Evaluation of Adhesion Using Different Formulations, Substrates, and Curing Protocols

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UV curable formulations must adhere to a wide range of substrates while also achieving a wide range of different material properties. In this study we evaluate adhesion of different formulations on a range of different substrates including polymer, metal, and glass. Urethane acrylates, epoxy acrylates, polyester acrylates, and thiol-ene based formulations are evaluated while systematically varying formulation viscosity and thickness. Formulations are cured using both broadband mercury as well as LED lights.

Introduction

UV cured polymers are ubiquitous in society today in products ranging from cell phones, to printing plates, to contact lenses. In many cases, a relatively thin film of resin material is placed onto a substrate or laminated between substrates. Upon curing the ensuing polymer must maintain good adhesion for proper functioning of the desired application. Adhesion to all types of different substrates is required commonly including glass, metal, and a wide variety of plastics. While the use of various adhesion promoters and formulations to achieve adhesion have been well established, formulations, applications, and curing techniques are constantly evolving. This necessitates the need to continually update and develop new formulations for adhesion to a wide variety of substrates for en ever evolving range of applications.

Adhesion to a substrate is achieved via either mechanical or chemical means. Mechanical adhesion results from surface roughness or porosity that enables the adhesive to physically form interpenetrating bonds into the surface of the material or simply creates a much greater surface area for adhesion. Mechanical adhesion is the strongest adhesion attainable and eliminates the need for specific adhesion promoters. However, if the desired surface to adhere to is not inherently rough or porous, physical abrasion or chemical etching is required adding additional steps and processing costs. For smooth surfaces, chemical adhesion is required and is achieved via chemical interaction of the formulation constituents with the surface. In these cases, selection of appropriate adhesion promoters and formulations that interact favorably with the surface of the material is required.

Most studies on adhesion focus on one or both of these types of adhesion in the development of adhesion promoters and protocols. Here, we utilize two common adhesion promoters, carboxy ethyl acrylate and phosphate acrylate, and evaluate how variations in the resin formulation, its application, and curing protocols affect adhesion to various substrates. We have evaluated the effect of several different curing protocols and parameters on adhesion to some typical substrates. The effects of polymer modulus and shrinkage stress are evaluated along with varying initiation conditions including different photoinitiator types and broadband versus LED curing.

Experimental

Materials

Ethoxylated trimethylolpropane triacrylate ($TMP(EO)_3TA$, Photomer 4149), 1-hydroxycyclohexyl-phenyl ketone (Omnirad 481) and 2,4,6-Trimethylbenzoyl-diphenyl phosphine oxide (Omnirad TPO) were purchased from IGM Resins. Aliphatic difunctional acrylate (PU2100), carboxy ethyl acrylate (CEA), and phosphate acrylate (SC1400A) were either purchased from or donated by Miwon. CPS 1020 is a proprietary thiol-ene based formulation. The substrates in this study included glass, acrylonitrile butadiene styrene (ABS), polycarbonate (PC), and structural steel.

Procedures

Coating. Substrates were cleaned using isopropanol and then coated to three different thicknesses (50 μm, 125 μm, and 250 μm) using wire wound drawdown bars.

Curing. Formulations were cured on a conveyor systems using a Heraeus F300 light with 300 W/inch H bulb. Formulations were cured using a 25 W 385 nm LED (Heraeus) or 405 nm LED. The 405 nm LED was donated by Dymax.

Adhesion. A cross hatch adhesion test was utilized to determine the level of adhesion to the different substrates. A 5 x 5 grid of ~1mm squares was cut into the substrate, and a strip of Scotch tape was smoothed onto the grid. The tape was pulled off of the substrate quickly and the number of squares remaining was counted to determine level adhesion. Substrates were scored between 1 – 5 where substrates with zero square remaining were given a score of 0 and substrates with all squares remaining were given a score of 5. For simplicity scores were grouped as 0-1, 2-4, and 5.

Results and Discussion

Three control systems were utilized to test adhesion, ethoxylated (3) trimethylolpropane triacrylate, an aliphatic difunctional acrylate, and a thiol-ene based formulation. These control formulations were utilized with two common adhesion promoters for promoting adhesion to the various substrates. The adhesion promoters included a phosphate acrylate and carboxy ethyl acrylate. The photoinitiators that were utilized were 1-hydroxycyclohexyl-phenyl ketone (Irgacure 184) and 2,4,6-Trimethylbenzoyl-diphenyl phosphine oxide (TPO).

Each of the formulations was evaluated for adhesion to glass, structural steel, polycarbonate, and ABS. The formulations were tested as control systems without any added adhesion promoters, with 10 wt% carboxy ethyl acrylate, and with 10 wt%, phosphate acrylate. The results are shown in Table 1.

