Study on Acrylic Oligomers for UV Adhesives Application

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Wraio Chemicals, CHINA
Presented by **Willy DU**

WRAIO

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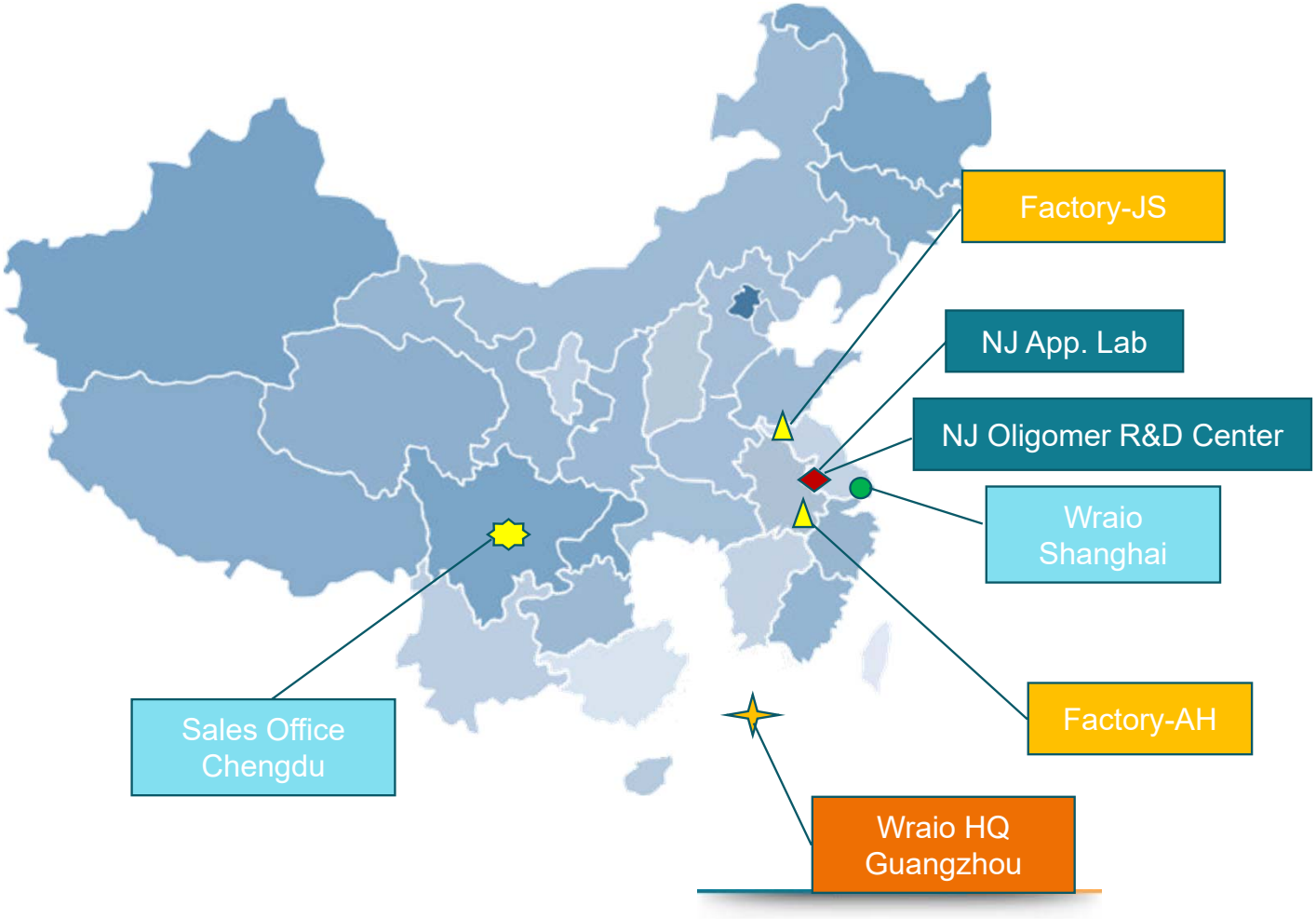
PART 01

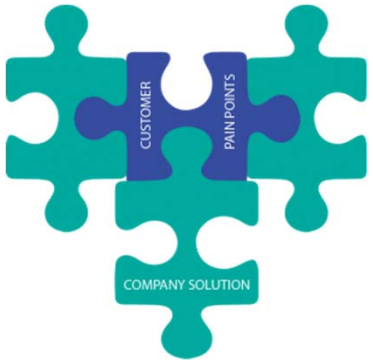
Profile of Wraio

Profile of Wraio

- 2008: Start up as a trading company of UV raw materials
- 2011: Establishment of Nanjing Technical Center
- 2012: Merging UG Chemicals
- 2014: Running of 1st factory of oligomers in Jiangsu, CHINA
- 2019: Running of 2nd factory of oligomers in Anhui, CHINA

Customer Support from Wraio





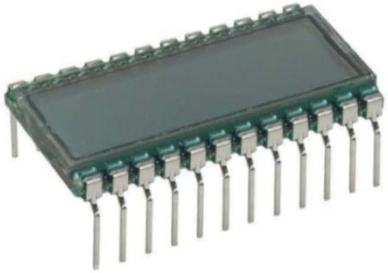
Market Focused

- UV Monocoat - Notebook
- UV PVD coatings - Mobile phones
- UV Coatings for Headlamp of vehicle
- UV Adhesives - Electronic products
- UV Nail Polish
- UV Coatings for Optical film (Hard coatings, BEF)
- UV Inks (LED)
- UV Matte coatings for PVC flooring
- ……

