PHOTOCURABLE DIELECTRICS FOR ELECTRONIC PACKAGING AND ENCAPSULANT APPLICATIONS

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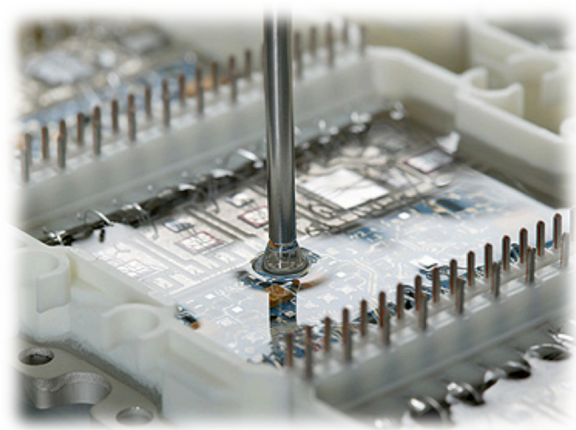
3D PEIM Symposium
6/14/2016

3D-PEIM

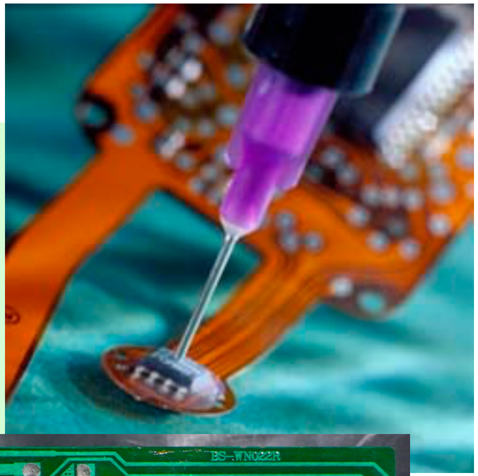
PennState



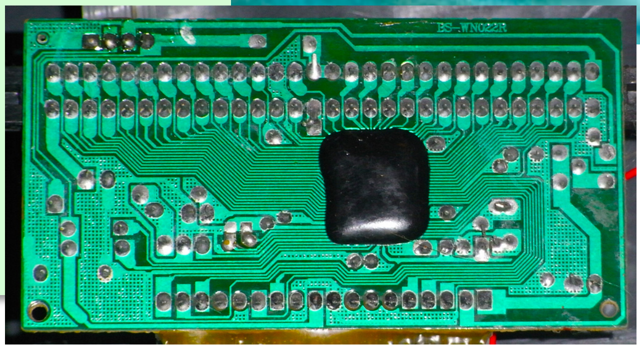
Electronic Packaging & Encapsulant Materials

- To protect microelectronics from mechanical stress, electrical breakdown, chemical/moisture erosion, radiation, and harsh environments

Requirements

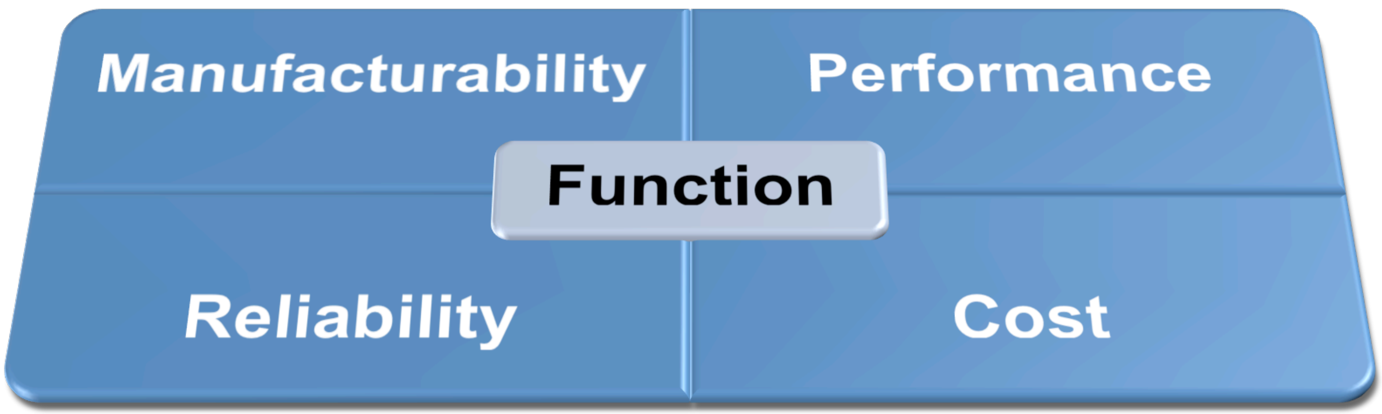


- High thermal conductivity (> 0.5 W/K.m)
- Low coefficient of thermal expansion (CTE)
- High thermal stability
- High dielectric strength (> 10 kV/mm)
- Low electrical conductivity
- Good mechanical strength
- Moisture and chemical resistance
- Easy and rapid processing
- Low cost of materials



Electronic Packaging & Encapsulant Materials

- Polymer-based materials are used extensively in electronic packaging and thermal managing systems.



- Applications: packaging moldings, encapsulations, passivation coatings, interlayer dielectric adhesives, PCB substrates, thermal interface materials

