Novel Polymeric Materials from Biological Oils

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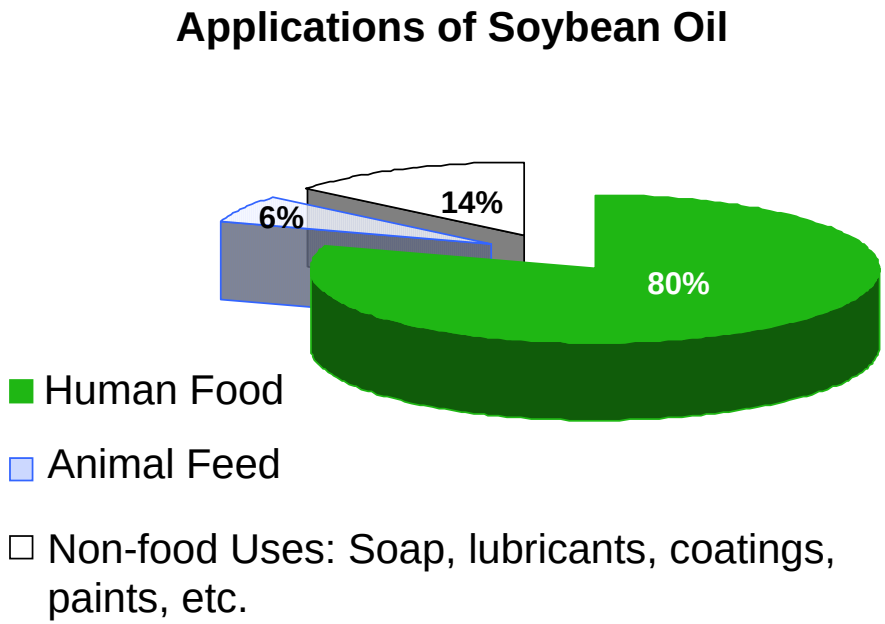
Applications of Soybean Oil

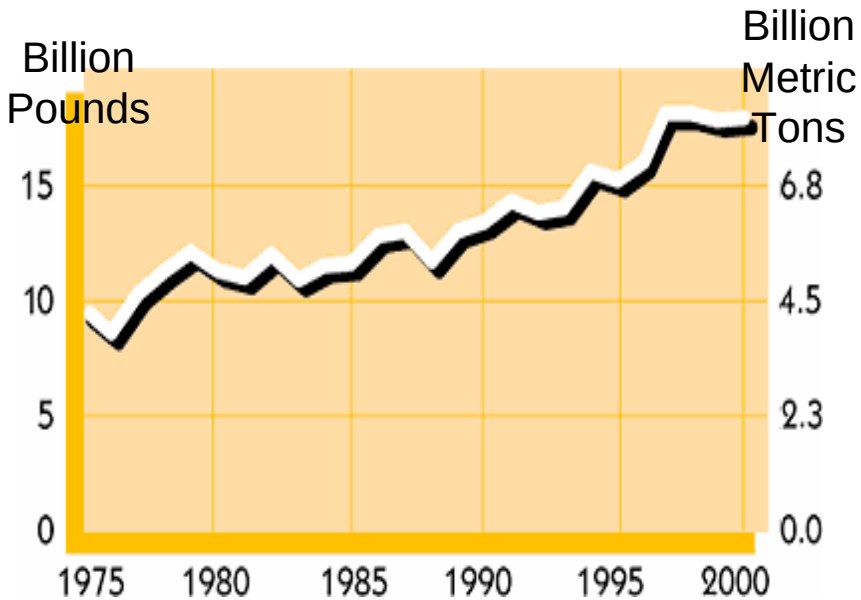
- Most soybean oil has been used for human food.
- The most promising new uses of soybean oil may be in non-food uses.



- Our interest is the conversion of soybean and other natural oils to industrially useful bulk polymers.