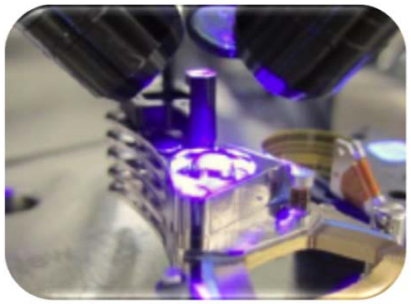
PART 02

Background Information

UV Adhesive Applications

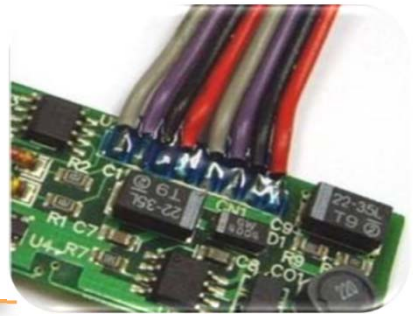


- Glass/Plastic/Metal structural bonding
- LCD pin fixing

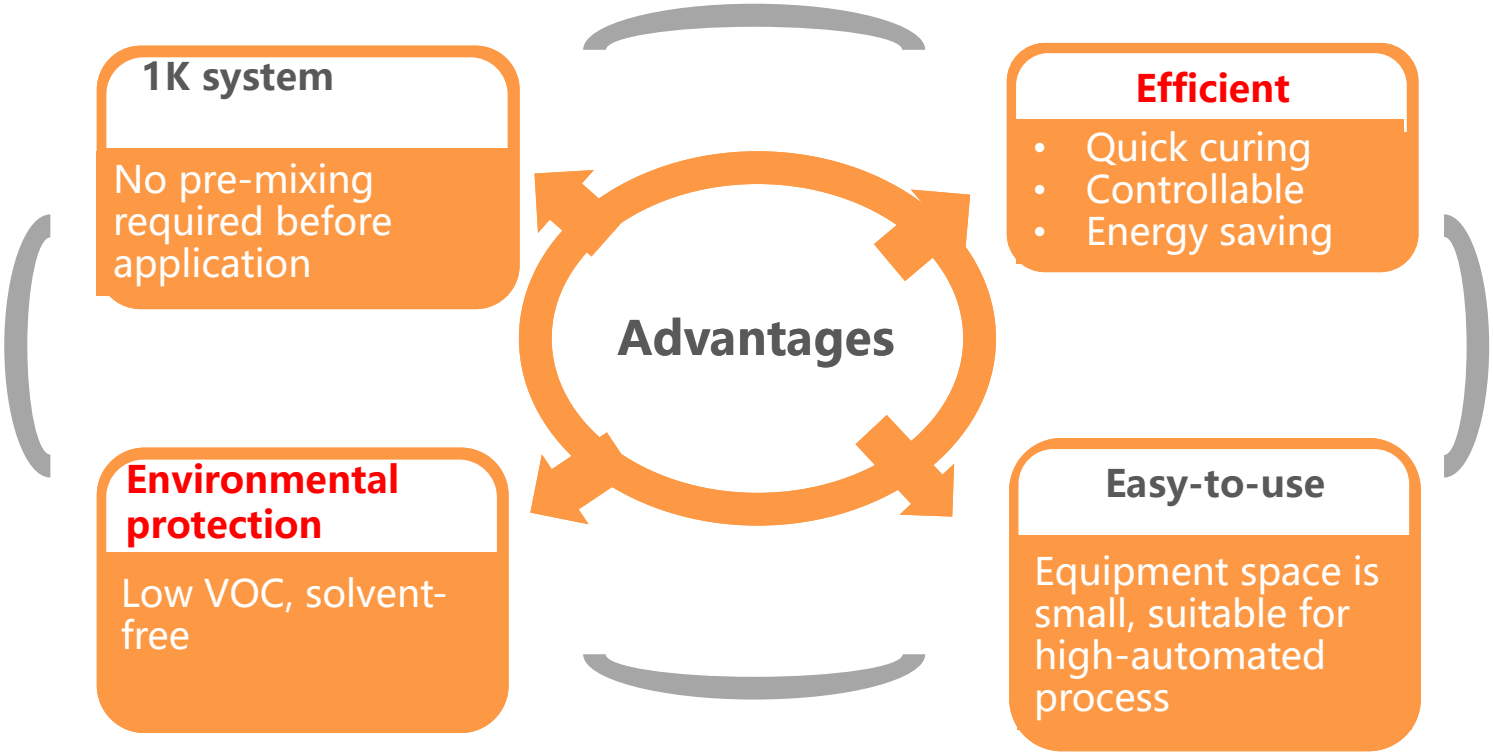


- Medical device bonding
- Spot protection line, reinforcement

- Circuit board coatings / conformal coatings
- Potting / sealing / UV sealant



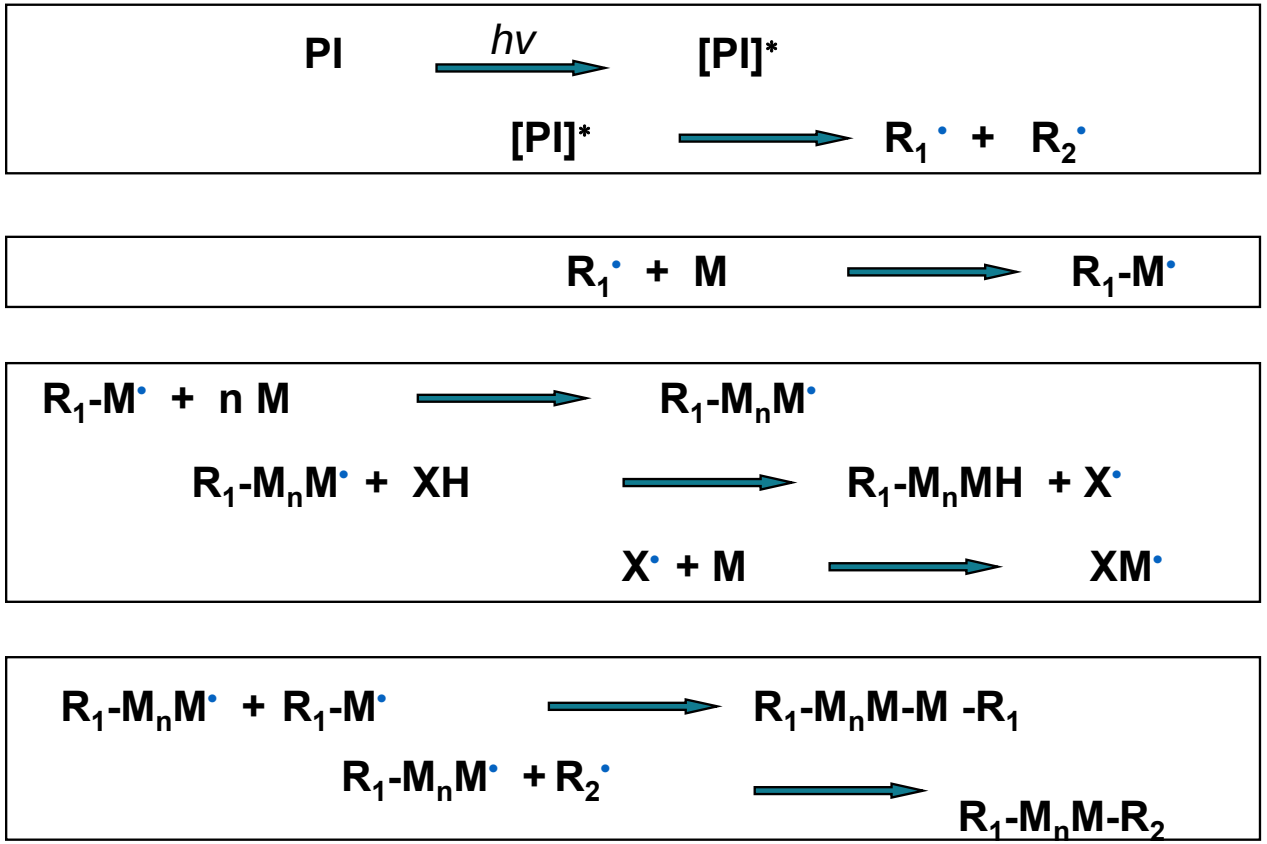
Pros of UV Adhesive



Cons of UV Adhesives

- Right source and enough intensity of light are required
- Limitations on substrates
  - The substrates have to be transparent on at least one side
  - Application to complicate-shape parts could be poor cured, other complementary curing methods could be required
- Curing equipment investment
- Mercury lamp produces ozone, exhausting system is necessary

