COMPARISON OF UV AND EB PROCESSING ON STRUCTURE PROPERTY RELATIONSHIPS

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SIMILAR BUT NOT THE SAME

UV

EB

- UV allows for easier controls of processing parameters
- EB has higher energy and can alter polymerization mechanism and processing

RADIATION CURE BENEFITS

- Green technology
- No solvent waste
- Low hazard

- Very low VOC emissions

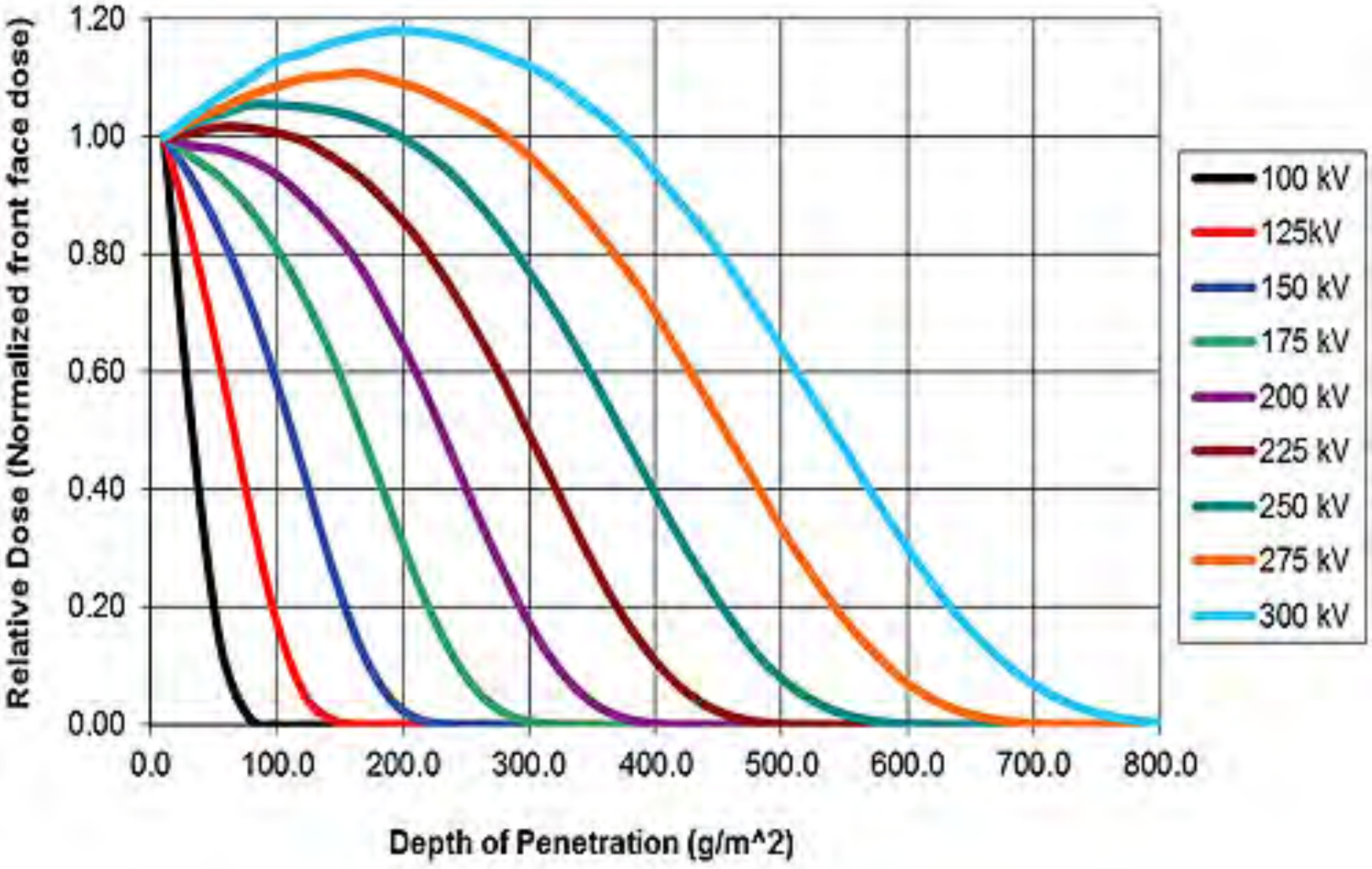
- Process efficiency and flexibility
- Room-temperature curing
- Low heat generation
- Simple adaptation to existing lines
- Ease of cleaning

- 10 times less space utilization than a conventional drying oven

- High productivity and cost savings
- Reduced cycle time
- Increased throughput
- Instant on/off
- Low energy consumption
- No solvent waste recycling
- Minor maintenance cost

- 4 times less energy consumption than thermal curing

DEPTH / DOSE CURVES



Source: Lapin, S.C. *RadTech Report* Modification of Polymer substrates using EB induced graft copolymerization

EFFECTIVE ELECTRON PENETRATION AT HIGH VOLTAGES

High Voltage kV	Depth Mils	Depth Gm/M^2
90	0.8	20.0
110	1.2	30.0
125	1.8	45.0
150	3.5	90.0
175	5.0	125.0
200	7.0	175.0
250	11.0	275.0
300	16.0	400.0

EB: IMPROVED DOT GAIN CONTROL

Conventional
Ink Dot Gain

EB
Ink Dot Gain

Source: ESI

INTERACTION WITH MATTER AND INITIATION MECHANISM WITH ACRYLATES

Energy loss events along the trajectory of a charged particle (“string of beads”)

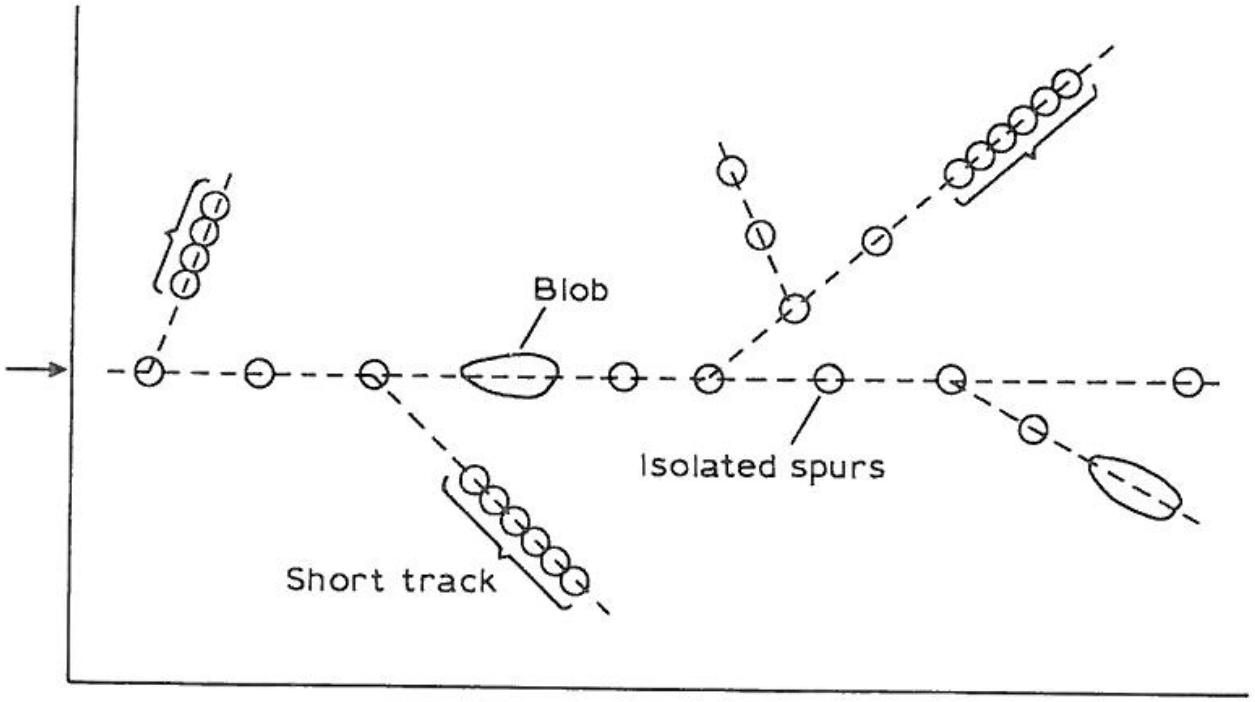


Fig. 9.12. Schematic diagram of track entities.

