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Abstract

As the automotive industry looks to become more eco-friendly, Original Equipment Manufacturers (OEMs) are looking to reduce the weight of vehicles, forcing the number of plastic parts in cars to be on the rise. Applications such as the use of decorative laminates that impart wood grain, brushed aluminum, chrome-like finishes can provide the look and feel of the material they are replacing at a reduced weights. Much like their conventional counterparts, these pieces must be formable while incorporating not only the chemical resistance but also the scratch and abrasion resistance that energy curing is known for. The high crosslink density that is so critical to the performance of these systems typically does not allow the ability to form three-dimensional or deep draw parts. The ability to create an energy curable coating layer that can be formed before or after curing will provide OEMs the ability to meet tougher scratch, abrasion and chemical standards while increasing throughput for next-generation products. The data presented will convey how energy cured materials can be used to create formable coatings that meet the scratch, chemical and abrasion resistance needs of the automotive industry.

Introduction

Energy curable coatings and thermoforming after cure are not phrases one would find synonymous with one another. Energy curable systems have been known for their rapid cure response, high crosslink density, outstanding chemical resistance and undeniable versatility and productivity. Such alluring properties have allowed the energy curable coating to become a staple in a host of packaging, inks, wood, display, and automotive coating applications. Many of these substrates are rigid in nature requiring little to no flex after cure. For those more pliable substrates, such as paper, foils or films, applicators or formulators can use lower coating thickness or add passive acrylates such as vinyl esters, non-acrylate functional polymers, or low acrylate functional oligomers to impart a degree of flexibility. The addition of these materials comes with a sacrifice in the scratch and chemical resistance.

For many decades, energy curable coatings and flat stock parts were a perfect marriage. While flat stock applications still have their place, consumers are looking for more of an interactive experience that is also more environmentally friendly. This has led to an evolution of plastics parts. Not only do they reduce weight but they open up freedom for designers in regard to potential design configurations. This freedom allows them to create a customizable world for the consumer. Conversely, the design freedom that plastic brings also comes with an age-old problem of how to protect the plastic substrates and meet more stringent performance needs and requirements such as flexibility and chemical resistance.

Traditional one- (1K) and two- (2K) component systems have been the solution, but the recent demands for better chemical and scratch resistance can leave something to be desired. For energy curable coatings, scratch and chemical resistance are not issues even under the more stringent performance requirements. However, there has been a technology gap for formability after UV exposure coupled with chemical resistance and hardness. Historically, formability has been limited to low acrylate functionality and high molecular weight chemistries but these give way to poor chemical resistance and blocking properties. Energy curable coatings have taken another step forward and now offer a variety of coating choices that allow applicators to thermoform before and/or after cure. This allows formulators to apply energy curable coatings to complex geometric shapes benefiting from the intrinsic nature of the acrylate chemistries. The toolbox has been expanded and now applicators can choose among energy curable waterborne

polyurethane dispersions, high acrylate functional and low molecular weight urethanes, and a hybrid technology that combines the 1K and 2K functionality into backbones with acrylate functionality.

Experiment

Table I: Formulations for first-generation thermoformable resins.

	1
RX 13000 Mono-functional high elongation urethane for thermoforming applications	100
1-hydroxycyclohexyl phenyl ketone	4

Table II: New Dual Cure formulation

Component I		1
	OH functional acrylic	26.7
	Butyl acetate	30-45
	Flow and leveling additive	0.3
	1-hydroxycyclohexyl-phenyl ketone	2.9
	Di-functional monomer	2.4
Component II	NCO-acrylate	33
Component III	Tin catalyst	200 ppm

This formulation is based on component I containing the OH functional part which is mixed just before application with component II (NCO containing part) and catalyst. A 5 % excess of the NCO equivalents versus the OH equivalents were used.