Mechanism of Free Radical Photocuring Polymerization



- Absorption of light
- Generates free radicals
- Initiate
- Chain growth
- Chain transfer
- Chain termination

Ultraviolet Source

UV curing applications normally use middle and near-ultraviolet light, usually subdivided to UVA, UVB and UVC

◆UVA(315~400nm)

Lower energy, deep curing, glass bonding

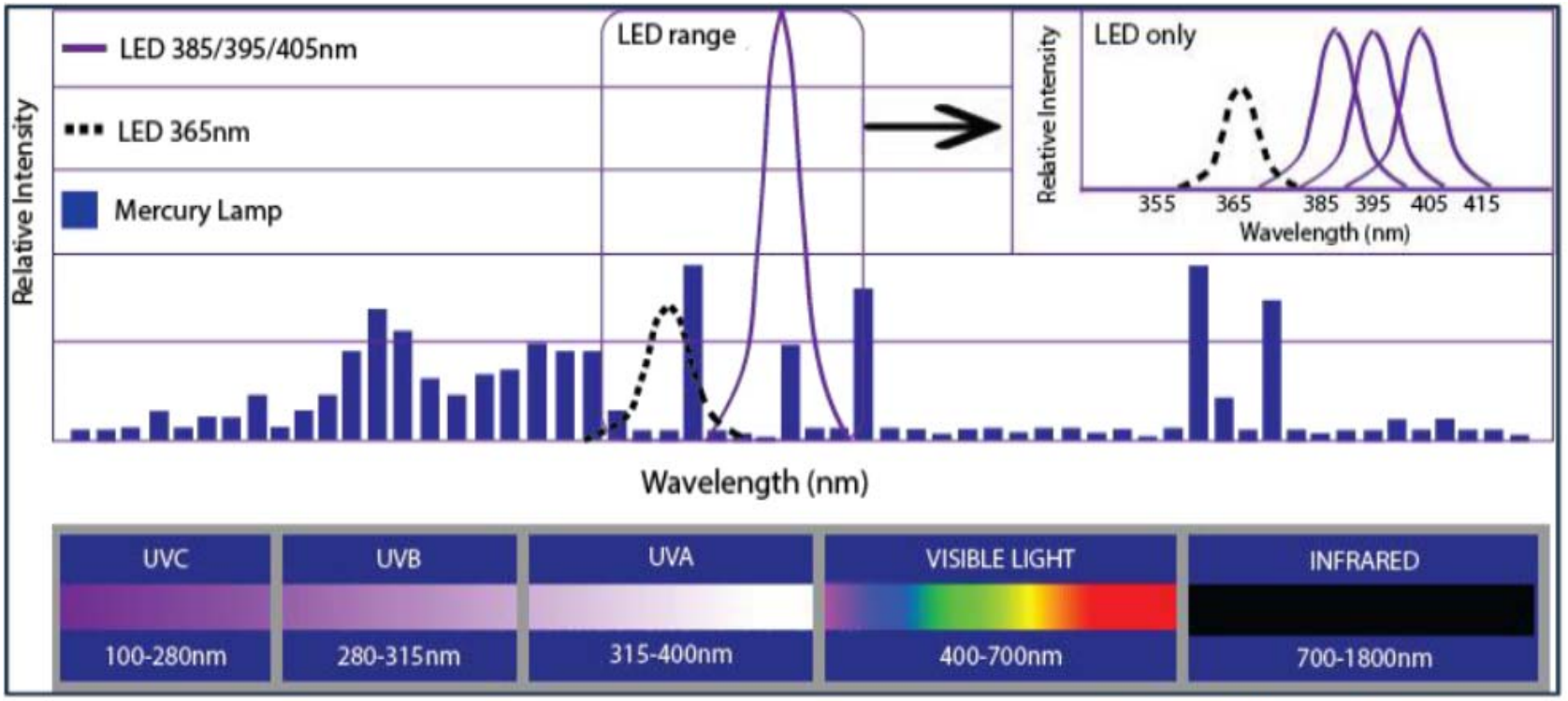
◆UVB(280~315nm)

Higher energy, surface curing, sealing/coating

◆UVC(200~280nm)

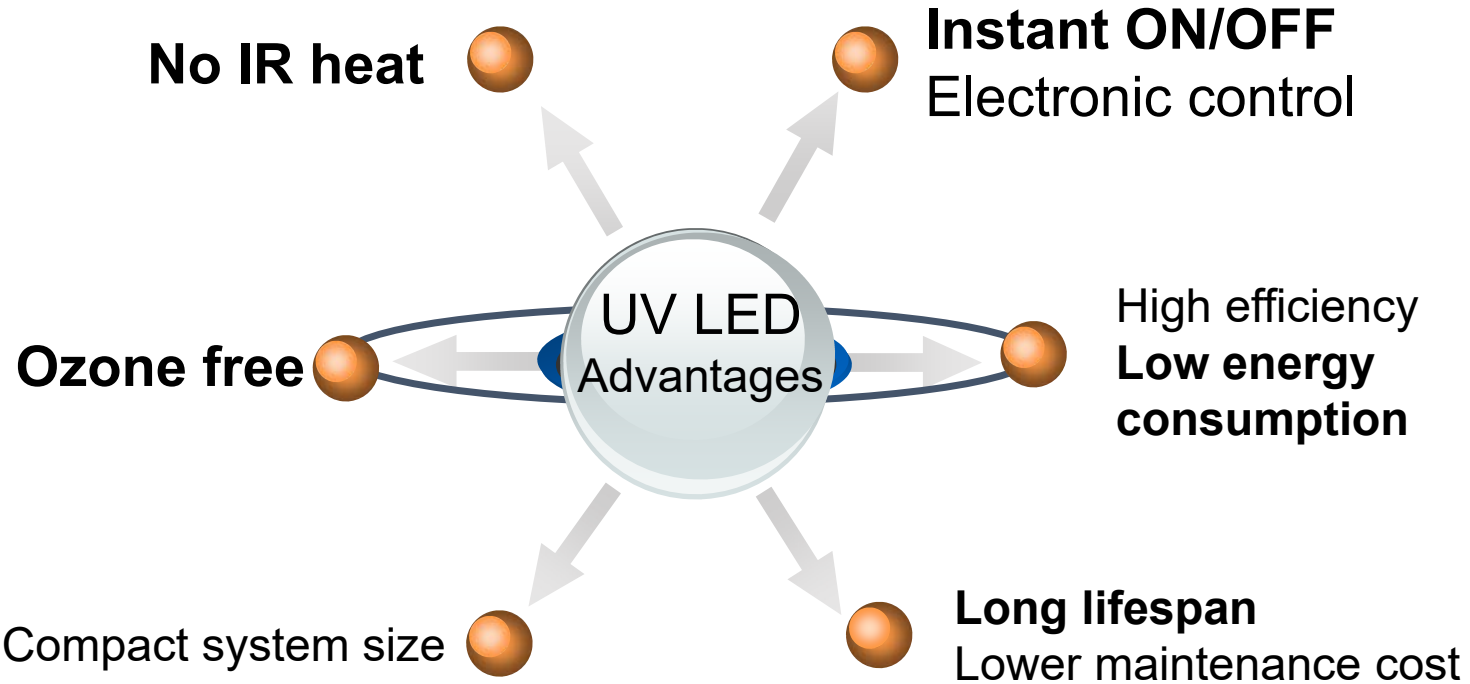
High energy, surface debonding, sterilization and disinfection