Table 1. Adhesion of ethoxylated trimethylolpropane triacrylate ($TMP(EO)_3TA$), aliphatic urethane acrylate, and a thiol-ene based formulation to glass, structural steel, polycarbonate, and ABS. Samples contained 4 wt% Irgacure 184 as the photoinitiator and were coated onto

substrates using a 125 μm drawdown bar and cured on a conveyor system with a Heraeus F300 broadband UV light source.

	$TMP(EO)_3TA$			**Aliphatic Urethane Acrylate**			**Thiol-Ene**		
	Control	CEA	Phosphate Acrylate	Control	CEA	Phosphate Acrylate	Control	CEA	Phosphate Acrylate
Glass	0	1	5	1	5	5	0	2	5
Structural Steel	0	1	5	3	5	5	0	2	5
Polycarbonate	5	5	5	5	5	5	5	5	5
ABS	5	5	5	5	5	5	5	5	5

Table 1 indicates that all of the formulations even without added adhesion promoter exhibit relatively good adhesion to ABS and polycarbonate. As such, with the inclusion of the CEA and phosphate acrylate adhesion promoters adhesion to both ABS and polycarbonate is maintained. None of the formulations exhibited good adhesion to glass or structural steel without the adhesion promoters. CEA improved the adhesion to both glass and structural steel, however overall adhesion was still poor. Presumably, increased levels of CEA in these formulations would result in improved adhesion to glass and structural steel. The addition of the phosphate acrylate resulted in complete adhesion of all formulations to glass and structural steel.

Thicker films are subject to greater shrinkage stress upon curing which can impact adhesion. In the case of the formulations evaluated here, as seen in Table 2, the thickness of the coating did not have a significant affect on adhesion. Likely, other types of formulations with different application methods would have a more significant impact on adhesion.

Table 2. Adhesion of ethoxylated trimethylolpropane triacrylate ($TMP(EO)_3TA$) with 10 wt% carboxy ethyl acrylate to glass, ABS, steel, and polycarbonate at 50 μm, 125 μm, and 250 μm. All formulations were prepared with 4 wt% Irgacure 184 and cured on a conveyor system using a Heraeus F300 broadband UV light source.

$TMP(EO)_3TA$				
Thickness	**Glass**	**ABS**	**Steel**	**Polycarbonate**
50 μm	0	5	1	5
125 μm	1	5	1	5
250 μm	1	5	2	5

Table 2 indicates that adhesion to various substrates with ethoxylated trimethylolpropane triacrylate was uninfluenced by film thickness. These results were consistent with the results of the aliphatic difunctional acrylate and thiol-ene formulations. These results do not change if the photoinitiator is switched from Irgacure 184 to TPO.

Different curing protocols were examined including broadband curing with 1-hydroxycyclohexyl-phenyl ketone and TPO and 385 nm LED curing with TPO. Different curing

protocols can affect the rate of polymerization and hence the final material properties and potentially levels of adhesion. In the case of the formulations evaluated in this work, as seen in Table 3, the type of irradiation source did not have any affect on adhesion.

Table 3. Adhesion of CPS 1020 thiol-ene based formulation after curing with different irradiation sources. CPS 1020 was cured on a conveyor system with both the Heraeus F300 H bulb and 385 nm LED. CPS1020 was also cured with continuous timed cure using a 405 nm LED. The film thickness of the coated substrates was 125 μm.

CPS 1020 at 125 μm and 4 wt% photoinitator				
	Glass	**ABS**	**Structural Steel**	**Polycarbonate**
Broadband UV	0	5	0	5
385 nm LED	0	5	0	4
405 nm LED	0	5	0	4

Conclusions

The phosphate acrylate adhesion promoter was found to be the most effective adhesion promoter across a range of different substrates. Carboxy ethyl acrylate is an adhesion promoter that results in clear formulations with improved adhesion, but more of the promoter is required in the formulations to achieve comparable levels of adhesion to the phosphate acrylate promoter.

TMP(EO)3TA, a glassy material, was coated at three different thicknesses on four different substrates and tested for adhesion performance. There were not any significant changes in adhesion performance as the thickness was varied. This was contrary to the expected trend, which suggests that thicker films will experience greater shrinkage and stress build-up during curing and reduce adhesion performance.

Different types of curing lights and photoinitiators did not have any significant effect on adhesion for any of the different formulations.

Acknowledgements

The authors gratefully acknowledge Miwon North America Inc for their ongoing support and discussions and for donating materials for this research.