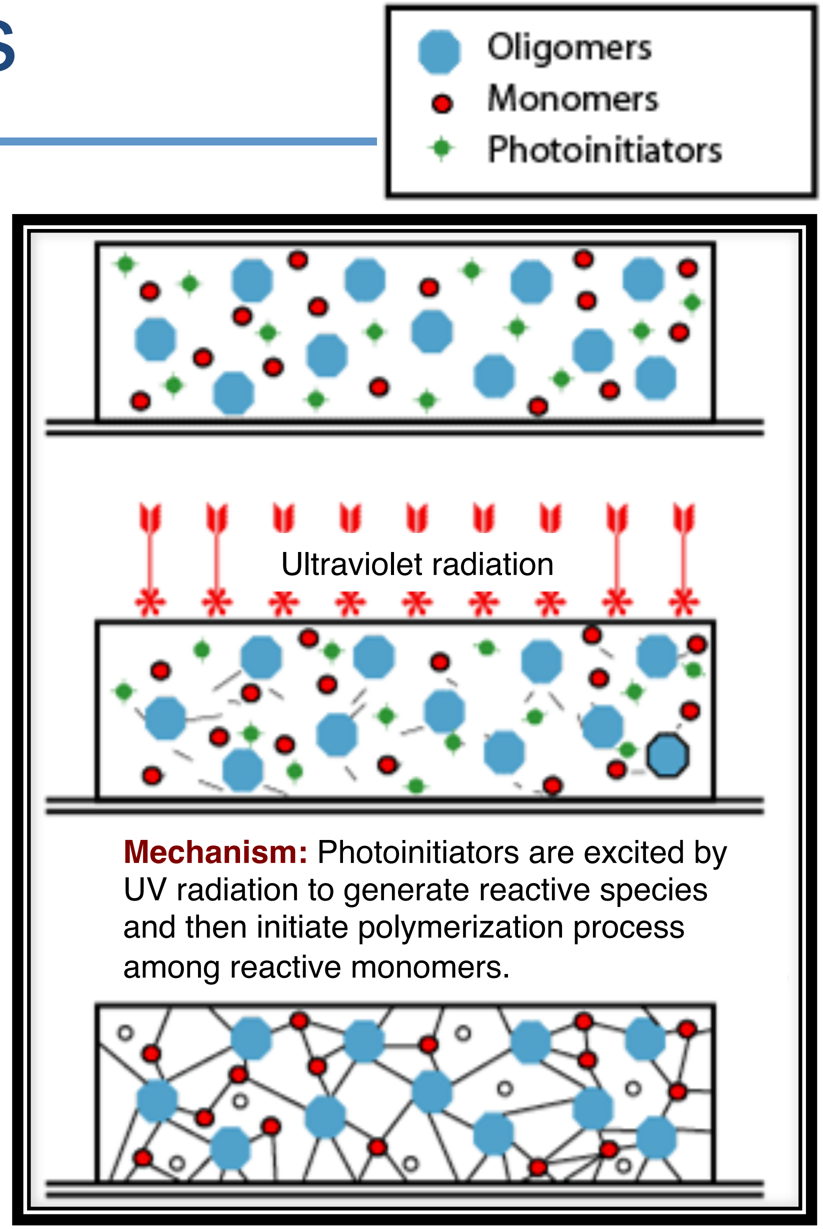
Photocurable Polymers

Advantages

- Cure-on-demand properties
- Low energy consumption
- High curing speed
- Ambient temperature processing
- Possibly solvent-free technology

Potential Applications

- Surface coatings
- Adhesives
- Sealants or encapsulants
- Photolithography
- 3D printing materials



Mechanism: Photoinitiators are excited by UV radiation to generate reactive species and then initiate polymerization process among reactive monomers.

Photocurable Polymers

Radical Polymerization	Cationic Polymerization

Radical Polymerization

- ➢ Acrylates, Thiol-ene

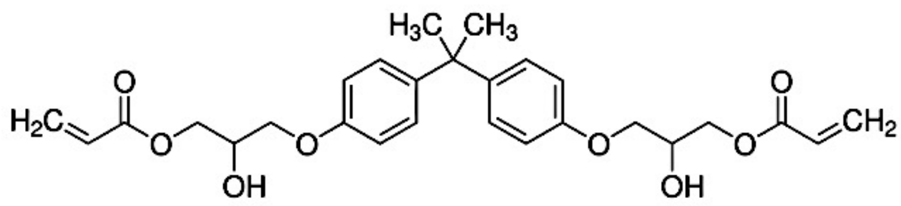
- Wide variety of materials
- Fast curing rate
- Larger depth of cure
- Lower cost of materials
- Inhibited by oxygen

Cationic Polymerization

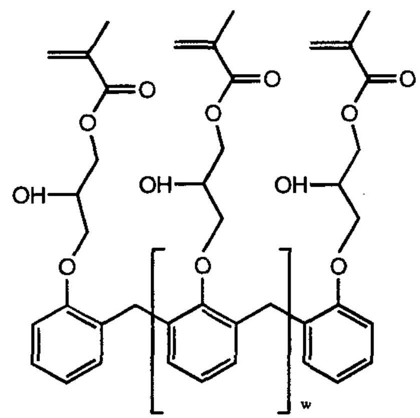
- ➢ Epoxides, Vinyl ethers

- Limited raw materials
- Slow curing rate
- Smaller depth of cure
- Higher cost of materials
- Inhibited by humidity and basic compounds

Epoxy Acrylate Resins



Bisphenol A Epoxy Acrylate



Novolac Epoxy Acrylate

Advantages

- High curing reactivity
- Thermal stability
- Hardness
- Adhesive properties
- Chemical resistance
- Electrical insulation
- Inexpensive

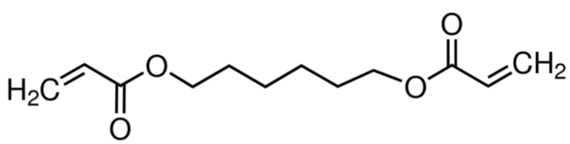
Limitations

- Relatively high viscosity
- Limited flexibility
- Brittle and low elongation

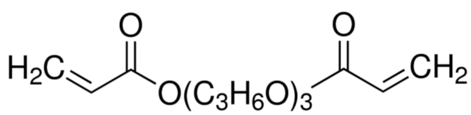
Epoxy Acrylate Resins

- The properties of epoxy acrylate resins could be modified by the introduction of additional comonomers, reactive diluents, or some additives.

