# Innovative Polyester Acrylates – Solutions for Industrial Market Needs

Jonathan Shaw, PhD May 17, 2016













## Agenda

- Energy Curing
  - Definitions and benefits
- Polyester Acrylates for IC Wood Applications
  - PEA 1 Low viscosity combined with high cure speed, high Tg, and low shrinkage
  - PEA 2 Raw materials from recycled plastic
- Performance
- Conclusions



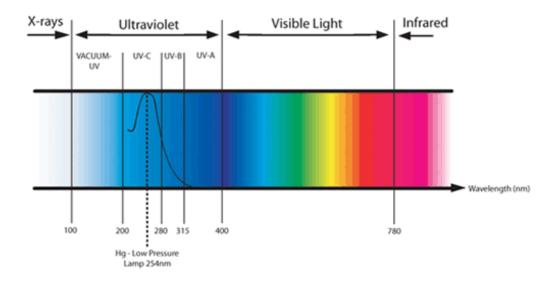
## What is Ultra-Violet (UV) curing?

- Using UV energy or visible light, as opposed to heat, solvent evaporation, or oxidation (air-drying), to convert a liquid formulation into a solid material
- Types of energy used:

Ultra Violet (UV): 200 - 400 nm

Visible light: typically 380 - 450 nm

#### **ELECTROMAGNETIC SPECTRUM**





# **Energy Curing Advantages**

#### **Productivity, Productivity, Productivity**

Seconds to cure vs. minutes or hours

# No reaction until exposure to UV energy

"Cure on Demand", long pot life and reduced waste

#### Single component formulas

Eliminates mixing errors found in 2 component systems

# **Lower Overall Cost (per cured part)**

100% solids, cure speed, recycling of coating, etc.

# **Regulatory concerns (VOC emissions)**

Low to no VOC

#### **Energy Costs**



# **Energy Curing Considerations**

#### Line of sight curing

- All areas of the part must be exposed to UV energy
- Lamp placement critical, but not difficult

#### **Absorbance of system**

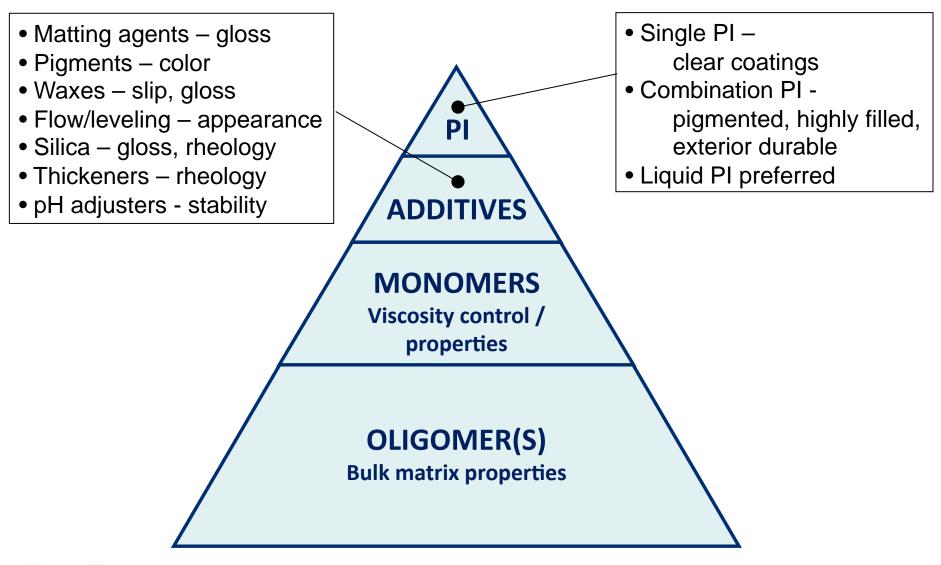
- Components that absorb/block UV may interfere with cure
- Select components that don't absorb UV or select PI that absorbs in another region of the UV spectrum

# Shrinkage

- All reactions generate shrinkage, which may lead to poorer adhesion
- Mitigate with selection of diluents, oligomers
- Use of WB systems can reduce shrinkage (no monomers needed to reduce viscosity)