Energy deposited:

- « spurs » < 100 eV
- « Blobs » 100 to 500 eV
- « Tracks » 500 to 5000 eV

Bond	Bond	Bond-dissociation energy at 298 K		
		(kcal/mol)	(kJ/mol)	(eV/Bond)
$H_3C–H$	Methyl C–H bond	105	439	4.550
$C_2H_5–H$	Ethyl C–H bond	101	423	4.384
$(CH_3)_2CH–H$	Isopropyl C–H bond	99	414	4.293
$(CH_3)_3C–H$	*t*-Butyl C–H bond	96.5	404	4.187
$(CH_3)_2NCH_2–H$	C–H bond α to amine	91	381	3.949
$(CH_2)_3OCH–H$	C–H bond α to ether	92	385	3.990

Source: wikipedia

Source: R.S.Davidson in « Radiation Curing in Polymer Science and Technology » Vol III

INITIATION MECHANISM WITH ACRYLATES

$$M \longrightarrow M^{+\cdot} + e^{-} \longrightarrow M^{*} \text{ or } M + \text{heat}$$

$ROH, H_2O, ..$

$-CH_2-C^{\bullet}H-CH_2-$

Branching & crosslinking

Scission

$CH_2{=}CHCO_2R$

$(CH_2{=}CHCO_2R)^{-\bullet}$

$ROH, H_2O, ..$

$CH_3-C^{\bullet}HCO_2R$

$n\ CH_2{=}CHCO_2R$

Polymer

Extent of C–C bond cleavage to C–H bond cleavage as a function of chain branching

	n-Hexane	3-Methyl-pentane	2,3-Dimethyl-butane	2,2-Dimethyl-butane
$\frac{G(C-C)}{G(C-H)}$	0·3	0·7	1·4	2·5

Source: R.S.Davidson in « Radiation Curing in Polymer Science and Technology » Vol III

INHIBITION / RETARDATION OF EB ACRYLATE POLYMERIZATION

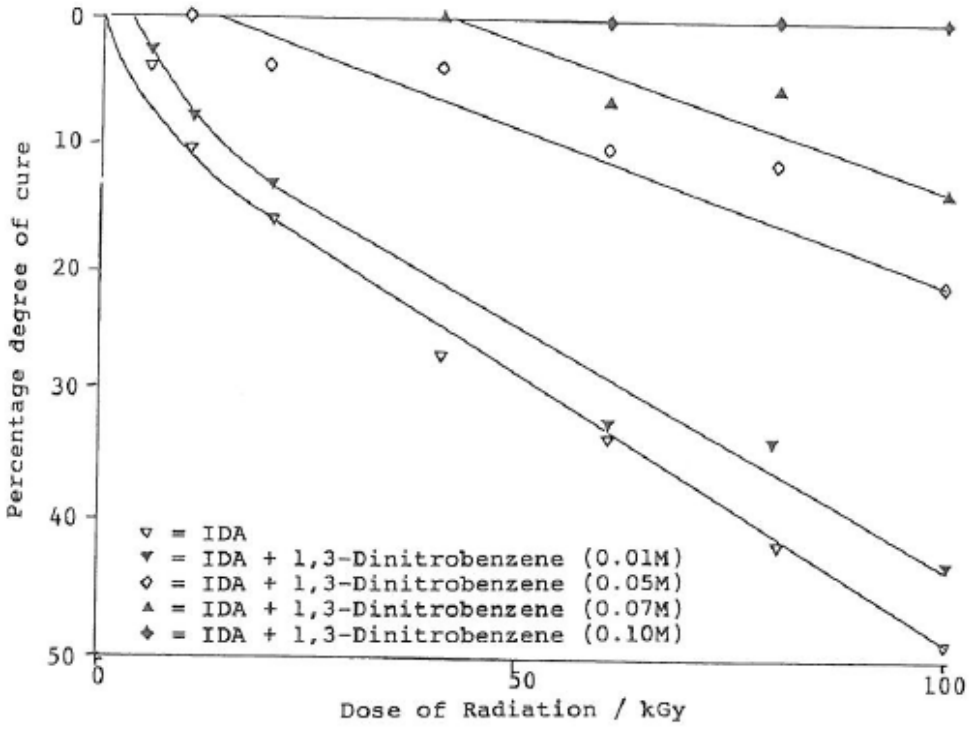
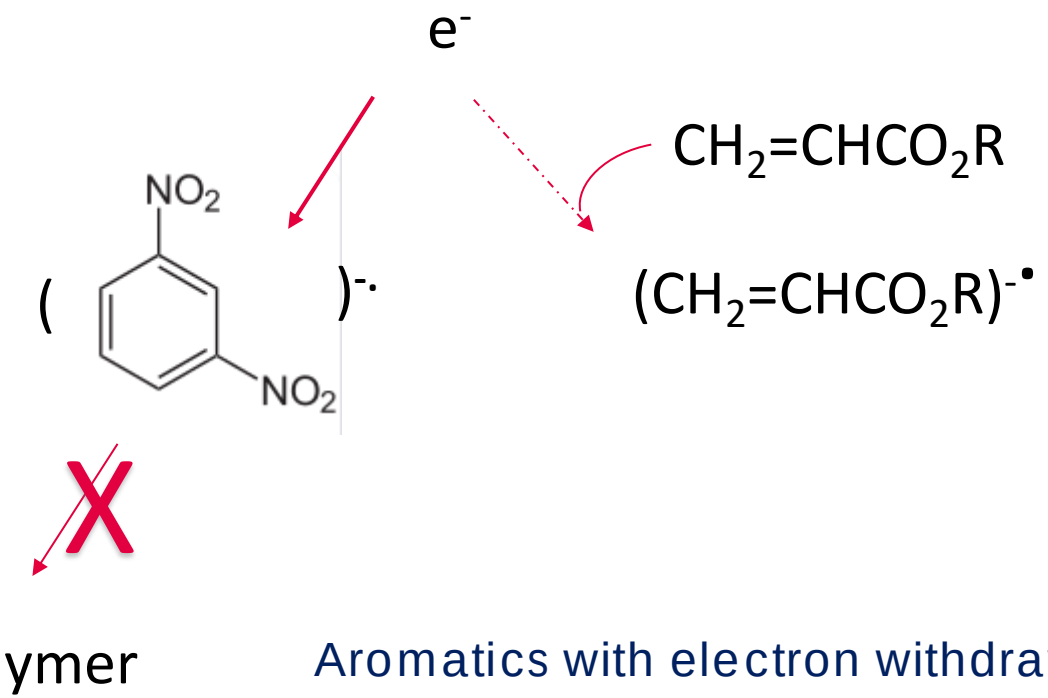


Fig. 9.19. Percentage degree of cure of IDA in the presence of 1,3-dinitrobenzene at various doses of radiation.

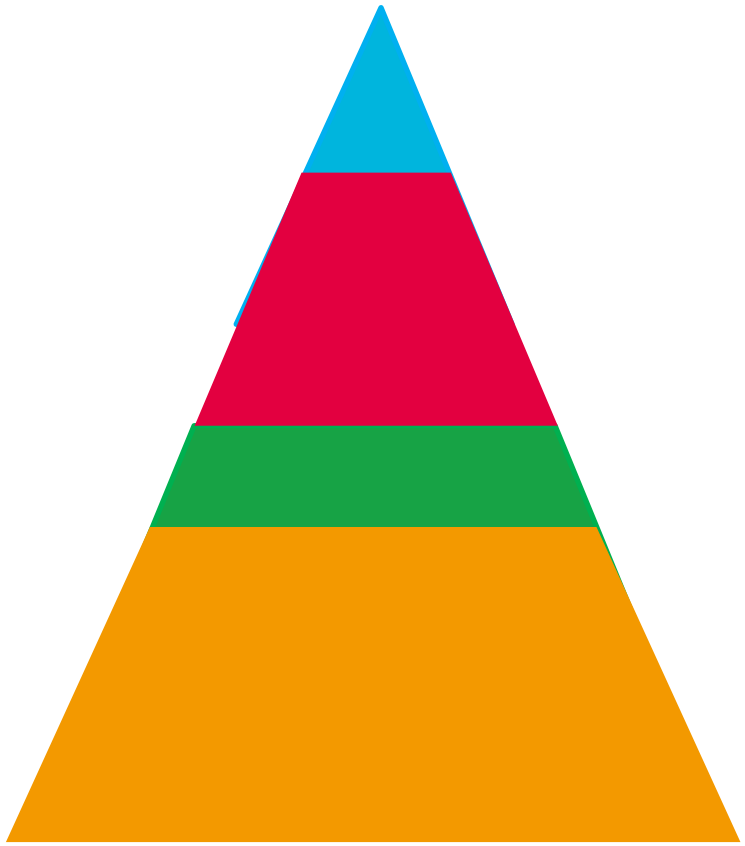


Aromatics with electron withdrawing groups

- Pigments based on quinones, azo dyes, phthalocyanines … ?
- Vinyl aromatics ?
- Unsaturated esters ?