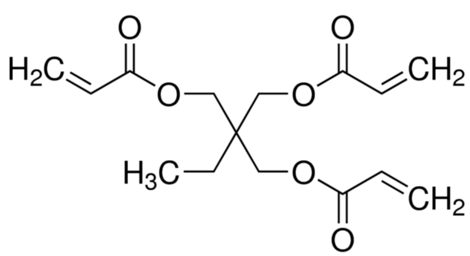
Comonomers



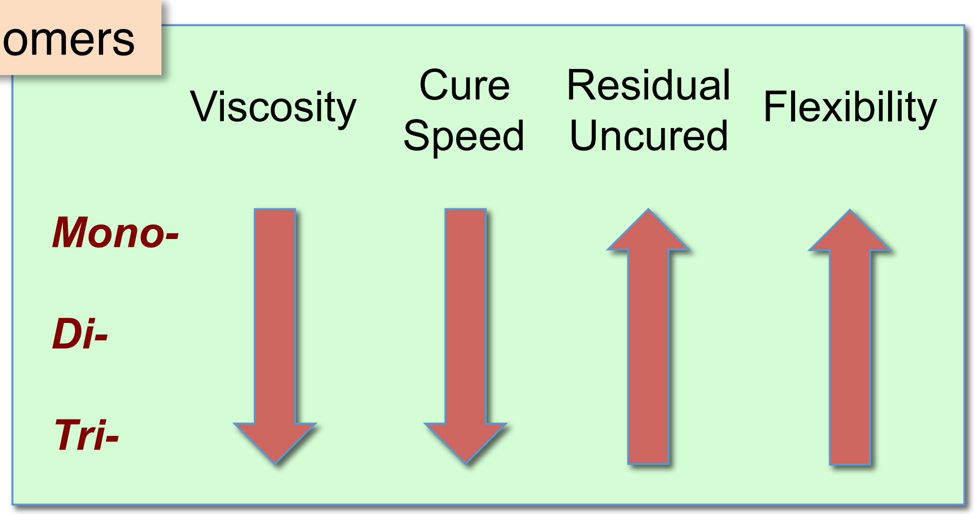
HDDA



TPGDA



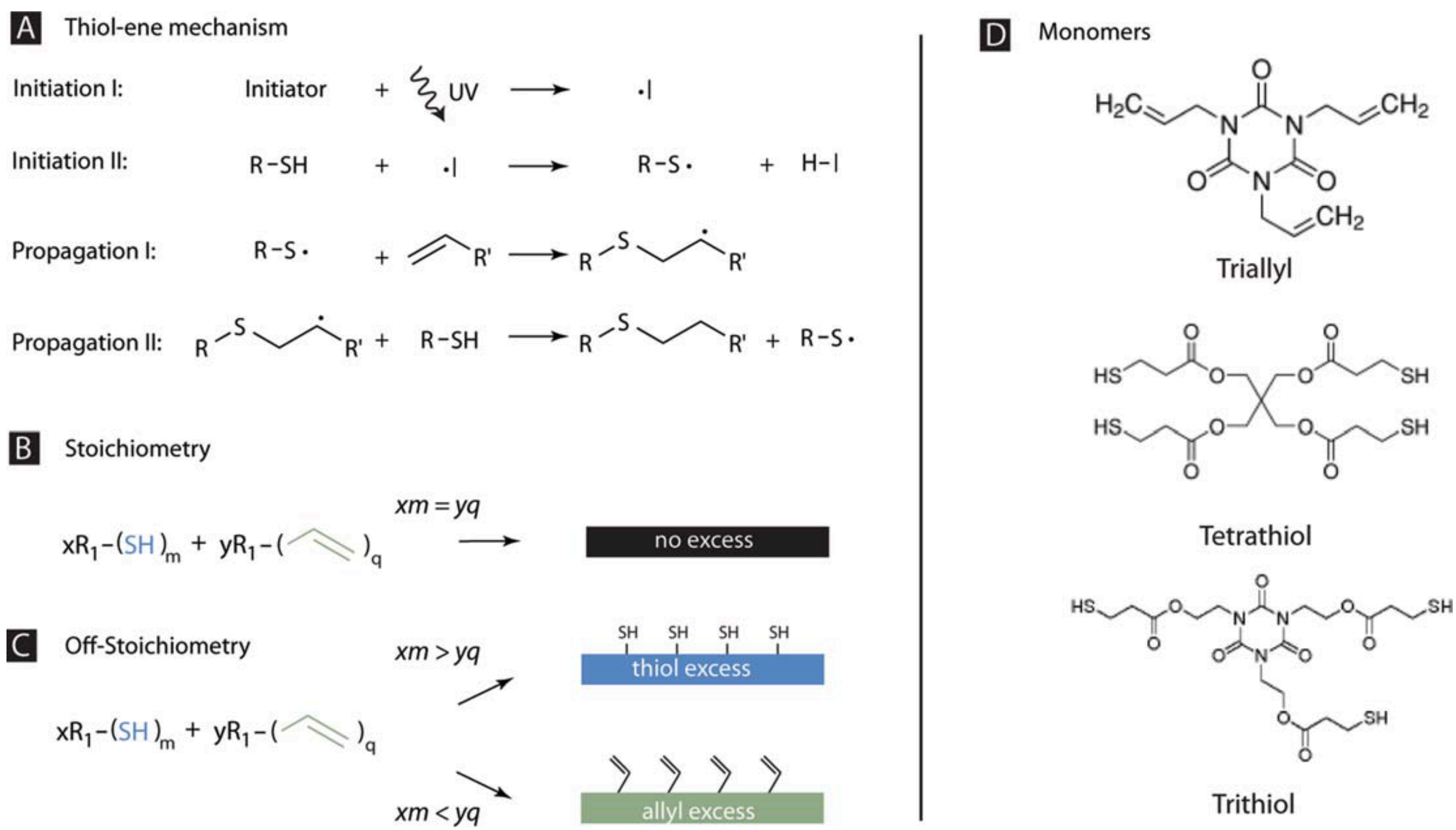
TMPTA



- Mechanical strength
- Hardness
- Thermal stability
- Chemical resistance

E-Journal of Chemistry **2008**, *5*, 521.
J. Appl. Polym. Sci. **2005**, *98*, 1180.