Conventional High Pressure Mercury Lamp vs. UV LED



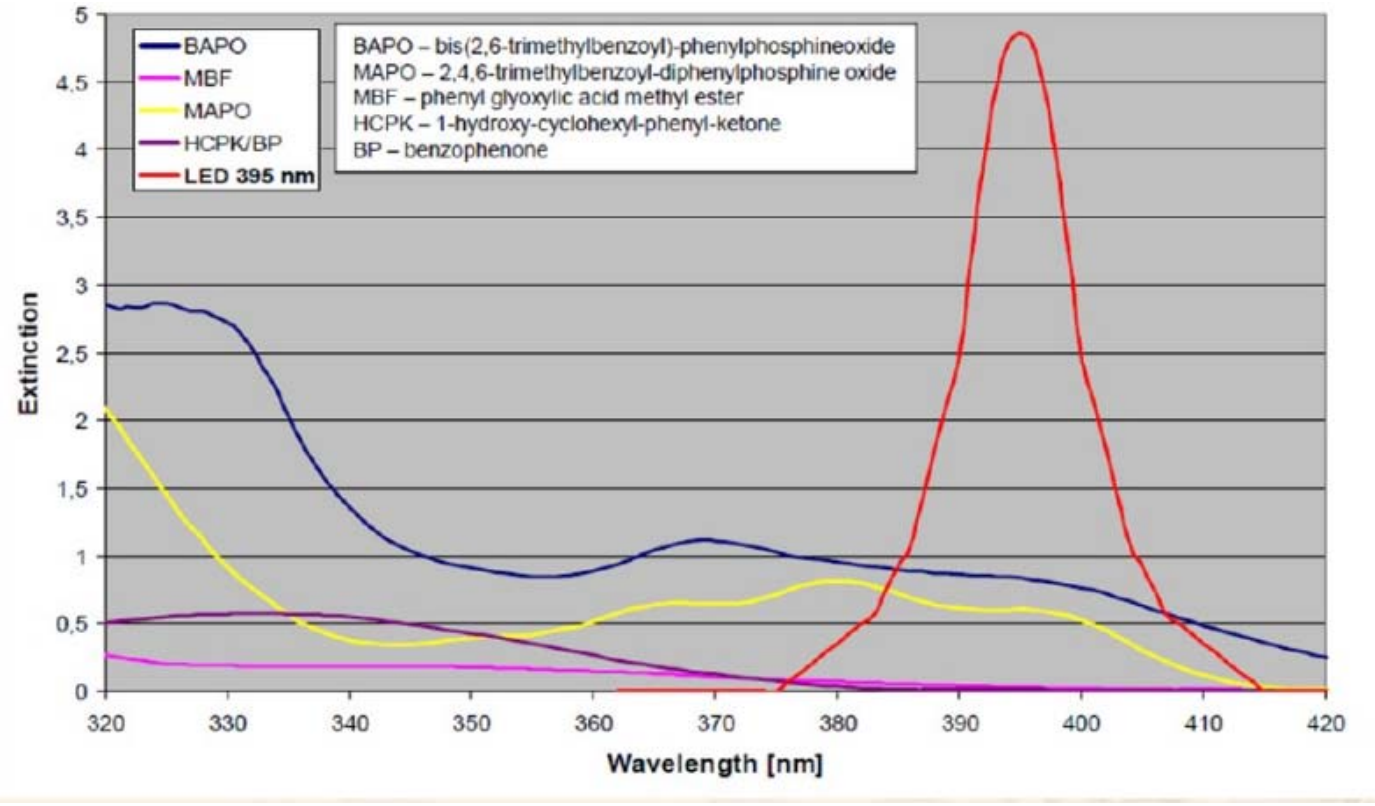
*courtesy of Phoseon Technology

UV LED Advantages



The Absorption Wavelength of Several Photoinitiators

Choose appropriate photoinitiators to match different light sources



UV Adhesive Development Trend

- Low energy, fast curing: high pressure mercury lamps are being replaced by **UV LED**
- **Hybrid Curing** (Photo + thermal / moisture): ODF frame glue, conformal coating
- Environment friendly: low VOC
- High cohesion and adhesion: replacing traditional structural adhesive applications (fast cure, low temperature, energy saving and environmental-friendly)
- **Low odor, low skin irritation**
- Universality: more diversified substrates(plastic, metal, glass, etc.)