Table III: Formulations

	1	2	3
RX 88960 – Low Tg Aliphatic urethane triacrylate for haptic coatings.	100		
RX 77000 – Tack free waterborne UV PUD with excellent hardness after water evaporation and cure		100	
RX 20086 – high elongation, moderate crosslink density			100
1-hydroxycyclohexyl phenyl ketone	3.2		4
50/50 blend of 1-hydroxycyclohexyl phenyl ketone and benzophenone		2.6	

Table IV: Material Properties

	RX 13000	RX 77000	RX 88960	RX 88960/88940	RX 20086	Dual Cure
Elongation - %	550	300-500, prior to cure	50	Not applicable	125	400, prior to cure
Tg by DMA - °C			-26	-8.8	51.9	
Functionality, theoretical	1	4 - 6	3	3	3-4	1-2

Applications and Testing Conditions

- Coating solutions described in tables I to III were prepared according to the formulas.
- Coating drawdowns were prepared on 8.5x11 inch polycarbonate; with a target dry film thickness of 5 to 7 microns. Formulations containing water or solvent were allowed to dry at 90°C for 5 minutes prior to UV curing, while dual cure coatings were dried at 80°C for 30 minutes prior to UV curing.
- After the thermal reaction was completed the coatings were exposed to 1200-2000 mJ/cm² using 236 watt/cm Fusion lamps equipped with two medium-pressure mercury bulbs as measured by an International Light's ILT 490 Profiling Belt Radiometer, initiated with 2-5% 1-hydroxycyclohexyl phenyl ketone or a 50/50 blend of 1-hydroxycyclohexyl phenyl ketone and benzophenone based on total formulation solids.
- Chemical resistance of the cured coating layer was evaluated through a chemical resistance test method, which entails the application of sun lotion and hand cream to the cured surface for 24 hours at 80°C. The gloss of the cured materials is measured before and after the test, using the BYK-Gardner tri-gloss meter, ASTM D 523.
- The abrasion test was performed using CS10F wheels, 500-gram weights, and a range of 100 to 500 cycles using Taber 5130 abraser. Scratch resistance was evaluated based on increases in a haze, measured by a BYK-Gardner Haze Gard plus, ASTM D1003.
- Outdoor durability was evaluated through accelerated weathering test using ASTM G154-UVA 340, cycles of 8 hours of irradiance at 0.89 W/cm² at 60°C, followed by 4 hours of dark at 50°C, for a total of 3500 hours. The gloss of the cured materials is compared before and after the test, using the BYK-Gardner tri-gloss meter, ASTM D 523.
- Adhesion was measured via cross-hatch adhesion, ASTM D3359.
- Formability was evaluated through the use of Formech's FS580, using a program that supplies heat at 65% power for 18 seconds followed by forming and then a cooling step for 15 seconds before separating the form from the formed films. The materials were then evaluated for delamination or cracking of the coating layer on the polycarbonate film. Pictures were taken to ensure a clear understanding of the performance formed parts.

Results and Discussion

First Generation


First generation products, such as RX 13000, allow OEMs the opportunity to form shapes with deep draws after exposure to UV light, unlike the materials in **Figure I**. This is made possible by its low acrylate functionality and compatibility with passive acrylates or non-functional acrylates. The drawback for the first generation products is poor chemical, scratch

Figure I: Formed part with cracking and delamination in the areas with a higher degree of thinning.



and blocking properties. **Table V** shows the generally expected properties of RX 13000 in regard to forming along with chemical and scratch resistance properties. Based on the information shown in **Table V**, it is apparent that the decreased crosslink density of the system inhibits the ability of the coating to resist scratches and chemical attacks. After abrasion test, the haze was more than 20% after only 100 cycles. Incorporating higher functional acrylates does reduce the haze increase, but more than 50% of tri or higher acrylate functional material is required to achieve <20% haze after 100 cycles, and coatings are no longer formable. The lack of crosslink density combined with low glass transition temperatures allow the sun lotion to quickly penetrate the coating during testing at an elevated temperature resulting in delamination, hazing, blistering, and eventually complete coating failure after only one hour at 80°C.

Table V: Properties of current technologies, RX 13000.

