Energy Curable Structural Adhesives

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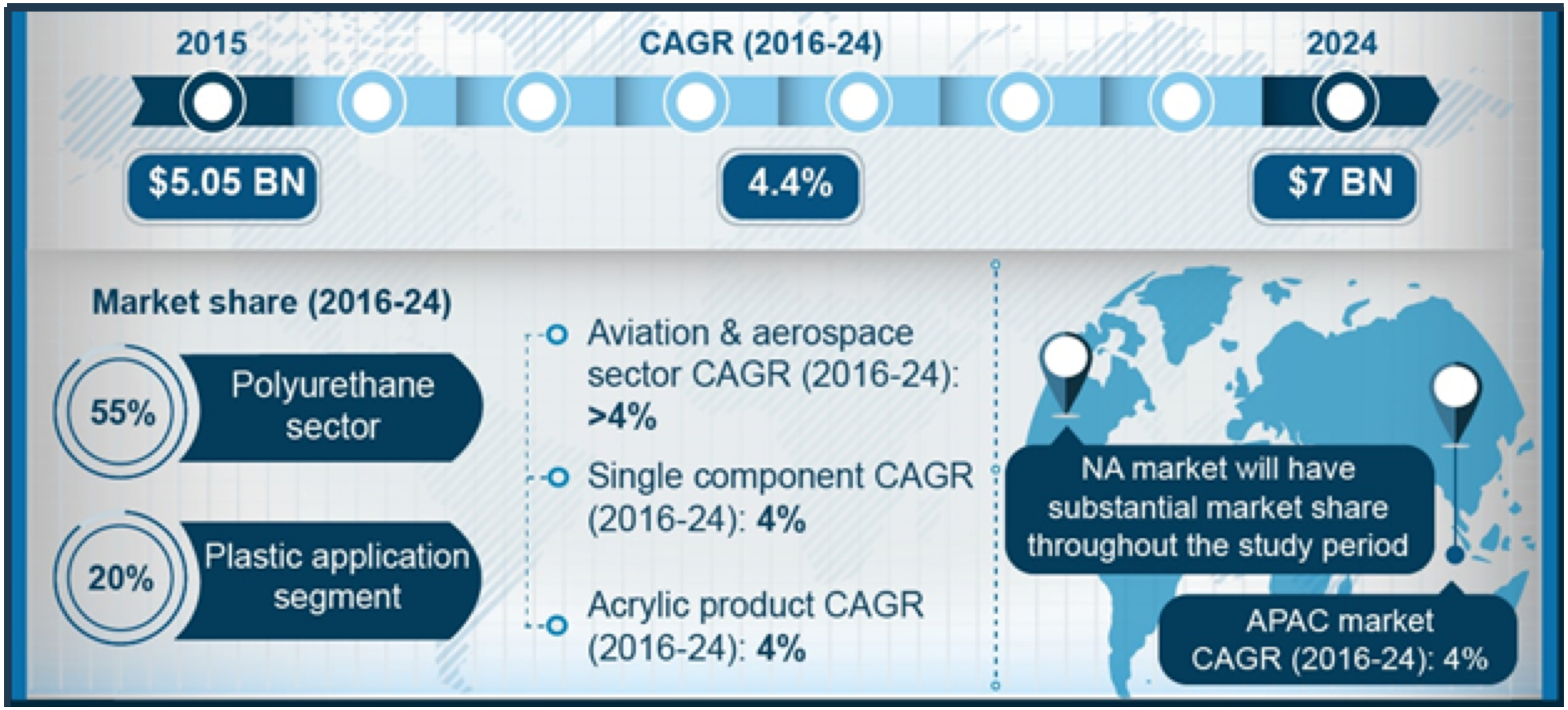
Structural Adhesives - Market

- CAGR of 4.4% between 2015 and 2024
- The growth of the market is mainly due to increased demand to lightweight vehicles
  - Transportation and aerospace applications.
    - Up to 6x more structural adhesive being used on newer vehicles.

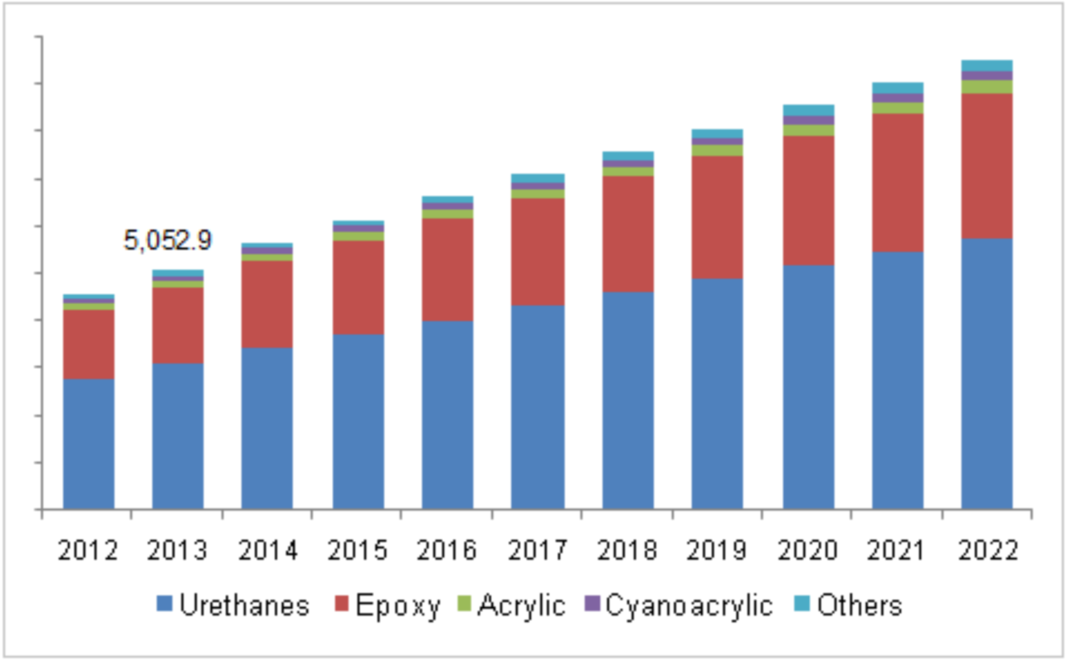


Graphic provided by Global Market Insights
https://www.gminsights.com/industry-analysis/structural-adhesives-market

Structural Adhesives - Market

- Global consumption is 10,000 – 13,000 kMT in 2018
- Global structural adhesives market size was 5,052.9 kMT in 2013 (~6500 kMto in 2018)

Global structural adhesives market share by product, 2012 - 2022 (Kilo Tons)



Structural Adhesives - Market

- **Structural Adhesives Market, by Substrate:**
  - Metals
  - Plastics
  - Wood
- **Structural Adhesives Market, by Application:**
  - Building & Construction
  - Automotive/Transportation
  - Aerospace
  - Others
- These materials can be used to bond together a multitude of similar and dissimilar substrates. This allows for faster curing times, reduced weight and improved durability. A major advantage to these systems is the reduction in manufacturing costs, due to decreased time needed for curing or reworking after conventional fasteners are used.

Structural Adhesives

- Structural Adhesives are materials used to produce load-bearing joints. Generally, adhesives are only referred to as structural adhesives if they have bond strength higher than 1000 psi, using the lap shear test method (ASTM D3163).
- Adhesives which fall into this class are typically composed of:
  - Epoxy
  - Polyurethane
  - Acrylic
  - Methyl Methacrylate
  - Cyanoacrylate

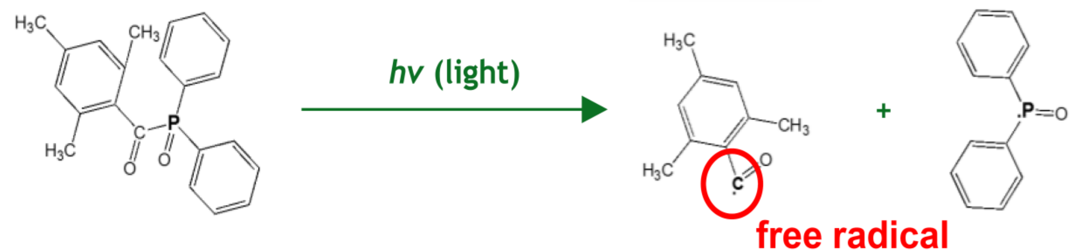
Structural Adhesives – UV advantages

- Advantages to UV Curable materials
  - Faster curing times
    - Only a few seconds to cure, not hours
    - Temperature and humidity have little effect on curing rate
  - Reaction doesn't take place until exposed to UV light
    - No extra waste
    - No pot life issues
  - No VOCs
    - No need for solvent
  - High degree of chemical resistance

UV Basics – Free Radical Polymerization

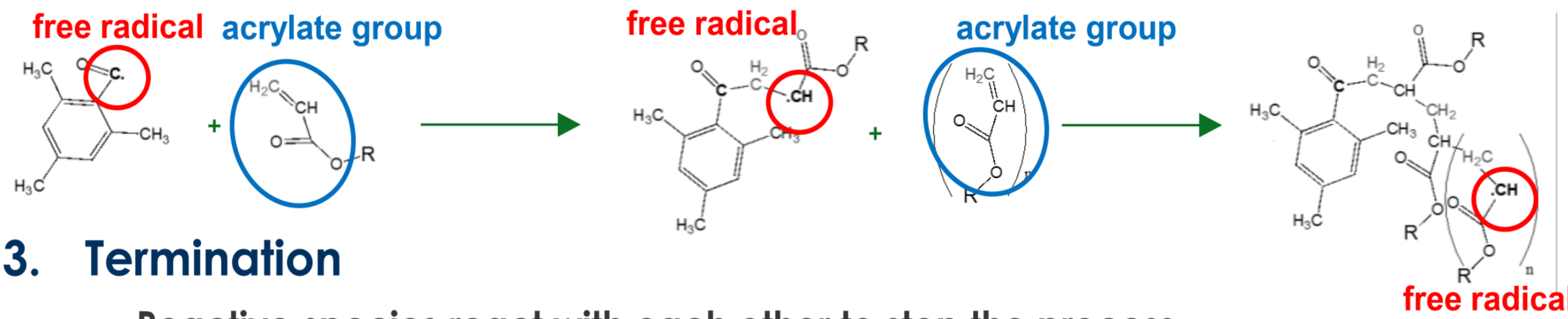
1. Initiation

- Matrix is excited with high energy source (electron beam)
- Initiators break apart into reactive species (thermal initiator or photoinitiator)



2. Propagation

- Reactive species add to vinyl bonds of monomers and oligomers
- Excited Monomers and Oligomers add to each other building molecular weight