# **Energy Curing 100% Solids Formulation**

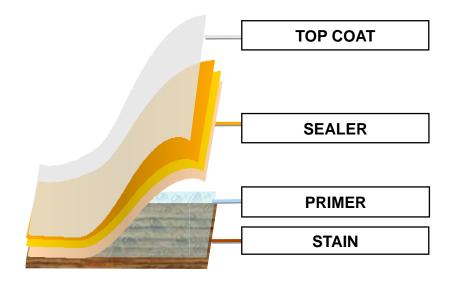




#### **UV Curable Coatings for Wood**

#### **Floor Coating Layers**

- Stain
- Primer functional layer for adhesion
- Sealer functional layer for abrasion resistance, may contain e.g. alumina to meet different abrasion tests (e.g. Taber, grit feeder or S42)
- Top Coat functional layer for scratch resistance, gloss



## **New PEA Resins for Industrial Wood Coatings**

# PEA 1 (experimental)

- Low viscosity combined with high cure speed and low shrinkage
- Good overall properties (hardness / flexibility) with high Tg
- Good component for UV LED due to high reactivity
- Biobased, 56% Renewable Content

## PEA 2 (experimental)

- Recycled raw materials for cost benefit
- Good performance properties
- Excellent flow when filled



# **PEA 1 Physical Properties**

Appearance	Yellow amber liquid
Viscosity 25°C mPa.s	5000
Color (Gardner)	3
Diluent content %	0
Tg °C $^{(1)}$ max Tan $\delta$ - DTMA	84
Tensile strength (1) MPa	16.5
Young modulus <sup>(1)</sup> MPa	1990
Elongation at break <sup>(1)</sup> %	0.9
Shrinkage – picnometer volume contraction (%)	6.52
<sup>(1)</sup> 80 μm film; electron beam cured	

PEA 1 shows excellent thermal and mechanical properties combined with low viscosity

# **PEA 1 Shrinkage Comparison**

UV Resin	% Volume shrinkage
PEA 1	-6.5
Bisphenol A based diacrylate	-6.2
Hard, trifunctional PEA	-8.1
Hard, hexafunctional UA	-8.4

PEA 1 has less volumetric contraction than hard PEA and UA

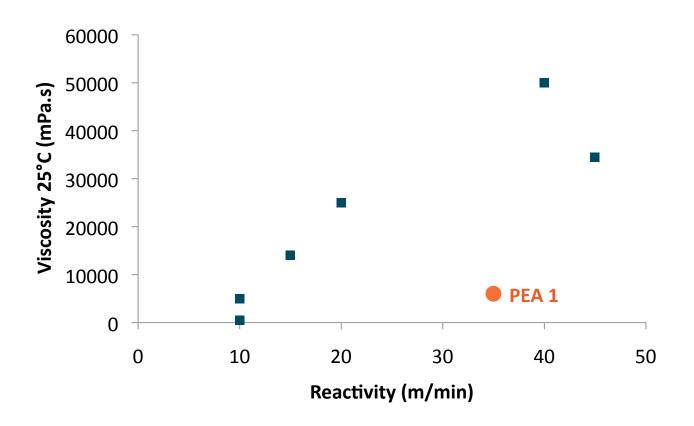
# **PEA 1 Cure Speed and Hardness**

Formulation	
PEA 1	100
Photoinitiator Blend	5
Total	105
Cure speed <sup>1</sup> & Hardness <sup>2</sup>	
Viscosity - c&p - CSR20 @ 25°C mPas	3330
Cure speed Fingernail scratch (m/min)	35
Cure speed 100 Acetone double rubs ( m/min )	< 50
Persöz hardness (s) Curing: 2 x 35 m/min	161

- (1)  $10 \mu m 80 \text{ W/cm Hg lamp}$
- (2)  $60 \mu m$  coat on glass cured at 2 x 35 m/min

PEA 1 shows high cure speed and hardness

# **PEA 1 Comparison with other PEAs**



PEA 1 combines a high reactivity with a low viscosity without the addition of a diluent

# **PEA 1 - Scratch Resistance Topcoat for Parquet SPF**

Formulation	Parts
PEA 1	55
DPGDA	29.5
Flow and Leveling Agent	0.5
Photoinitiator 1	4
Photoiniitator 2	1
Silica 1	8
Silica 2	1
Wax	2
Substrate Wetting Agent	1