	RX 13000		
Forming abilities			
Sun lotion Resistance, gloss		20°	60°
	Before	88.6	123
	After	19.1	59.3
	Δ	-69.5	-63.7
Hand cream resistance, gloss		20°	60°
	Before	84.8	119
	After	4	17.9

	Δ	-80.8	-101.1
Haze after taber, CS10F, 500grams, 100 cycles	72.2		


New Technologies

Formable before UV exposure – Waterborne polyurethane and Dual Cure technologies

It is clear that the first generation products leave a lot to be desired. Therefore resin developers have pushed the development envelope of high molecular weight acrylates. This has led to the development of waterborne and dual/ hybrid energy curable technologies. For dual cure technology, formulators can use a poly-addition reaction of hydroxyl (OH) and isocyanate (NCO) functional groups that are attached to an acrylate functional backbone. Such chemistries can offer tack-free surfaces after water or solvent evaporation with more than 400% elongation that offers limitless formability before UV cure. Additionally, such chemical routes offer excellent non-blocking properties that allow the applicator to wind and/or store coated parts that can be shipped or moved to another station for finishing and UV curing. These materials can achieve 40 to 45% thinning after forming, while maintaining acceptable chemical and scratch resistance. **Tables VI and VII**, illustrate the performance and thermoforming ability where the part is coated, formed, and UV cured at different stations or locations.

Energy curable waterborne polyurethane dispersions have advanced a long way over the past 10 years. Clarity and low gloss limited their use to flooring or matte applications that could hide coating imperfections. New developments such as RX 77000 offer high gloss and clarity and perform quite well in regard to thermal forming abilities, prior to being cured with UV light. These materials are physically solidified and can be wound into rolls, and formed without any imperfections due to tack free and non-blocking surfaces. Prior to UV exposure, these materials have between 300 and 500% elongation, which allows for forming into complex shapes and parts. After UV exposure the elongation drops to less than 10%, crosslink density is increased and mechanical properties such as scratch, abrasion, and chemical resistance are imparted in the final film. The resulting thermoformed coating offers performance on par with higher acrylate functional counterparts. Compared to RX 13000, RX 77000 offers a significant improvement in surface properties and excellent formability with only a small change in processing, UV curing after forming.


Table VI: Waterborne polyurethane dispersion material properties.

	RX 77000		
Forming abilities			
Sun lotion Resistance, gloss		20°	60°
	Before	173	163

	After	151	159
	Δ	-22	-4
Hand cream resistance, gloss		20°	60°
	Before	171	163
	After	169	168
	Δ	-2	5
Haze after taber, CS10F, 500grams, 500 cycles	37.44		

With dual cure, applicators can enjoy the same processing as traditional 1K and 2K systems with a similar twist as UV waterbased and that is UV curing after forming. These materials use conventional thermally cured NCO-OH reactions to create urethane linkages that can be tack free and non-blocking after the polyaddition reaction. A coating based on dual cure technology can offer further performance enhancements due to acrylate functionality contained in the same backbone. This allows the coating to benefit from thermoplastic behavior and offer higher initial elongation, leading to a more readily formable part. The conversion of isocyanates and polyols can inhibit the ability of the coating to form, and must be taken into consideration when formulating for these types of applications. Once the materials are exposed to UV energy, the crosslink density is greatly increased, elongation goes from >400% to <10%, and the result is excellent chemical and scratch resistance for automotive applications, **Table VII**.

Table VII: Dual cure technology material properties.

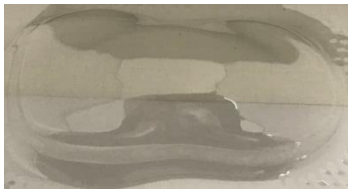
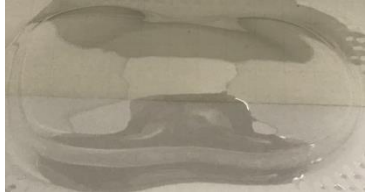
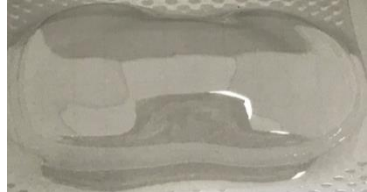
	Dual Cure		
Forming abilities			
Sun lotion Resistance, gloss		20°	60°
	Before	180	189
	After	170	185
	Δ	-10	-4
Hand cream resistance, gloss		20°	60°
	Before	174	188
	After	175	188
	Δ	1	0
Haze after taber, CS10F, 500grams, 500 cycles	12.9		