3. Termination

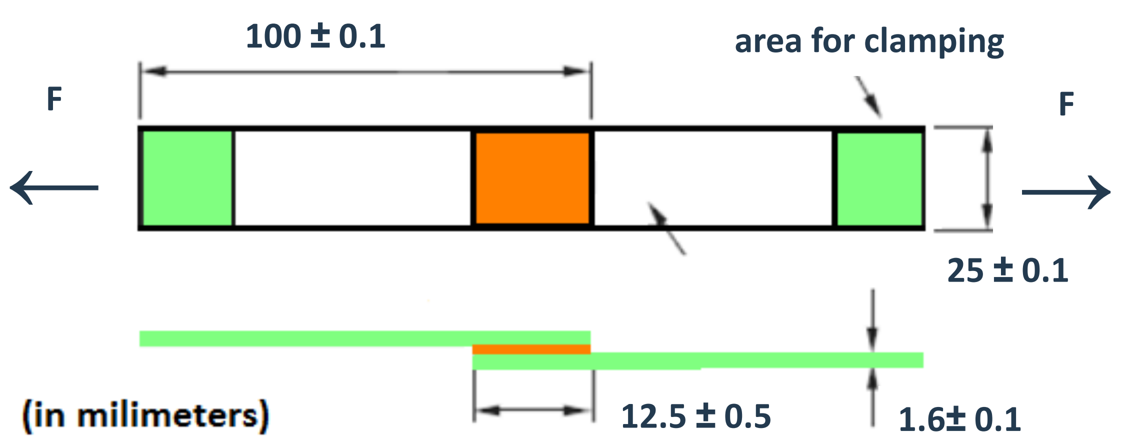
- Reactive species react with each other to stop the process

Formulation Components

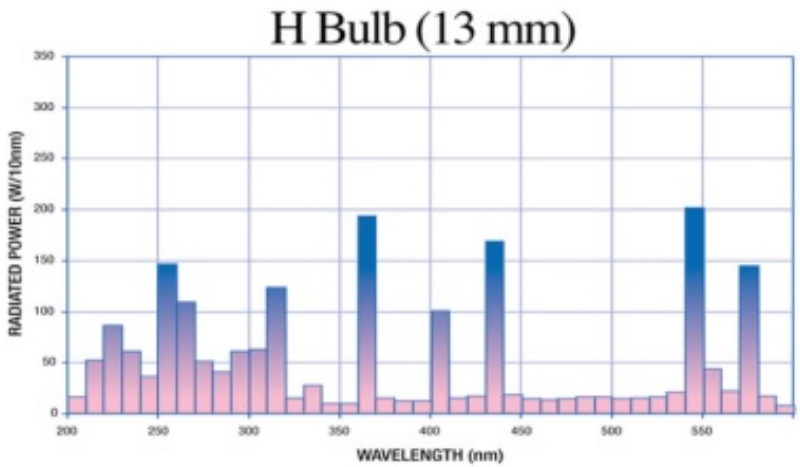
- Oligomers
  - Provide much of the shear strength
  - Contribute to reactivity, chemical resistance, and heat resistance
  - Influence T_g of final formulation
- Monomers
  - Reactive diluents – lowers the viscosity of the total formulation
  - Influence substrate wetting, leveling and final properties
  - Influence crosslink density, T_g, cure speed, chemical resistance, thermal resistance, flexibility
- Photoinitiators
  - Responsible for curing the material
    - Application/Curing method must be considered in selection to ensure appropriate crosslinking
- Additives
  - Adhesion promoters, amine synergists, etc.

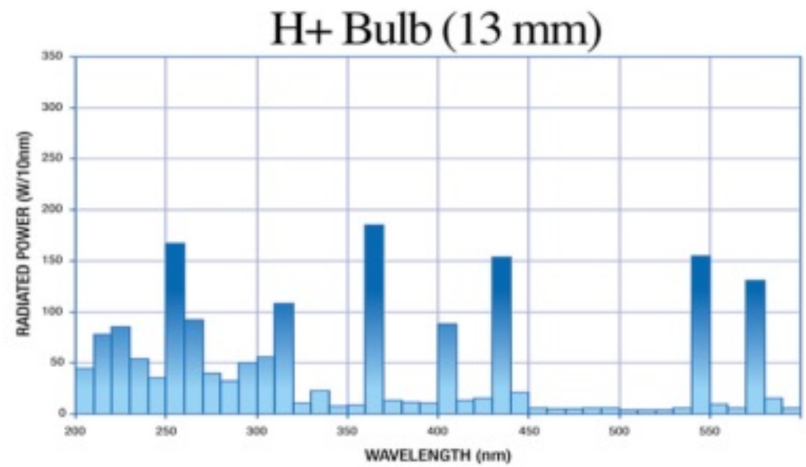
Test Method – Lap Shear

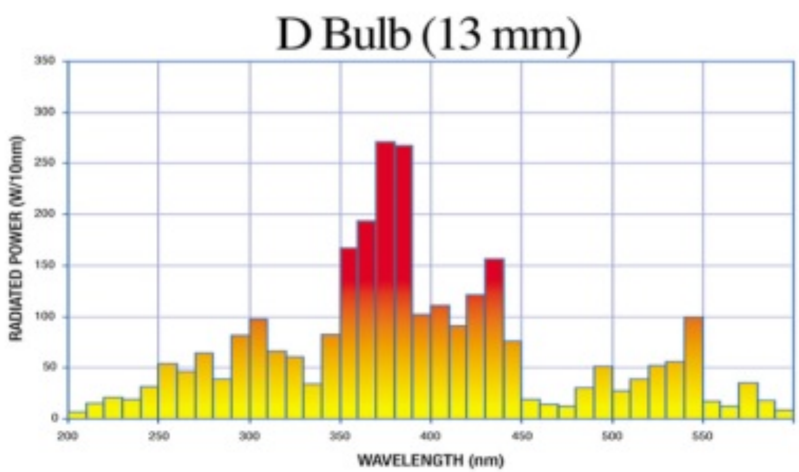
- Lap Shear – ASTM D3163
  - ASTM D3163 is used to measure the strength of a cured bond. This property is critical to any type of adhesive. This standard is specific to the shear properties of rigid plastic assembled parts. Data collected using this method allows for the comparison of bond strength between not only different substrates, but also different substrate surface treatments.

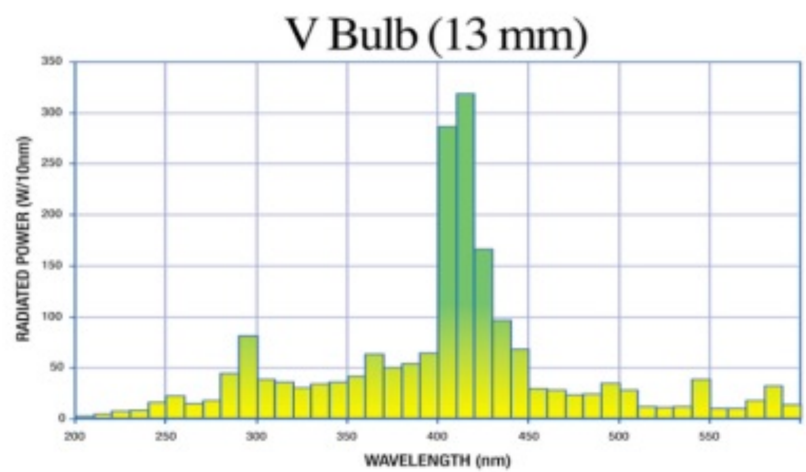


UV Lamps – Substrate Influence









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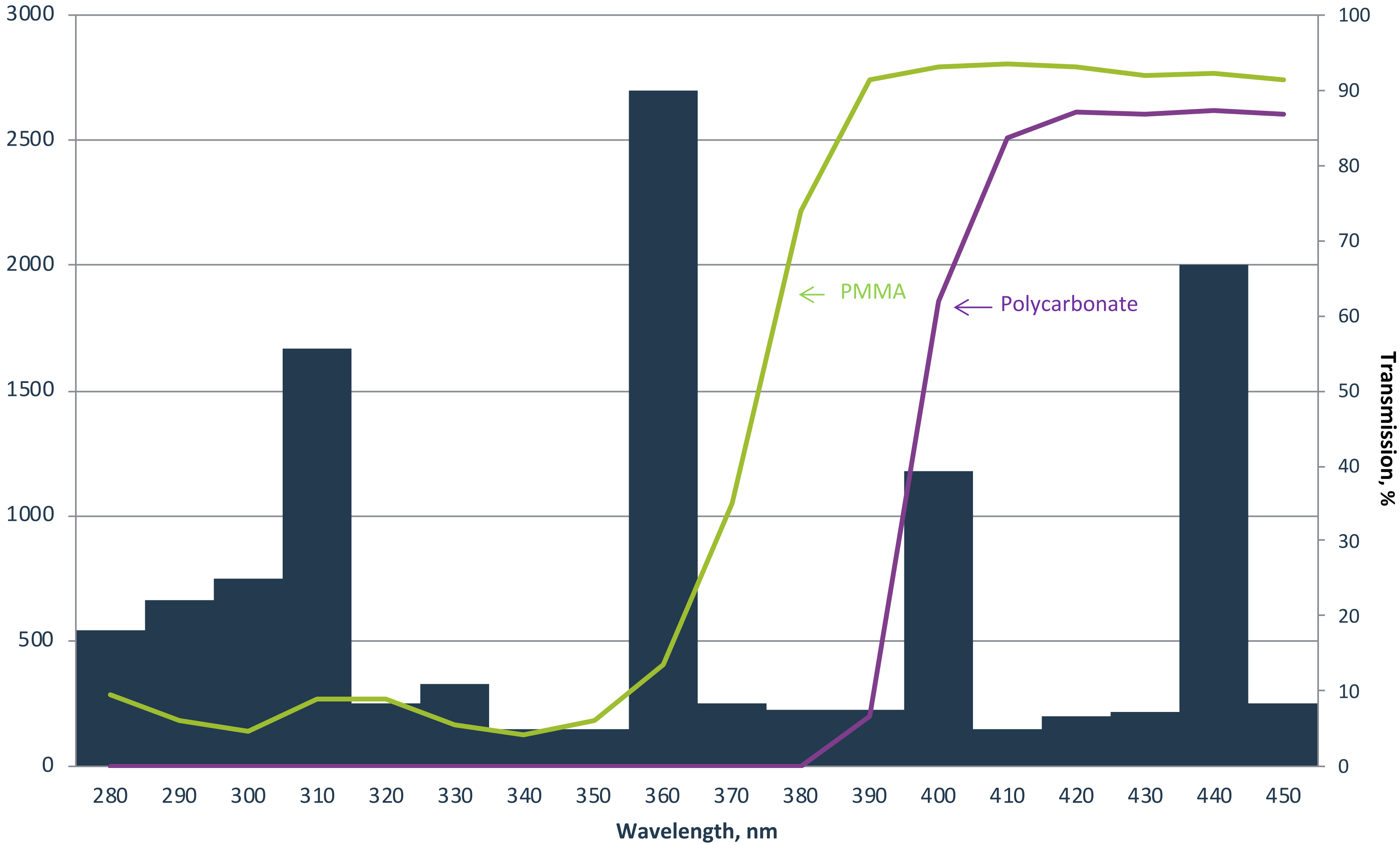
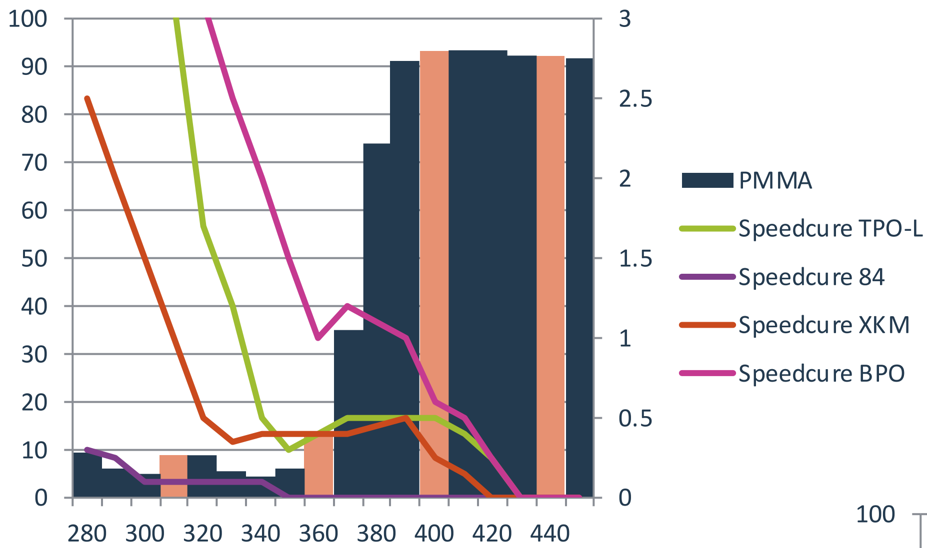
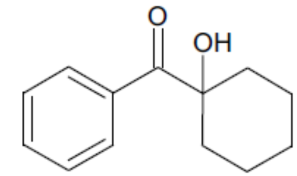
Substrate Dependency



