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Thermosetting polymers and composites from agricultural oils

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Thermosetting Polymers and Composites from Agricultural Oils

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Outline

- Plastics from vegetable oils (thermosets)
  - Free radical polymerization
  - Cationic polymerization
  - Ring-opening metathesis polymerization
- Composites
- Polyurethane Coatings

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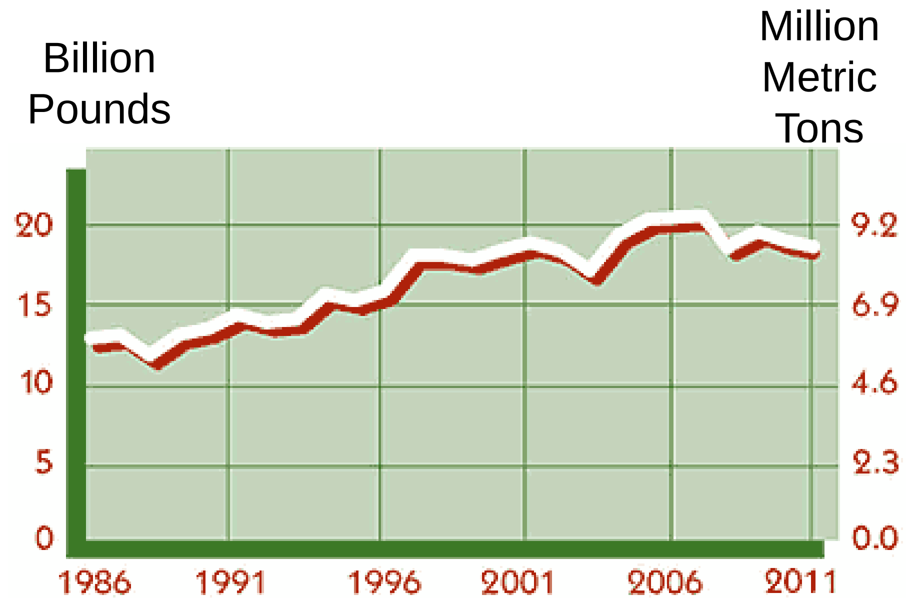
Advantages of Natural Oils

- Readily available on a huge scale.
- Very inexpensive.
- Natural and renewable.
- High purity.
- Relatively high molecular weight.
- Can be genetically engineered.



U.S. Soybean Oil Production. Source: USDA

- Many structurally related natural oils are readily available.

Soybean Oil Structure

$$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2CH_2$$

$$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7CO_2CH$$

$$CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_7CO_2CH_2$$

Oleic acid	22%
Linoleic acid	54%
Linolenic acid	8%

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Natural and Conjugated Oils

Oil	C=C Bonds		% Composition		
	Conjugated	No.	C18:1	C18:2	C18:3
Regular soy oil (SOY)	no	4.5	22	54	8
LoSatSoy oil (LSS)	no	5.1	20	64	9
Conjugated LSS (CLS)	yes	5.1	20	64	9
Linseed oil (LIN)	no	5.8	19	15	57
Conjugated linseed oil (CLIN)	yes	5.8	19	15	57
Tung oil (TUN)	yes	8.2	5	7	85[a]

[a] α-Eleostearic acid (9,11,13-octadecatrienoic acid)