Source: R.S.Davidson in « Radiation Curing in Polymer Science and Technology » Vol III

FORMULATION FOR UV AND EB



UV and UV-LED

Photoinitiator

Additives & pigments

Monomers

Oligomers

Nitrogen

EB

MONOMER STUDIES

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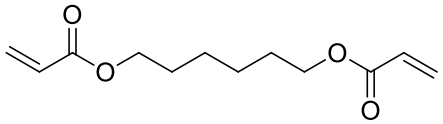
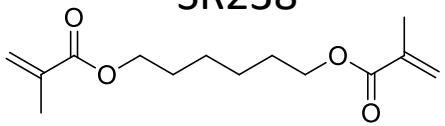
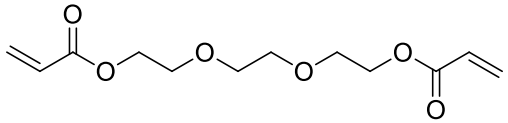
DIFUNCTIONAL MATERIALS - CURE



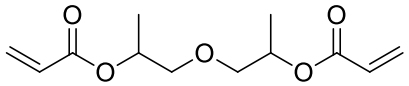
SR238



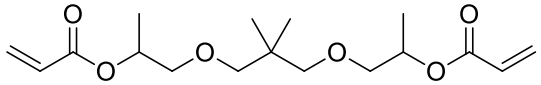
SR239



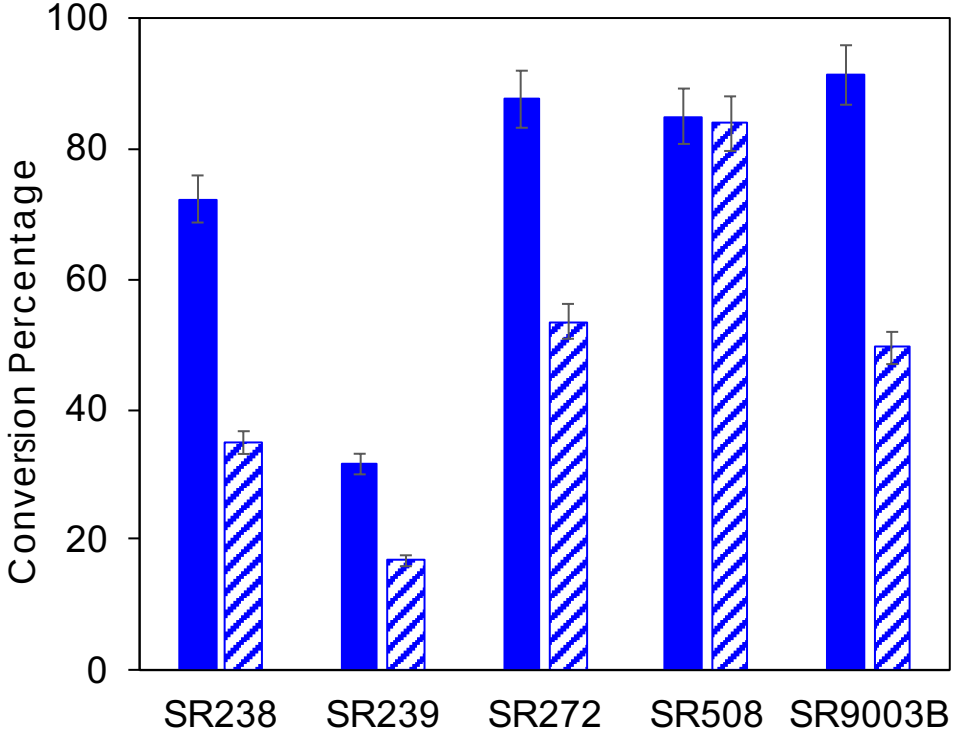
SR272

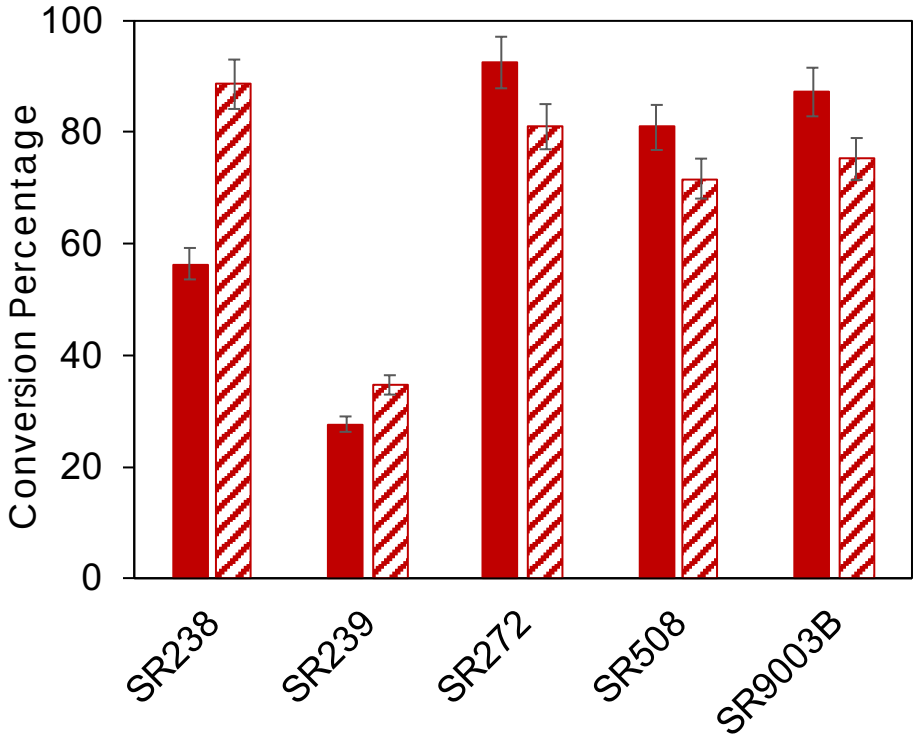


SR508



SR9003B





UV cured film top surface

UV cured film bottom surface

EB cured film top surface

EB cured film bottom surface

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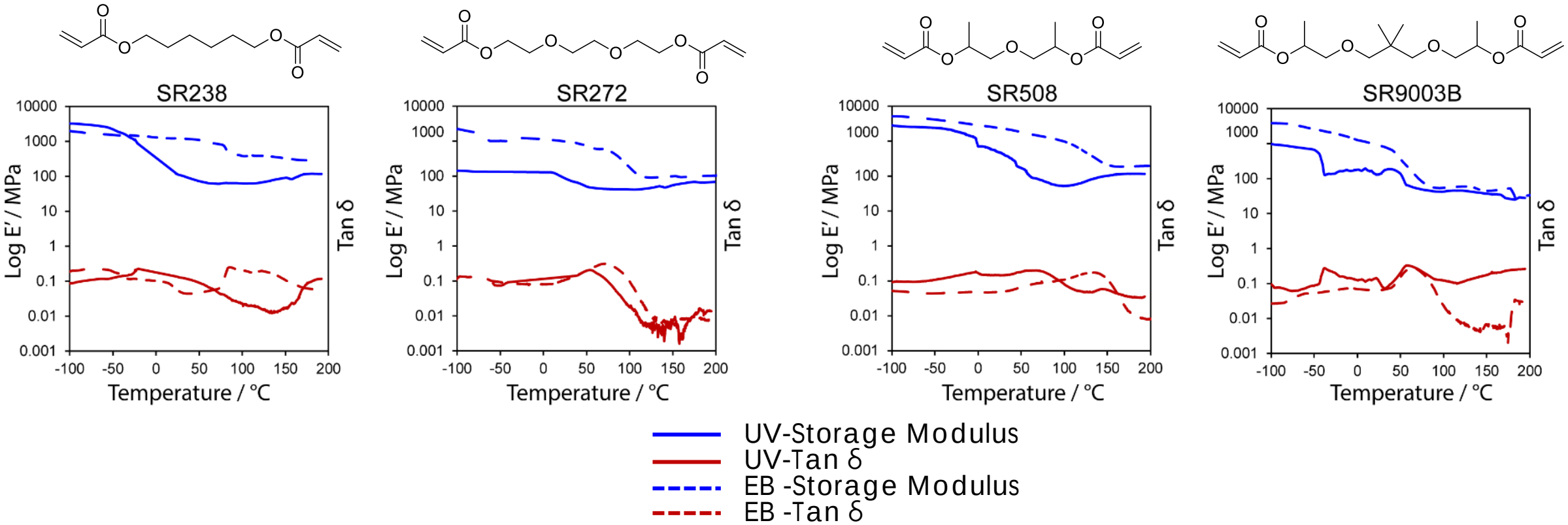
DIFUNCTIONAL - TG