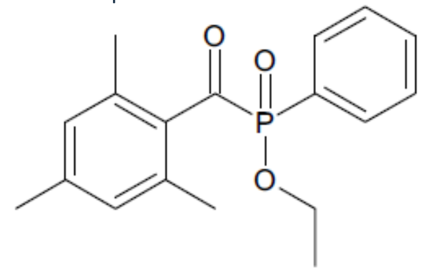
Matching Photoinitiators to Lamps and Substrates



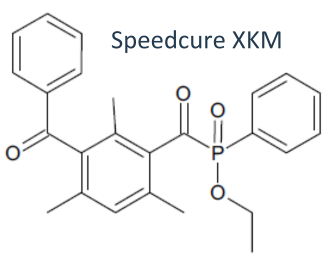
Speedcure 84



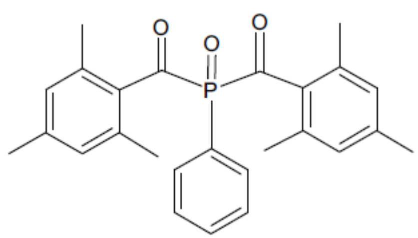
Speedcure TPO-L

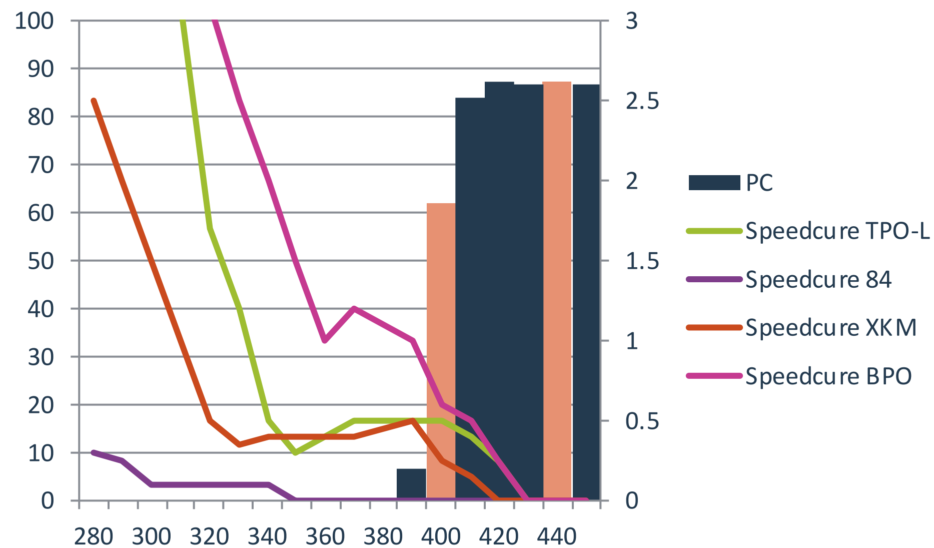


Speedcure XKM



Speedcure BPO

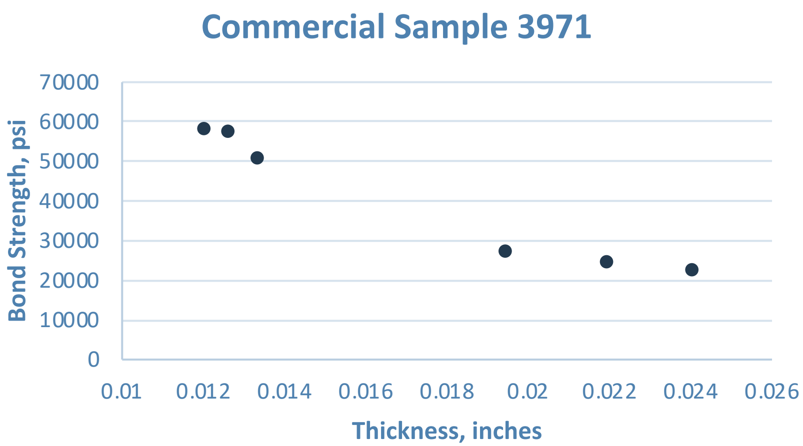


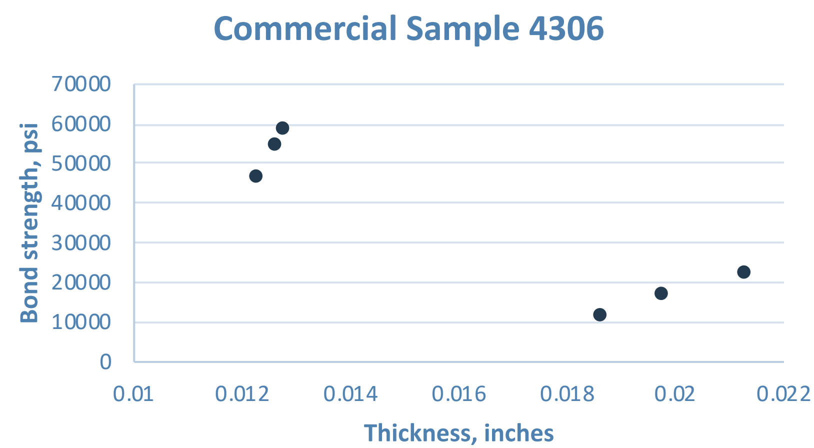


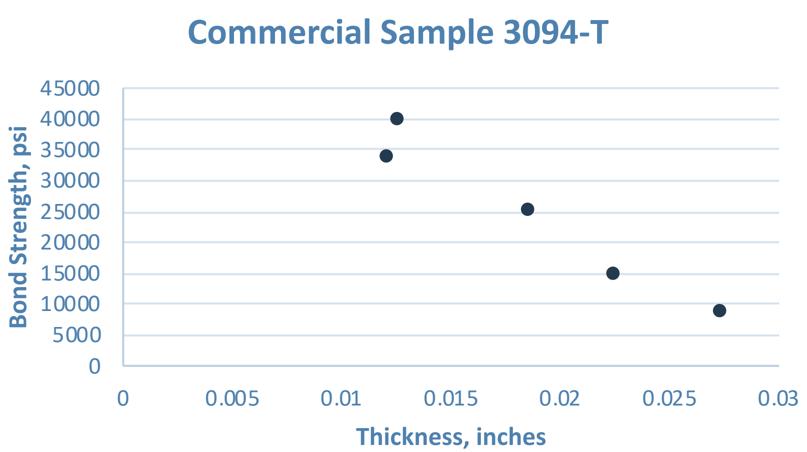
Structural Adhesives Study

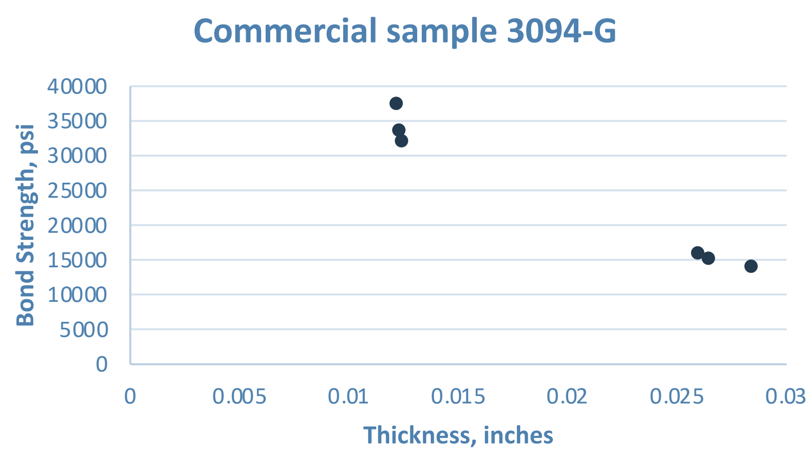
Commercial Benchmarking

Commercially Available Benchmarks









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Curing conditions – through PC film - 2000 mJ/cm2 from the radiometer

Summary - Commercially Available Benchmarks

- Based on the benchmarks the parameters for these materials were decided.
  - The material needs to have good adhesion to both the plastic (PC) and the metal.
  - The thickness target needs to stay between 0.008 and 0.015 inches
  - The bond strength needs to be greater than 30,000 psi
  - Cure using mercury bulbs through PC
  - Tg target of less than 60°C
  - Viscosity less than 4,000 cps at 25°C

Oligomers

Oligomers	Description	Functionality	Tg
RX 4513	Aliphatic urethane acrylate	3.2	10°C
RX 4858	Low viscosity aliphatic urethane diacrylate	2	54°C
RX 4738	Aliphatic urethane acrylate	3	80°C
RX 20139	Low Viscosity aliphatic urethane dimethacrylate	2	60°C
RX 8402	Low viscosity aliphatic urethane diacrylate	2	14°C

Monomers

Diluting Monomers	Functionality	Glass transition temperature
TCD monoacrylate	1	100°C
2-HEA	1	-16°C
2-phenoxyethyl acrylate	1	5°C
THFMA	1	-12°C