$$-CH_2-CH{=}CH-CH_2-$$
$$-CH_2-CH{=}CH-CH_2-CH{=}CH-CH_2-$$
$$-CH_2-CH{=}CH-CH_2-CH{=}CH-CH_2-CH{=}CH-CH_2-$$

In SOY and LSS oils

$$-CH_2-CH{=}CH-CH_2-$$
$$-CH_2-CH{=}CH-CH{=}CH-CH_2-$$
$$-CH_2-CH{=}CH-CH{=}CH-CH{=}CH-CH_2-$$

In CLS, C_{100}LIN, C_{87}LIN and TUN oils

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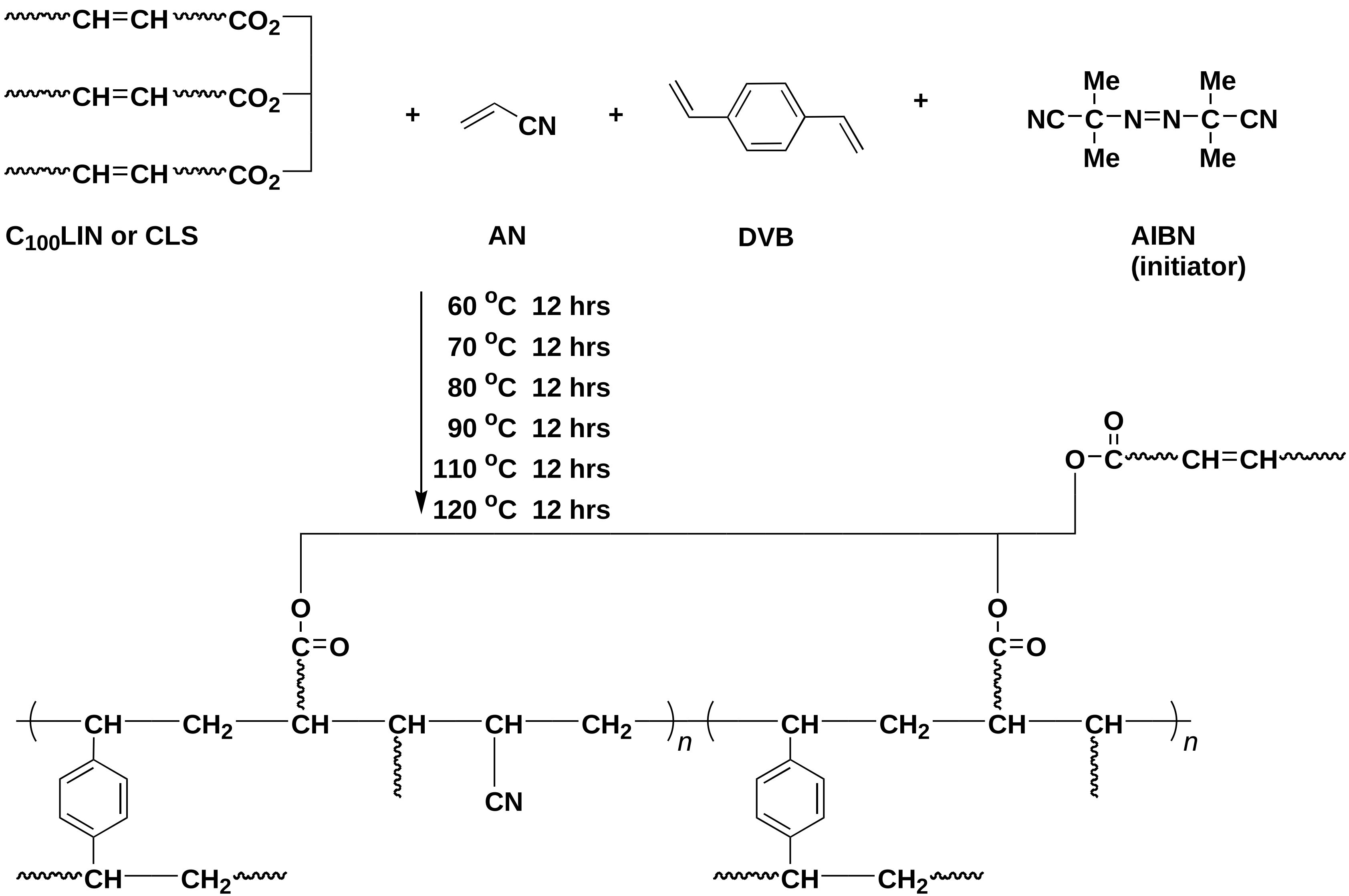
Free Radical Polymerization



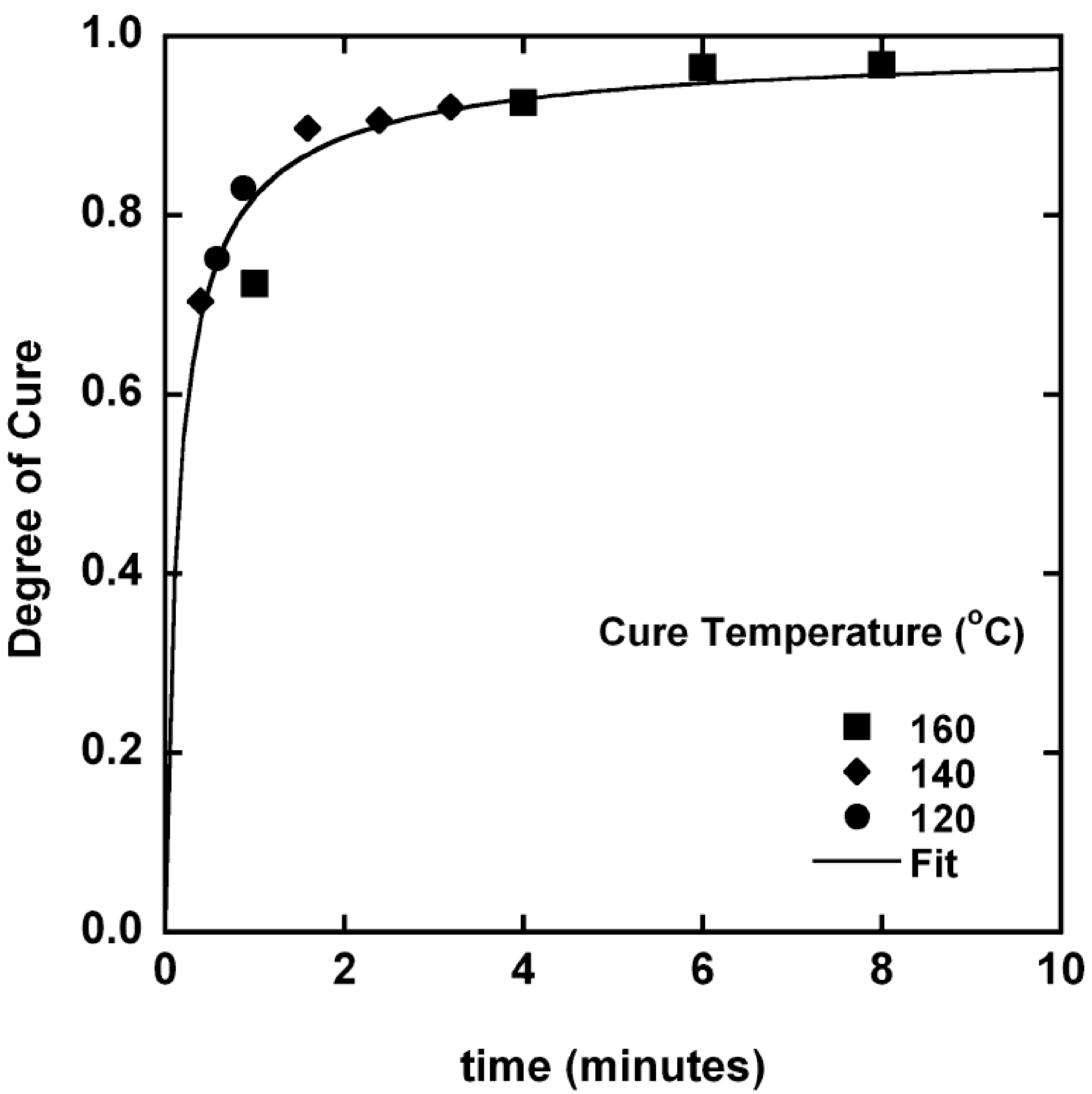
Free Radical Polymerization of Conjugated Soybean Oil