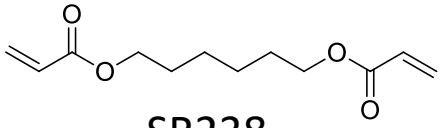


- Alterations to curing mechanism through increased side reactions lead to increased modulus and T_g

DIFUNCTIONAL HARDNESS/TENSILE

- Increased crosslinking from side reactions through monomer choice increases hardness

- Solvent resistance for neat monomers remains low



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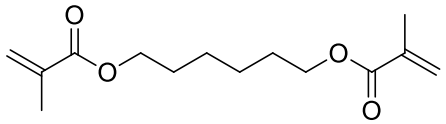

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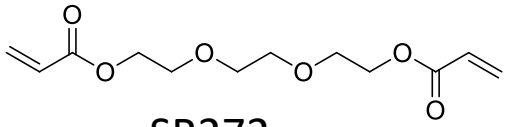

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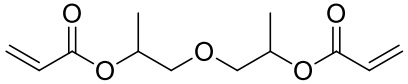

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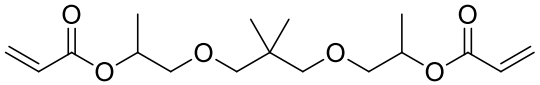
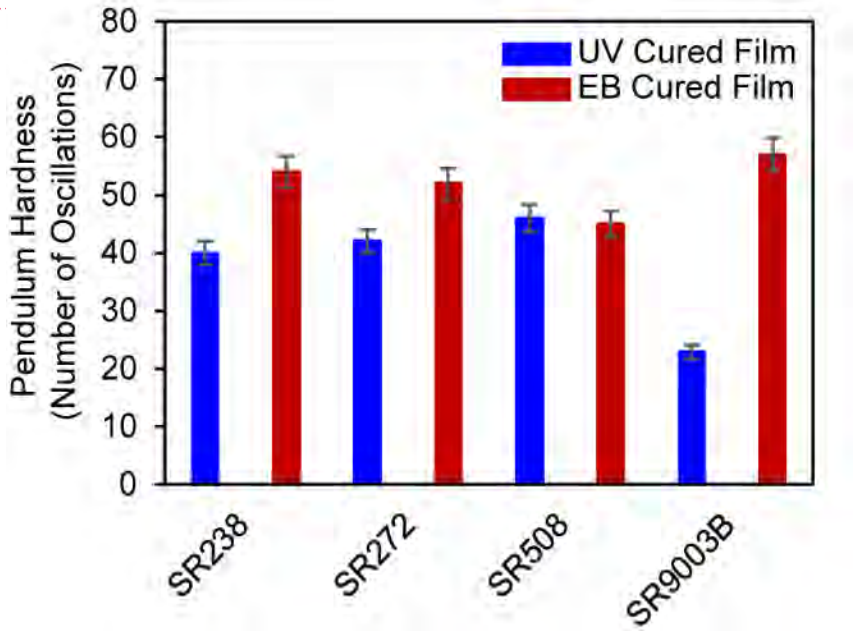
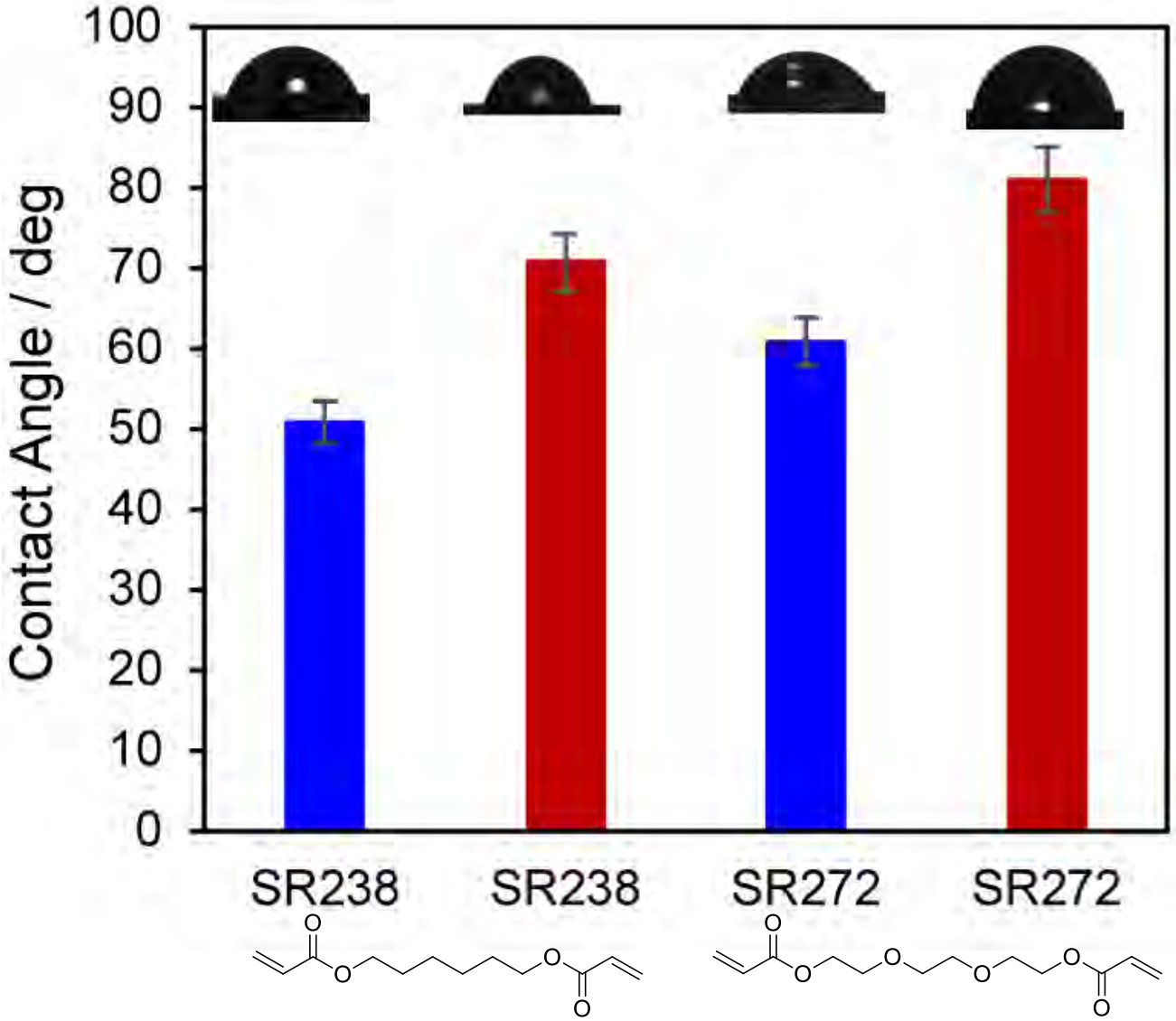