Thiol-Ene Polymer Systems

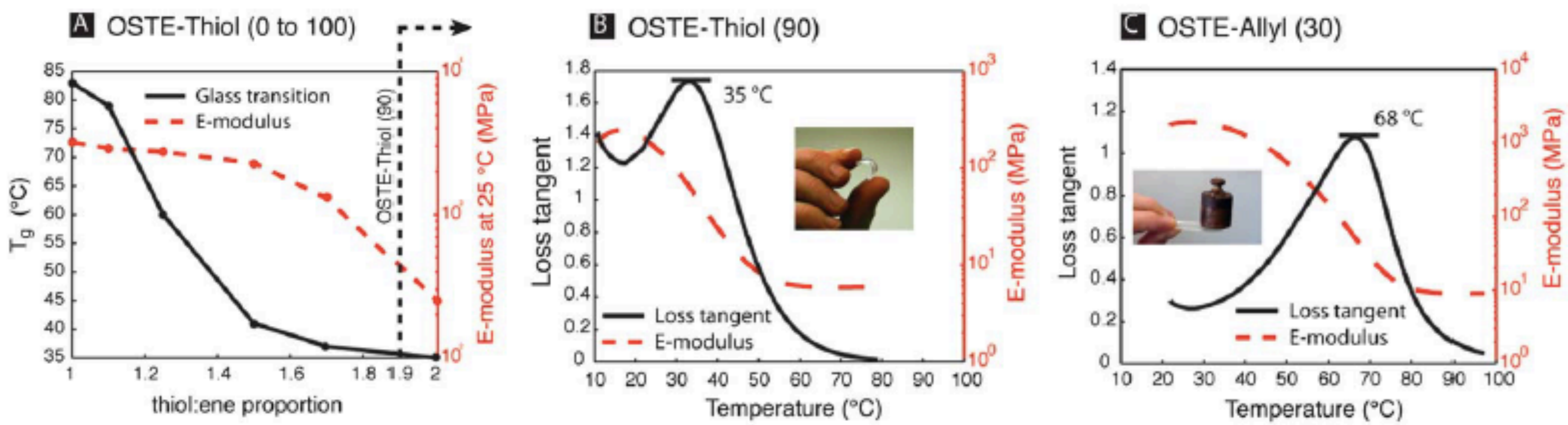


Lab. Chip. **2011**, *11*, 3136.

Thiol-Ene Polymer Systems

Table 1 Properties of the demonstrator OSTE-materials and reference materials

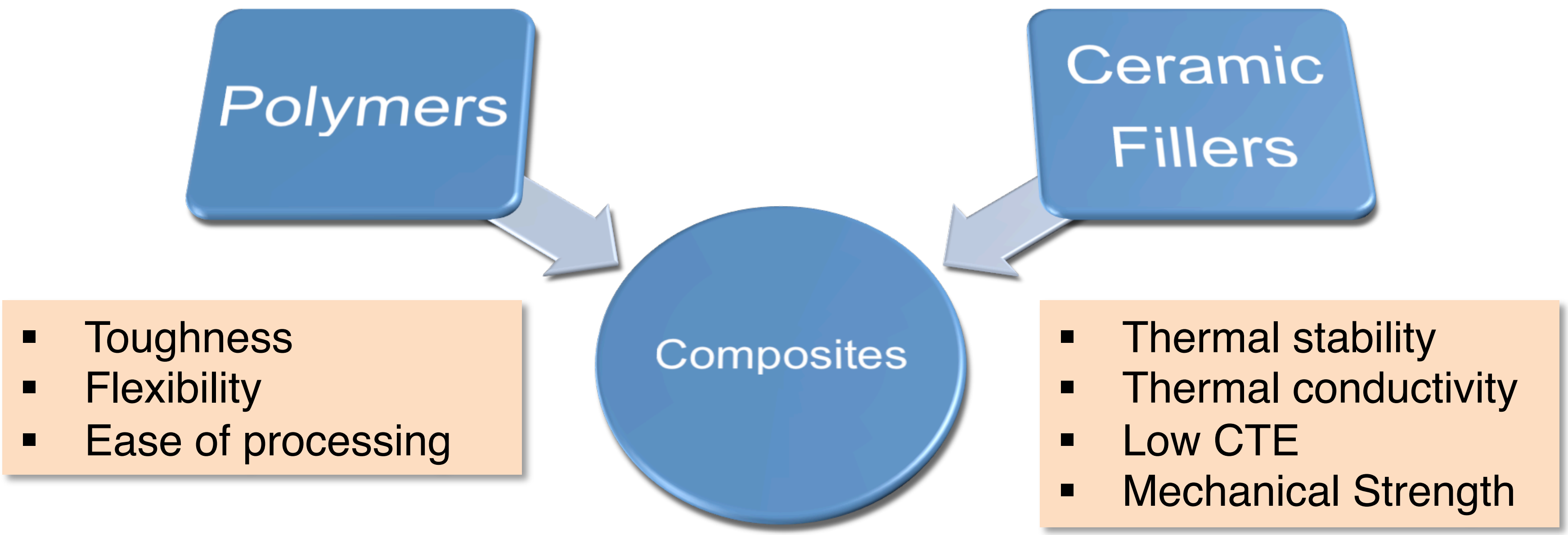
Sample material	Monomers	Functionality mixing ratio	E-modulus @ 25 °C/MPa	T_g/°C
OSTE-Thiol (90)	Tetrathiol : triallyl	1.9 : 1	250	35
OSTE-Allyl (30)	Triallyl : trithiol	1.3 : 1	1740	68
OSTE-PDMS (20)	Thiol-PDMS : vinyl-PDMS	1.2 : 1	0.33	−36
References				
PDMS (Sylgard 184)	Vinyl siloxanes	1 : 1	0.8	−135
PMMA (Plexiglas®)	Methacrylates	1 : 1	1800	105
NOA 81 (Norland Products)	Thiol and ene monomers	1 : 1	1400	75



Lab. Chip. **2011**, *11*, 3136.

Photocurable Composites

- To improve properties of photocurable polymers, some ceramic fillers can be incorporated into the polymer matrix to perform photocurable composites.



