

ADHESIVES FOR THE ASSEMBLY OF HARD-TO-BOND PLASTICS

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Abstract

Many modern plastics used in a variety of industries are formulated specifically for their resistance to harsh chemical and environmental conditions. As a result, these substrates also tend to be difficult to chemically bond. Bonding, however, remains the preferred joining method particularly when dissimilar substrates are involved and/or solvent welding or mechanical fastening is not desired. Polyolefin plastics are the most common type of hard to bond plastics because of their low surface energy. Examples of polyolefin plastics are polypropylene and polyethylene.

Fortunately, advances in adhesive chemistries and surface preparation techniques have given us the tools we need to achieve strong bonds to even the most difficult to bond polymer substrates. Topics covered will include identification of “difficult to bond” plastics, chemical surface treatments, mechanical surface treatments, and adhesive selection guidelines.

Defining Hard-to-Bond Substrates

Thermoset plastics are resins that cannot be melted or reformed once polymerized, and include polyester, phenolic and epoxy resins. Thermoplastics are resins that can be reflowed under heat following final processing, and include Acrylonitrile Butadiene Styrene (ABS), polyamide (nylon), polycarbonate, and polyolefins such as polyethylene and polypropylene.

Characterized by either linear or branched carbon chain polymers, low surface energies, low porosity, and non-polar or non-functional surfaces, hard-to-bond substrates feature no functional sites or surface roughness onto which an adhesive can secure itself.

Low Density Polyethylene (LDPE) is a semi-crystalline thermoplastic produced via a free-radical polymerization reaction. Although LDPE typically has lower strength and hardness properties, it offers numerous benefits including flexibility, clarity and enhanced impact and stress cracking resistance.

High Density Polyethylene (HDPE) is similar to LDPE in the polymerization process used to obtain the resin. However, the density of the polyethylene increases,

resulting in higher strengths, increased hardness, and enhanced chemical and abrasion resistance. Common uses for polyethylenes include packaging containers for food, chemicals, and automotive fluids; films used for shrink wrapping, packaging and drum lining; and various other medical device, electrical component, and appliance applications.

Polypropylene (PP) is a crystalline thermoplastic known for its excellent thermal and chemical resistance properties. In addition to high moisture resistance, PPs are often selected for their good mechanical properties. The primary disadvantage of PP is its low-temperature impact resistance, a property directly related to the polymer's degree of crystallinity. Like polyethylenes, PP is commonly used in the packaging, appliance, medical, electrical and fiber industries.

Fluoropolymers such as Teflon[®] are highly crystalline thermoplastics produced using a free radical polymerization reaction. Fluoropolymers are characterized by superior thermal and chemical resistance, low coefficients of friction, excellent weatherability and low flammability. With typical service temperatures of approximately 500°F, fluoropolymers work well in high temperature applications in the electrical, mechanical, chemical, home appliance and packaging industries. The high per pound cost of some grades of fluoropolymers is a potential drawback of these substrates over other thermoplastics.

Acetal Homopolymer (acetal) resins are thermoplastics that are produced through a polymerization reaction involving formaldehyde. Typical characteristics of acetals include excellent impact strength, good dielectric properties, low permeability and moderate temperature resistance (~ 221°F). Many grades of acetal homopolymers are UL94HB rated. Primary disadvantages of acetals include UV degradation and poor resistance to strong acids. Because of their enhanced wear resistance, acetals are often used in automotive components, industrial machines, plumbing, electronics and various other consumer items.

Classified as thermoplastic elastomers, thermoplastic vulcanizates (TPVs) are sometimes considered hard-to-bond plastics. Formed by combining polypropylene with a vulcanized rubber, TPVs offer excellent thermal, weathering, and chemical resistance. Because of their inherent flexibility, TPVs exhibit excellent flexural resistance, abrasion

resistance and tensile strength properties. These materials are used in a wide variety of industries including automotive, construction, electrical and medical.

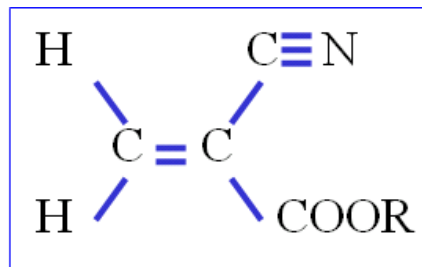
Surface Energy of Multiple Surfaces	
SURFACE	SURFACE ENERGY (Dynes /cm)
Copper	1,103
Aluminum	840
Glass	250 to 500
High Surface Energy	
Kapton	50
ABS	42
Polycarbonate	42
Low Surface Energy	
Polyethylene	31
Polypropylene	29
Teflon	18

Surface Energy of Various Materials

Adhesives for Hard-To-Bond Plastics

Hard-to-bond plastics are most often assembled using adhesives¹. While adhesives are the most versatile assembly method for plastics, capable of joining thirty-six types of plastics, only a few industrial adhesives offer consistently high bond strengths on hard-to-bond plastics. Cyanoacrylate, light curing cyanoacrylate, hot melt and occasionally light curing acrylic adhesives have exhibited high bond strengths on typical difficult to bond substrates including PE, PP, acetal, fluoropolymers and TPVs. A new breed of acrylic adhesive is also designed for use with hard-to-bond plastics.

