

Adhesion to Plastic

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Abstract

A plastic can be described as a mixture of polymer or polymers, plasticizers, fillers, pigments, and additives which under temperature and pressure can be molded into various items¹. Plastic materials have become a staple of our everyday life in applications ranging from food packaging to home construction. In automotive applications alone, over four billion pounds² of plastic were used in cars and light trucks and that figure is expected to grow 30 percent by 2011. The demand for plastic is growing at a rate faster than metal because of advantages such as reduced weight, reduced material cost, corrosion resistance and increased durability over metal. As the demand for plastic increases, the need to effectively and efficiently coat plastic parts will also increase. For most plastics, that will mean starting with a good primer coating. This paper will present three new ultraviolet (UV) curable resins that may be used to formulate primers for a variety of plastic substrates.

Introduction

Once a plastic part is formed, a coating is usually applied for decorative or protective purposes. Typically, that starts with a primer coating. There are many factors that positively affect the adhesion of the primer to the substrate, and several will be discussed here. One of the more important properties in achieving adhesion is the ability of the coating to wet the substrate³. In order for wetting to occur, the surface tension of the coating must be less than the surface energy of the substrate. Plastics are often comprised of long chain non-polar materials, with inherently low surface energies. Achieving adhesion to plastics that have a surface tension of 32 dynes/cm or lower can be problematic since most coatings have surface tensions in this range as well. The general literature suggests the plastic part needs to have a surface energy 8-10 dynes/cm greater than the liquid to obtain optimal adhesion³. In addition, surface energy can vary across a plastic due to the plastic being a blend of polymers. A successful primer coating allows for good wetting of the substrate regardless of that substrate's surface energy or uniformity of that surface energy. Table I lists surface energies for some commonly used plastics:

Table I.⁴

Plastic	Surface Energy dynes/cm	Plastic	Surface Energy dynes/cm
Polypropylene	29-31	Polyethylene	30-31
ABS	35-42	Polyester	41-44
PET	41-44	Polycarbonate	46
Polystyrene	38	Nylon	33-46
PBT	32	Rigid PVC	39
Plasticized PVC	33-38	Polyphenylene oxide (PPO)	47

Wetting is not the only factor to consider when trying to achieve good adhesion. The morphology/structure of the plastic also influences adhesion. If the structure of the plastic is amorphous, the molecules at the surface tend to be loosely packed; in a semi-crystalline configuration, the molecules at the surface tend to be more tightly packed. Amorphous materials are generally easier to adhere to than substrates with moderate or high degrees of crystallinity. This is observed in a semi-crystalline form of PET. PET has a surface energy between 41-44 dynes/cm, but achieving adhesion is difficult. The reason is because of its high degree of crystalline structure. Due to the surface being tightly packed, forming any type of mechanical bonding is difficult. Figures 1 and 2 show a more detailed view of an amorphous structured plastic versus a semi-crystalline structure at room temperature:



Figure 1: Amorphous



Figure 2: Semi-crystalline

The temperature of a plastic part also can influence the ability to achieve good adhesion. Applying heat before coating a plastic part can soften the surface and increase surface energy thus making the part easier to coat. The softer surface may also allow for some penetration of the coating into the substrate, creating greater adhesion through physical entanglement of the coating and substrate polymers. A few plastic substrates are exceptions to this phenomenon and the adhesion of a coating may actually be adversely affected by heating. Heating these plastics prior to coating may cause a drop in surface tension thus making the plastic harder to coat and exposure to heat after coating may cause a post adhesion loss of adhesion. Table II lists several plastics that exhibit a drop in surface tension upon heat exposure:

Table II.

Plastic	Surface Tension dyne/cm at 20°C	Surface Tension dyne/cm at 140°C
Polyethylene ⁵	35.7	28.8
Polycarbonate ⁶	42.9	35.1
Polystyrene ⁷	40.7	32.1

Upon cure, most reactive coating systems, including UV coatings, undergo volumetric shrinkage. This volumetric shrinkage can cause a loss of adhesion. Because UV systems mainly adhere to substrates through mechanical bonding, a volumetric shrinkage can increase the internal stresses in a coating, leading to loss of adhesion. Table III list some common shrinkage values for UV materials:

Table III.