Photocurable Composites

Formulations for Photopolymerizable Liquid Encapsulants (PLEs)

▪ Epoxy Novolac-based Vinyl Ester Resin	~25 wt.%
▪ Fused Silica	70-74 wt.%
▪ Photoinitiator (BAPO)	0.2 wt.%
▪ Silane Coupling Agent	1 wt.%

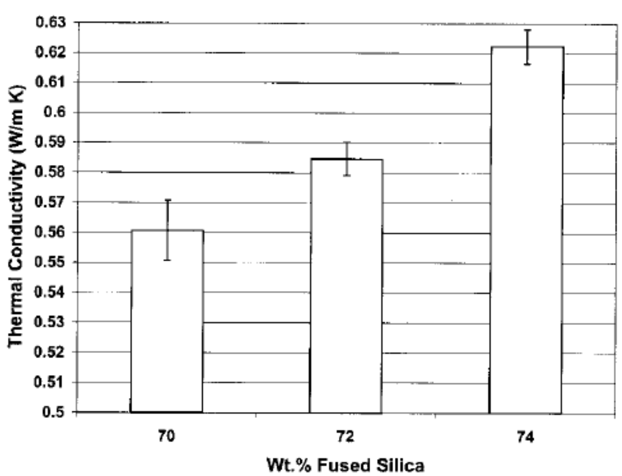


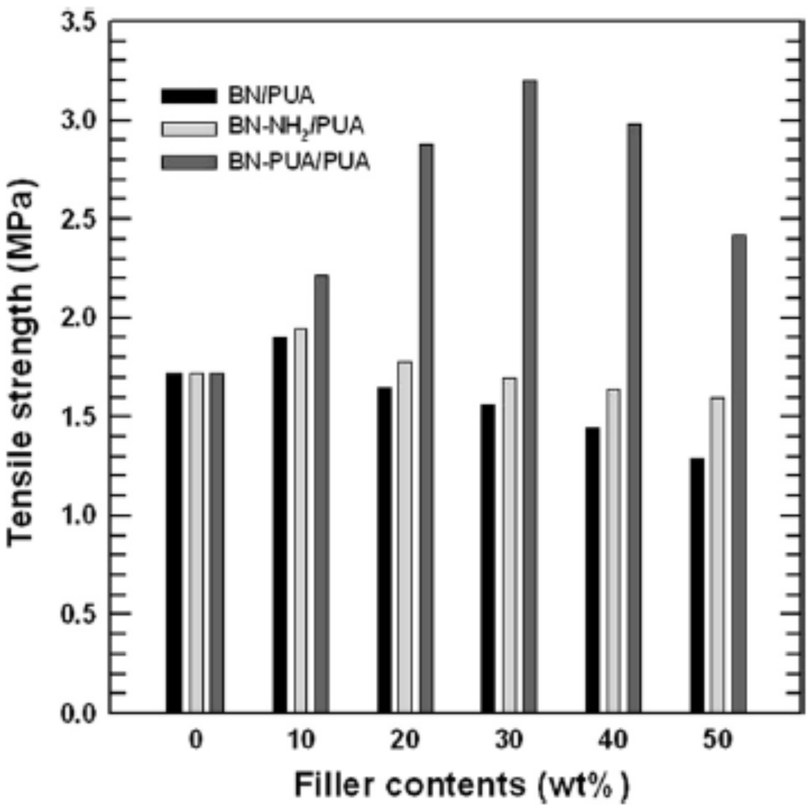
Table 2. Comparison of material properties between PLEs and conventional molding compounds

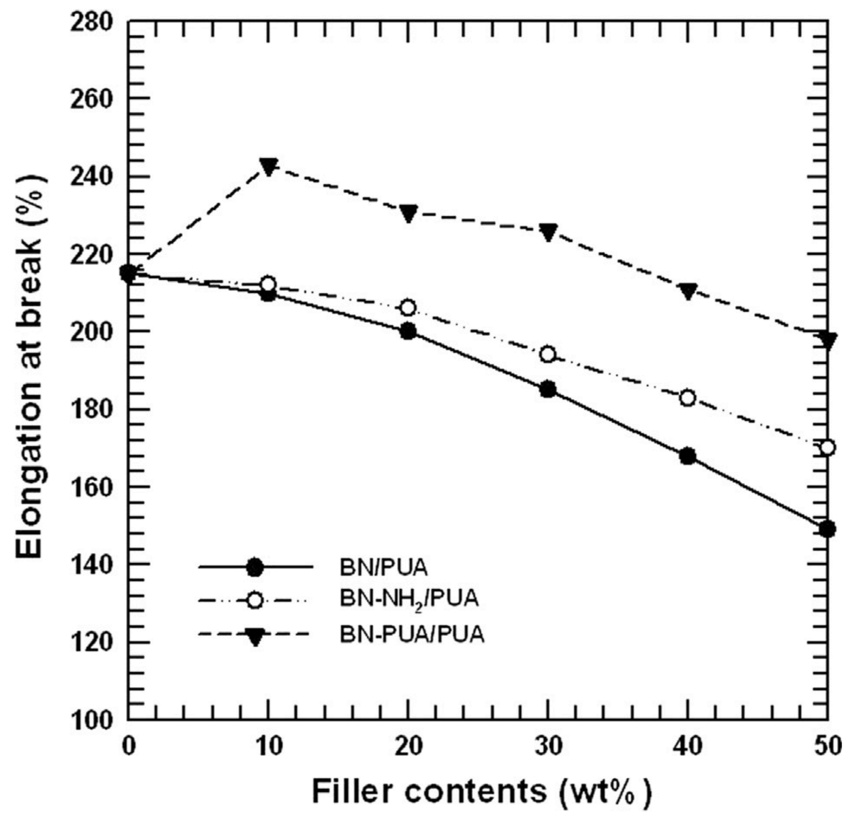
	PLE	*Molding Compound (6)*
Viscosity (cP)	5,000 – 30,000 @ 30°C	1,5000 – 100,000 @ 170°C
Flexural Modulus (kg_f/mm^2)	1,000 – 1,200	1,000 – 1,500
Flexural Strength (kg_f/mm^2)	9 – 11	9 – 15
CTE (μm/m°C)	19 – 22	16 – 25
T_g (°C)	145 – 155	140 – 180
Thermal Stress Parameter (kg_f/mm^2)	0.6 – 1.3	0.5 – 1.5
Thermal Conductivity (W/m·K)	0.56 – 0.62	0.50 – 0.70

Polymer **2001**, *42*, 431.

