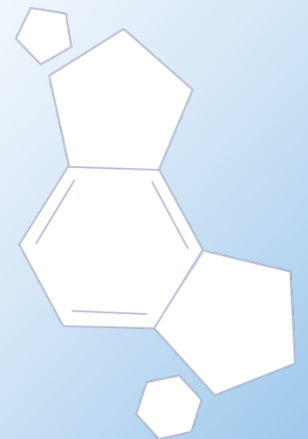




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Curing of Non-Styrene Based Thermosetting Resins

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Abstract

- With the challenges to current industry practices, it is common to say "How do I approach using resins that aren't based on styrene?". In the face of new regulatory standards, it is possible to use alternative resin technologies. While many non-styrene resins are not effectively cured using traditional methods, acceptable curing and processing times can be achieved with some of the newer resins currently being sold and developed.
- New resin technology seeks to eliminate styrene emissions in one of two ways: 1) through use of an alternative monomer, or b) by elimination of monomer altogether and using a resin with a shortened backbone chain which will be a flowable liquid until the cure cycle is executed. These changes have brought about some unique challenges in curing resins.
- This talk will inform end-users of alternative resin technologies available, and what some of the processing consequences are for each option. This talk does not attempt to debate whether styrene regulation is justified or not, rather it will offer alternatives to these users wishing to move away from styrenated resins.





Outline

- 1) A Brief Review of Polymer Resins
- 2) Background to Organic Peroxide Chemistry
- 3) Types of Non-Styrene Resins
- 4) Curing Alternative Monomer Resins
- 5) Curing no monomer resins
- 6) Summary and Conclusions



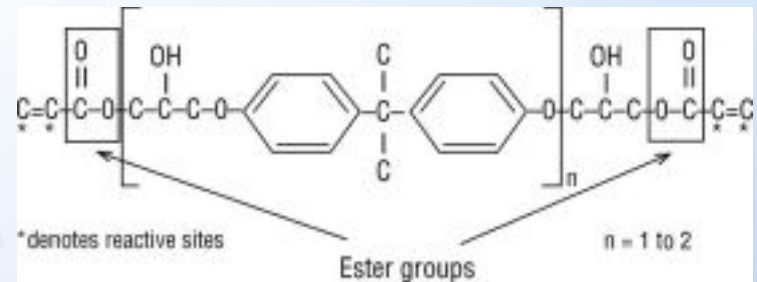
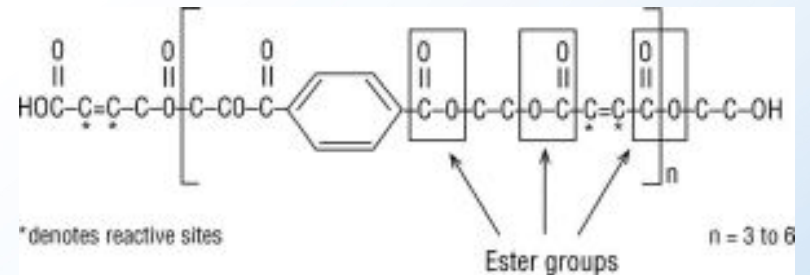
A Brief Review of Polymer Resins

- Thermosetting resins have two components that actively participate in the cure mechanism, a backbone polymer and a monomer.
- How the resin assembles is greatly effected by which backbone polymers and/or monomers are used.
- Each particular type of monomer and polymer react differently, and the rate of cure and amount of exotherm are dependant on the assembly.



Types of Backbone Polymers

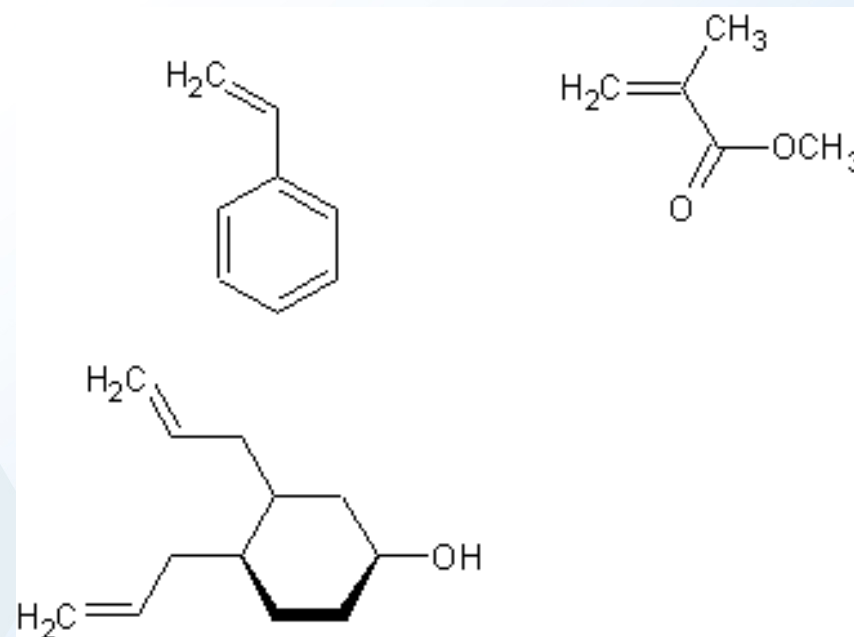
- Unsaturated Polyester
Reactive groups are in the middle of the polymer
- Vinyl Ester
Reactive groups on the end of the polymer
- DCPD
Dicyclopentadiene
- Others
Acrylics, etc.