SR9003B



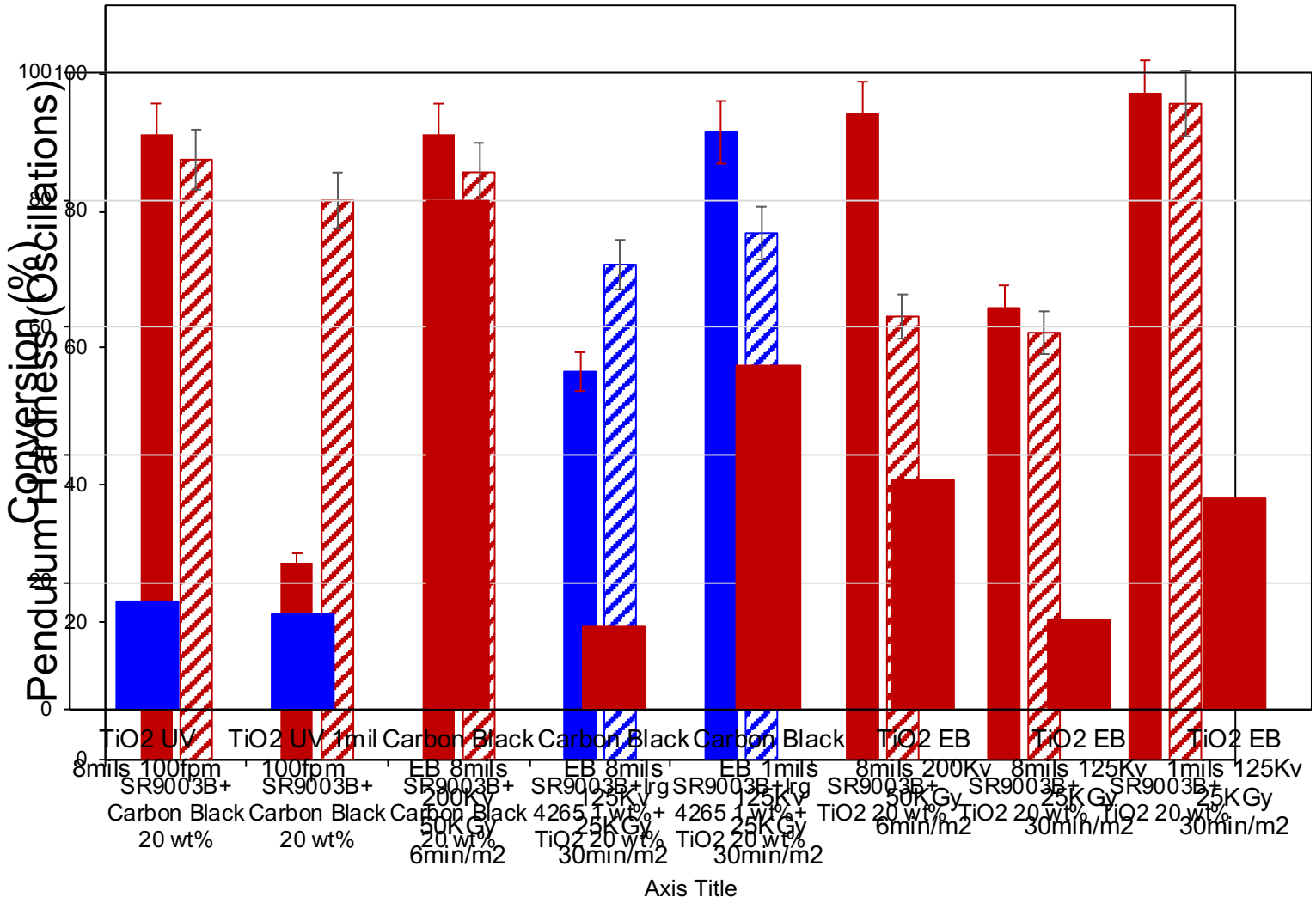
Composition	50 Cycles	100 Cycles	150 Cycles	200 Cycles
SR238 UV	haze	haze	haze	haze
SR238 EB	haze	haze	haze	haze
SR239 UV	*	*	*	*
SR239 EB	*	*	*	*
SR272 UV	haze	haze	haze	haze
SR272 EB	haze	haze	haze	haze
SR508 UV	haze	haze	haze	haze
SR508 EB	haze	haze	haze	haze
SR9003B UV	haze	haze	haze	haze
SR9003B EB	haze	haze	haze	haze

RADIATION CURING EFFECTS ON SURFACE CHEMISTRY



- Interactions between EB source and surface chemistry reacts to increase contact angle of water

EFFECTS OF FILLERS



- EB can cured more highly filled systems than UV/Visible light sources
- Fillers can have complex interactions in EB curing