Advantages of Natural Oils

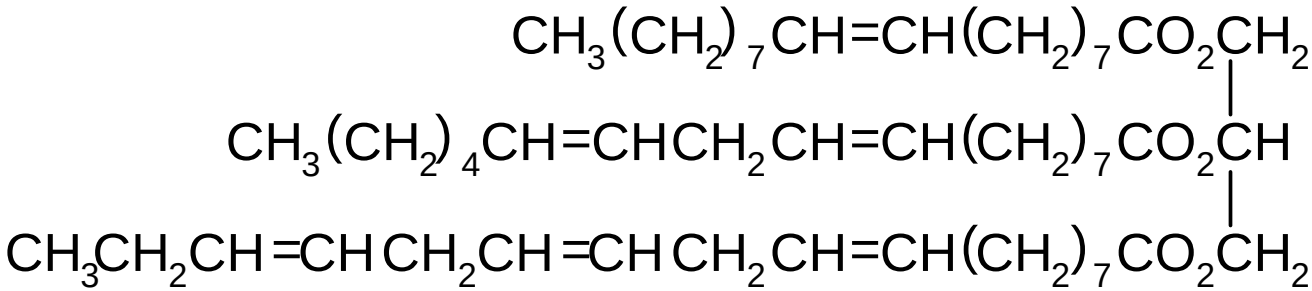
- Readily available on a huge scale.
- Very inexpensive.
  - Soybean oil ~23 cents/lb.
  - Corn oil ~25 cents/lb.
- Natural and renewable.
- High purity.



U.S. Soybean Oil Production. Source: USDA

- Relatively high molecular weight.
- Can be genetically engineered.
- Many structurally related natural oils are readily available.

Soybean Oil Structure

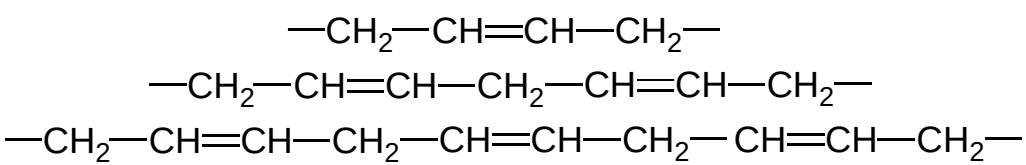


Oleic acid	22%
Linoleic acid	54%
Linolenic acid	8%

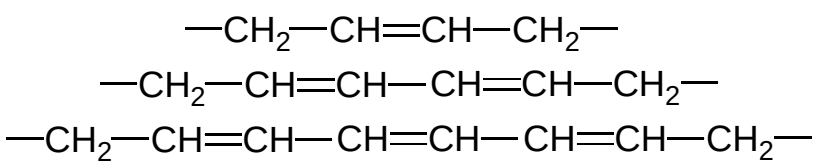
Natural and Conjugated Oils

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 ($C_{100\ or\ 87}$LIN)	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)