Types of Monomers

- There are also a large number of monomers available

1. Styrenics
2. Acrylics
3. Vinylics
4. Allylics



Background to Organic Peroxide Chemistry

Organic Peroxide initiators undergo two types of decomposition:

- Thermal (such as peresters)
 - The advantage to thermal decomposition is that initiator use is much more efficient, the down side is, heat is required to carry out curing.

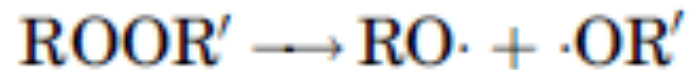
Promoted (MEKPs)

- Contrarily, promoted decomposition can allow RT cure, but more initiator is needed because of poor efficiency.



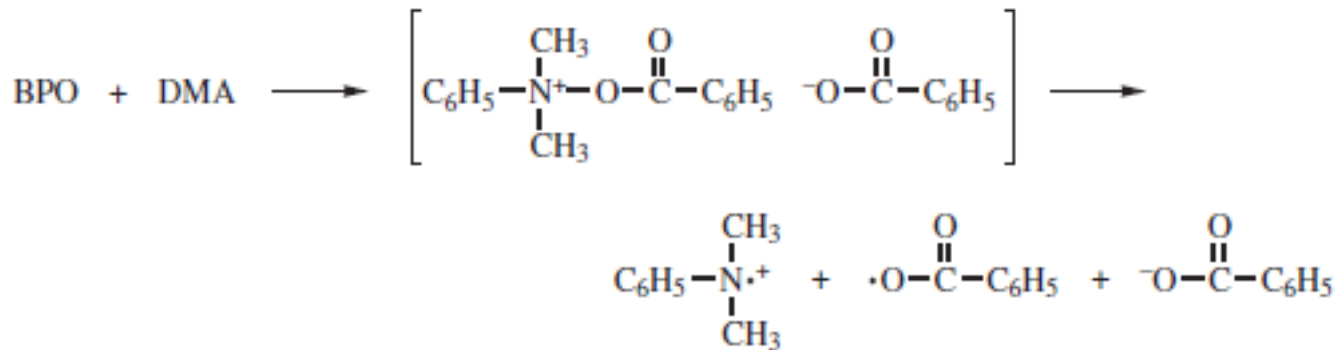
Thermal Decomposition

- Thermal decomposition occurs when heat causes a decomposition that splits the O-O bond exactly in half.
- This is called homolytic cleavage



Promoted Decomposition

- Promoted decomposition occurs when a peroxide is exposed to an external agent like a metal ion, that will cause the initiator to cleave in a way where equal numbers of radicals are not produced.
- This is called heterolytic cleavage.



Types of Non-Styrene Resins

• With all of this set forth, we see that the two primary methods for making a “non-styrene” resin are:

- Using an alternative monomer, such as Vinyl Toluene
 - Alternative monomer resins crosslink as normal, but the monomers may be expensive, or hard to find.
- Using a modified resin with no monomer
 - No monomer resins rely on reactive crosslinking only at reactivity points.
 - In general, these reactive points are more hindered and less reactive, requiring a more aggressive initiator.



Challenges of Curing Alternative Monomer Resins

Other styrenic monomers:

- Vinyl Toluene has been used, but there are problems:
 - 1) VT is not available in sufficient supplies to meet the needs of the composites industry.
 - 2) VT goes through the same chemistry in the body as styrene, and may eventually be regulated also.

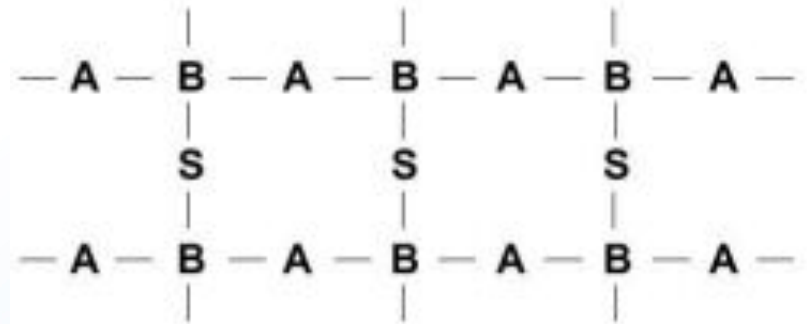
Acrylic monomers:

- MMA would be an obvious choice, but some caveats:
 - 1) MMA requires much more energy to initiate than styrene. As such MEKP/cobalt will not work well.
 - 2) BPO/DMA will work, but color and haze issues could be a problem. Not an easy promoted system for acrylic.

