or surface treatment to increase the surface energy of the plastic. Table 3 shows the improvement in adhesion to polyethylene as compared to an epoxy or urethane adhesive without any surface treatment on the plastic.

Table 4: Strength of new low surface energy adhesive compared to standard epoxy and standard urethane adhesive. All of the samples were bonded without any surface treatment.

	Polyethylene Adhesive Shear Strength
Loctite 3035 Low Surface Energy Adhesive	2.42 MPa
Epoxy Adhesive	0.48 MPa
Urethane Adhesive	0.40 MPa

Adhesive Solutions for Difficult to Bond Plastics

As shown in the previous section, surface treatments modify a plastic's surface to increase surface energy. This increase allows adhesives to wet out the surface more easily and improves adhesion. Innovative adhesive solutions are available to overcome the issues associated with difficult to bond plastics.

Cyanoacrylate adhesives are commonly used for difficult to bond materials, based on their compatibility with the primer systems. The cyanoacrylate adhesive with primer show very high bond strength to these materials and result in substrate failure of some plastics. Structural acrylic adhesives are also commonly used to bond some of the low surface energy plastics. Henkel Corporation has developed a new methacrylate adhesive specifically designed for polyolefin bonding.

Cyanoacrylates

Cyanoacrylate adhesives are one component adhesives that bond very well to a variety of different substrates including plastics. Cyanoacrylate adhesives are also known as instant adhesives, because they build strength very quickly when enclosed between two substrates. The chemistry behind the cyanoacrylates is an acid base chemical reaction. The cyanoacrylate adhesive is stabilized in the container prior to use by a weak acid. The moisture on the surface of a part is a weak base that reacts with the adhesive to overcome the acid stabilizer and allow the adhesive to start curing. The adhesive cures into a thermoplastic adhesive when the curing is complete. A thermoplastic adhesive is an adhesive that softens when it is exposed to very high temperatures. Some of the most important processing benefits of the cyanoacrylates are that they are single component materials that do not require any mixing and that they cure under ambient conditions without the need for any external energy source. One of the most important performance benefits of the cyanoacrylate is the ability to bond low surface energy plastics through the use of a cyanoacrylate primer, as shown in Figure 2.

Cyanoacrylate adhesives are used in a wide variety of different bonding applications, such as medical devices, appliances, and sports equipment.

Structural Acrylics

Structural acrylics are adhesives that show very high shear strength and impact strength values. These adhesives are two component materials that require static mixing to cure. The curing reaction takes place via a free radical polymerization, which forms a crosslinked thermoset acrylate adhesive. The adhesive and the activator need to be mixed in the correct ratio in order to develop the high strength properties of the adhesive. The typical ratios of structural acrylic adhesives are 1:1 and 10:1 (adhesive: activator). As mentioned above, these adhesives have very high shear, impact and peel strength. The high strength is due in part to the level of rubber modifiers built into the adhesive's network. These materials are designed for bonding a variety of different substrates including metals, plastics, and composite materials.

Structural adhesives are used in applications that require a large impact resistance or toughness. Some examples of typical applications are truck panels, hand held devices, wind blades and appliances.

Conclusions

Hard to bond plastics are very popular due to the benefits they provide to manufacturing, such as improved heat and chemical resistance. The difficult to bond materials are also typically less expensive, which drop the overall cost of the assemblies being produced.

One technique to improve the overall adhesion of difficult to bond materials is to select a surface treatment process that can increase the surface energy of the plastic prior to applying the adhesive. There are a variety of different surface treatments available, including plasma treatment, corona treatment, flame treatment and application of a primer. The surface treatment should be selected based on the substrate being testing, the adhesive selected for the application and the ability to implement the process into manufacturing.

There are also various adhesive options available for bonding difficult to bond plastics, such as polyolefin substrates. Cyanoacrylate adhesives and structural acrylic adhesives are the two most commonly used adhesives to bond low surface energy plastics.

References

1. Henkel Plastic Bonding Guide, Volume 6, 2011.

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