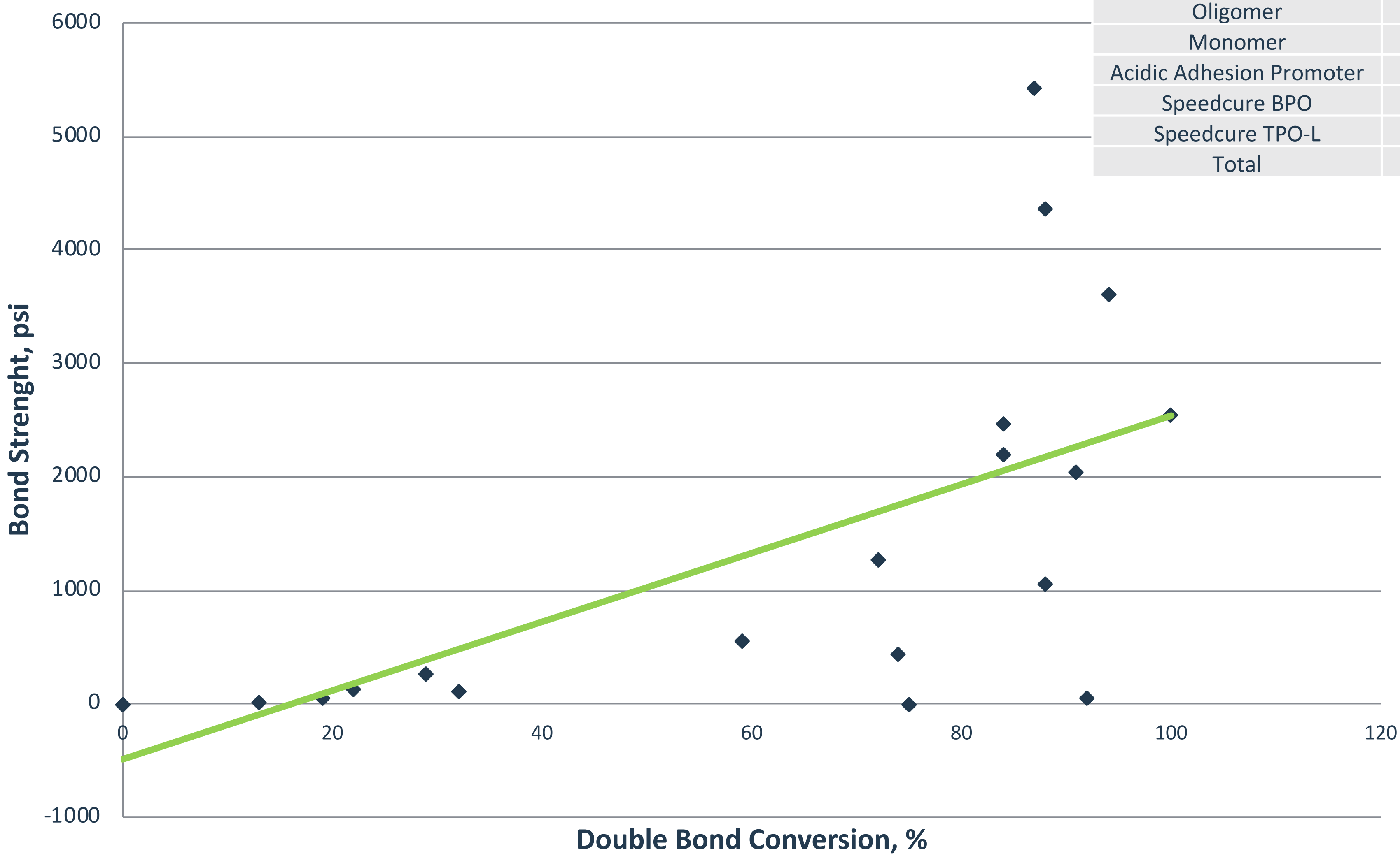
Target Specifications

- Based on learnings from commercially available samples
  - Bond strength – >30,000 psi
  - Color – clear to pale yellow
  - Thickness target – 0.008-0.015 inches
  - Substrates – Polycarbonate bonded to metal
  - Maximize double bond conversion, curing through substrate with mercury bulbs
  - Tg target of less than 60°C
  - Viscosity less than 4,000 cps at 25°C

Study Results

- Identified 6 formulations that meet the targets for bond strength and viscosity
  - Various oligomers and monomers
- Identified parameters for thickness of adhesive
- Identified parameters for curing
  - Mercury lamps
  - Photoinitiator blend (TPO and BPO)
  - Energy dosage (2000 mJ/cm^2)
  - Double bond conversion (80-100%)

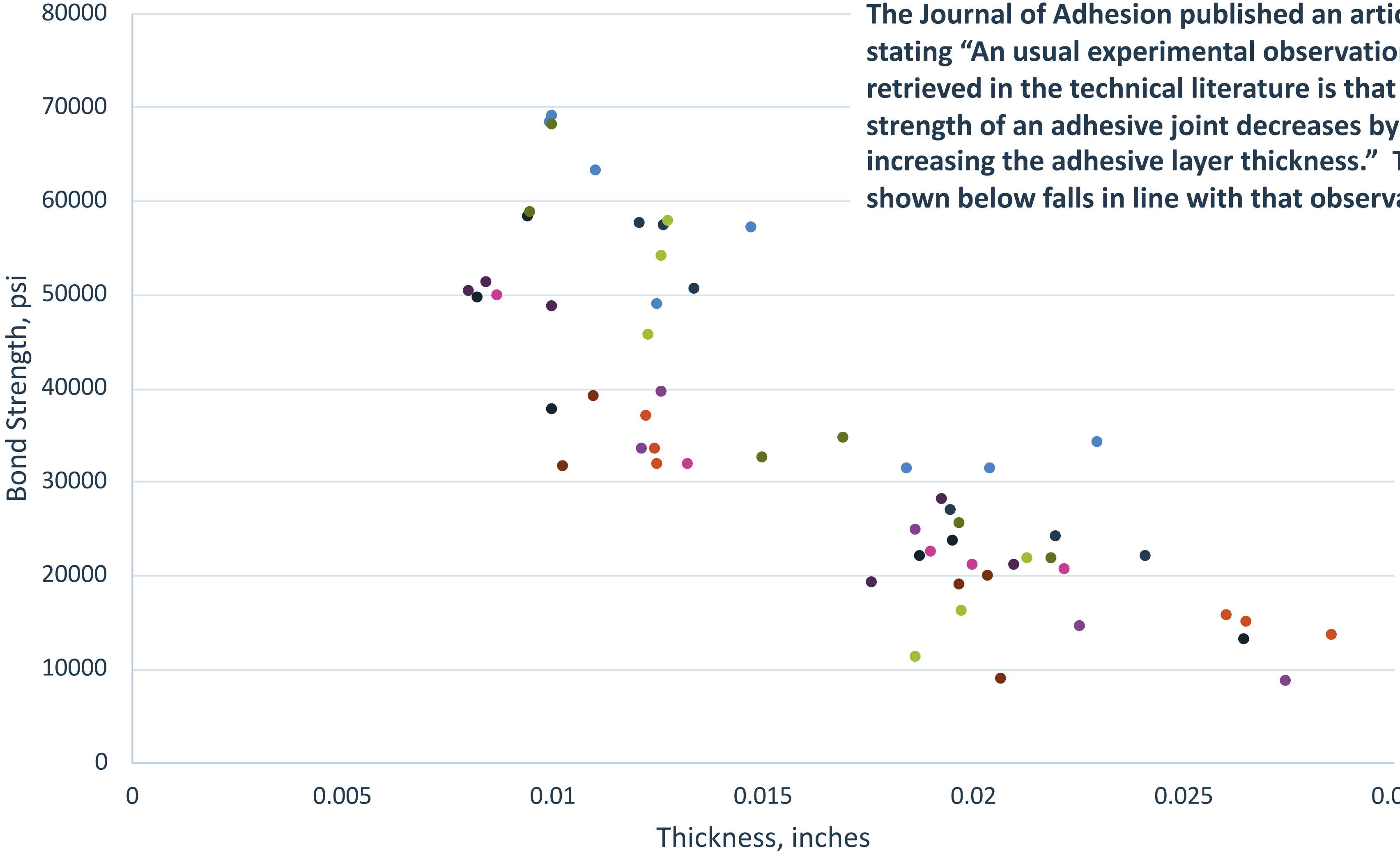
Comparison of Double Bond Conversion with Bond Strength



	%
Oligomer	45-65
Monomer	25-50
Acidic Adhesion Promoter	0.93
Speedcure BPO	1.87
Speedcure TPO-L	3.74
Total	100.00

Influence of Thickness

The Journal of Adhesion published an article stating "An usual experimental observation retrieved in the technical literature is that the strength of an adhesive joint decreases by increasing the adhesive layer thickness." The data shown below falls in line with that observation.