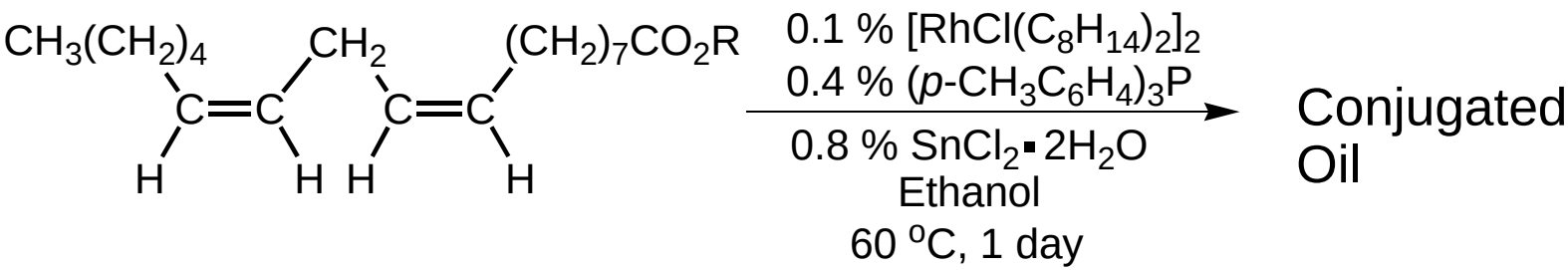


In SOY and LSS oils



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

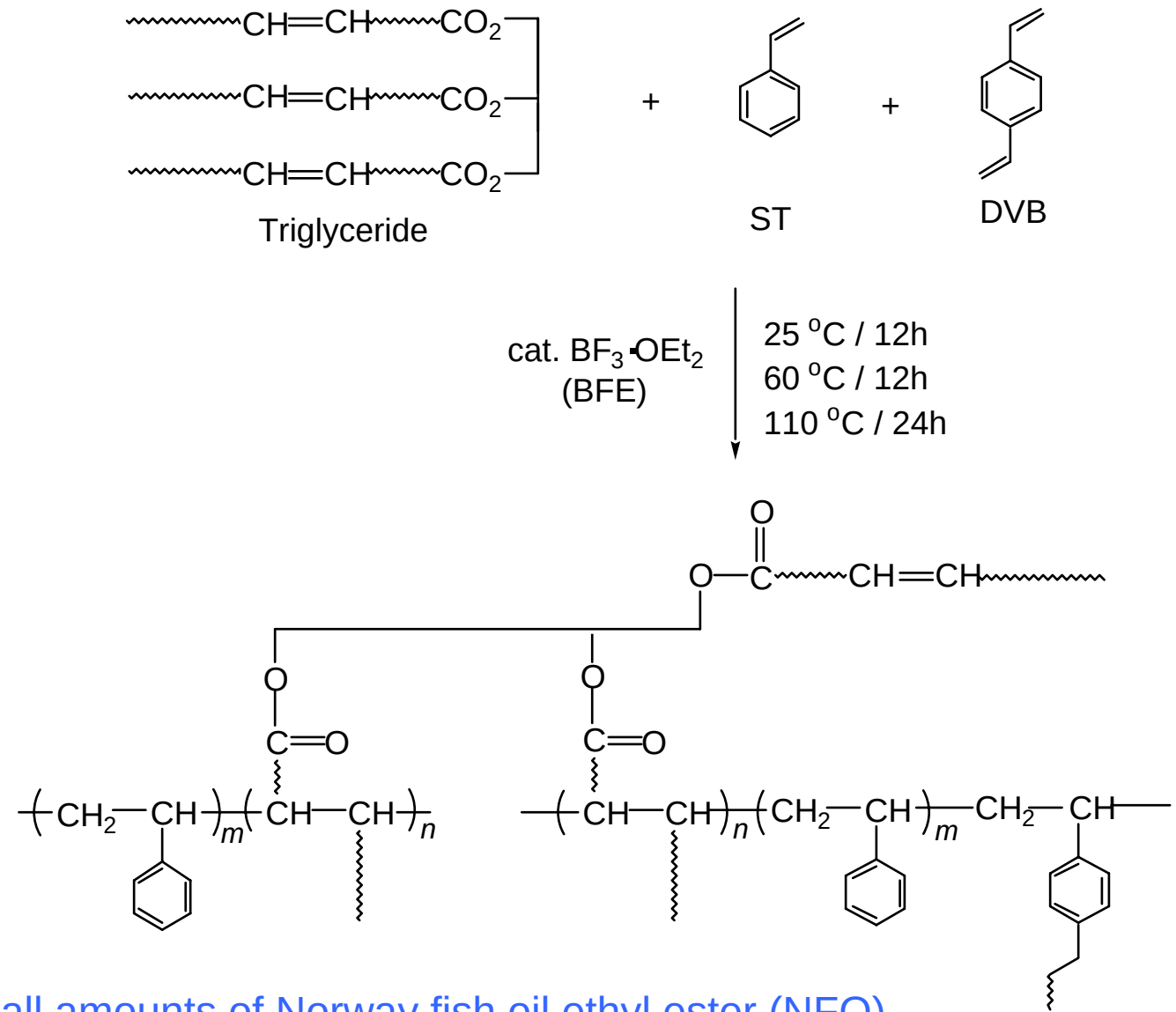
Conjugation of Natural Oils



Oil	% Conjugation
Linseed	100
Walnut	85
Safflower	91
Sunflower	82
Soy	100
Corn	78
Sesame	74
Peanut	70