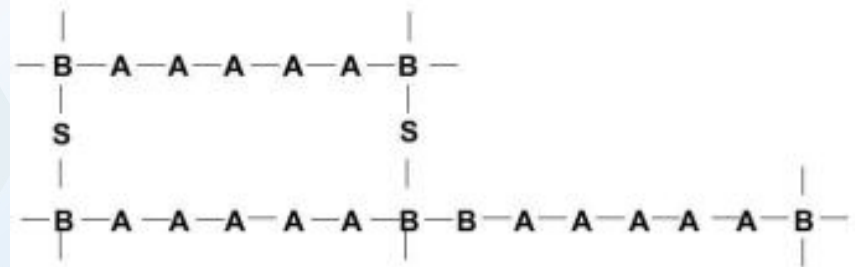


Curing Alternative Monomer Resins

- Alternative monomer resins will cure much like traditional styrene containing resins.
- The S-chains would be replaced with the alternative monomer.



Schematic Representation of Polyester Resin (Cured)

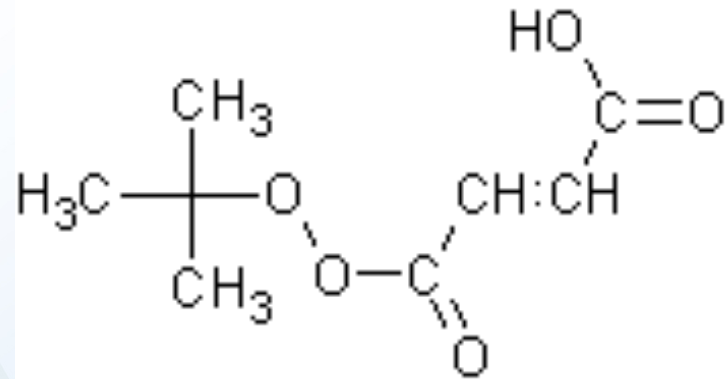


Schematic Representation of Vinylester Resin (Cured)



Curing Alternative Monomer Resins

- A good alternative for curing acrylic based resins is the molecule t-butyl peroxy maleic acid.
- This material is well known to the cast polymer industry, as it is commonly used for acrylic solid surface castings.
- The unique characteristic of this initiator is that it can be used either thermally, or in one of two promoted states.
- As a result, it is capable of either elevated temperature or room temperature curing.



Curing Acrylics with PMA

- The hemi-perester of peroxy maleic acid can be promoted with a variety of heavy metal bases.
- A mercapto ester is used in conjunction to achieve room temperature curing.

TABLE I

Example	Metal salt of hemi-perester	Basic compound	Average Gel time (minutes)
1	Calcium	Hydroxide	3.9
	do	Oxide	21.7
2	Sodium	Acetate	11.1
	do	Aluminate	20.3
	do	Benzoate	13.3
	do	Carbonate	10.2
	do	Bicarbonate	53.3
	do	Cyanide	7.9
	do	Thiocyanate	33.0
	do	Formate	21.4
	do	Methacrylate	14.2
	do	Methoxide	6.4
	do	Dihydrogen phosphate	22.7
	do	Orthophosphate	9.8
	do	Stearate	12.1
	do	Sulfide	13.9
3	Potassium	Carbonate	12.4
4	Magnesium	Acetate	14.9
	do	Hydroxide	27.8
	do	Oxide	32.1
5	Barium	Hydroxide	13.7
6	Copper	Acetate	61.4
7	Strontium	do	43.5
	do	Hydroxide	7.7
8	Zinc	Acetate	6.8
9	Lead	do	4.5
10	Cobalt	do	50.6
11	Manganese	do	8.7
Control	(Hydrogen)	None	>275



Additives to Modify PMA Cures

- Curing can be optimized by varying the level of metal base.
- Curing can also occur with a low level of peroxide, as long as the base and mercaptan are present.