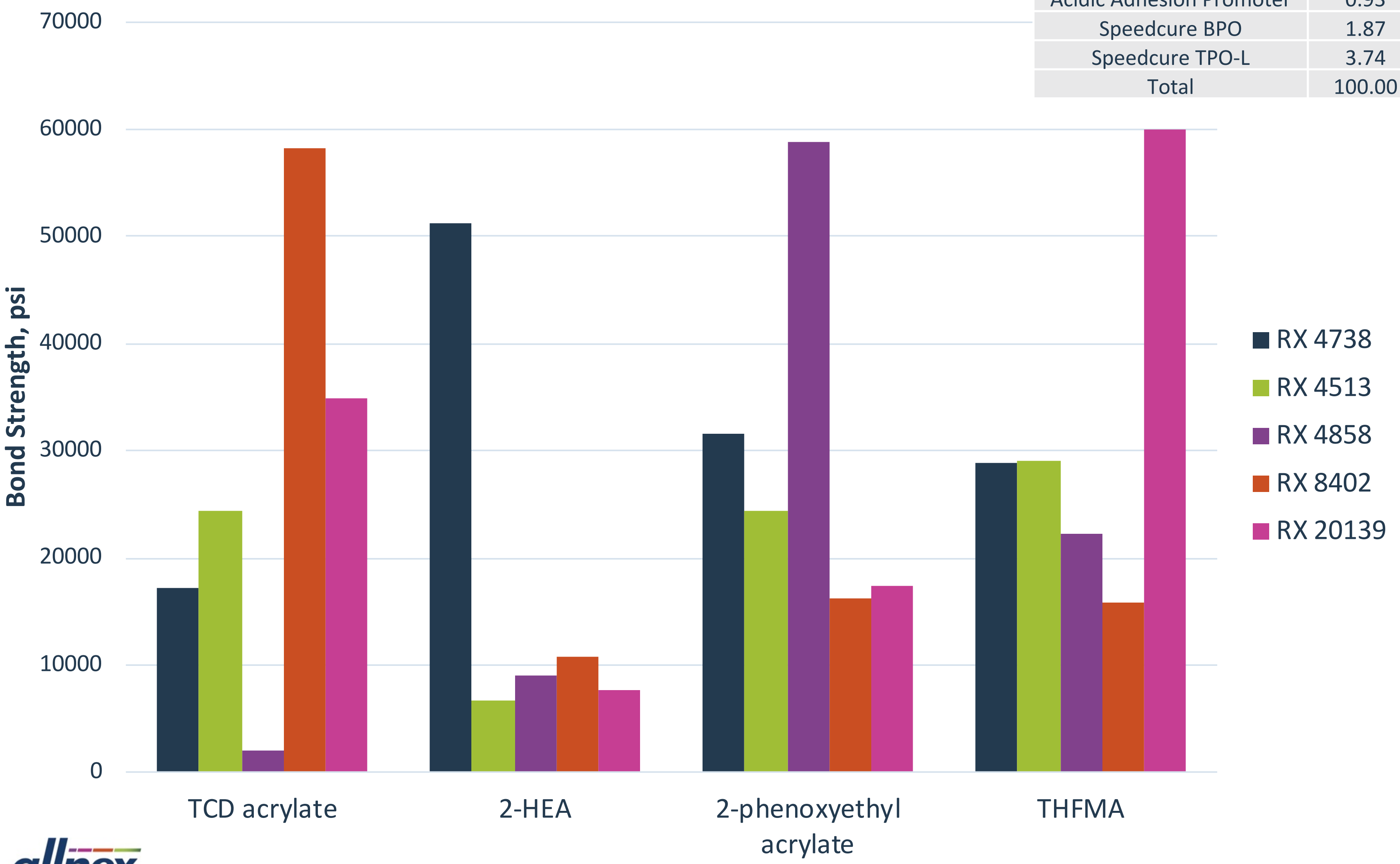


General trend for all formulations

Curing conditions – through PC film - 2000 mJ/cm2 as measured by radiometer

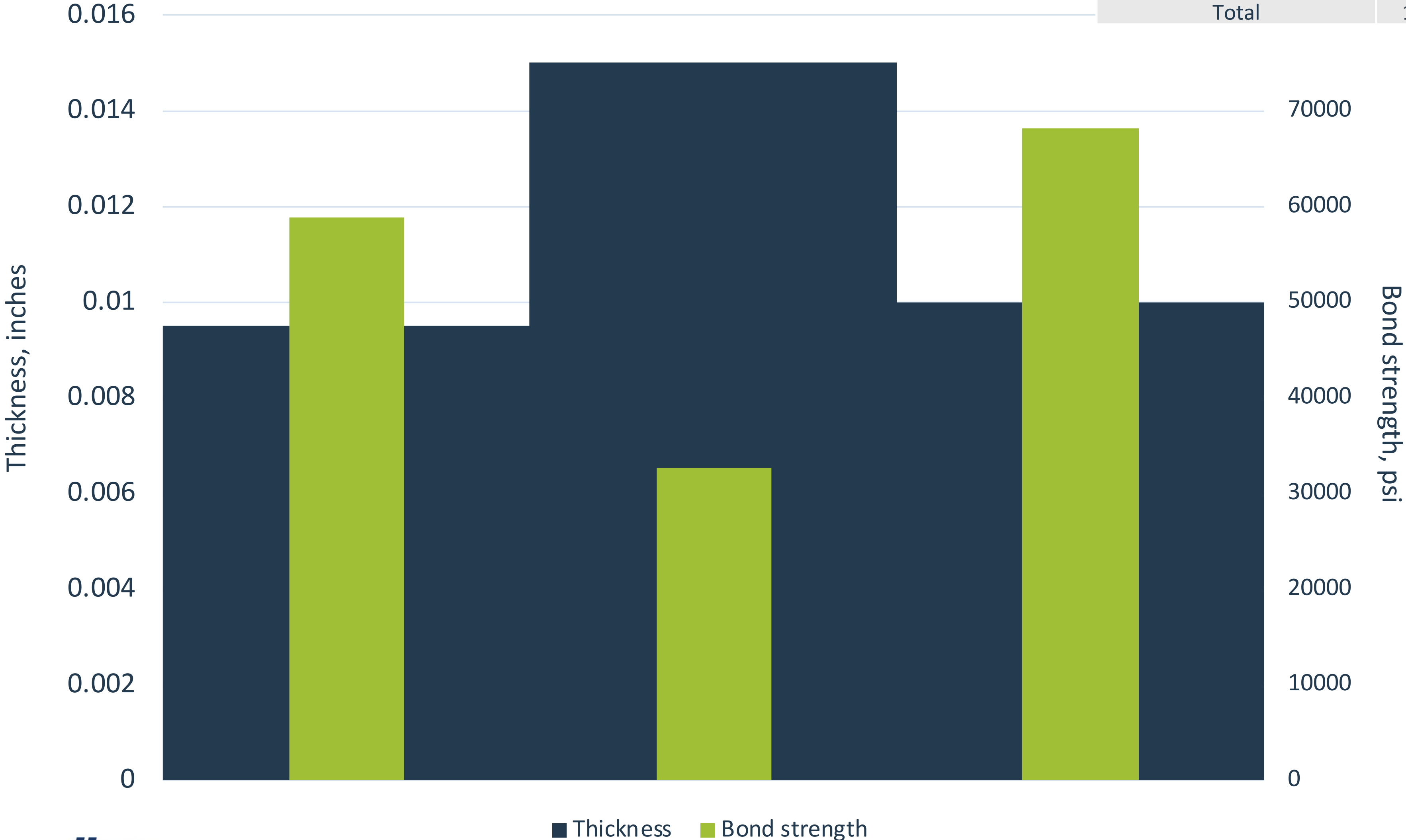
Effect of Monomer

	%
Oligomer	45-65
Monomer	25-50
Acidic Adhesion Promoter	0.93
Speedcure BPO	1.87
Speedcure TPO-L	3.74
Total	100.00



RX 4858 with 2-phenoxyethyl acrylate

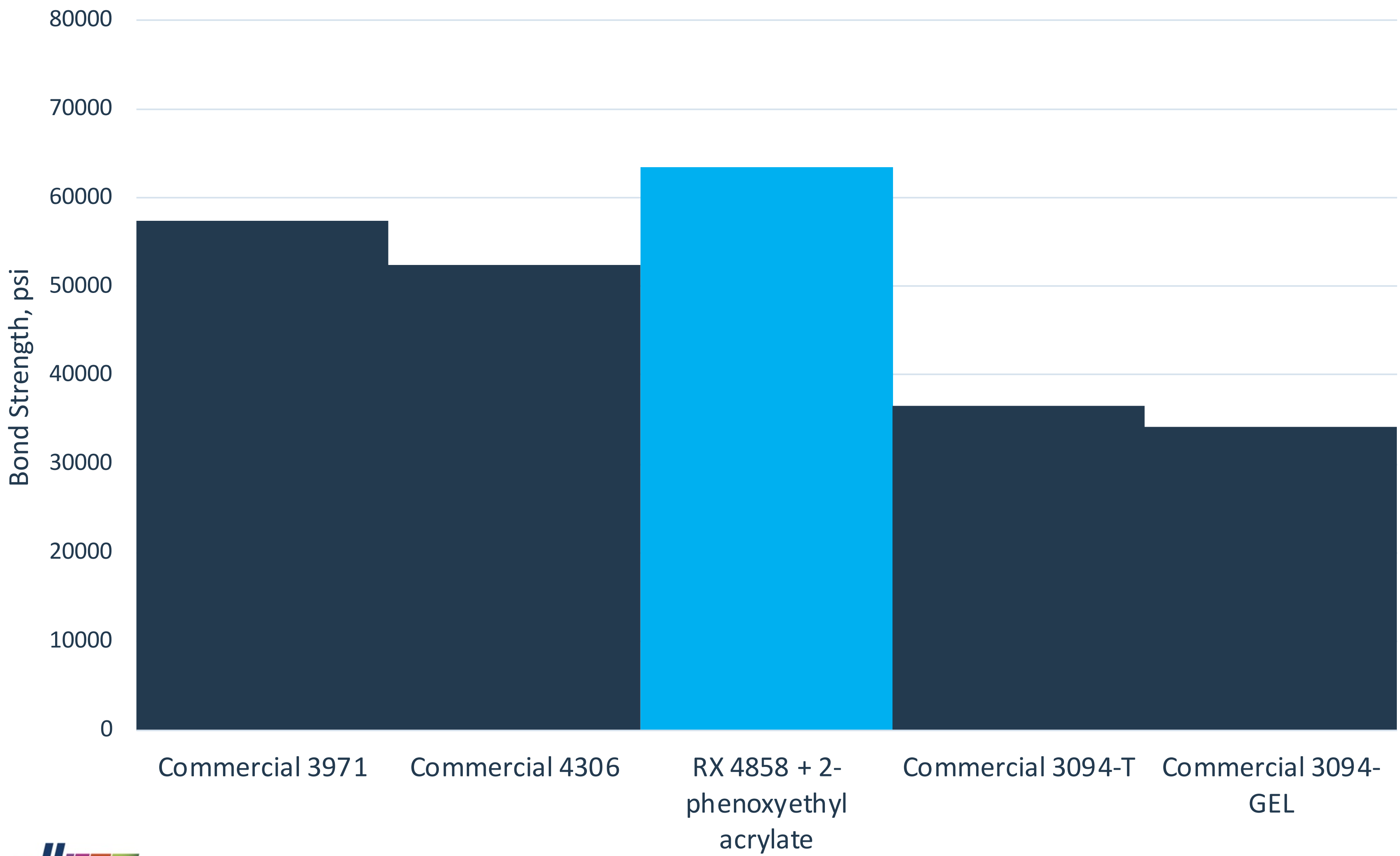
	%
RX 4858	65.42
2-phenoxyethyl acrylate	28.04
Acidic Adhesion Promoter	0.93
Speedcure BPO	1.87
Speedcure TPO-L	3.74
Total	100.00