Sample	T_g (ºC)	Tan Delta	T_{10} (ºC)	T_{50} (ºC)	T_{max} (ºC)	% Sol	% Insol
CLS40-AN54-DVB6-AIBN1	102	0.36	-	-	-	1.6	98.4
CLS50-AN45-DVB5-AIBN1	95	0.35	-	-	-	2.1	97.9
CLS60-AN36-DVB4-AIBN1	74	0.36	-	-	-	4.5	95.5
CLS70-AN27-DVB3-AIBN1	49	0.36	-	-	-	6.8	93.2

Sample	T_g (ºC)	Tan Delta	T_{10} (ºC)	T_{50} (ºC)	T_{max} (ºC)	% Sol	% Insol
CLS40-AN54-DCP6-AIBN1	107	0.49	389	488	458	0.9	99.1
CLS50-AN45-DCP5-AIBN1	84	0.45	419	484	490	1.8	98.2
CLS60-AN36-DCP4-AIBN1	65	0.46	426	491	499	2.7	97.3
CLS70-AN27-DCP3-AIBN1	32	0.47	433	502	524	7.5	92.5

DCP = dicyclopentadiene

Cationic Polymerization



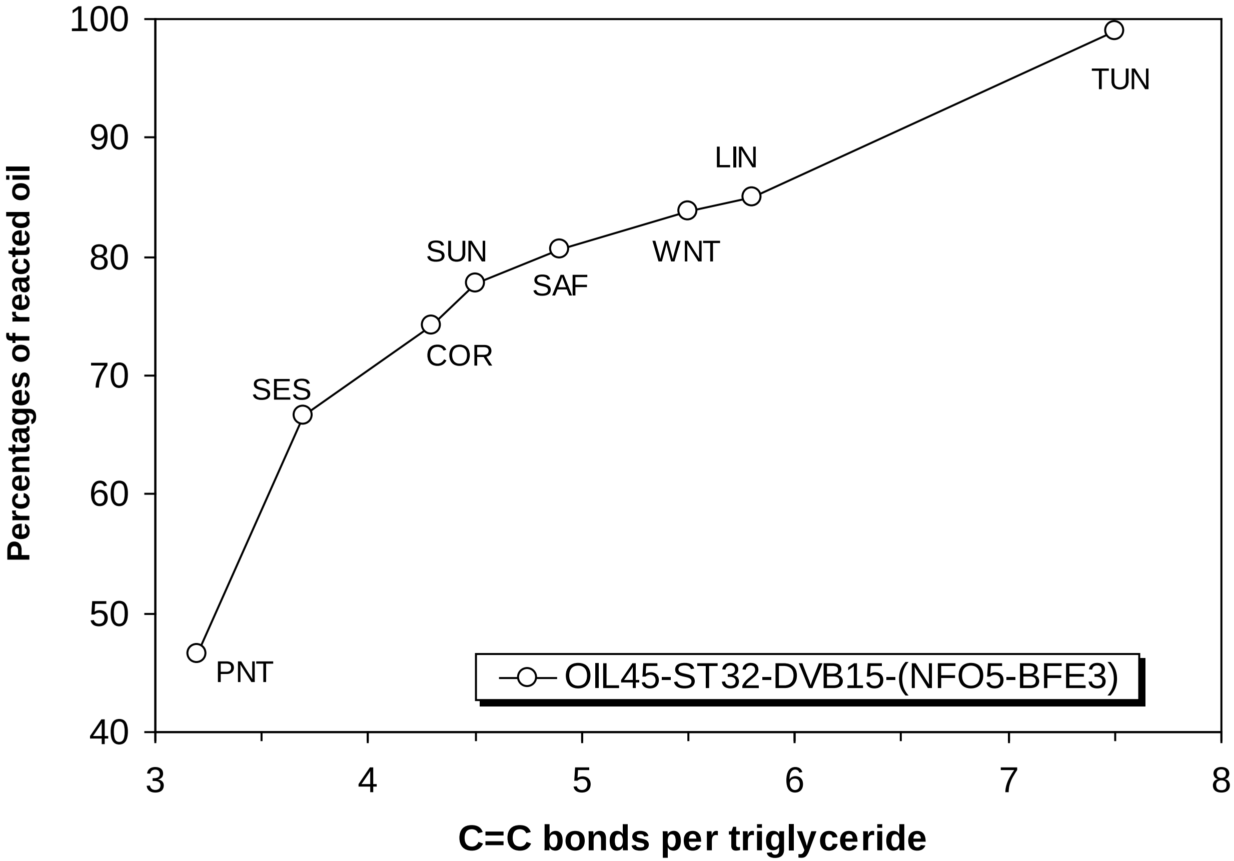
Mechanical Properties of Soybean Oil Polymers