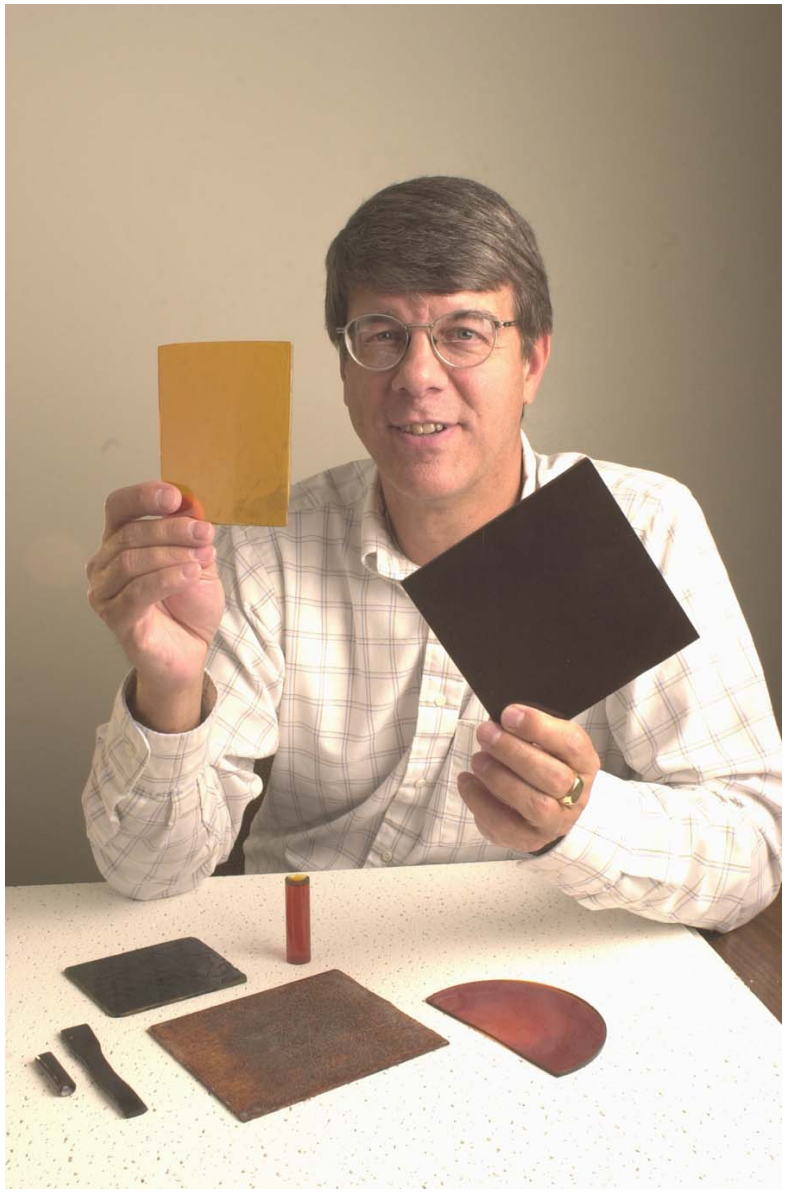
J. Am. Oil. Chem. Soc. 78, 447 (2001)