# **PEA 1 - Scratch Resistance Topcoat for Parquet SPF**

Stain resistance	80 μm coat on Leneta	120 μm coat on beech with WB primer
	24 hours Stain	test ( 1 – 5 rating )
Bleach water	5	3
ETOH/ water 1/1	5	5
10% Na <sub>2</sub> CO <sub>3</sub>	5	3
Coffee	5	5
Mustard	5	5
Adhesion/flexibility	120 μm coat on beech with WB primer	
Hamberger (N)	38<	
Erichsen (N)	27	
Coin test	OK	
Gloss on Black Leneta	80 μm coat on Leneta paper	
20° 60°	7 40	

Coating on Beech and Leneta paper cured with 80-120W Hg lamp

**PEA 1 can be used as Topcoat for Parquet Flooring** 

# **PEA 1 Sprayable High Gloss Pigmented Topcoat SPF**

Formulation	Parts
Trifunctional, hard PEA	35
PEA 1	35
DPGDA	30
White pigment paste	10
Wetting agent	0.5
Antisettling agent	2
Photo-initiator blend	3

Viscosity Cup 4 25°C: < 1 min 35 sec

# **PEA 1 Sprayable High Gloss Pigmented Topcoat SPF**

Stain- & solvent resistance	80 μm coat on Leneta paper	
	24 hours Stain test (rating 1 – 5)	
Bleach water	3	
EtOH/ water 1/1	5	
10% Na2CO3	3	
Coffee	5	
Mustard	3	
Acetone DR	>100	

80 μm wet coat	80 μm coating on MDF with 100% solids primer and sealer
Coin test	Pass without burnish mark

Gloss on Black Leneta	80 μm coat on Leneta paper
20°	36
60°	73

PEA 1 can be used as 100% sprayable formulation for Furniture

# **PEA 1 LED Curing with Co-Initiator SPF**

Formulation	Α	В	С
PEA 1	50	65	75
Hexafunctional UA	25	10	
Co-Initiator	25	25	25
Phosphine Oxide Photo initiator	5	5	5
Cure speed : 10 μm on Leneta paper			
Surface cure (m/min) measured by fingernail	1x10	1x5	2x5
Through cure measured by number of double acetone rubs	>100	>100	>100

Curing: 8W/cm2 - 395 nm - 1 cm distance

#### **New PEA Resins for Industrial Wood Coatings**

## PEA 1 (experimental)

- Low viscosity combined with high cure speed and low shrinkage
- Good overall properties (hardness / flexibility) with high Tg
- Good component for UV LED due to high reactivity
- Biobased, 56% Renewable Content

# PEA 2 (experimental)

- Recycled raw materials for cost benefit
- Good performance properties
- Excellent flow when filled



#### **Raw Materials From Recycled Plastics**





Europe (2011): 1.6 million tons of PET bottles collected 1.12 million tons of PET flake produced

- Different scrap shapes: cut, grinded, extruded pellets
- Different colors
- Different qualities





## **Raw Materials From Recycled Plastics**

m > n

#### PET glycolysis

Influence of:

- Diol and stoichiometry
- Catalyst
- Temperature
- Time
- On
- Color
- Viscosity
- Crystallinity
- Molecular Weight



Properties	PEA 2
Viscosity 25°C (mPa.s)	17000
% recycled / renewable content	33
FORMULATION	
Polyester acrylate	80
TPGDA	20
ВСРК	4
Viscosity 25°C (mPa.s)	1950
RESULTS	
Graphite (m/min)	7
Acetone Double rubs at 2x5 m/min	> 100
Persoz hardness (Seconds)	200



Graphite test



Acetone double rubs test



Persoz hardness



# **Physical Properties of PEA 2**

TYPICAL PHYSICAL PROPERTIES	VALUE	
Appearance	Clear liquid	
Color, Gardner scale	<5	
Density, g/ml at 21.5°C	1.28	
Functionality, theoretical	2	
Resin solids, %	100	
Viscosity, 25°C, mPa·s	5000	
Tensile strength, psi (MPa)	>2000	
Elongation @ break, %	~1	
Young's Modulus, psi (MPa)	>275,000	
Glass Transition temperature, °C	>80	