Characteristics of soybean oil polymers

Polymer	Tg (°C)	ν_e (mol/m^3)	T_{max}[a] (°C)	E[b] (MPa)	σ_b[c] (MPa)	ε_b[d] (%)	Toughness (MPa)
Polyethylene (LDPE)	-68	-	355	370	9.6	46	5.2
Polystyrene	90	-	420	1330	30.3	4	0.5
CLS45-ST47-DVB00-(NFO5-BFE3)[e]	10	1.0×10^2	**448**	12	1.3	**300**	2.0
CLS45-ST32-DVB15-(NFO5-BFE3)[f]	76	2.2×10^3	**475**	225	11.5	41	4.0
CLS35-ST39-DVB18-(NFO5-BFE3)[g]	82	3.4×10^3	**477**	**500**	**21.0**	3	0.8
SOY45-ST32-DVB15-(NFO5-BFE3)	68	1.8×10^2	**468**	71	4.1	57	1.7
LSS45-ST32-DVB15-(NFO5-BFE3)	61	5.3×10^2	**470**	90	6.0	64	2.9
CLS45-ST32-DVB15-(NFO5-BFE3)	76	2.2×10^3	**475**	225	11.5	41	4.0

[a] The temperature at the maximum degradation rate
[b] Young's modulus
[c] Break strength
[d] Elongation at break
[e] A typical elastomer
[f] A ductile plastic
[g] A rigid plastic

Polymers from Other Vegetable Oils



- All oils have a triglyceride structure composed primarily of oleic acid, linoleic acid and linolenic acid.
- Generally, higher unsaturation results in a plastic with higher mechanical properties.

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Polymers from Other Vegetable Oils

Table. Tensile mechanical properties of other natural oil-based plastics

Samples	E (MPa)	σ_b (MPa)	ε_b (%)	Toughness (MPa)
PNT45-ST32-DVB15-(NFO5-BFE3)	32	2.5	20.0	0.27
SES45-ST32-DVB15-(NFO5-BFE3)	48	3.8	48.1	1.46
COR45-ST32-DVB15-(NFO5-BFE3)	48	4.0	51.7	1.64
SUN45-ST32-DVB15-(NFO5-BFE3)	49	5.1	55.7	1.78
SAF45-ST32-DVB15-(NFO5-BFE3)	76	4.5	48.1	1.79
WNT45-ST32-DVB15-(NFO5-BFE3)	85	6.1	62.1	2.97
LIN45-ST32-DVB15-(NFO5-BFE3)	75	7.0	60.4	3.22

- The agricultural oil-based polymers exhibit characteristics ranging from soft to tough plastics.
- Generally, a higher degree of unsaturation in the oil results in a plastic with higher mechanical properties.

Outline

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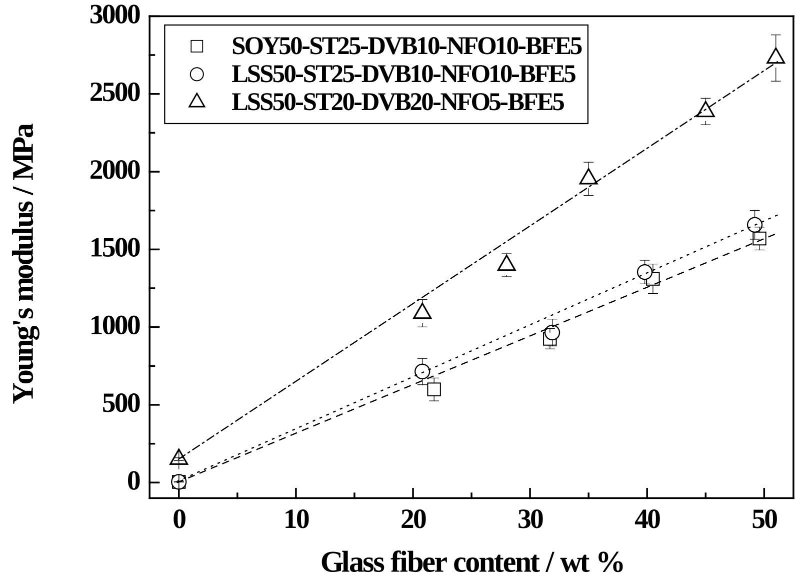
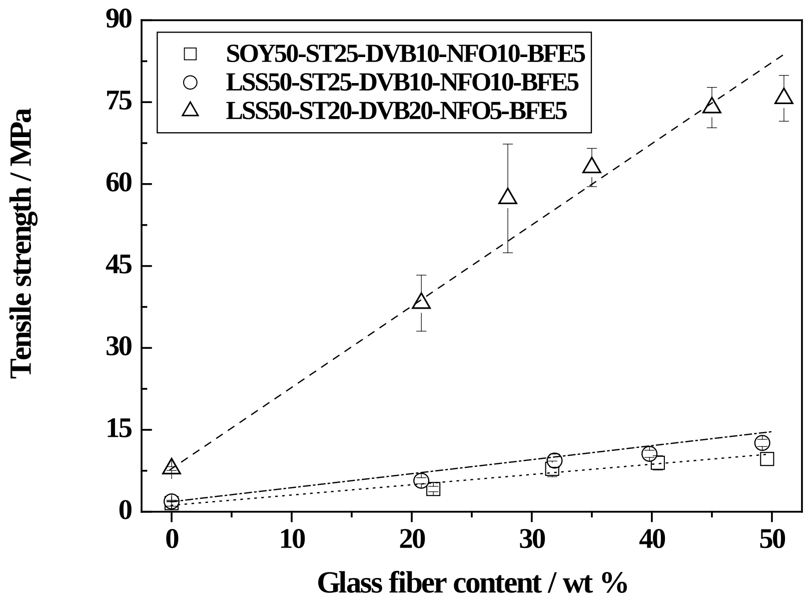
Soy-Glass Fiber Composites