TABLE II

Hemi-perester (parts)	Calcium Hydroxide (parts)	Exotherm Time (minutes)
0.75	7.50	14
0.75	3.00	13
0.75	1.50	12
0.75	0.75	13
0.75	0.30	11
0.75	0.15	18
0.75	None	168

TABLE III

Hemi-perester (parts)	Calcium Hydroxide (parts)	Exotherm Time (minutes)
0.15	0.45	39
0.15	0.30	48
0.15	0.15	50
0.15	0.075	56



Another Example of PMA Curing

- 35 parts of acrylic syrup
- 65 parts of alumina trihydrate
- 0.30 part of a 30% paste of calcium hydroxide in the syrup
- 0.80 part of a 25% solution of mono-tertiary-butyl peroxy maleate in a 1:2 by weight solution of methanol and methyl methacrylate
- 0.5 part of a 33% aqueous solution of sodium metabisulfite corresponding to bisulfite: hemi-perester ratio of 1:1.4
- Prior to the addition of the last ingredient, the mixture is heated to 30.degree. C.
- The final mix is cast in 2.5 inch diameter dishes to have a thickness of 0.75 inch.
- Curing is obtained in 7.5 minutes.
- The cured sheet is translucent and shows no blushing (whitening) after immersion in 70.degree. C. water for 16 hours.



Curing No Monomer Resins

- No monomer resins are more difficult to cure for a couple of important reasons:
 - 1) Since there is no monomer in the mixture, everything there is a high molecular weight material. These are more difficult to compatibilize with additives.
 - 2) Since there are no additives to accelerate cure, the cure mechanism will be limited to thermally initiated systems.



No Monomer Resins

- These types of resins will tend to be stronger, and possibly could be more like thermoplastics (partially recyclable?)
- These resins would work ideally where thermal initiation is already used (pultrusion, compression molding, filament winding, etc.)
- The initiators used could be higher reactivity, and potentially low temperature storage.



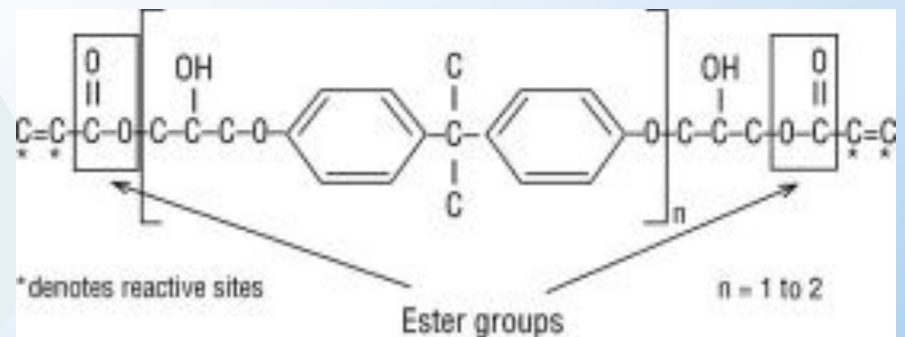
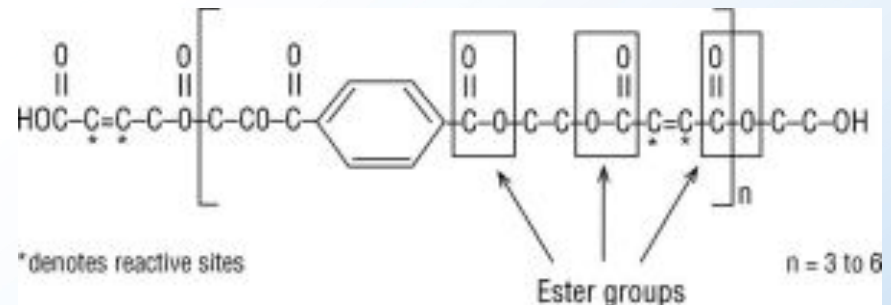
No Monomer Resins: Initiator Choice

- Some of the popular solid initiators used in some applications (pultrusion, CIPP, etc) would not be usable in these resins. Solid initiators will not dissolve in these resins.
- Some low melting point initiators such as the non-BPO diacyl peroxides could be useful here.
- For higher temperature applications, initiators with high stability and low melting points could also be used (i.e. “bis” peroxide).



Role of Reactive Groups in Non-Monomer Resins

- Some further things to consider:
- End group resins will be more typical in this category. Reactive groups in the middle of chains (maleate) will be difficult to crosslink. Maleates do not react well with themselves.
- End group resins with acrylates are easier to crosslink.



Summary

- The main challenge with curing resins based on alternative monomers lies in the fact that most other monomers other than styrene are more difficult to cure due to the fact that they require higher energies to initiate curing. In free radical initiators, this could mean a move away from traditional MEKPs for primary curing.
- The other alternative, monomerless resins, pose the challenge that you are curing a polymer, not a monomer. As a result, more aggressive curing agents must sometimes be used.
- In either case, switching to a styrene-free resin can be done, as long as the end-user is willing to consider alternative ways of curing.



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Questions?

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