Cyanoacrylate adhesives are polar, linear molecules that undergo an anionic polymerization reaction. A weak base, such as moisture, triggers the reaction causing the linear chains to form. The products are maintained in their liquid form through the addition of weak acids that act as stabilizers. A wide variety of cyanoacrylate formulations are available with varying viscosities, cure times, strength properties and temperature resistance.



The Cyanoacrylate Monomer

Cyanoacrylates form thermoplastic resins when cured. Standard unfilled ethyl monomer based cyanoacrylates typically exhibit low impact and peel strengths, low to moderate solvent resistance, and maximum operating temperatures of 160 – 180°F. They will fixture in as little as three seconds.

Rubber modified cyanoacrylate formulations offer greatly improved peel and impact strengths over standard cyanoacrylates. The compounded rubber added to ethyl formulations does slightly increase fixture time to 30 seconds to two minutes.

“Blooming” or “frosting” is the presence of a white haze around a bondline. A selection of cyanoacrylate adhesives offer monomers with a higher molecular weight and lower vapor pressure, which minimizes blooming/frosting. The change in monomer can affect the adhesive’s cure speed, physical properties, and operating temperatures.

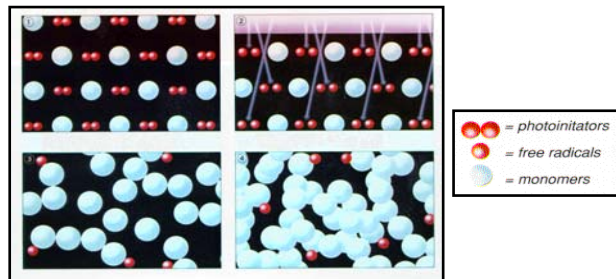


Blooming on Steel Specimens

Thermally resistant ethyl cyanoacrylates can withstand continuous exposure to test temperatures up to 250°F. Available in both black and clear versions, these modified toughened cyanoacrylate products also have increased fixture times.

Although light curing acrylics do not offer the significant performance strength of cyanoacrylates on hard-to-bond substrates, they do offer moderate performance on several of the cited plastics including acetal and polyethylene (Table 1).

Light curing acrylics cure via a free radical reaction to form thermoset resins when exposed to light of the appropriate wavelength and intensity. Like cyanoacrylates, light curing acrylic adhesives are available in a wide range of viscosities from low (~ 50 cP) to thixotropic gels. In addition, light curing adhesives vary in final cured form from hard and glass-like to soft and flexible resins.



The Light Cure Polymerization Reaction

With these adhesives, light must reach the entire bondline in order to achieve full cure. Any adhesive remaining in shadowed areas will remain liquid. Light curing acrylics fixture rapidly and cure in as little as 5 seconds following light exposure. Because the final resins are thermoset plastics, light curing acrylics offer enhanced thermal, chemical and environmental resistance over Cyanoacrylate adhesives. Table 1 shows typical bond strengths on hard-to-bond substrates using a standard ultraviolet and/or visible curing adhesive.

LIGHT CURING ACRYLIC BLOCK SHEAR STRENGTH (in PSI per ASTM 4501)	
SUBSTRATE	LIGHT CURING ACRYLIC
Acetal	250
Fluoropolymer	150
Polyethylene	350
Polypropylene	100
TPV	120

(from *The Loctite Design Guide for Bonding Plastics*)

Table 1: Typical Bond Strengths of Light Curing Adhesives

Light curing cyanoacrylates are ethyl based products that have photoinitiators added to the formulation, allowing them to fixture rapidly on exposure to low intensity light, and to cure in shadowed areas. Physical performance characteristics of these adhesives are similar to those of traditional cyanoacrylates. Light cure cyanoacrylates minimize blooming/frosting since exposed uncured cyanoacrylate can be immediately cured using ultraviolet and/or visible light. While traditional cyanoacrylate cure to a maximum of 0.010 inches, cure depths in excess of 0.5” have been achieved with light curing cyanoacrylates. These adhesives are compatible with primers for hard-to-bond plastics. The bond performance of light curing cyanoacrylates on difficult to bond substrates is similar to that of traditional ethyl cyanoacrylates.