Mechanical properties

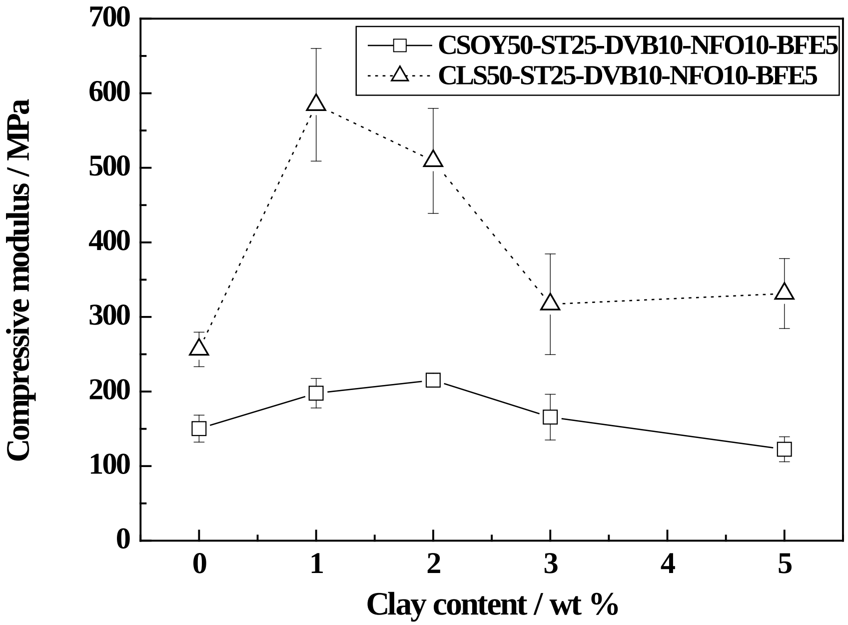


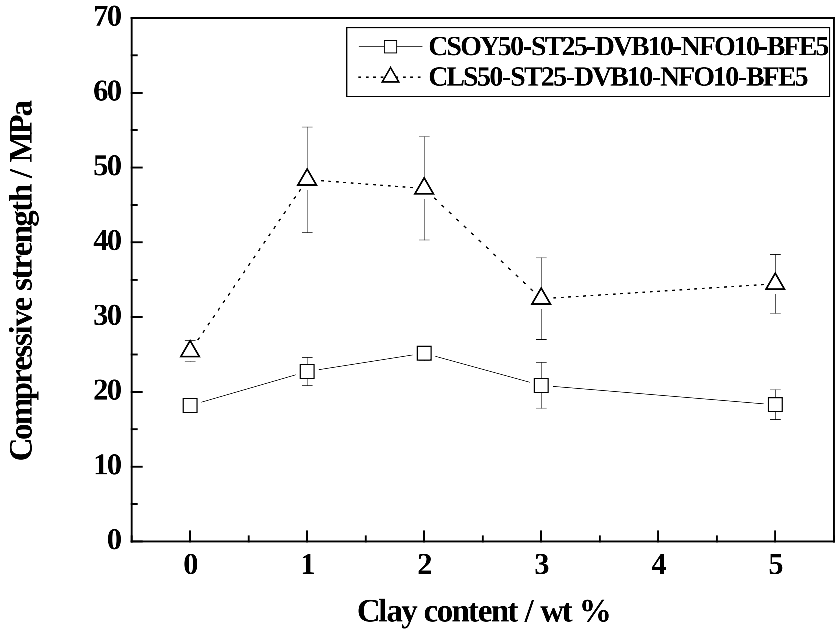


- Incorporating glass fiber into the soy-based polymer results in good composites with improved properties.
- Increasing crosslinking of the polymer matrix can dramatically increase the mechanical properties.
- Fiber surface modification and compatibilization efforts are currently underway