Our Method: Cationic Polymerization



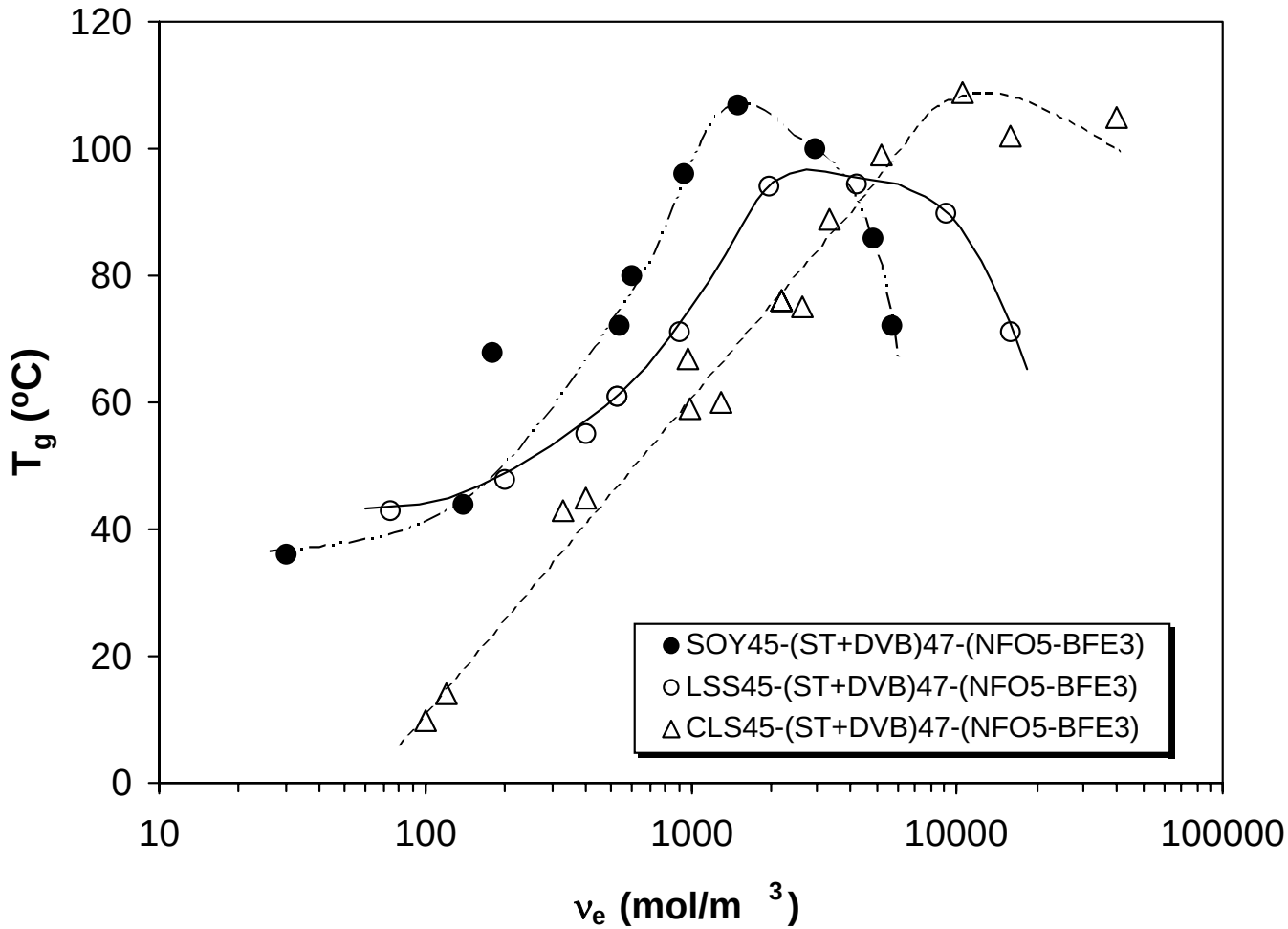
Note: small amounts of Norway fish oil ethyl ester (NFO) are added for homogeneity.