Formable after UV exposure – Urethane acrylates

In the past, UV curable materials have been one of two things, either scratch resistant or formable, without any overlap between the two material properties. Generally, lower functionality materials responsible for creating formable coatings possess poor chemical and scratch resistance, while hexa-functional urethane acrylates provide films with superb scratch and chemical resistance, but no forming abilities. Newly developed materials, allow for forming after UV exposure, reaching 40-45% thinning, while maintaining a high level of scratch and chemical resistance due to higher acrylate functionality. Customarily, thermoforming after curing has been limited to materials with less than two acrylate functional groups. RX 88940, RX 88960 and RX 20086 offer more than three acrylate functional groups and can be formed to a multitude of shapes and draws after UV cure. RX 88960 is a low glass transition temperature (-26°C) urethane acrylate that imparts the foundation for achieving haptic coatings. RX 88940 has a higher glass transition temperature (60°C) that increases chemical and humidity resistance without impacting the tunable nature of the haptic ability. RX 20086 is a trifunctional urethane acrylate that offers >100% elongation that is designed for high gloss automotive interior applications where the system needs a combination of hardness, chemical resistance, and flexibility.

To achieve haptic feels, resins have to be modified with inert resins or fillers that impart feel. The addition of such material often creates a disadvantage in scratch, abrasion, and chemical resistance. In **Table VIII**, this is observed when blending RX 88960 with necessary additives to divulge the velvet feel to the coatings. At elevated temperatures, the coating experiences extreme attack due to the low glass transition temperature despite the high acrylate functionality. Blending RX 88940, a higher glass transition temperature oligomer, with RX 88960 the chemical resistance can be significantly improved even with the presence of required fillers and additives that adjust the haptic feel. This increase in the glass transition temperature while maintaining the same acrylate functionality allows the coating to obtain chemical resistance but also allows sufficient flexibility to form effortlessly after cure.

Table VIII: Material Properties of Urethane acrylates

	RX 88960			RX 88960/88940			RX 20086		
Forming abilities									
Sun lotion Resistance, gloss retention		20°	60°		20°	60°		20°	60°
	Before	100	100	Before*	100	100	Before	100	100
	After	20.39	51.5	After*	96.73	97.56	After	95.03	96.36
	Δ	-79.61	-69.52	Δ	-3.27	-2.44	Δ	-4.97	-3.64
Hand cream resistance, gloss retention		20°	60°		20°	60°		20°	60°
	Before	100	100	Before*	100	100	Before	100	100
	After	69.06	75.74	After*	96.94	98.54	After	96.57	97.58
	Δ	-30.94	-24.26	Δ	-3.06	-1.46	Δ	-3.43	-2.42
Haze after taber, CS10F, 500grams, 500 cycles	44.8			41.8			27.2		

* Formulation contains soft feel additives and fillers to create a velvet haptic coating

Formulating a coating with <30% haze after 500 cycles (CS10F, 500g) has been a challenging task, especially where the coating elongation needs to exceed 100%. RX 20086 offers a unique solution with optimized chain length, structural hindrance, and functionality into the backbone. The result is a multifunctional urethane that has more than three acrylate functionality after dilution with reactive diluents. This is almost a double improvement in elongation when compared to first generation forming after cure products such as RX 13000. After cure, RX 20086 offers >40% thinning, a tack-free surface, and low haze after abrasion test. In data not shown, after 100 cycles, RX 20086 showed <10% increase in haze after abrasion. It is important to note that testing various automotive crèmes, at elevated temperatures, showed no visual attack or loss of adhesion after testing.

Conclusion

The development of formable materials requires a delicate balance of crosslink density, chemical structure hindrance, and glass transition temperature. The recent innovation of energy curable waterborne polyurethanes, the emergence of dual cure coatings and the evolution of higher functional and ductile urethane acrylates, provide formulators a plethora of technologies that allow them to achieve their goals. The combination of scratch resistance, chemical resistance, and heat shaping abilities that have been misnomers are now a reality thanks to energy curable coatings. The data presented above demonstrates that energy curable coatings are the next big thing for foils, films, and sheet applications used in the automotive interior. These new technologies cover a multitude of technical paths, providing formulators more flexibility and tool selection than ever before. With continuous process improvements, expanded material properties and the ability to form any number of shapes and substrates, energy curable coatings are not only ready for demanding markets such automotive but also primed to be sustainable for many decades to come.