254.6 cps at 25°C

Curing conditions – through PC film - 2000 mJ/cm2 as measured by radiometer

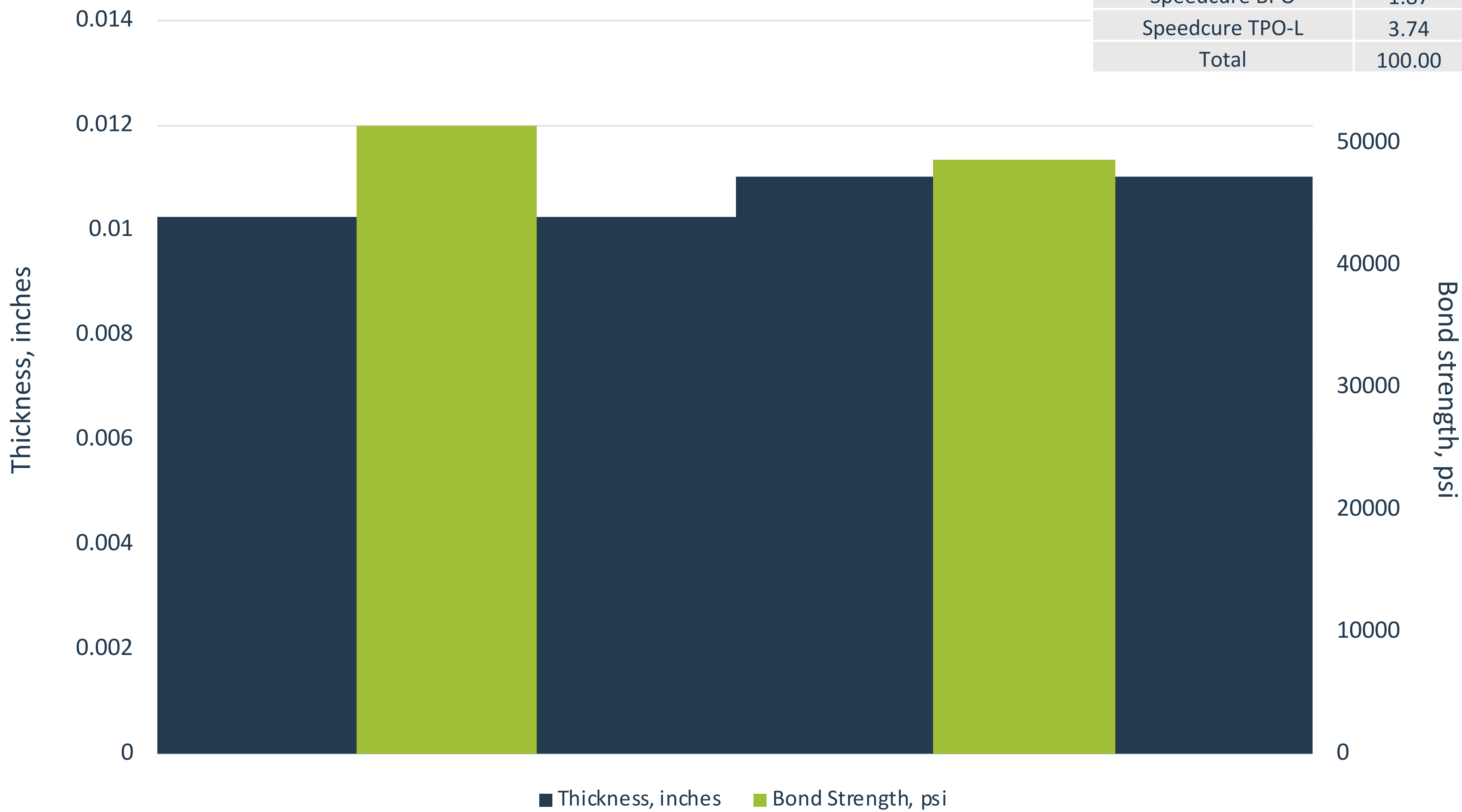
RX 4858 with monomer compared to commercially available materials.



Curing conditions – through PC film - 2000 mJ/cm2 as measured by radiometer

RX 4738 with EBECRYL 114

	%
RX 4738	46.73
2-phenoxyethyl acrylate	46.73
Acidic Adhesion Promoter	0.93
Speedcure BPO	1.87
Speedcure TPO-L	3.74
Total	100.00

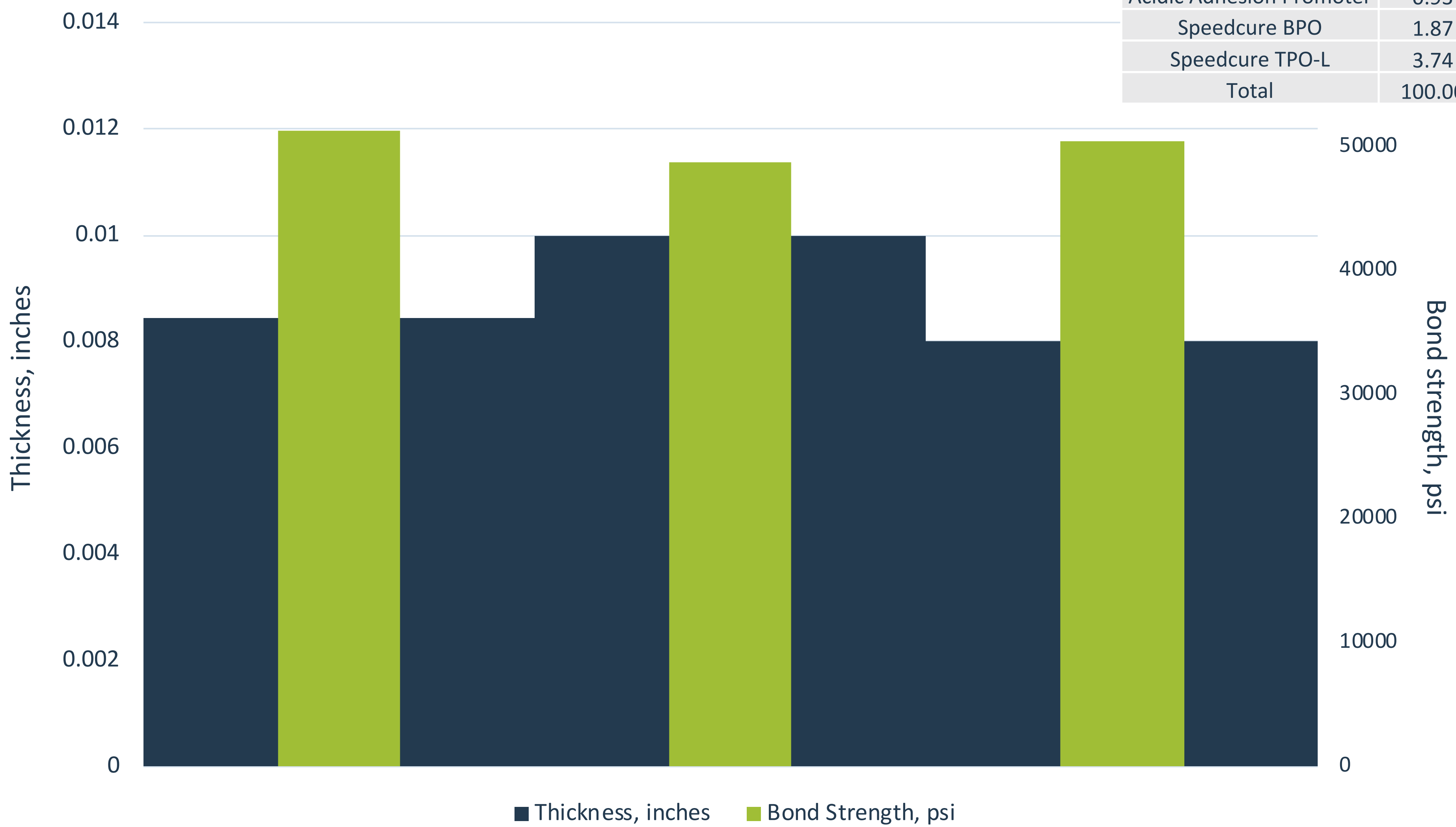


199.1 cps at 25°C

Curing conditions – through PC film - 2000 mJ/cm2 as measured by radiometer

RX 4738 with 2-HEA

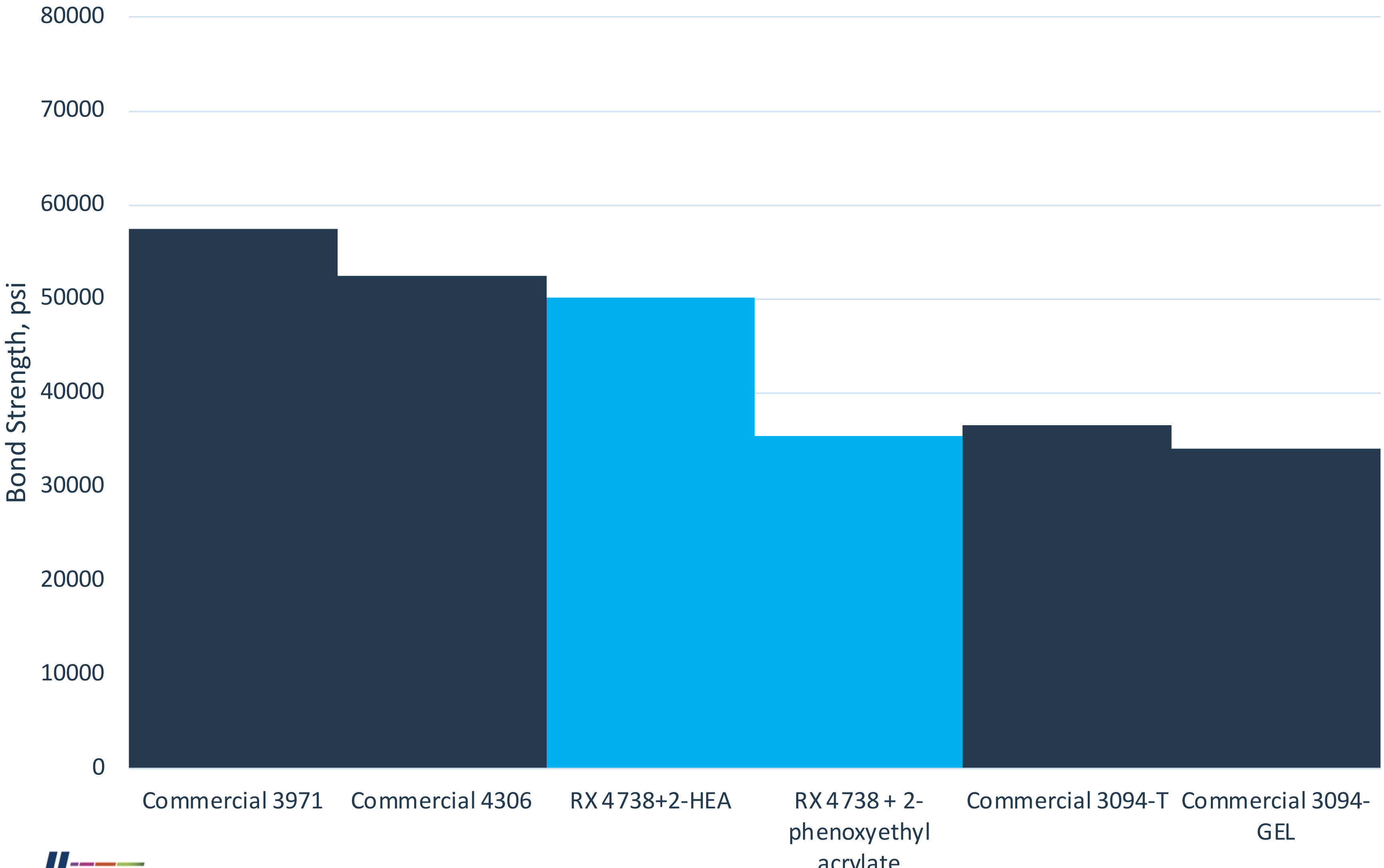
	%
RX 4738	46.73
2-HEA	46.73
Acidic Adhesion Promoter	0.93
Speedcure BPO	1.87
Speedcure TPO-L	3.74
Total	100.00