Cure through Depth of Light Curing Cyanoacrylates

Polyolefin hot melts provide good resistance to moisture as well as excellent resistance to polar solvents, acids, bases, and alcohols. The polyolefin family of hot melts offers superior adhesion to polypropylene when compared to the other types of hot melts.



Hot Melt Adhesives in Various Solid Form

Reactive urethane hot melts perform well on hard-to-bond plastics. Whereas most traditional hot melts are thermoplastic resins that can be repeatedly reheated, reactive urethanes form thermoset plastics when fully processed. Although initial strength develops a bit slower than traditional thermoplastic hot melts, fully cured reactive urethanes are superior performers. In addition to offering good bond strengths to difficult to bond materials, reactive urethanes process at temperatures of approximately 250°F, as much as 200°F cooler than EVA, polyamide, and polyolefin hot melts.

HOT MELT BLOCK SHEAR STRENGTH (in PSI per ASTM 4501)		
SUBSTRATE	POLYOLEFIN HOT MELT	REACTIVE URETHANE HOT MELT
Acetal	609	344
Low Density Polyethylene	161	189
High Density Polyethylene	298	197
Polypropylene	163	373

Hot Melt Adhesive Performance on Select Hard-to-Bond Plastics

A new two-part acrylic-based adhesive offers superior performance on materials such as polyethylene and polypropylene. The two-part acrylic offers tenacious bond strength without surface preparation, creating not only mechanical but also chemical attachment to mated surfaces. In addition to its performance on hard-to-bond plastics, the acrylic adhesive provides in excess of 1000 PSI on many traditional metal and plastic materials including polycarbonate, PVC, steel and aluminum.

Surface Preparation Methods

In order to enhance adhesion, materials designated as hard-to-bond require surface preparation prior to joining. Surface preparation methods for hard-to-bond plastics include both chemical and physical treatments designed to increase reactivity and roughness on the surface of the substrate. Common methods include plasma or corona treatment, flame treatment, chemical etching or surface priming.

Plasma treatment is used on a wide variety of substrates including polyolefins and polyester. A gas such as oxygen, argon, helium, or air is excited at low pressure, resulting in the production of free radicals. The ions generated bombard the substrate surface and form reactive groups that increase surface reactivity and wettability.

One of the major drawbacks with plasma treatment is its potentially short shelf life. Most substrates treated with plasma must be assembled within a very short period of time since the reactive surface is re-exposed to air and rapidly reverts back to its normal state.

Plasma treatment is frequently used with cyanoacrylate, light curing acrylic, and light curing cyanoacrylate adhesive technologies. Since each plasma gas imparts different characteristics onto a substrate, end-users should consult their adhesive and substrate suppliers to determine the optimum gas for the materials used.

Similar to plasma treatment, corona discharge uses ionization of a gas to effect surface reactivity and roughness. Reactive groups such as carbonyls, hydroxyls, hydroperoxides, aldehydes, ethers or esters are introduced to the surface. Corona discharge has a limited shelf life and requires parts to be assembled in a limited time period. Corona discharge is commonly used on polyolefin substrates. Both plasma and corona treatment require an investment in capital equipment or outsourcing of treatment.

Like plasma exposure, corona treatment is most frequently used on polyolefin substrates bonded with cyanoacrylate or light curing acrylic adhesives. The treatment generates reactive groups that serve as potential bonding sites for the adhesive, and result in a significant enhancement of bond strength.

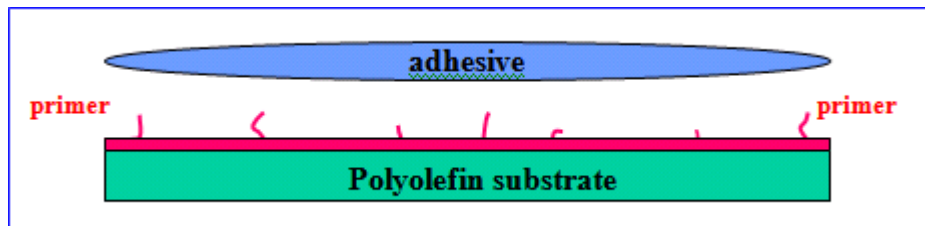
Chemical treatment methods such as chromic acid etching are often used on polyolefins and acetals. Like other surface treatment methods, chromic acid etching adds reactive species to a surface. Because it can be hazardous, chemical treatment is used on a limited basis to treat a variety of substrates prior to bonding with cyanoacrylate and light curing acrylic adhesives.

Handling and storage of hazardous substances is one potential drawback of chemical treatments. Surface changes are controlled by two variables: the solvent selected and the overall exposure time.