Soy-Organomodified Clay Nanocomposites

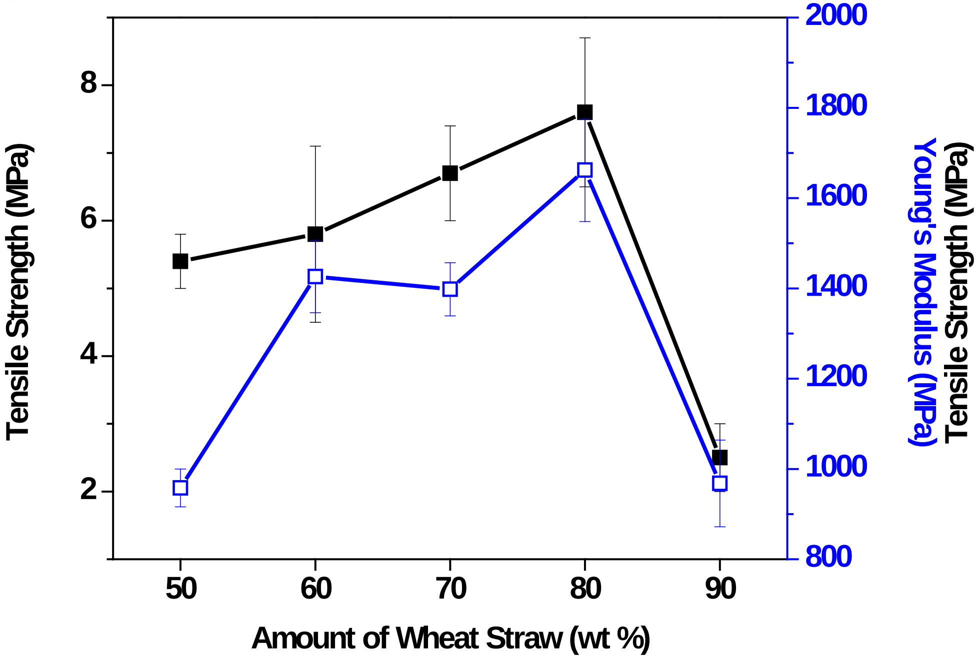
Mechanical properties

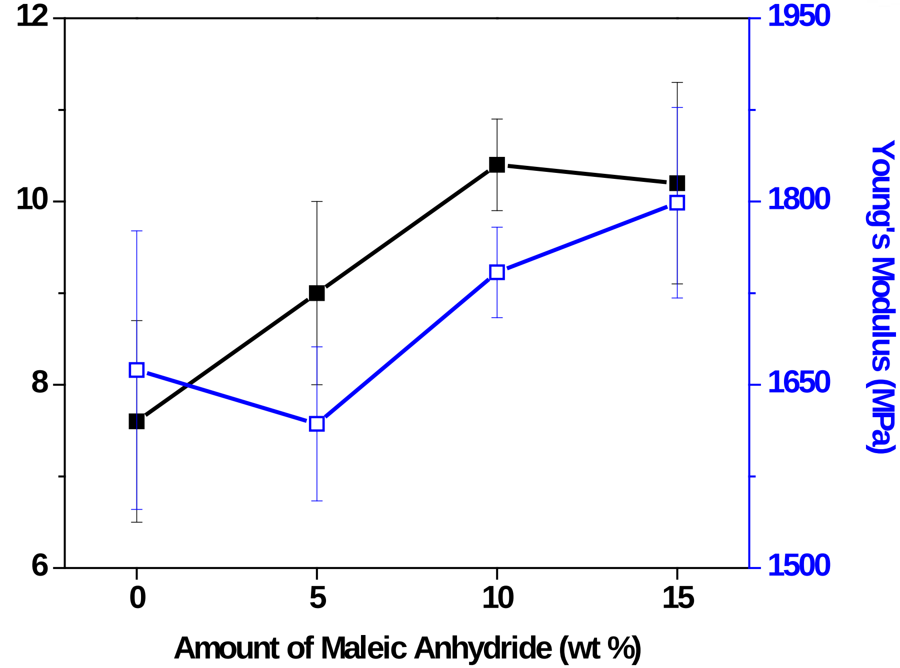




- 1-2 wt % clay can significantly increase the mechanical properties.
- CLS affords better mechanical properties than CSOY.

Wheat Straw Biocomposites





Matrix: CLIN50-BMA35-DVB15-TBPO5

Filler: 2 mm Wheat Straw

Matrix: (CLIN)50-(BMA + MA)35-DVB15-TBPO5

Filler: 2 mm Wheat Straw (80 wt %)

- Good mechanical properties can be maintained using as much as 80 wt % of wheat straw.
- Maleic anhydride (MA) is an effective compatibilizer between the filler and matrix and significant increases in the mechanical properties result by the addition of MA.