Reactive Diluents	Shrinkage, %	Oligomers Type	Shrinkage, %
Isobornyl acrylate (IBOA)	5.2%	Acrylate Bisphenol A epoxy	10.8%
Octadecyl acrylate (ODA)	8.3%	Di-functional urethane acrylate	1.0-5.0%
Ethoxylated bisphenol A acrylate	7.1%	Hexa-functional urethane acrylate	9.0-10%

Neopentyl glycol diacrylate (NPGDA)	9.0%	Multi-functional amine modified polyester acrylate	4.0-6.0%
Hexane Diol Diacrylate (HDODA)	19%	Tetra-functional polyester	6.0-14.0%
Trimethylolpropane triacrylate (TMPTA-N)	25.1%	Modified acrylated Bisphenol A epoxy	2.0-8.0%

The most commonly used method for increasing adhesion to plastic is surface preparation/treatment. Surface treatments can be used to activate the surface of the substrate to increase its surface energy. This will allow for improved wetting of the surface by the primer coating. Surface preparation can be anything from plasma treatment to functionalizing the surface or corona treating the surface all of which increase surface tension. For example, if a charge is passed (corona treatment) over polypropylene, the surface energy increases from 29-31 dynes/cm to over 40 dynes/cm. These procedures involve an extra step for the manufacturer that could be eliminated with the proper primer.

Most UV curable formulations contain reactive diluents or materials that may interact with the surface of the plastic and provide some adhesion benefits. Some of the reactive diluents listed in Table III can be used to improve mechanical adhesion through etching or swelling of the plastic substrate.

An etched surface provides more sites for mechanical adhesion while swelling the surface can increase adhesion through greater commingling of the substrate and coating resins, even to the point of forming an interpenetrating network. However, swelling or etching can have an adverse effect on some plastics. This technique can cause haze and other visual distortions (“rainbow effect”) upon cure in a number of plastics such as polycarbonate. Materials that have primary or secondary hydroxyls or other secondary functionality can react with the surface or materials and produce chemical bonding which can be stronger than mechanical bonding.

This paper will present three acrylic resins that demonstrate good adhesion to a variety of plastic substrates without the need to resort to surface treatments or the use of attacking diluents.

Experimental Procedures

The experimental acrylic resins are proprietary in nature and were prepared in our laboratories. The three commercial blends used for comparative purposes are made from commercially available materials and used as received. Each of the resins was formulated into a primer by adding four percent, by total weight of solids, of 1-hydroxy-cyclohexylphenyl ketone photoinitiator. The viscosity of the proprietary acrylics was adjusted through the addition of a solvent, Aromatic 100.

Each formulation was applied to the plastic substrate by drawing it down using a wire wound bar to achieve a cured film thickness between 7.5-8.0 microns. The plastic substrate was not solvent wiped

or prepared in any other way prior to application of the primer. The solvent was flashed off at 60°C with a dwell time of five minutes before cure.

Also, each formulation was cured by exposure to a 600 WPI medium pressure mercury lamp with each formulation receiving an energy density of 950 mJ/cm². Crosshatch adhesion was measured as in ASTM D 3359 using 3M's 898 tape and assigned a rating (0B – 5B, 5B is best) as described in the ASTM method. Post adhesion was measured after 240 hours of exposure at 80°C and 70% humidity, and was rated using the same method as for the original adhesion ratings. Recoatability was determined by applying a 25 micron (cured or dried thickness) coating applied to each acrylic primer coating and testing for adhesion using the above method.

All viscosities were measured on a Brookfield brand viscometer at the temperature reported in Table IV. Surface tensions were determined using Kruess' Processor Tensiometer K12. Shrinkage was determined by comparing the densities of the liquid and solid (cured) formulations. Surface energies of the cured films were estimated using dyne pens.

Results and Discussion

The three experimental acrylic resins are proprietary acrylate functional acrylic oligomers. Blends 1-3 are mixtures of commercially available materials. Blend 1 is comprised of a hexafunctional acrylated urethane, an acrylated acrylic, and a monofunctional monomer; Blend 2 contains an acrylated acrylic; and Blend 3 is an acrylated acrylic in an acrylate modified phenoxy resin. The properties of the resins used in this work are listed in Table IV.

Table IV.