	PEA 2	
TABER HAZE:  10-15u coatings on PC sheet  Cure 2x5m/min @ 300 WPI  CS10F wheels, 500g, 100 cycles	9.8	
ABER ABRASION:  25u coatings on PVC  Cure 3x5 min @ 300 WPI  CS17, 1 kg. load, wt. loss after  100/300 cycles	3.9 / 12.8	Taber CS 10F/ CS
exibility: Mandrel test Su coating ure 2x5 min@ 300 WPI on Al / PC	5mm / 4mm	7
Coin Test: 25u coating on oak Cure 2x5 m/min @ 300 WPI (0=bad, 5=good)	3	Cylindrical mandrel flexibility (BS EN 435



	PEA 2	
<b>Adhesion</b> : cure 2x5 m/min @ 300WPI, cross hatch adhesion		
25u on sanded oak	80%	
40u on sanded oak	80%	
25u on PVC floor	100%	
Stain/Solvent resistance – 25u white Leneta chart (5=best, 0=worst)		
Olive oil (16h)	5	
Coffee (16 h)	3	
Black marker (5 min)	2	
Betadine (16 h)	3	
Mustard (16 h)	3	
Ammonia 10% (16 h)	4	
Ethanol 48% (16 h)	5	



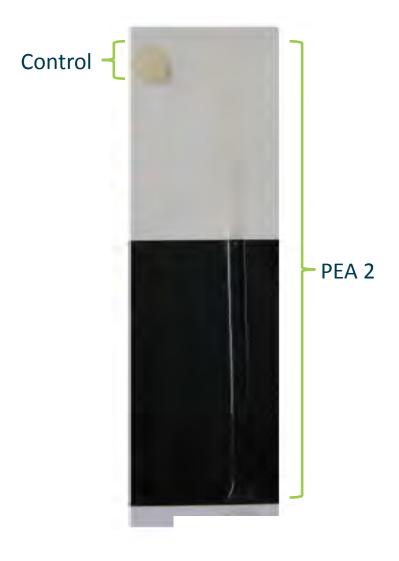
Cross hatch adhesion test



Stain resistance



	Control	PEA 2		
<b>Flow</b> : 1 gram coating (4% silica) on vertical Leneta chart, cm				
Flow after 1 minute	0.1	10.5		
Flow after 5 minutes	0.2	> 20		





#### **Conclusions**

- Two new PEAs are in development which give formulators greater latitude
- PEA 1 delivers high cure speed, high Tg and low shrinkage at low viscosity, with the additional benefits of high reactivity for LED curing and high renewable content for our environment
- PEA 2 delivers good performance properties with excellent flow when filled with the additional benefit of using recycled raw materials for cost control and for our environment

# **Acknowledgements**

# Allnex, Drogenbos, Belgium

- Hugues Van den Bergen
- Stephan Peeters
- Paul Gevaert
- Luc Lindekens



# Thank you for your attention!

For more information, please visit us at Booth #301 or at www.allnex.com.

Contact Name: Jon Shaw

Office Phone: 770-280-8370

E-mail: jon.shaw@allnex.com













# www.allnex.com

Disclaimer: Allnex Group companies ('Allnex') decline any liability with respect to the use made by anyone of the information contained herein. The information contained herein represents Allnex's best knowledge thereon without constituting any express or implied guarantee or warranty of any kind (including, but not limited to, regarding the accuracy, the completeness or relevance of the data set out herein). Nothing contained herein shall be construed as conferring any license or right under any patent or other intellectual property rights of Allnex or of any third party. The information relating to the products is given for information purposes only. No guarantee or warranty is provided that the product and/or information is adapted for any specific use, performance or result and that product and/or information do not infringe any Allnex and/or third party intellectual property rights. The user should perform its own tests to determine the suitability for a particular purpose. The final choice of use of a product and/or information as well as the investigation of any possible violation of intellectual property rights of Allnex and/or third parties remains the sole responsibility of the user.

Notice: Trademarks indicated with the ®, ™ or \* are registered, unregistered or pending trademarks of Allnex IP Sarl or its directly or indirectly affiliated Allnex Group companies.

©2016 Allnex Group. All Rights Reserved

#### **Helios Products for Wood Floors – ABRASION RESISTANCE**

#### **Abrasion Testing**

- Related to toughness
- Different tests require different sealers to pass
- Taber abrasion more common in NA



S 42
Rubber wheels +
Abrasive Paper



Taber CS 10/CS 17 CS 10/CS17 wheels