BA = Butyl Metacrylate

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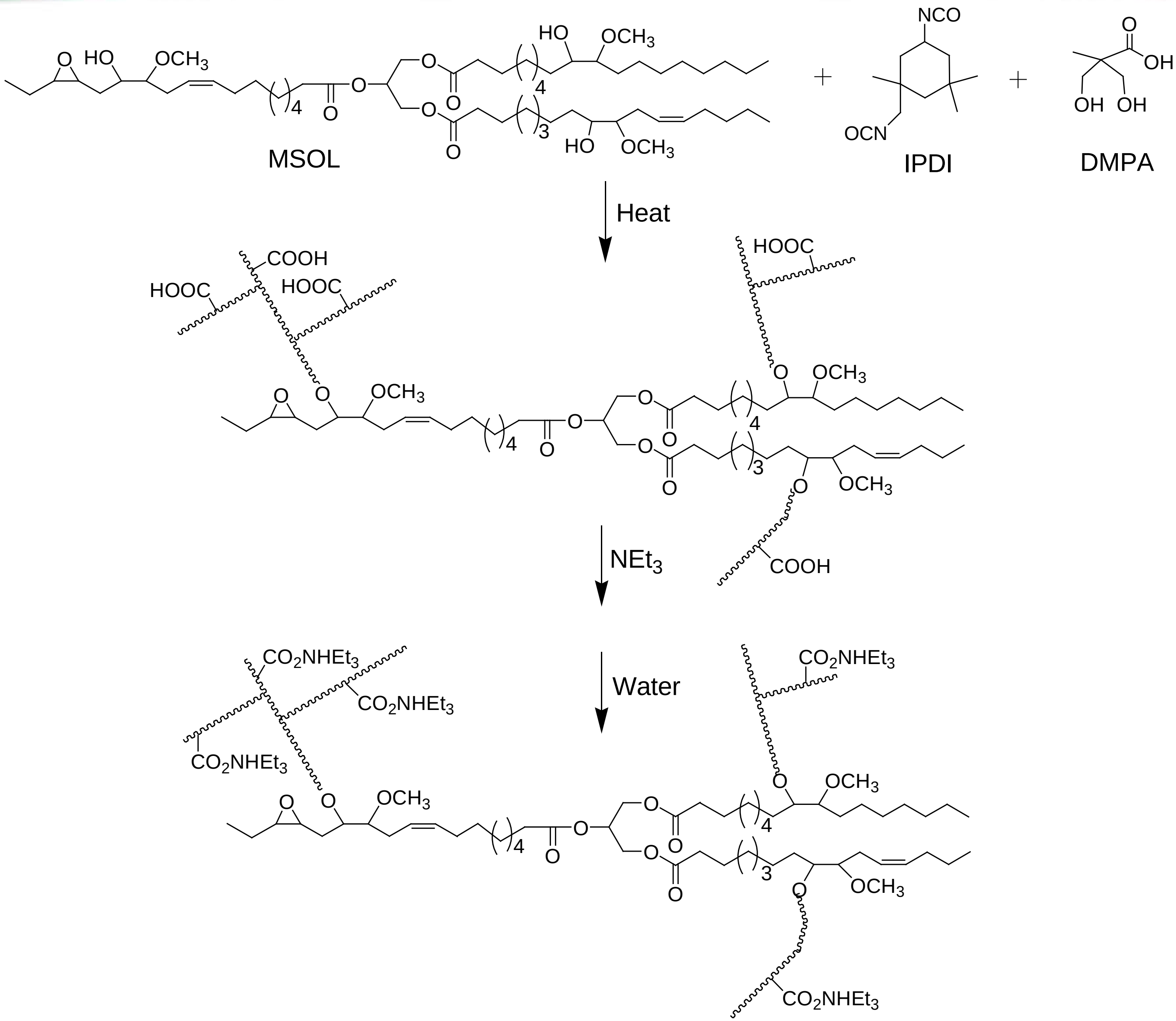
Vegetable Oil-Based Dispersions



Soybean Oil-Based Waterborne Polyurethane Dispersion (SPU)

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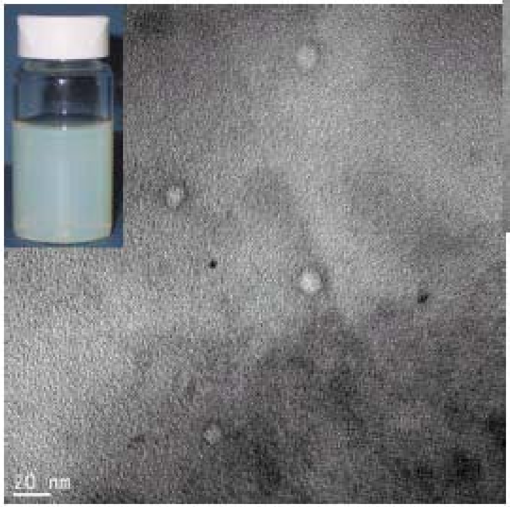
Vegetable Oil-Based Dispersions