OLIGOMER STUDIES

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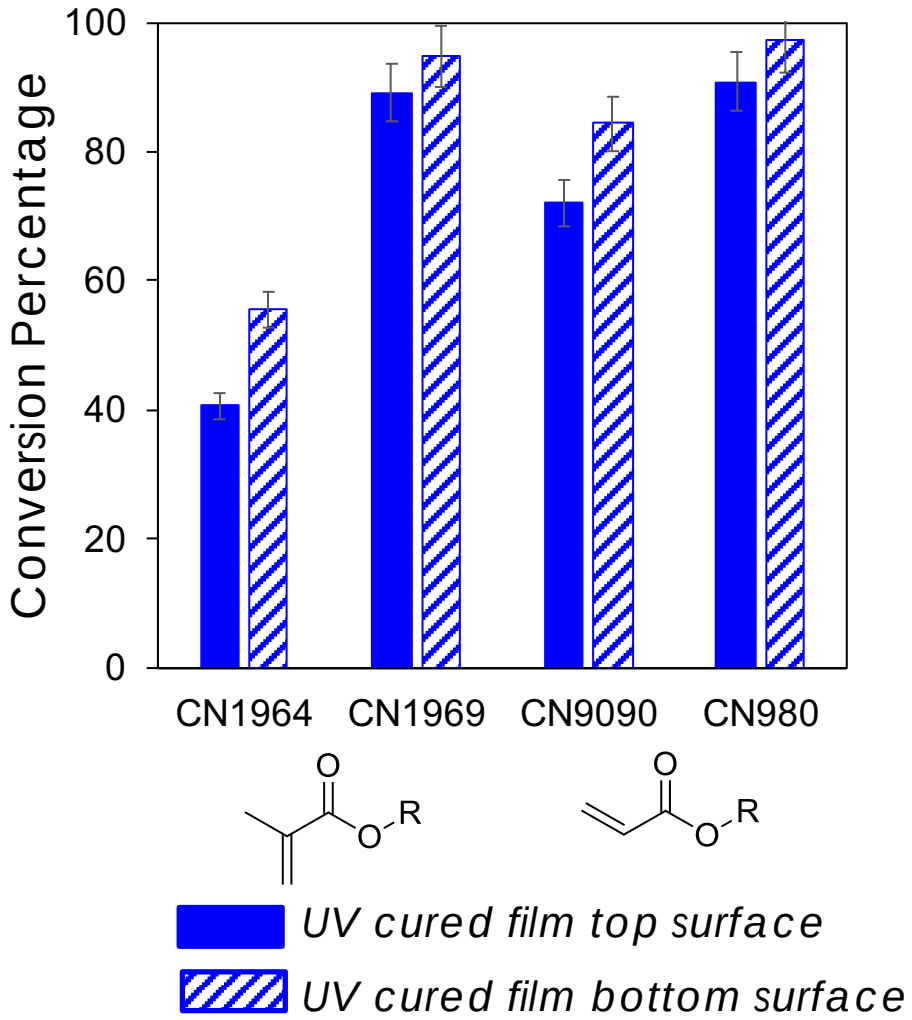
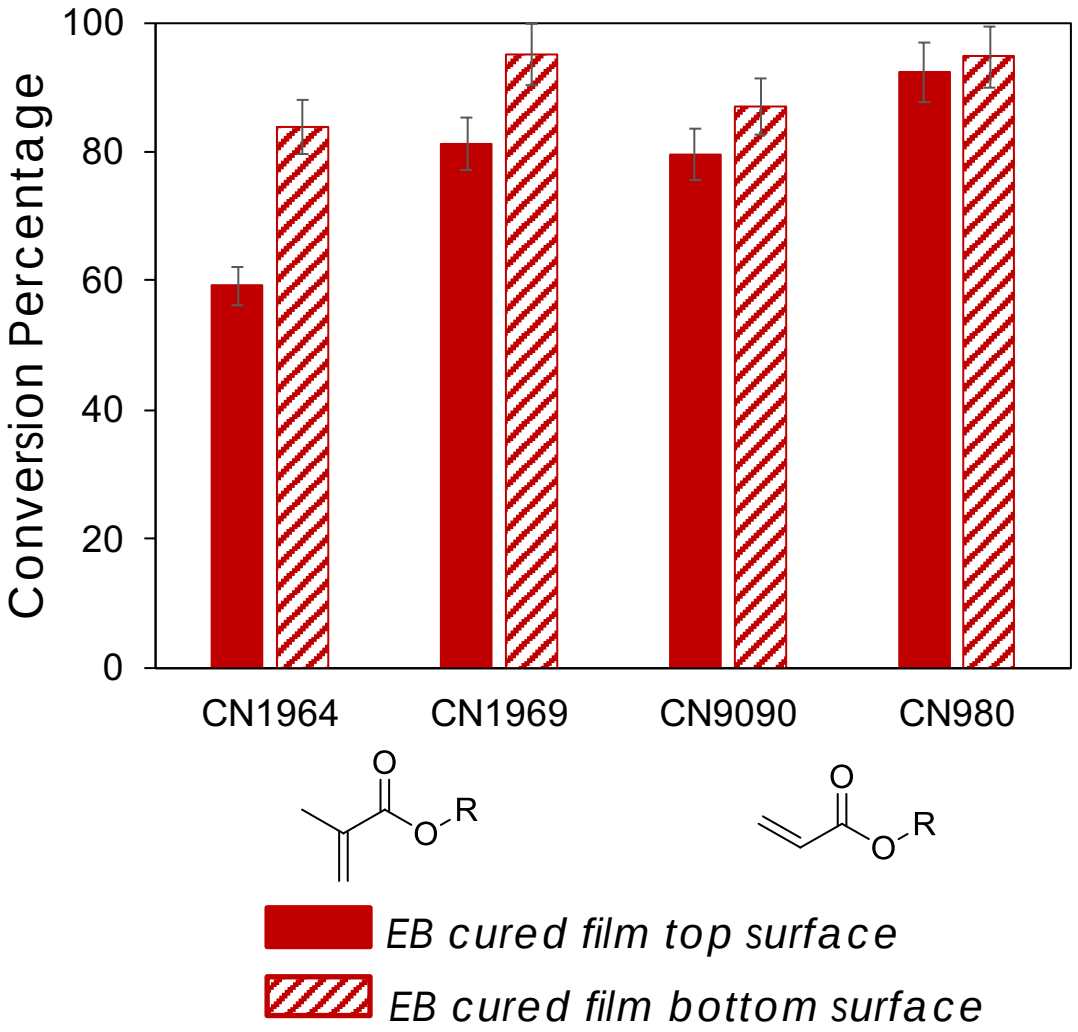
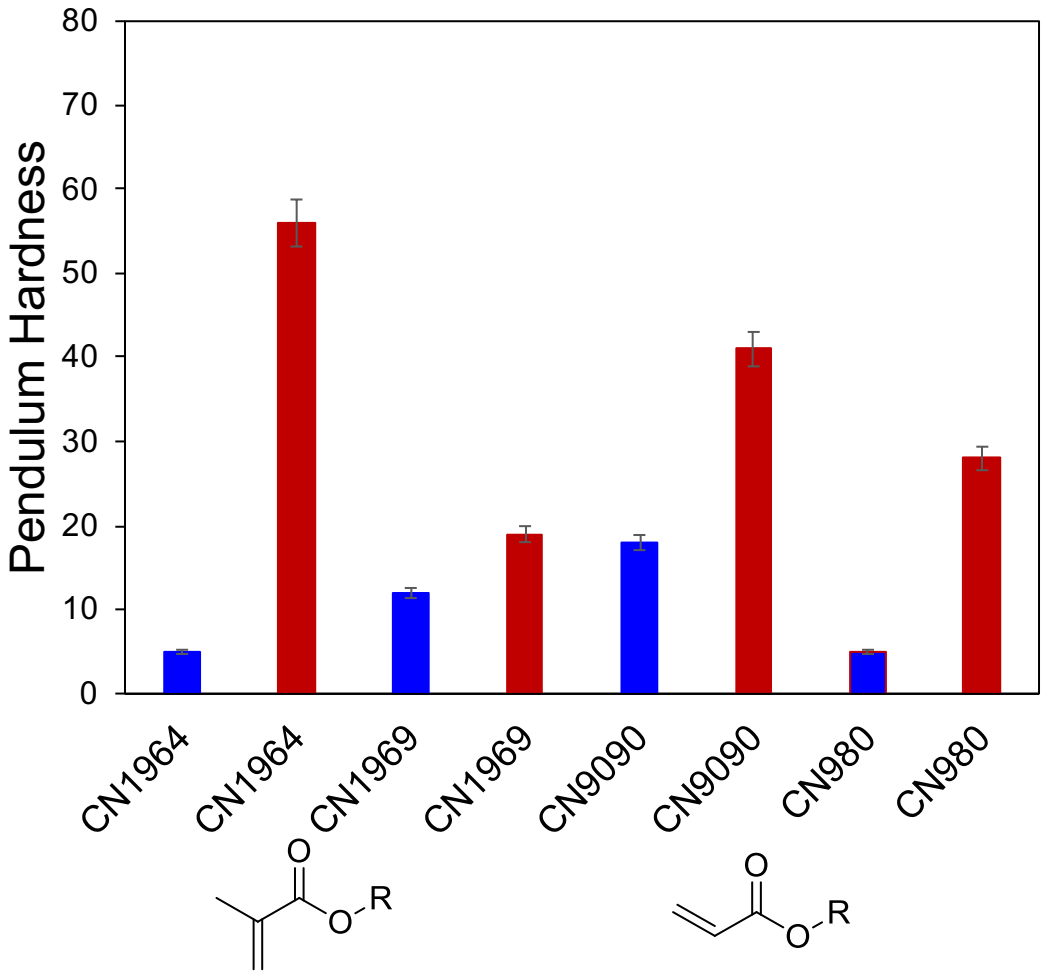
URETHANE ACRYLATE VS URETHANE METHACRYLATE





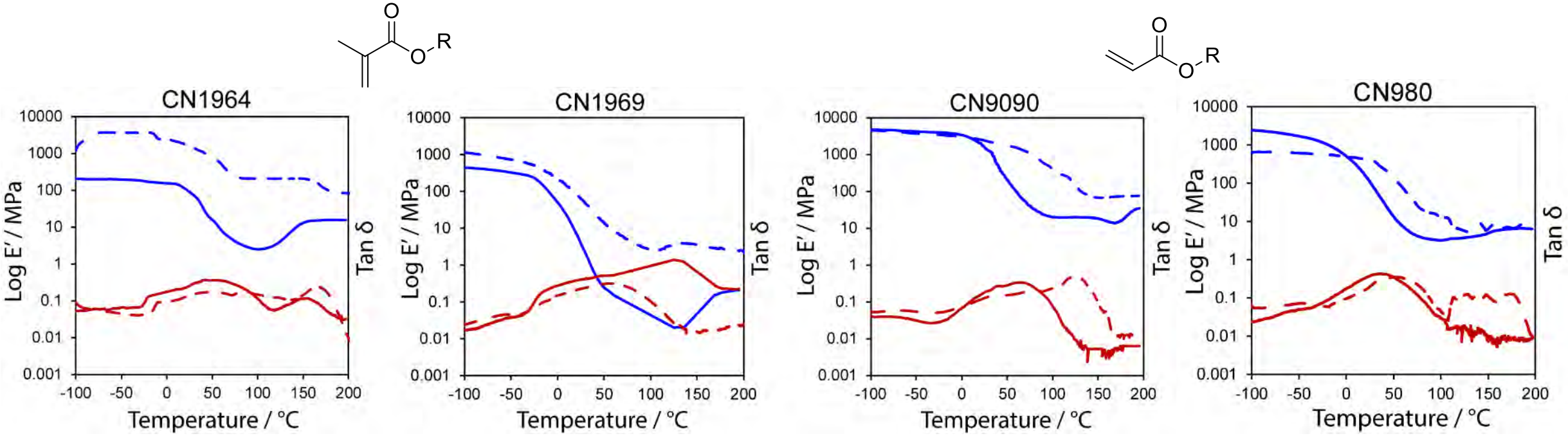
DIFUNCTIONAL MATERIALS-CURE



Composition	50 Cycles	100 Cycles	150 Cycles	200 Cycles
CN980	no haze	no haze	low haze	haze
CN980	no haze	no haze	no haze	no haze
CN1969	low haze	haze	haze	haze
CN1969	no haze	no haze	no haze	low haze
CN9090	haze	haze	haze	haze
CN9090	no haze	no haze	low haze	haze
CN1964	haze	haze	haze	haze
CN1964	no haze	no haze	no haze	low haze