75.7 cps at 25°C

Curing conditions – through PC film - 2000 mJ/cm2 as measured by radiometer

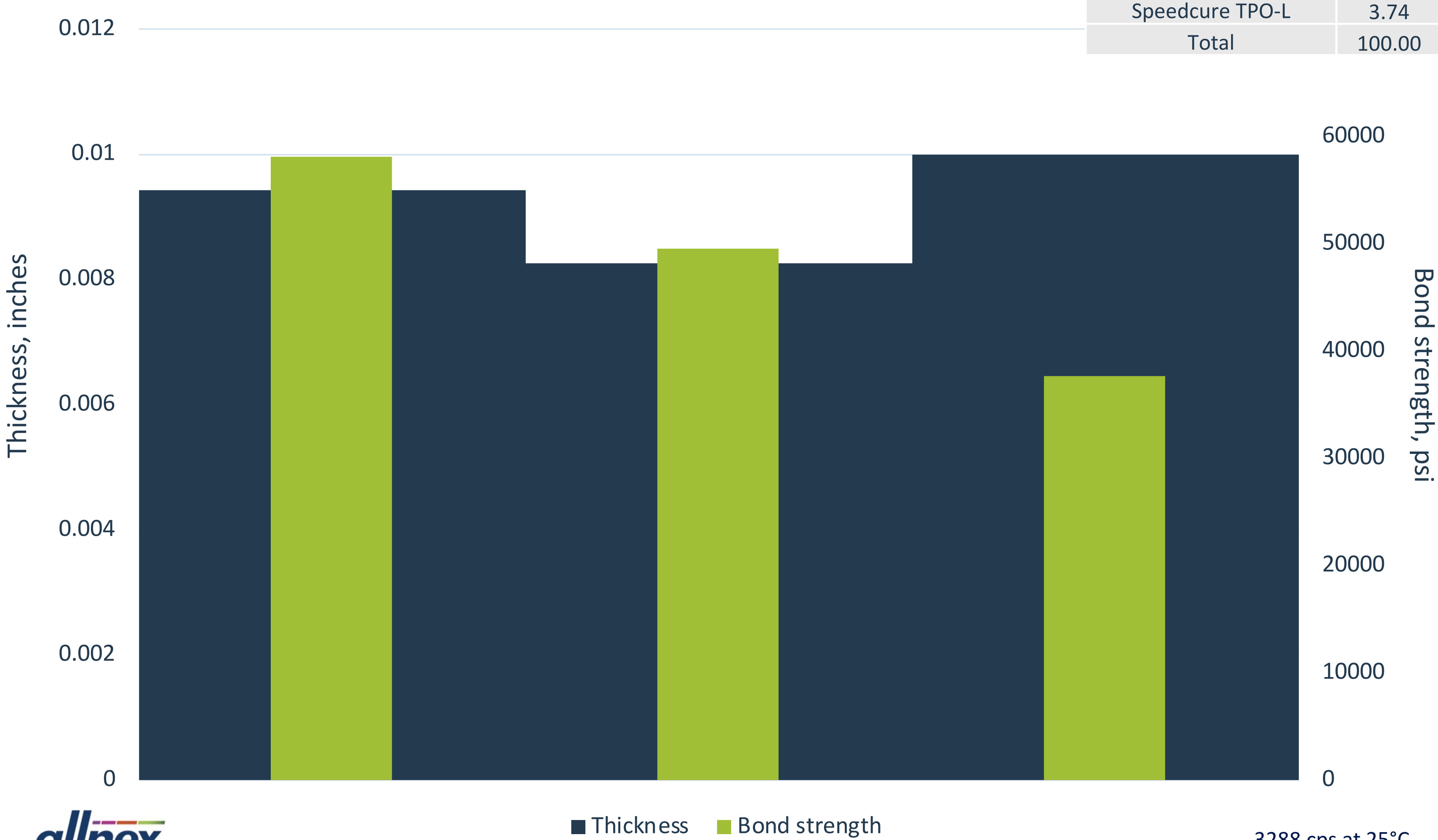
RX 4738 with monomers compared to commercially available materials.



Curing conditions – through PC film - 2000 mJ/cm2 as measured by radiometer

EBECRYL 8402 with TCD Acrylate

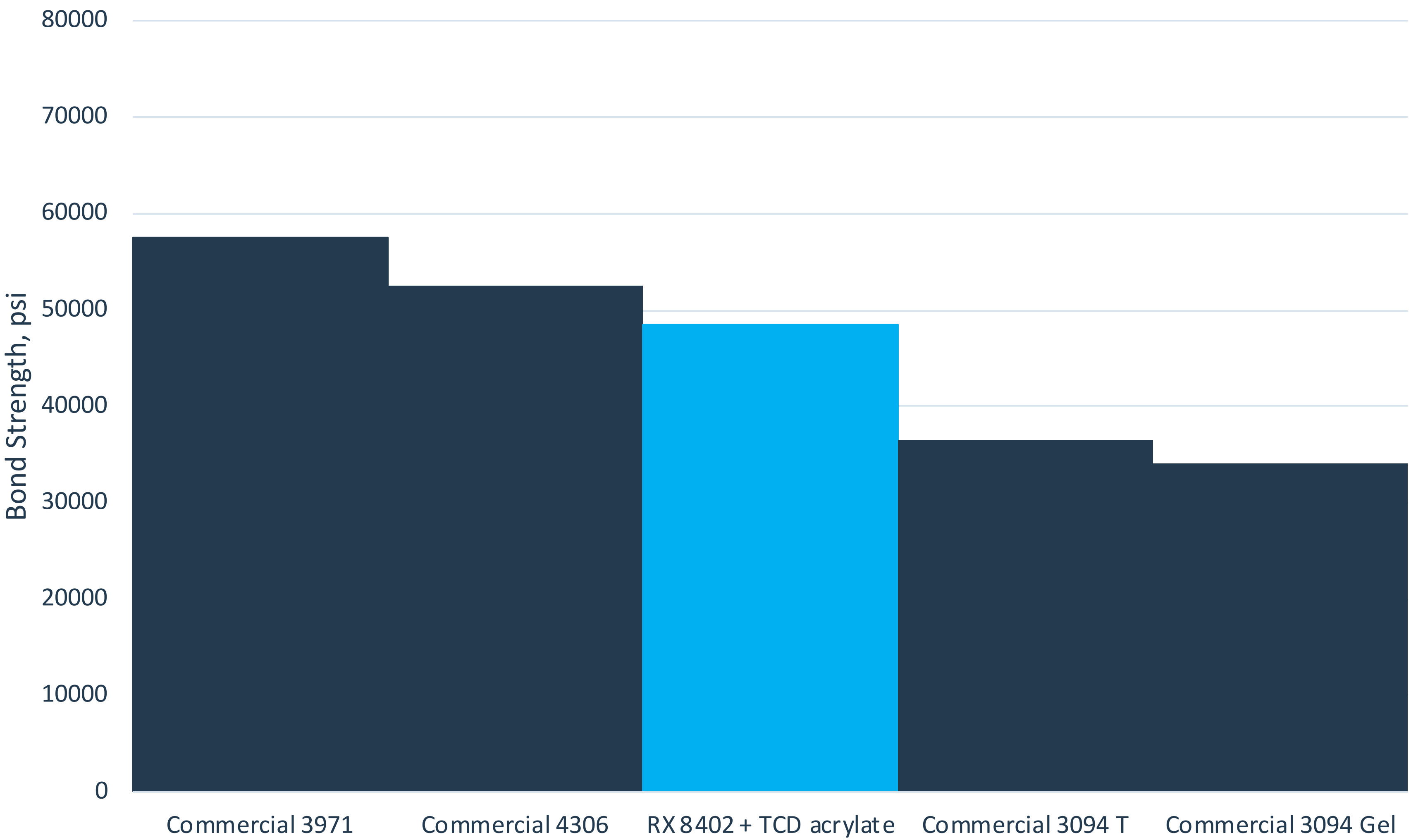
	%
RX 8402	65.42
TCD Acrylate	28.04
Acidic Adhesion Promoter	0.93
Speedcure BPO	1.87
Speedcure TPO-L	3.74
Total	100.00



3288 cps at 25°C

Curing conditions – through PC film - 2000 mJ/cm2 as measured by radiometer

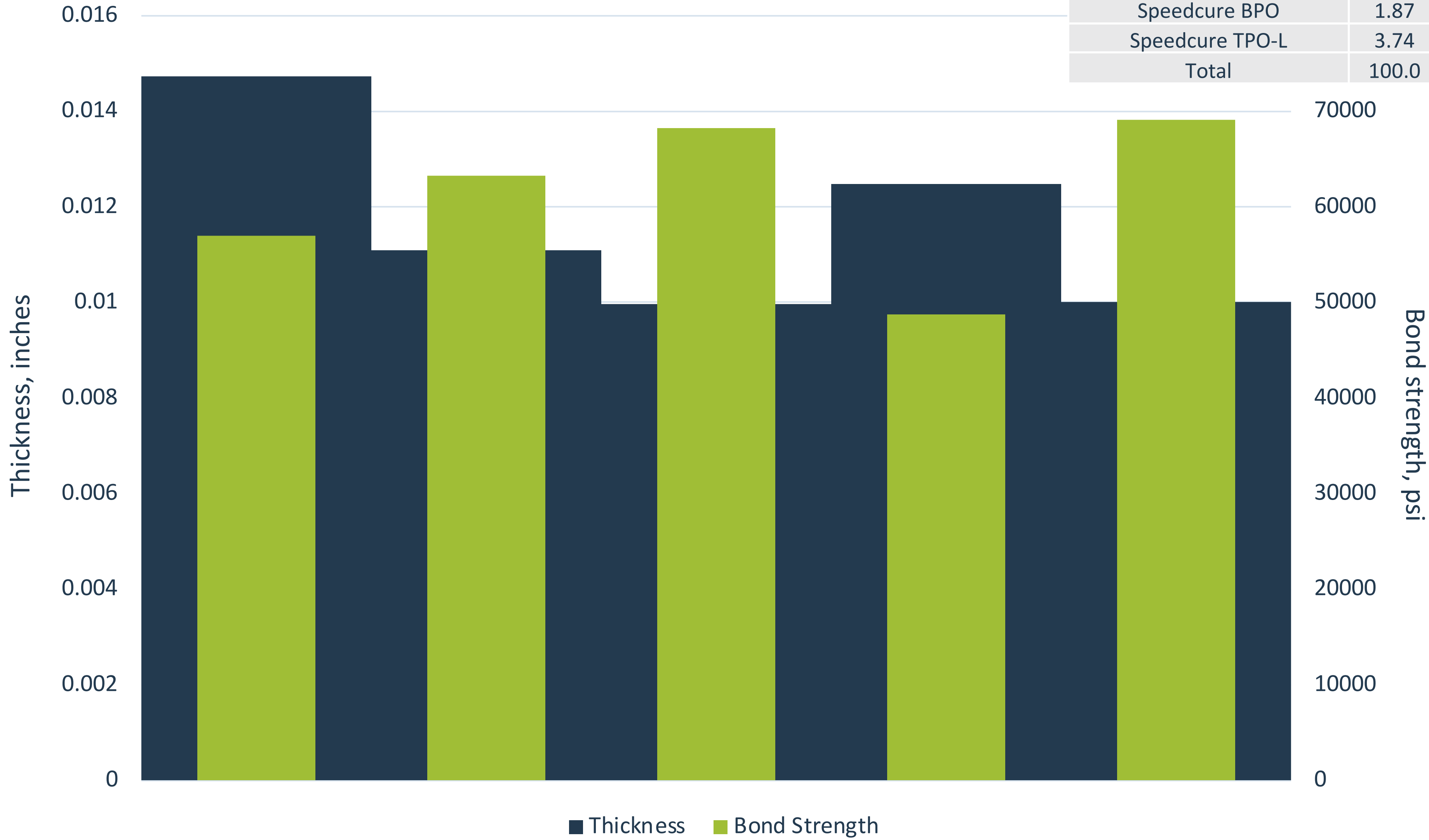
RX 8402 with monomer compared to commercially available materials.