Photocurable Composites

- Polyurethane acrylate composites with surface-modified boron nitride for underwater sonar encapsulants





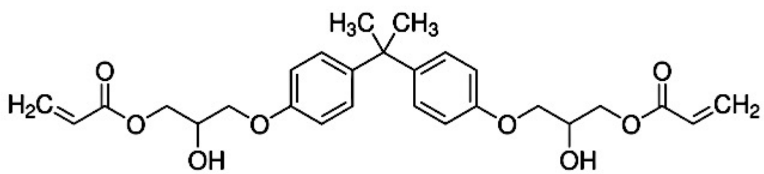
Ceram. Int. **2014**, *40*, 10933.

Purpose of Work

- To develop some novel photocurable dielectrics that have potential for electronic packaging and encapsulant applications
    - Epoxy acrylate-based polymers
    - Thiol-ene polymer systems
    - Photocurable composites
- To investigate variation and effects of photocurable formulations on their properties

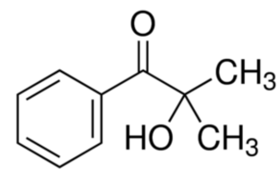
Materials

Epoxy Acrylate Base Resin



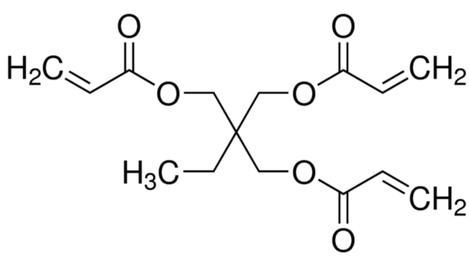
BPAGDA

Photoinitiator

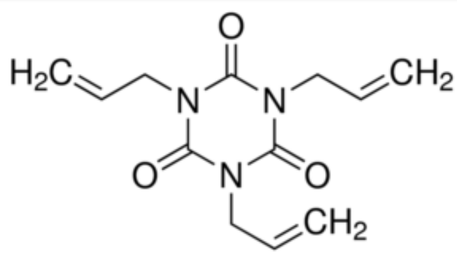


HMPP

Crosslinking comonomers

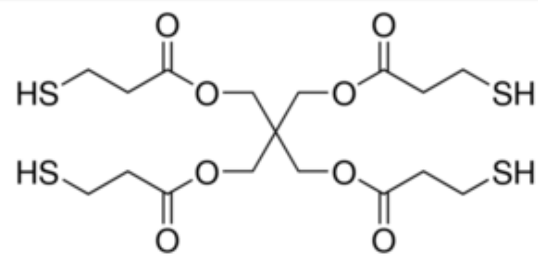


TMPTA



TAIC

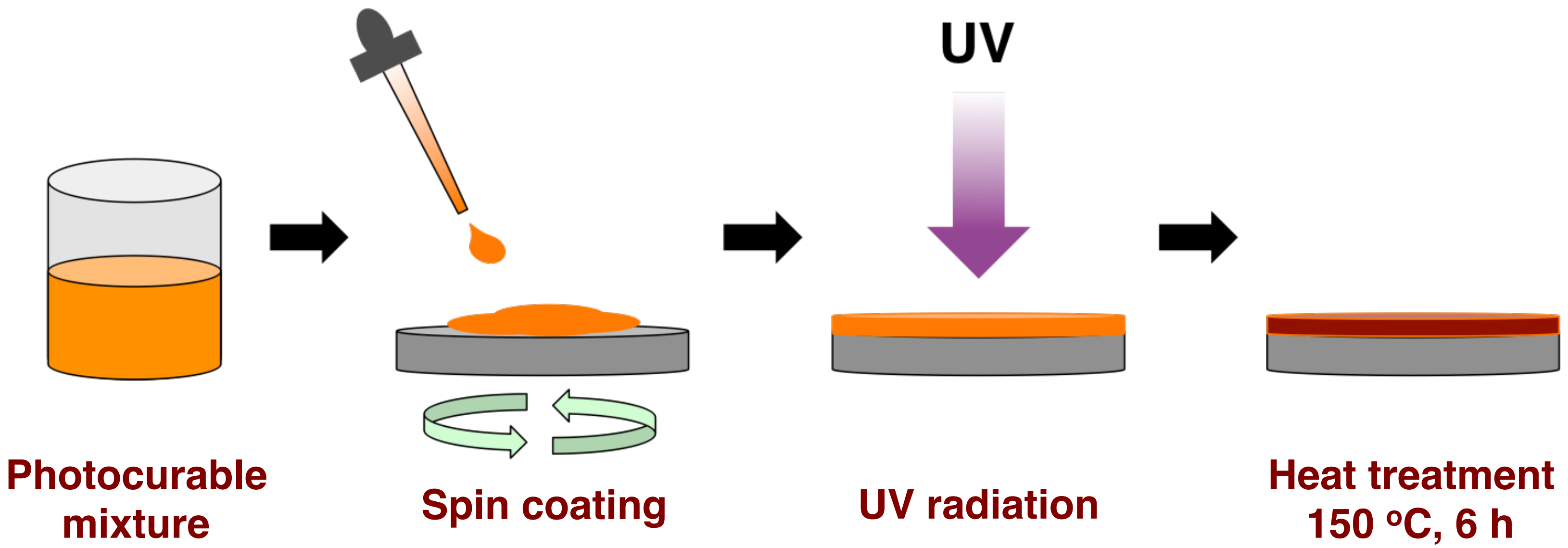
- Mechanical strength
- Thermal stability
- Breakdown strength



PETMP

- No photoinitiator required
- Tunable mechanical properties

Preparation of Materials



Epoxy acrylate base resin	BPAGDA
Crosslinking comonomer	TMPTA, TAIC, PETMP
Solvent	THF
Photoinitiator	HMPP
Filler	BNNs, Functionalized BNNs