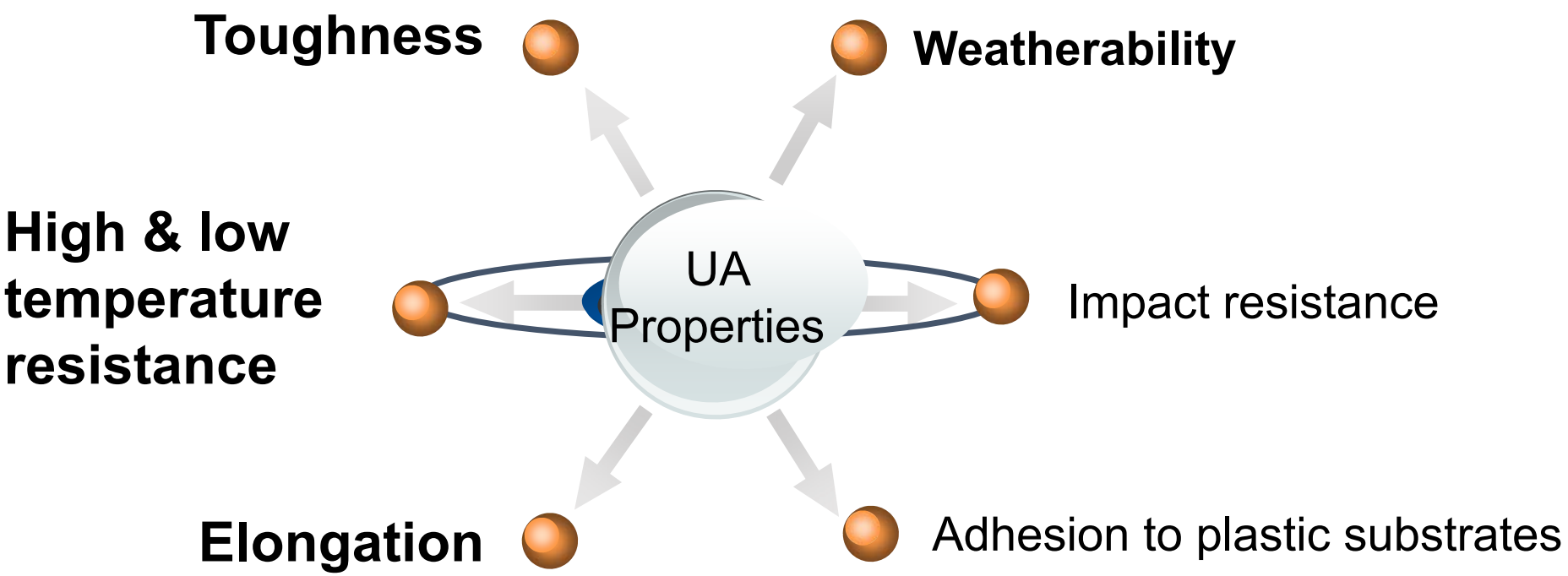
PART 03

Oligomers for UV Adhesives

Pros & Cons of Different Types Oligomers

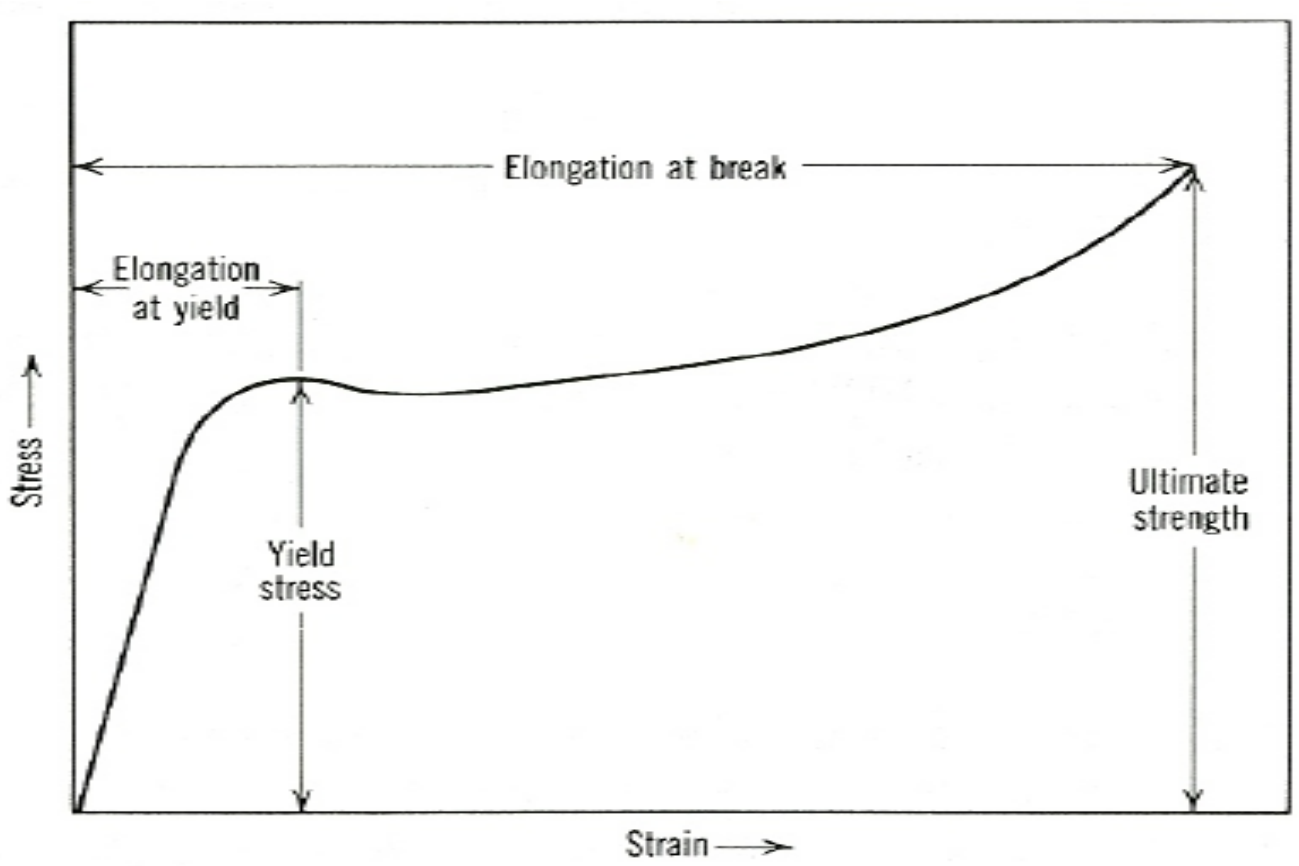
Type	Pros.	Cons.
Epoxy Acrylate	Fast curing, chemical resistances	Poor weatherability, brittle
Urethane Acrylate	**Good comprehensive properties, cohesion, and elongation**	Higher cost
Polyester Acrylate	Low viscosity, good performance-to-cost ratio, faster curing	Low cohesion
Polyether Acrylate	Low viscosity, flexibility	Low mechanical strength
Full Acrylics Acrylate	Adhesion, flexibility	Slow curing, low mechanical strength
Thiol Modified Resin	non-sensitive to oxygen inhibition	Smell, stability