Curing conditions – through PC film - 2000 mJ/cm2 as measured by radiometer

RX 20139 with THFMA

	%
RX 20139	65.42
THFMA	28.04
Acidic Adhesion Promoter	0.93
Speedcure BPO	1.87
Speedcure TPO-L	3.74
Total	100.0

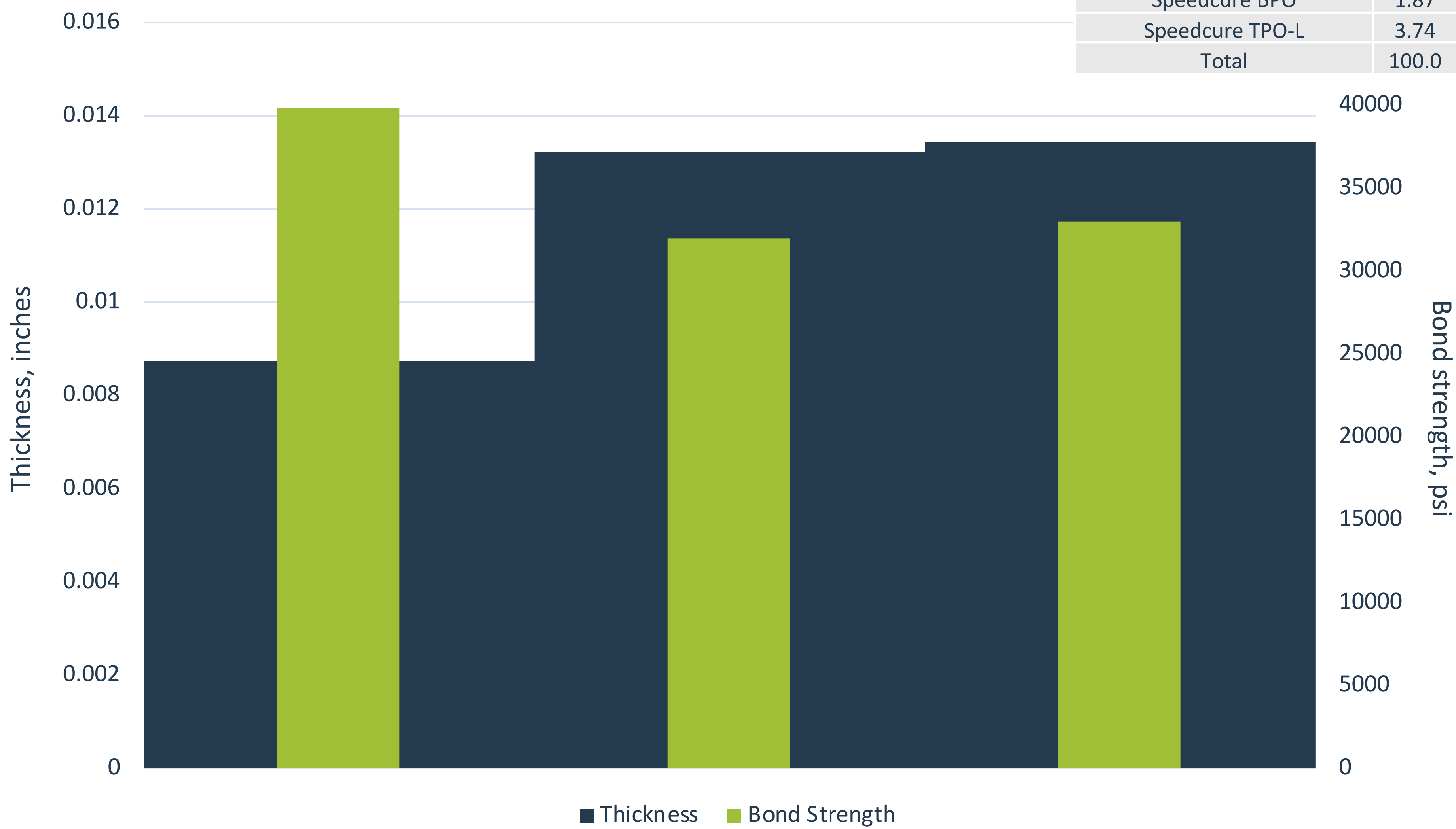


2528 cps at 25°C

Curing conditions – through PC film - 2000 mJ/cm2 as measured by radiometer

RX 20139 with TCD acrylate

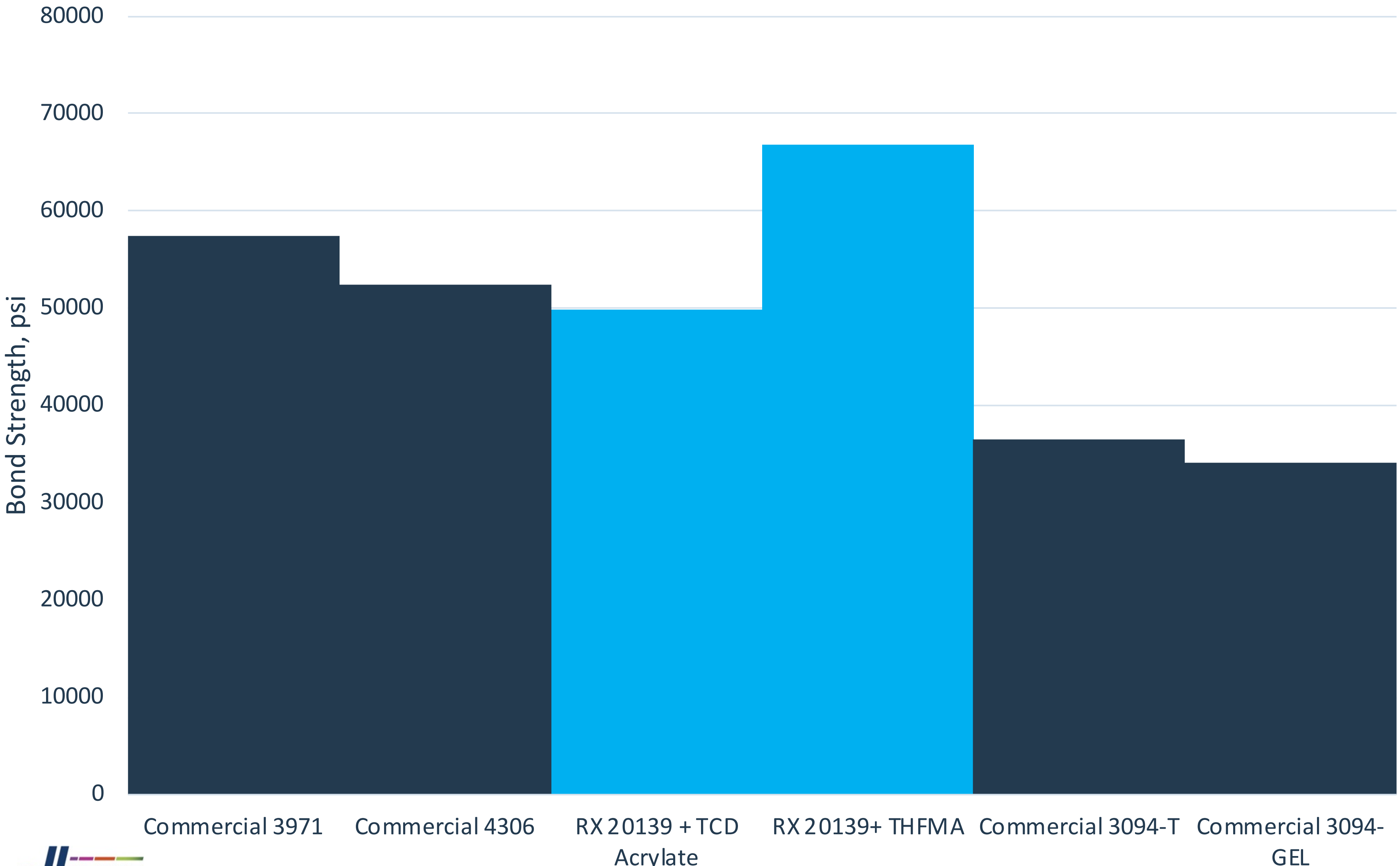
	%
RX 20139	65.42
TCD Acrylate	28.04
Acidic Adhesion promoter	0.93
Speedcure BPO	1.87
Speedcure TPO-L	3.74
Total	100.0



252.9 cps at 25°C

Curing conditions – through PC film - 2000 mJ/cm2 as measured by radiometer

RX 20139 with monomers compared to commercially available materials.



Curing conditions – through PC film - 2000 mJ/cm2 as measured by radiometer

Conclusions

- It is important to match the photoinitiator system with the lamps and light that is able to pass through the substrate being used.
- Double bond conversion is important to overall bond strength
  - Higher conversion gives higher bond strength
    - Depth of cure is incredibly important to final properties
- The glass transition temperature of final adhesive is important to the bond strength
  - Lower glass transition temperatures lead to materials with the ability to handle larger amounts of stress prior to failure
    - More malleable resin after curing
- The use of various chemistries is able to achieve a variety of bond strengths
  - A large product portfolio allows for customization of blends to achieve the perfect bond strength between two dissimilar substrates

Thank you

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Any questions ?

PLEASE CONTACT:

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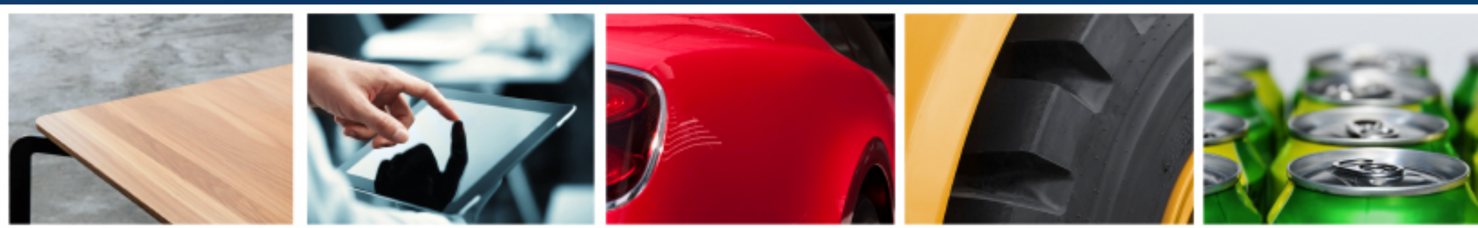

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