In flame treatment, various reactive groups such as hydroxyls, carbonyls and carboxyls are introduced to bonding surfaces through an oxidation reaction when the substrate is exposed to flame. In addition, flame treatment lowers the surface energy of the substrate surface, allowing for better wetting. Flame treatment is commonly used on polyolefins and polyacetals, and is most frequently used when bonding with cyanoacrylate adhesives.

Surface roughening results in mechanical interlocking sites and causes bond strength to increase dramatically. A surface roughness of approximately 63-125 micro-inches is often used as a guideline for assemblies that are to be bonded with adhesives. Surface roughening will significantly increase the bond strength of most adhesive technologies, and is highly recommended for both hard-to-bond and traditional substrates.

Primers are solvent-based systems in which a reactive species is dissolved. Applied to a surface using a brush or spray, the primer's solvent evaporates, leaving behind the reactive species on the substrate. The reactive species acts as a linking pin or bridge between an adhesive and the substrate.



A Cyanoacrylate Primer acts as a Bridge or Link between the Adhesive and the Substrate

A variety of substrates exhibit enhanced bond strengths following treatment with primers, including polyolefins, acetals, fluoropolymers and TPVs. Although using a surface primer is often viewed as a two step bonding process, primers can be applied with little to no capital expenditure and many remain active on substrates for more than eight hours.

Polyolefin primers are frequently used on hard-to-bond substrates joined with traditional and/or light curing cyanoacrylate technologies. Introducing the active species to the substrate surface generally increases bond strength three-fold for traditional ethyl cyanoacrylate adhesives.

CYANOACRYLATE BLOCK SHEAR STRENGTH			
(in PSI per ASTM 4501)			
SUBSTRATE	ETHYL CA W/O PRIMER	TOUGHENED ETHYL CA W/O PRIMER	ETHYL CA WITH PRIMER
Acetal	200	100	1700
Fluoropolymer	350	200	1050
Polyethylene	150	<50	500
Polypropylene	50	50	>1950
TPV	80	20	220

(from The Loctite Design Guide for Bonding Plastics)

A Comparison of Cyanoacrylate Performance on Select Hard-to-Bond Plastics with and without Primer

Mechanical Fasteners	Solvent Welding	Ultrasonic Welding	Vibration Welding	Heated Tool Welding	Adhesive Assembly
<p>Benefits:</p> <ul style="list-style-type: none"> ◆ Ease of use ◆ Full strength immediately ◆ Removable <p>Limitations:</p> <ul style="list-style-type: none"> ● Stress concentrator ● No seal ● Large # of parts ● Difficult to automate 	<p>Benefits:</p> <ul style="list-style-type: none"> ◆ Low cost ◆ Simple ◆ Fast <p>Limitations:</p> <ul style="list-style-type: none"> ● Not usable on thermosets ● Can cause stress cracking ● Health & safety issues ● Poor gap filling 	<p>Benefits:</p> <ul style="list-style-type: none"> ◆ Easily automated ◆ Simple ◆ Fast <p>Limitations:</p> <ul style="list-style-type: none"> ● Not usable on thermosets ● Plastics must be compatible ● Poor gap filling ● Capital cost ● Must remove or hide weld flash 	<p>Benefits:</p> <ul style="list-style-type: none"> ◆ Simple ◆ Fast ◆ Surface prep not required <p>Limitations:</p> <ul style="list-style-type: none"> ● Not usable on thermosets ● Plastics must be rigid/flat ● Capital cost ● Must remove or hide weld flash 	<p>Benefits:</p> <ul style="list-style-type: none"> ◆ Easily automated ◆ Simple ◆ Fast <p>Limitations:</p> <ul style="list-style-type: none"> ● Not usable on thermosets ● Surfaces must be clean/flat ● Capital cost ● Must remove or hide weld flash 	<p>Benefits:</p> <ul style="list-style-type: none"> ◆ Join dissimilar materials ◆ Even stress distribution ◆ Fill large gaps ◆ Seal and bond ◆ Easily automated ◆ Aesthetically acceptable <p>Limitations:</p> <ul style="list-style-type: none"> ● Requires cure ● Requires fixture time ● Can be messy ● Chemical in plant

Comparison of “Hard-to-Bond” Plastic Assembly Methods

Footnotes & References:

¹*“Engineer’s Guide to Plastics” published by Materials Engineering*

The Loctite Design Guide for Bonding Plastics, Volume 2, LT-2197A

The Loctite Design Guide for Bonding Rubber and Thermoplastic Elastomers, Volume 1, LT-2662

Handbook of Plastics Joining, A Practical Guide, copyright 1997 by Plastics Design Library, published by Plastics Design Library, Norwich, NY

<http://machinedesign.com/article/bonding-low-surface-energy-plastics-0615>