- Increased performance of EB materials likely due to increased crosslinking

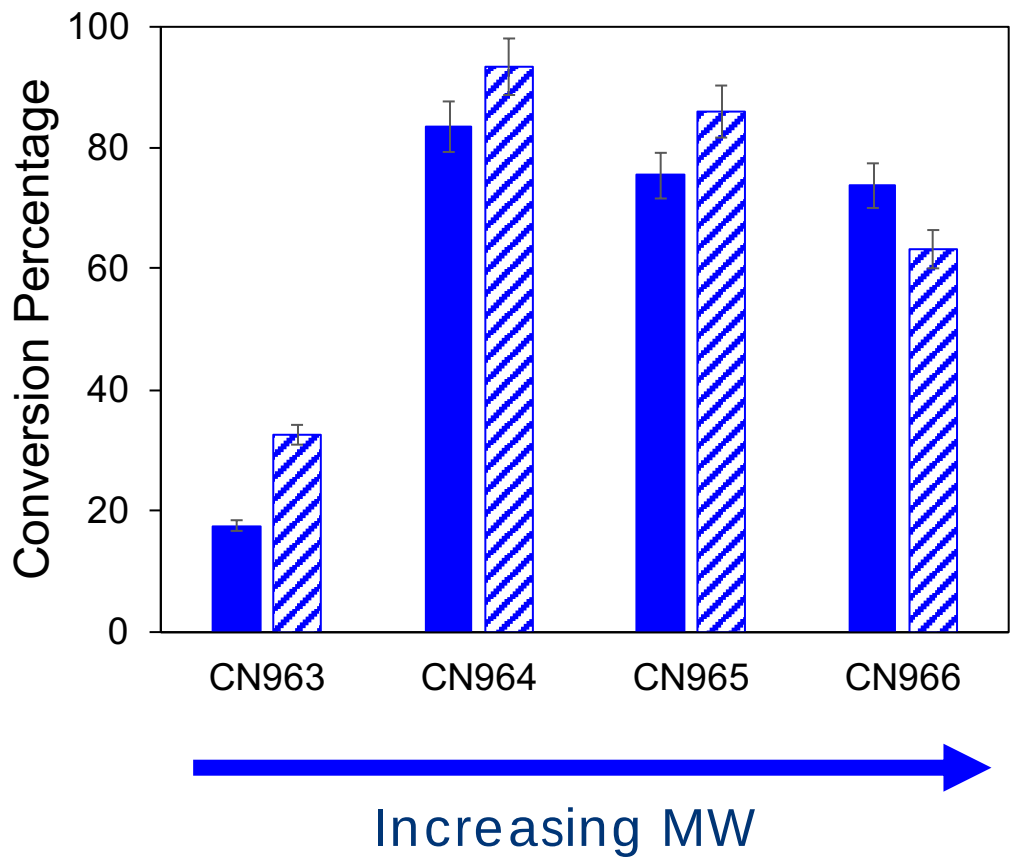
POLYURETHANE (METH)ACRYLATE THERMOMECHANICAL STUDIES

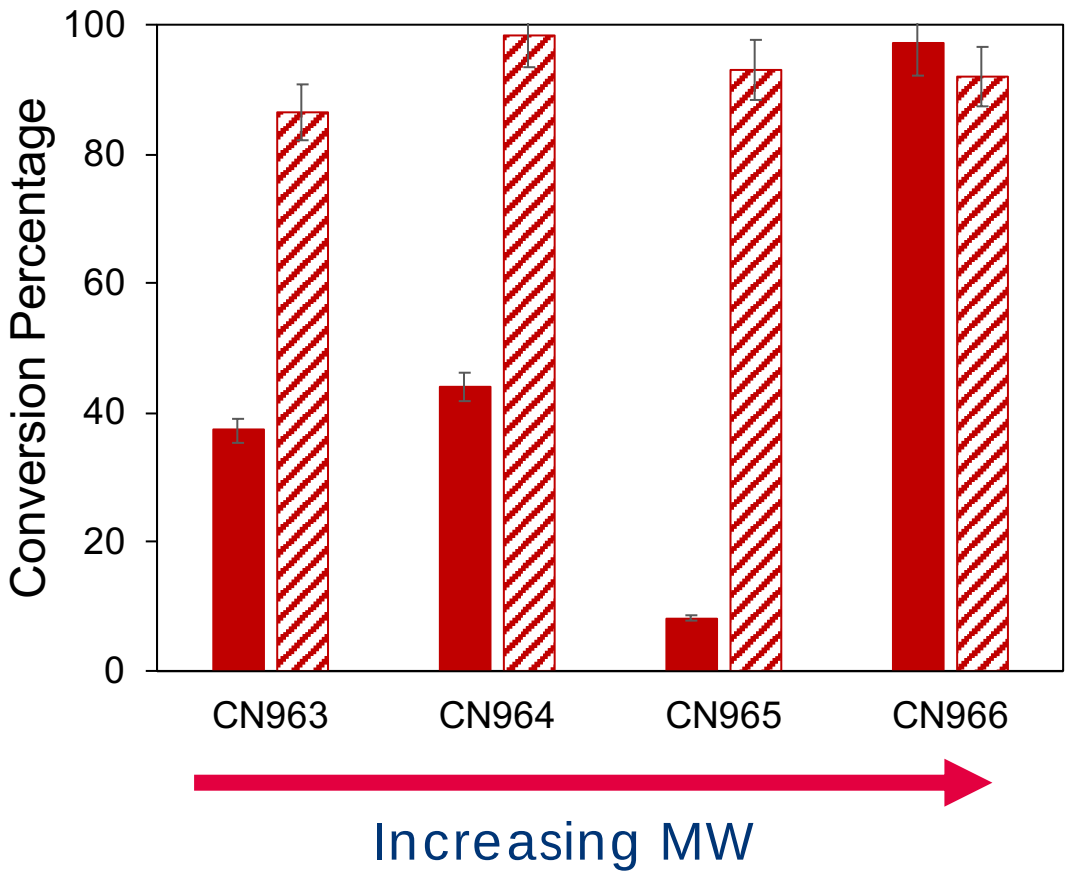


- UV Cure of methacrylate oligomers show increased storage modulus due to interactions between urethane and polyol backbone chemistry