Urethane Acrylate

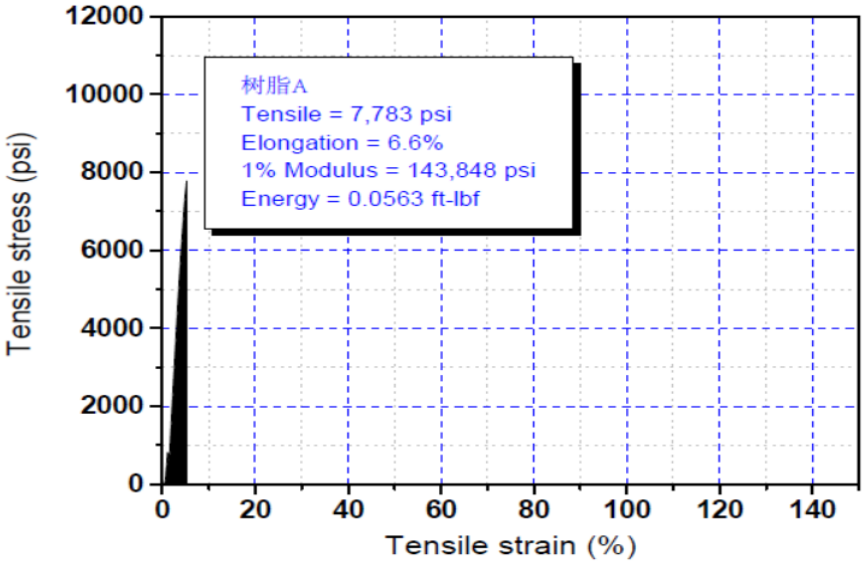


Important Specs. of UV Adhesive Resin

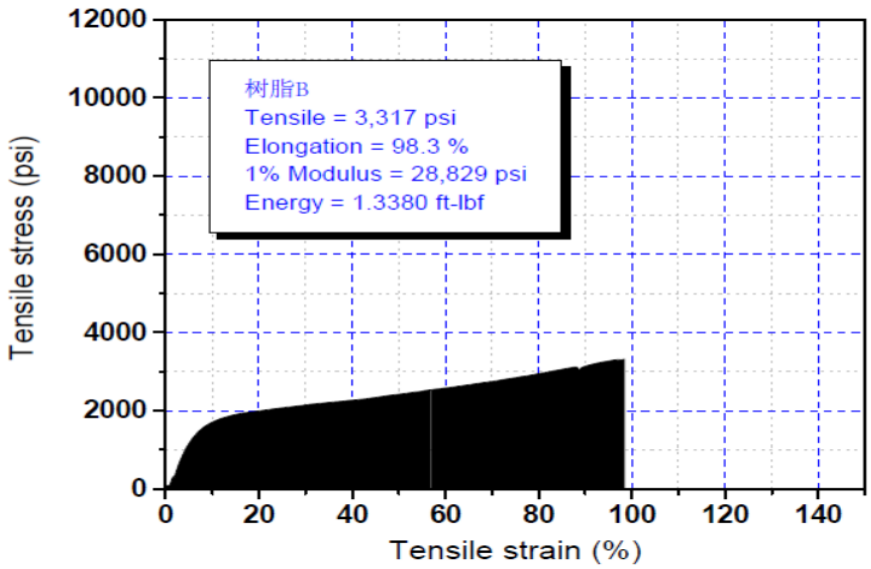
Stress-strain curve



Examples of Stress-strain Curves



Hard and strong



Soft and medium toughness

UV Adhesive Resin Performance Test

Major parameters

- **Curing speed** – surface & deep curing
- **Hardness** - Shore hardness
- **Elongation** – pure resin strain
- **Bonding property** - strain shear, compress shear
- **Aging test** – high temperature & humidity, boiling water resistance, cold and hot cycle
- **Water absorption** - weight change after water boiled
- **Modulus** -mechanical property
- **Tg** - effects on bonding properties, strength

The Infulence of Isocyanates

IPDI vs. HMDI

Product Structure	Hardness	Tensile strength, MPa	Elongation at break, %	Shear strength PC/PC MPa	Water absorption %
HEA-[IPDI-(Polyol 1)]4-IPDI-HEA	D60	17	30	8.0	1.0
HEA-(IPDI-Polyol 2)4-IPDI-HEA	D55	15	120	7.5	0.9
HEA-[HMDI-(Polyol 3)]4-HMDI-HEA	D65	20	200	9.5	1.4
HEA-(HMDI-Polyol 4)4-HMDI-HEA	D60	19	180	8.5	0.7

The Effect of Molecular Weight

Product Structure	Hardness	Tensile strength MPa	Elongation at break %	Shear strength PC/PC MPa	Water absorption %
HEA-[IPDI-(Polyol 1)]$_4$-IPDI-HEA	D60	17	30	8.0	1.0
HEA-[IPDI-(Polyol 1)]$_7$-IPDI-HEA	D55	16	55	8.5	0.9
HEA-[HMDI-(Polyol 5)]$_4$-HMDI-HEA	D65	22	185	9.0	2.0
HEA-[HMDI-(Polyol 6)]$_4$-HMDI-HEA	D62	18	240	8.5	1.4

The Effect of Capping Group

HEA vs. CA vs. HBA

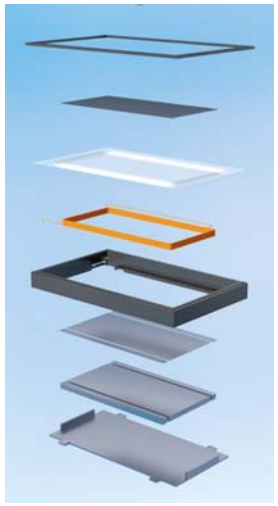
Serial number	Hardness	Tensile strength MPa	Elongation at break %	Shear strength PC/PC MPa	Water absorption %
HEA-[IPDI-(Polyol 1)]$_4$-IPDI-HEA	D60	17	30	8.0	1.0
HBA-[IPDI-(Polyol 1)]$_4$-IPDI-HBA	D55	15	45	7.0	1.1
CA-[IPDI-(Polyol 1)]$_4$-IPDI-CA	D55	14	60	5.5	0.8
HEA-[HMDI-(Polyol 5)]$_4$-IPDI-HEA	D65	22	185	9.0	2.0
HBA-[HMDI-(Polyol 5)]$_4$-IPDI-HBA	D60	20	200	9.0	1.8
CA-[HMDI-(Polyol 5)]$_4$-IPDI-CA	D55	17	230	8.5	1.8

PART 05

R&D Case Study

1st Case: Oligomers for UV Adhesives

UV Adhesives for Electronic Module



Mini loudspeaker

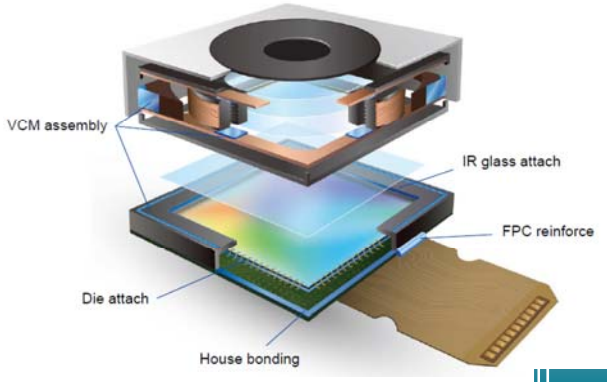
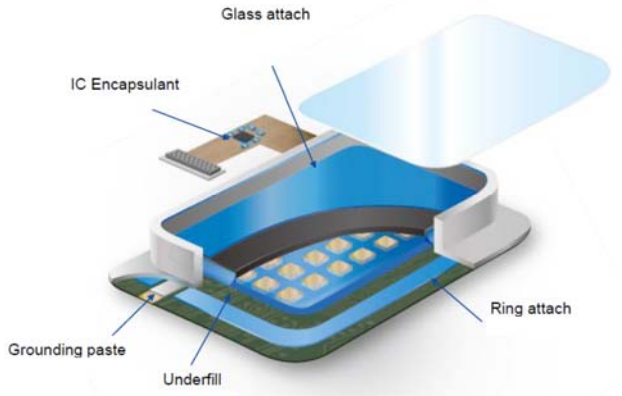


Image Sensor



Fingerprint sensor

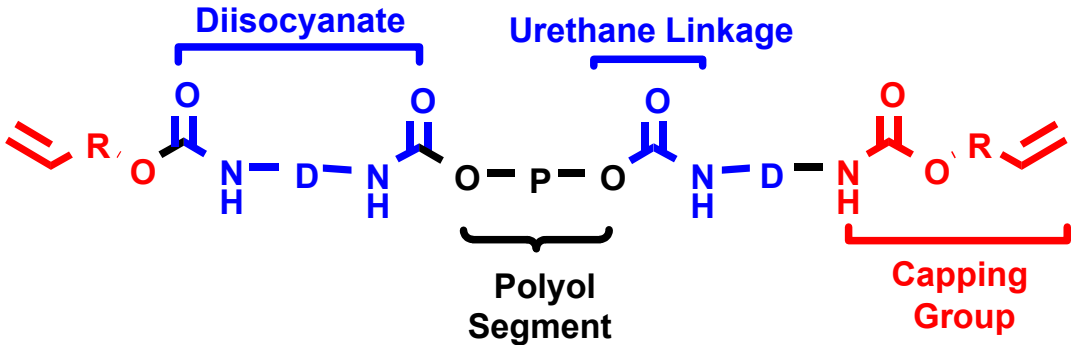
UV Adhesives for Plastics

Items and Requirements		Main Properties
UV Lamp	Hg or LED	■ UV and visible light, fast curing ■ Broad viscosity range for different applications ■ Colorless clear, low odor ■ Excellent bonding to plastics, especially PC and PMMA ■ Excellent aging resistant performance
Minimum Curing Energy	1,200mJ/cm^2	
Tensile Strength, Mpa	18-20	
Elongation at Break	150-250%	
Shore Hardness	60D-70D	
LSS PC/PC, Mpa	10-12	