	Viscosity centipoise (T)	Surface Tension dynes/cm	Shrinkage, %
Acrylic 1 – 100% solid, low viscosity acrylated acrylic	900 (25°C)	36.13	5%
Acrylic 2 – 100% solid, low viscosity acrylate acrylic	5800 (60°C)	35.00	8%
Acrylic 3 – 55% solids, acrylated acrylic diluted in Aromatic 100	350 cP (25°C)	33.50	10%
Commercial Blend 1	1000 (25°C)	44.00	8%
Commercial Blend 2	15000 (25°C)	35.00	5%
Commercial Blend 3	2000 (25°C)	40.00	5%

Table V.

Substrate	Acrylic 1	Acrylic 2	Acrylic 3	Commercial Blend 1	Commercial Blend 2	Commercial Blend 3
Polypropylene	5B	5B	5B	5B	5B	5B
Thermoplastic (TPO)	0B	5B	5B	0B	0B	0B
Valox*	5B	5B	5B	0B	0B	0B
Noryl GTX 907*	5B	5B	5B	3B	0B	5B
Acrylonitrile Butadiene Styrene (ABS)	5B	5B	5B	0B	0B	0B
Polycarbonate	5B	5B	5B	5B	5B	5B
High Density Polyethylene (sheet)	5B	5B	5B	0B	0B	0B
Sheet Molded Compound (SMC)	5B	5B	5B	0B	0B	3B
Bulk Molded Compound (BMC)	4B	5B	5B	0B	0B	0B
PET	5B	5B	5B	0B	0B	0B
PVC	5B	5B	5B	0B	0B	0B
Xenoy*	5B	5B	5B	0B	5B	0B

0B=no adhesion 5B=100% adhesion

*Registered trademarks of the General Electric Company

Upon cure, the coatings were all tack free, clear, and with high gloss. With the exception of the adhesion of acrylic 1 to TPO, the adhesion of the acrylic primers was excellent. All formulations tested demonstrated excellent adhesion to polycarbonate. The excellent adhesion result over polycarbonate is believed to be related to the amorphous nature of this substrate. Only one commercially available UV formulation demonstrated excellent adhesion over more than one type of plastic substrate.

The post-adhesion results for Acrylic 2 and 3 remained consistent at 5B. Acrylic 1 had the worst post adhesion results. Initial adhesion was 5B, but after temperature and humidity exposure, the adhesion dropped to 2B. The post adhesion loss is related to poor water resistance of Acrylic 1 in general. Only one commercially available acrylic acrylate passed the post adhesion testing and it did so only over polypropylene.

The recoatability results are in Table VI. Each UV curable topcoat was exposed to three times the required energy density to pass the finger scratch test without marring. If the UV system contained solvent, the solvent was flashed off at 60°C with a dwell time of five minutes before cure. The nitrocellulose lacquer, acrylic lacquer, solventborne conventional aliphatic were cured as outlined in the literature.

Table VI.

Topcoat Type or Base Oligomer Type	Acrylic 1	Acrylic 2	Acrylic 3
Tetra functional aliphatic urethane in HDODA	3B	4B	4B
Di-functional aliphatic urethane	5B	5B	5B
Acrylated bisphenol A epoxy	5B	5B	5B
Hexa-functional urethane acrylate	5B	5B	5B
Polyester acrylate	5B	5B	5B
Aromatic di-functional urethane acrylate	5B	5B	5B
Solventborne conventional aliphatic urethane	5B	5B	5B
Nitrocellulose lacquer	5B	5B	5B
Acrylic lacquer	5B	5B	5B
Acrylate cyclic oligomer	3B	3B	3B

With the exception of the tetra-functional urethanes and cyclic monomers, adhesion to the primer coating was easily achieved. The loss of adhesion between the tetra-functional urethane and the acrylated cyclic oligomer is believed to be related because they have similar cyclic structure. Work is continuing to understand the relationship between the structure of the materials and its effect on adhesion.

Conclusions

New materials for UV curable coatings have been developed that provide adhesion to a number of different substrates with varying surface tensions and crystalline structures, enabling the formulator to create a more universal primer system for plastics. Surface treatments for some plastics can be eliminated if these primers are used while other plastics may simply require wiping down or rinsing the surface with a solvent prior to primer application.

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