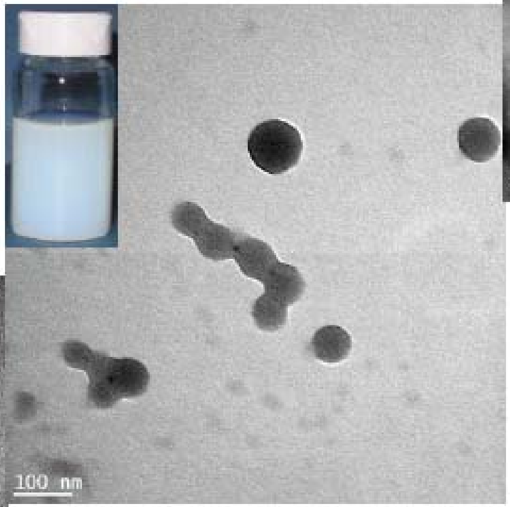
Appearance and particle sizes

15 nm



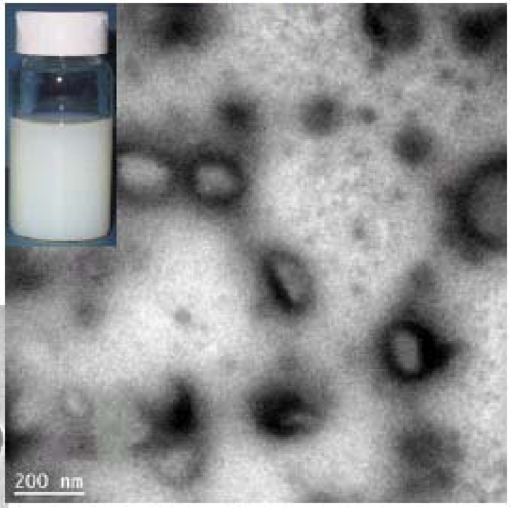
SPU-135 (2.4)

60 nm



SPU-149 (2.8)

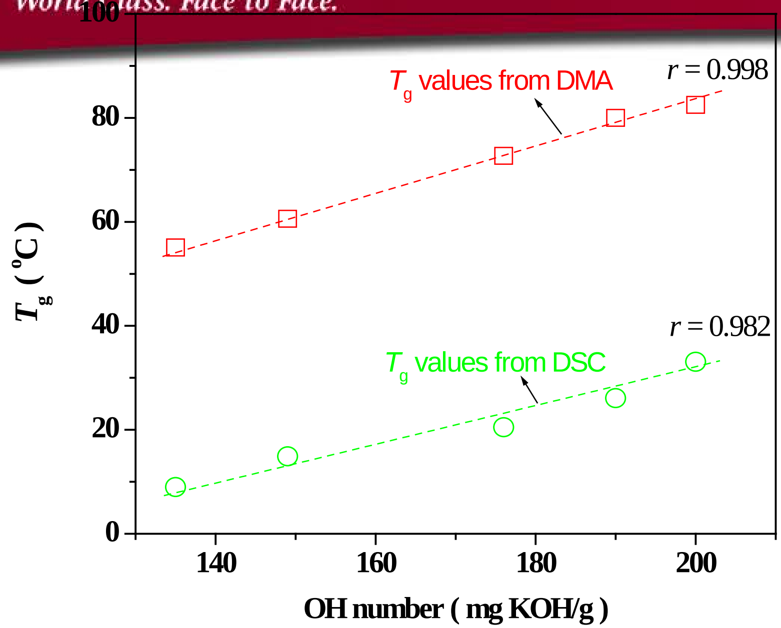
130 nm

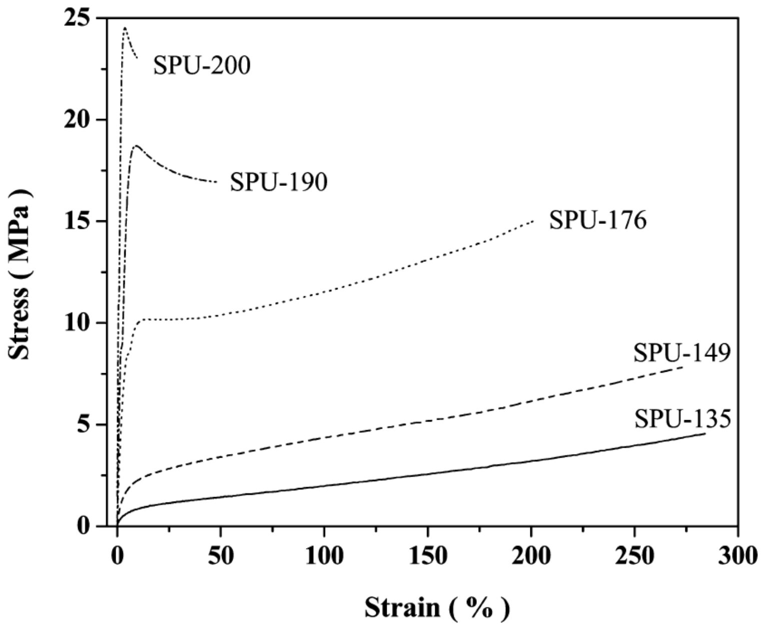


SPU-200 (4.0)

- The particle size of the SPU dispersions increases with the increasing OH functionality of the polyol.

Vegetable Oil-Based Dispersions





- The T_g of the SPU films increases linearly with an increase in the OH functionality.
- The mechanical properties of the SPU films increase with the OH functionality.
- The mechanical properties of the SPU films change from those of an elastomer to a ductile polymer and eventually to a hard plastic with an increase in the OH functionality.

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Summary

- Industrially promising biopolymers ranging from elastomers to rigid plastics have been prepared.
- These biomaterials have excellent thermal and mechanical properties.
- Work with other comonomers, oils and processes is underway.
- Biocomposites can be made from a variety of materials.
- Work on biobased coatings and adhesives is promising.