- FTIR
- Gel Content
- SEM

Research Progress

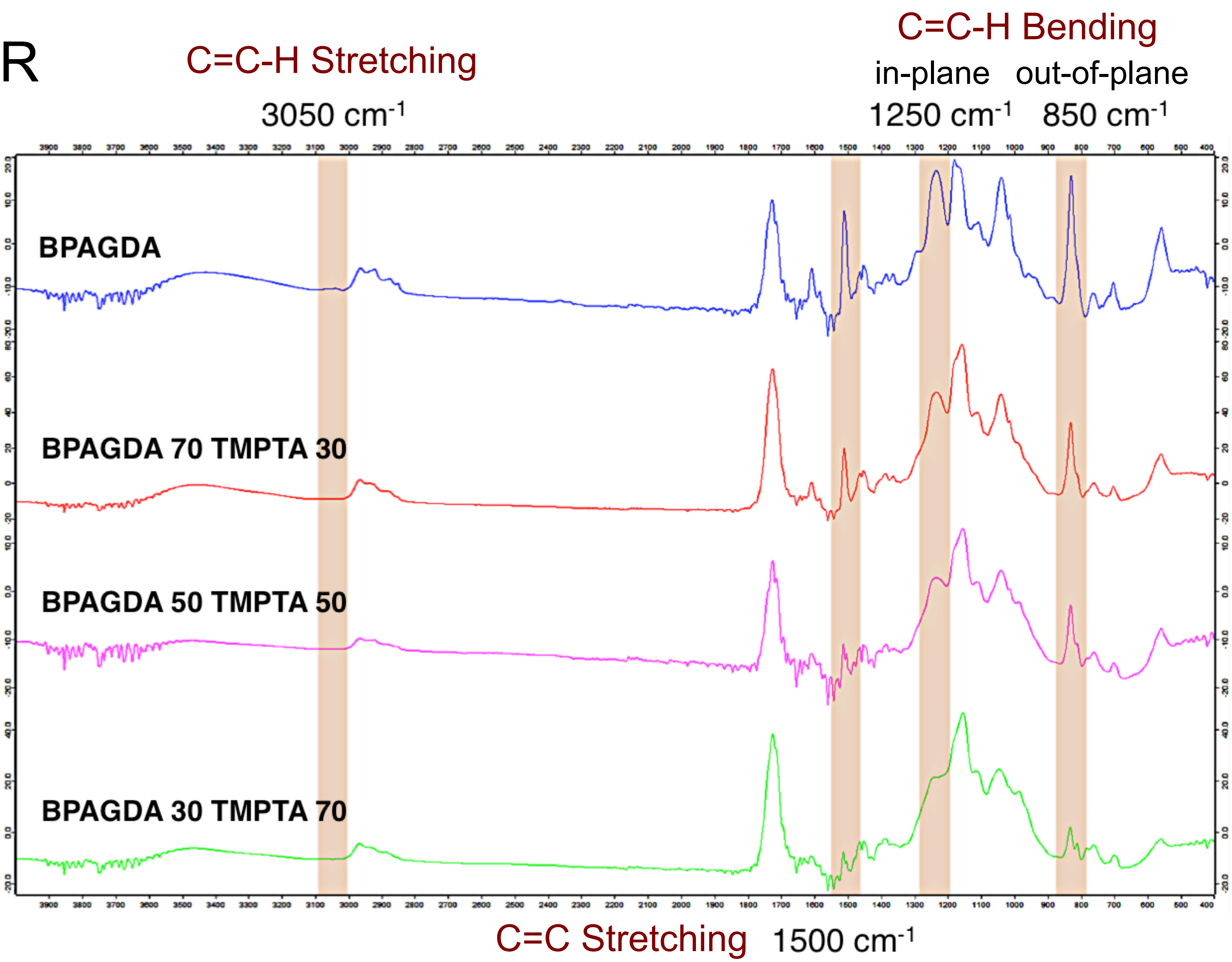
- BPAGDA-TMPTA

Sample	% Weight		
	BPAGDA	TMPTA	HMPP
1	100	-	3
2	90	10	3
3	70	30	3
4	50	50	3
5	30	70	3

- ❑ Spin coating (THF) on Si wafer
- ❑ UV radiation (254 nm): 10 min → Thin film (thickness: 15-50 μm)
- ❑ Thermal treatment at 150 ^{o}C, 6 h

BPAGDA-TMPTA

- FTIR



BPAGDA-TMPTA

- Gel Content & Thermal Stability

General Procedure:

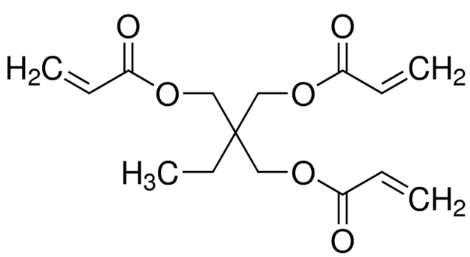
- Reflux the cured specimen in THF at 60 ^{o}C for 24 h
- Dry the specimen in vacuum oven at 60 ^{o}C for 24 h

$$\textbf{Gel Content} = \frac{\textbf{Final weight}}{\textbf{Initial weight}}$$

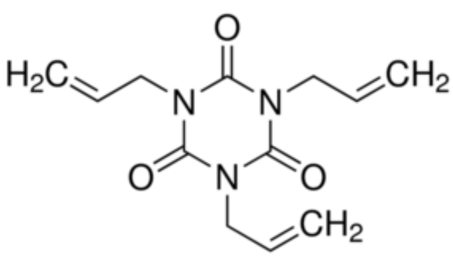
Sample	% Weight		Gel Content	T_d (^{o}C) *
	BPAGDA	TMPTA		
1	100	-	0.67	424
2	90	10	0.72	460
3	70	30	0.74	462
4	50	50	0.75	464
5	30	70	0.81	464

* T_d is observed by TGA

Mechanical Strength



Crosslinking comonomers

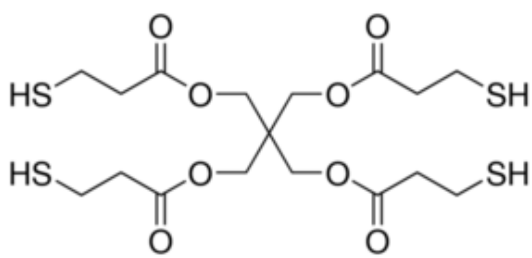


% Weight		Tensile Strength (MPa)	Young's Modulus (GPa)	Elongation (%)
BPAGDA	TMPTA			
100	-	24.2	1.9	1.3
90	10	40.6	1.4	2.8
70	30	41.4	2.6	1.6
50	50	12.0	2.2	0.6