General Glass / Metal UV Adhesives

Items and Requirement		Main Properties
UV Lamp	Hg or LED	■ UV and visible light, fast curing ■ Suitable viscosity and Ti for easy processing ■ Colorless clear and low odor ■ High bonding Strength for glass and other substrates(glass, metal, etc) ■ Excellent aging resistant performance
Minimum Curing Energy	500mJ/cm^2	
Tensile Strength, Mpa	14-22	
Elongation at Break	150-250%	
Shore Hardness	50D-60D	
LSS Glass/Glass, Mpa	5-8	

Properties Matrix - Urethane Acrylate



Polyester-UA
Synthesized with polyester polyol, adipic ester or polycarbonate ester type

High mechanical strength, elongation and modulus

Polyether-UA
Synthesized with polyether polyol

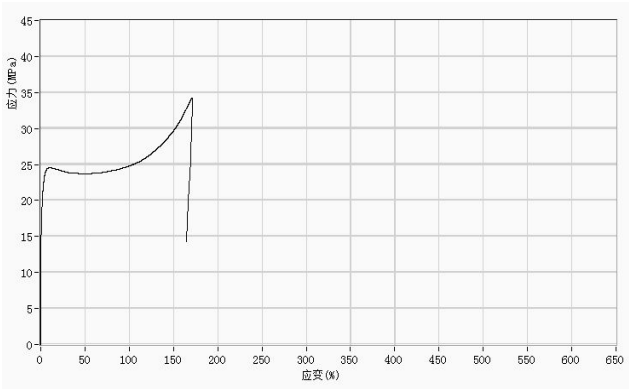
Low cohesive energy. **Excellent flexibility,** low temperature resistance, hydrolysis resistance. Poor strength and heat resistance

Performance	Modulus	Yield Stress	Break Strength	Elongation at break
Soft, weak	low	low	low	medium
Soft, tough	low	low	high	high
Hard, brittle	high	Very high	medium	Low
Hard, strong	medium	high	high	Medium
Hard, tough	medium	medium	high	high

Customized Oligomers with SPF- General Purpose UV Adhesives for Plastics

Cure speed mJ/cm²	Water absorp. %	Elong. at break%	Tensile strength MPa	Deep cure	High temp. & humity resis.	LSS/MPa			
						PC/PC	PC/PVC	PC/ABS	PC/Glass
800	1.74	220	36.2	3.4mm	Excellent	9.5	8.5	7.1	4.2
3.5	4.5	4	5	3	5	4	4	4	3

Grade：0~5, higher is better



FSP8674(Polyester-UA)

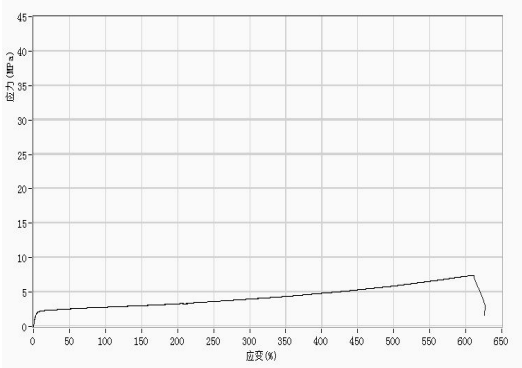
SPF	
Comp.	**%**
FSP8674	50-60
DMAA	5-10.0
IBOA	20-30
MMA	2-5
184	2.5
TPO	1.0
Additive	2-4
Total	100

Substrates	LSS/MPa	
	RT	85℃ & 85% humidity for 48h
PC/PC	10.4	9.9
PC/PS	9.6	9.3
PC/PVC	9.2	8.8

Customized Oligomers with SPF- General Purpose UV Adhesives for Glass / Metal

Cure speed mJ/cm^2	Water absorp. %	Elong. at break %	Tensile strength MPa	High temp. & humidity resist.	LSS/MPa			
					PC/PC	GL/GL	GL/Al	GL/SS
2500	1.82	600	8.2	Excellent	2.5	4.5	5.9	5.2
1	4.5	5	2	5	1	4	4	4

Grade：0~5, higher is better.



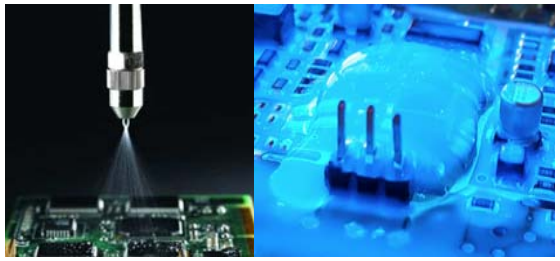
FSP8054(Polyether-UA)

SPF	
Comp.	**%**
FSP8054	30-40
IBOA	45-55
R9107	2.0
AA	2-4
184	2.5
TPO	1.0
Additive	1.5
Total	100

Substrates	LSS/Mpa	
	RT	85℃ & 85% humidity for 48h
Glass/Glass	5.2(Glass break)	5.1(Glass break)
Glass/Al	6.2(Glass break)	6(Glass break)
Glass/Steel	5.7(Glass break)	5.5(Glass break)

2nd Case: Oligomers for UV+Moisture Cured Conformal Coatings

Moisture resistance | Salt resistance | Static resistance

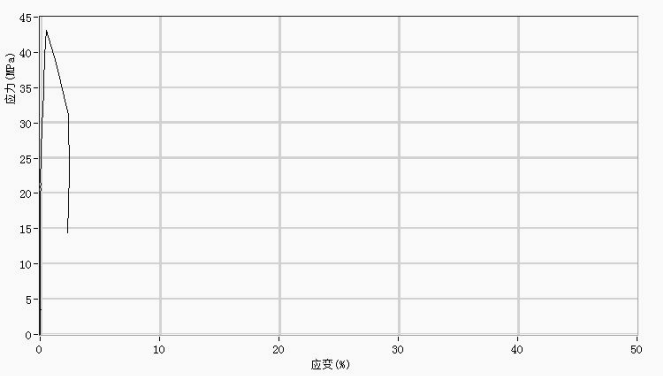


Oil resistance | Dust resistance | Temp. resistance

Items and Requirement		Main Properties
Curing	UV + Moisture	■ UV and moisture curing ■ Low viscosity for conformal coating and high viscosity & Ti for circuit board protection with color changing ■ Low odor ■ Excellent protection for PCB and electronic components, especially from moisture, salt fog, dust, temperature, etc.
Minimum Curing Energy	2,000mJ/cm^2	
Tensile Strength, MPa	10-15	
Depth/um	50-100	
Elongation at Break	50-150%	
Shore Hardness	70D-75D	
LSS Glass/Glass, MPa	5-10	

Customized UV Oligomer for Conformal Coatings

Shore Hardness	Cure speed (LED)	Boiling water resis.	Adhesion	Tensile strength	Toughness	Depth Curing	Yellowing	Pigment wetting
75D	<500 mJ/cm²	85℃ 1h，5B	PC，Glass 5B/4B	30.2MPa	Excellent	5.2mm	△b=2.26	good
1-4	4	3	4	5	5	5	2	4
Grade：0~5, higher is better.								