- Urethane acrylates show increased T_g as well as increased crosslinking

EFFECTS OF URETHANE ACRYLATE MW ON CONVERSION





UV cured film top surface

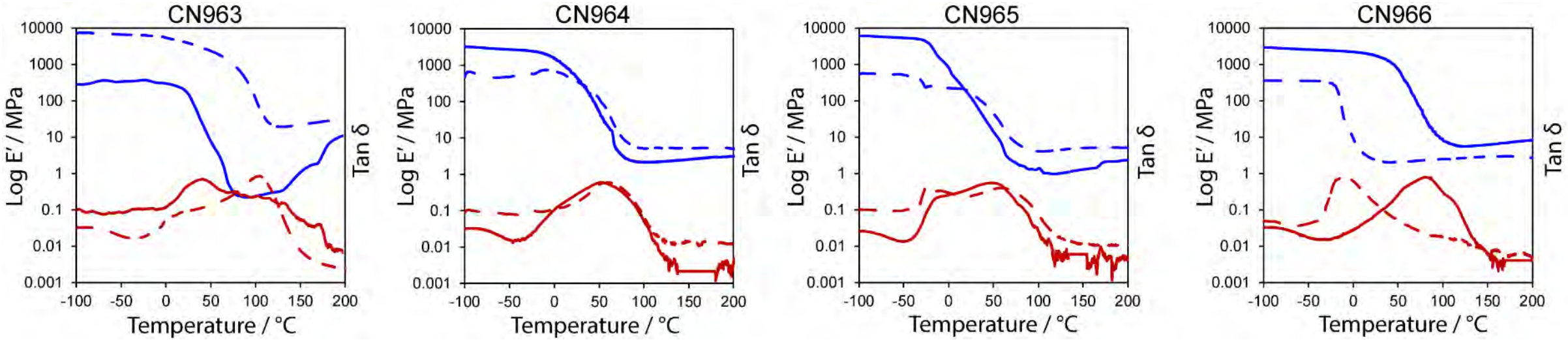
UV cured film bottom surface

EB cured film top surface

EB cured film bottom surface

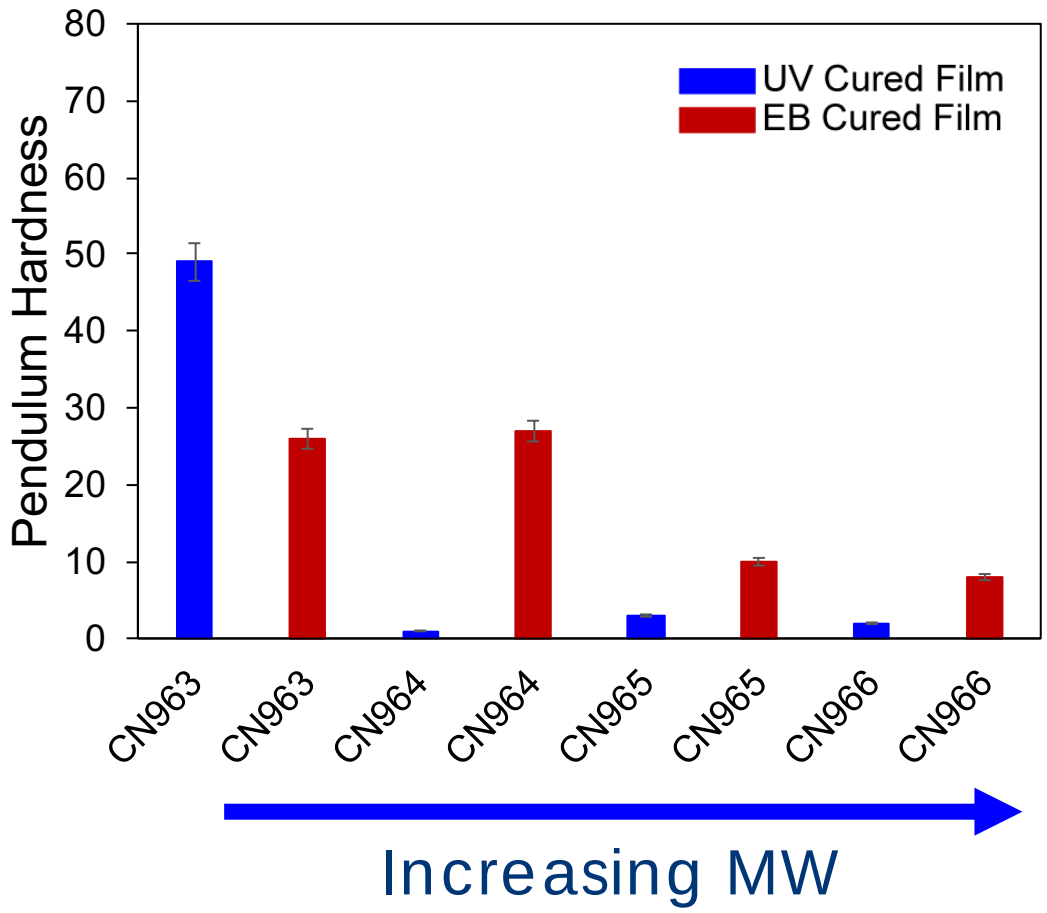
EFFECTS OF POLYURETHANE MOLECULAR WEIGHT

Increasing MW



- Increasing polyester content leads to interesting EB cure behavior
- Increasing chain scission lowers T_g and modulus

POLYURETHANE ACRYLATE MW HARDNESS



Composition	*50 Cycles*	*100 Cycles*	*150 Cycles*	*200 Cycles*
CN963 UV	no haze	no haze	no haze	low haze
CN963 EB	low haze	haze	haze	haze
CN964 UV	haze	haze	haze	haze
CN964 EB	no haze	no haze	no haze	no haze
CN965 UV	low haze	haze	haze	haze
CN965 EB	no haze	low haze	haze	haze
CN966 UV	no haze	low haze	haze	haze
CN966 EB	low haze	haze	haze	haze

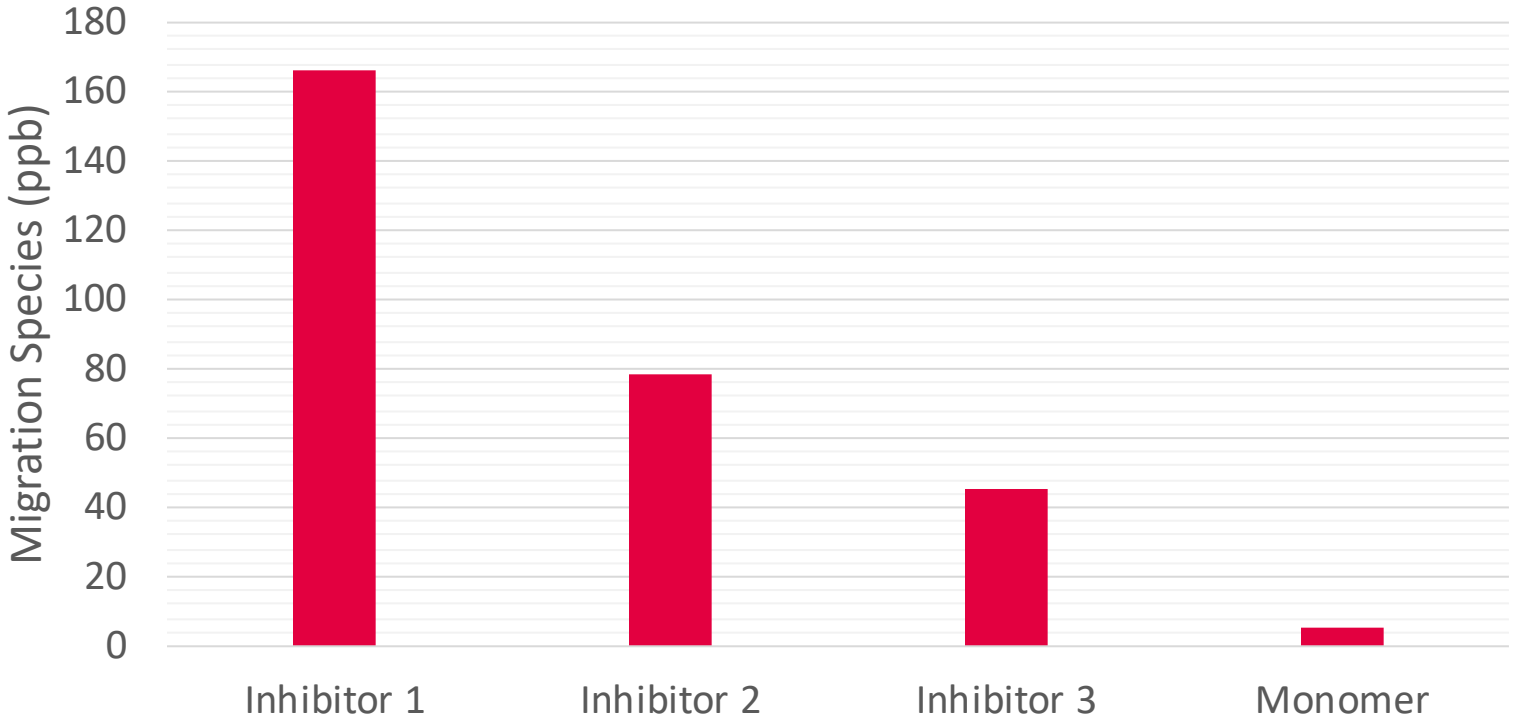
- Balancing polyester content and reactivity is necessary to maximize performance

ENERGY CURABLE PSA PRODUCTS

Property	UV cured	EB cured
Viscosity at 25°C (cP)	6,650	6,650
Cured PSA Thickness (mil)	2.7	2.1
Curing Method	UV (H Bulb)	EB
Energy (J/cm^2)	0.49	10 Mrad/175 kV
180° Peel on Stainless Steel; 1 day (lb/in)	7.6	4.2
180° Peel on Polypropylene; 1 day (lb/in)	4.8	4.5
Probe Tack (lb)	2.26	2.06
Room Temp Shear 2 kg (hr)	34	>167
Room Temp Shear 1 kg (hr)	84	>167
SAFT (^{0}F)	185	435
Refractive Index	1.49	1.49

- Modifications to PSA rheology change properties to increase shear and adhesion failure temperature tests.

MIGRATION IN EB CURABLE FILMS



→ Ongoing work to limit migratable species and formation.

→ Inhibitors selection is important to limit small molecule species

→ Single ppb or no monomers detected

CONCLUSIONS

- UV and EB processing create different polymerization methods with significantly different side reactions
- Polymer backbone and reactive groups further impact the types of side reactions
- The increased crosslinking in EB processing can lead to much lower levels of migratables in polymer films

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