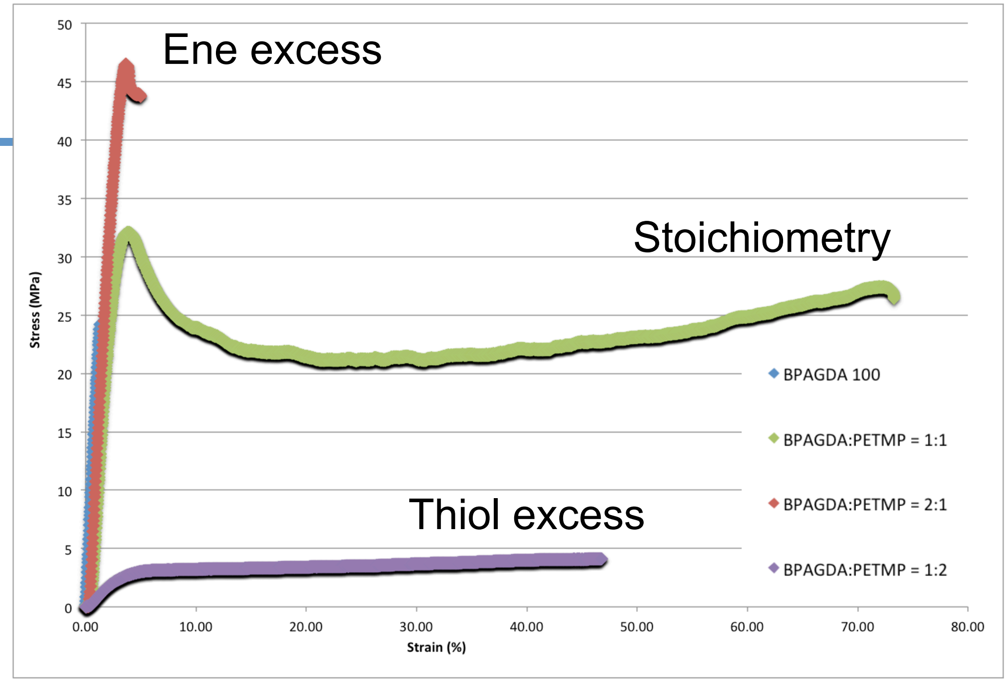
% Weight		Tensile Strength (MPa)	Young's Modulus (GPa)	Elongation (%)
BPAGDA	TAIC			
100	-	24.2	1.9	1.3
90	10	42.6	1.8	2.7
70	30	76.3	2.6	3.3
50	50	26.1	2.6	1.7

BPAGDA-PETMP

- Mechanical Strength



PETMP

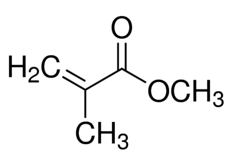


	Thiol-Ene Mole Ratio		Tensile Strength (MPa)	Young's Modulus (GPa)	Elongation (%)
	BPAGDA	PETMP			
	1	0	24.2	1.9	1.3
Stoichiometry	1	1	32.1	1.4	73.3
Ene excess	2	1	46.5	1.7	5.0
Thiol excess	1	2	4.1	0.1	46.8

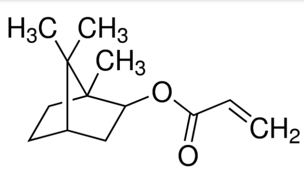
Ongoing Research & Future Works

- Investigation of thermal, electrical, and viscoelastic properties of the prepared films
- Studies on formulations of photocurable dielectrics without solvent by using reactive diluents

Reactive Diluents



MMA



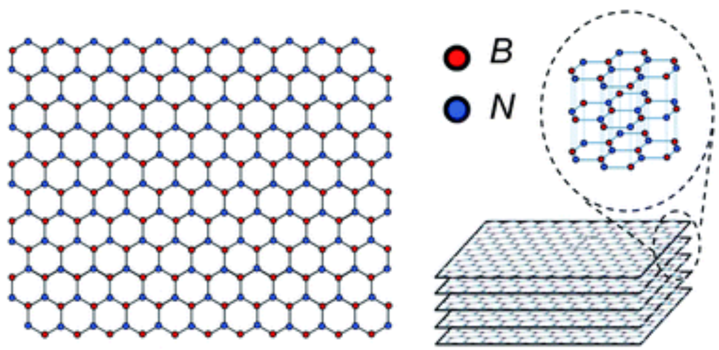
IBA

- Reduce viscosity of epoxy acrylates
- Generate solvent-free systems

Ongoing Research & Future Works

- Studies on composites between selected photocurable polymer systems and ceramic fillers such as BNNs

Ceramic Fillers



Boron Nitride Nanosheets (BNNs)

- High thermal conductivity (up to 275 W/K.m)
- Low CTE (1 μm/m.^{o}C)
- High thermal stability
- High electrical resistivity
- Low dielectric constant
- Low density

Summary

Photocurable Polymers → **Composites** ← **Ceramic Fillers**

- Epoxy acrylate-based resins
- Thiol-ene polymer systems

- BNNs
- Functionalized BNNs

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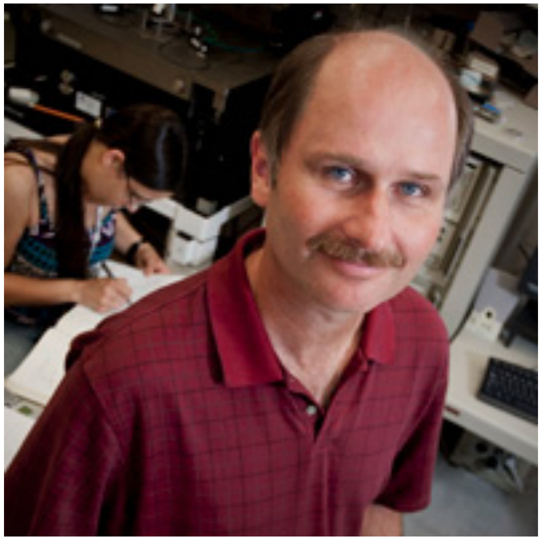
High Performance
Electronic Packaging & Encapsulant Materials

Acknowledgements & Contacts



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