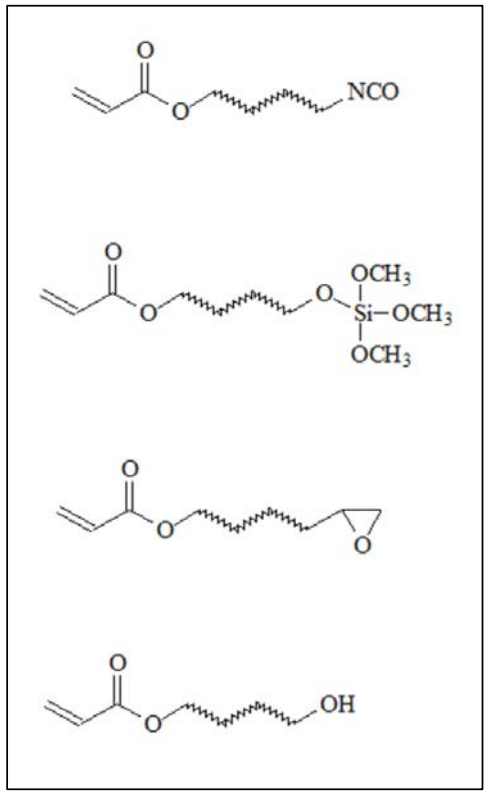
FSP8672

Start Point Formulation	
Comp.	**%**
FSP8672	30.0
THFA	15.0
IBOA	40.0
UV/Moisture Dual Cure Resin (BASF)	12.5
184	2.0
819	0.5
合计	100.0

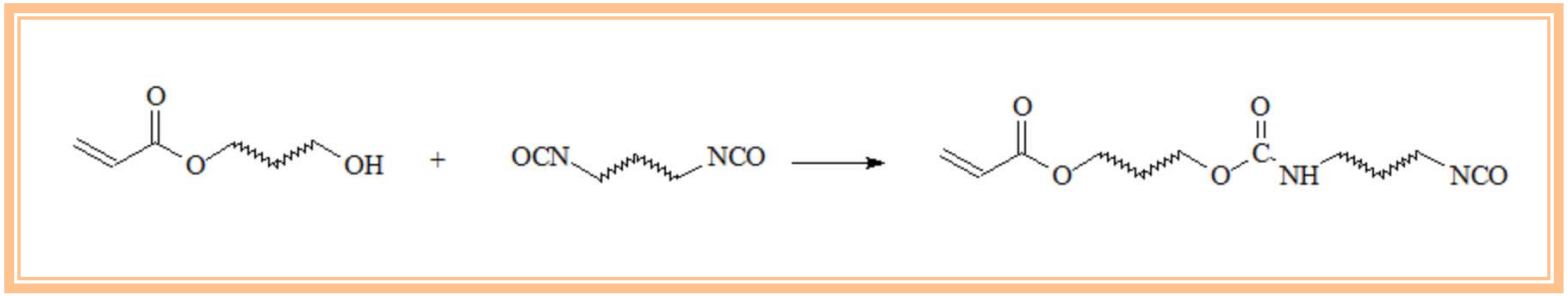
Test Result	
Visco., cps @ 25℃	500
Cure energy, mJ/cm²	1500
Water absorp.%	2.2
Cured depth	>7mm
Adhesion	5B
Hardness	D32
Elongation at break, %	160
Tensile Strength, MPa	6.2

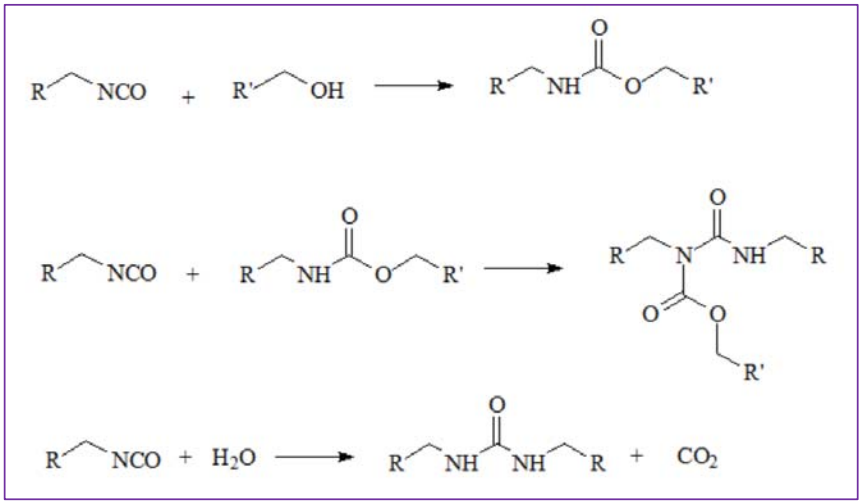
Customized UV / Moisture Dual Cure Resins for Conformal Coatings (Ongoing Project)

Different Types of Dual Cure Resins



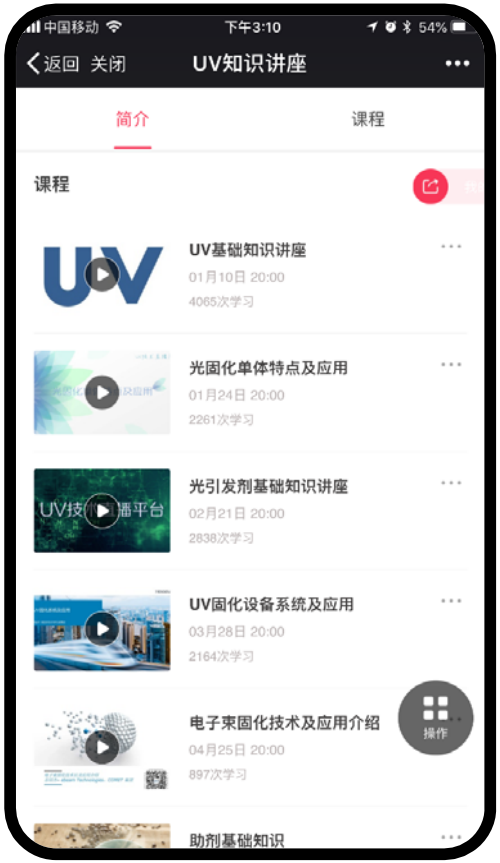
Synthesis of UV / Moisture Dual Cure Resin





Reactions mechanism of moisture curing

“Photocure New Materials” WeChat Official Account



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Thanks for Your Attention!

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WRAIO