An Overview of the Soybean Oil Polymers



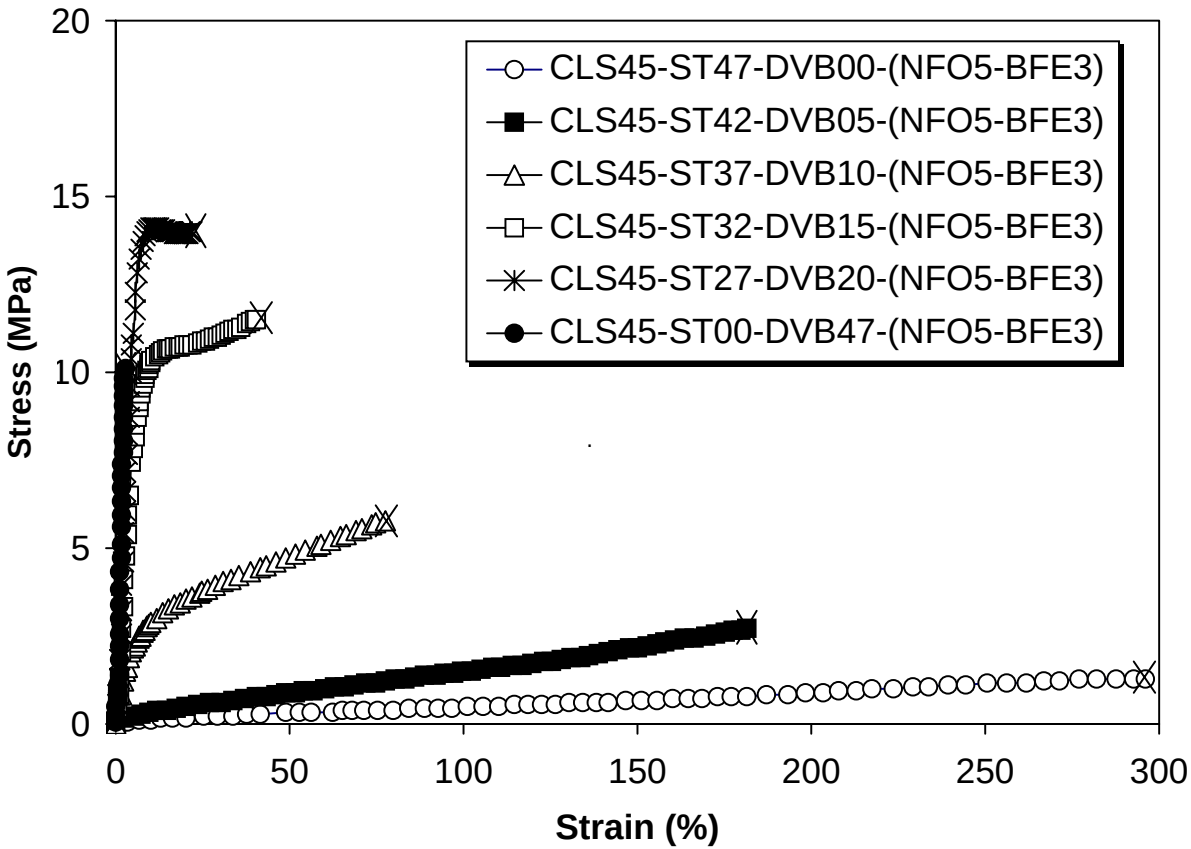
- The cationic copolymerization of different soybean oils with various alkene comonomers results in thermoset polymers with a glossy dark brown color.
- The polymers can be made into various shapes by *in situ* reaction molding or cutting.

Glass Transitions of the Soybean Oil Polymers



- A variety of polymeric materials have been prepared with their glass transition temperatures ranging from 10 to 110 °C.

Mechanical Properties of Soybean Oil Polymers



- A typical soy oil-based elastomer shows an elongation at break of 300%.
- A typical soy oil-based ductile plastic shows yielding behavior, followed by strain softening and strain hardening.
- A typical soy oil-based rigid plastic shows an ultimate tensile strength of 43 Mpa.

Mechanical Properties of Soybean Oil Polymers

Characteristics of soybean oil polymers

Polymer	Tg (^oC)	ν_e (mol/m^3)	T_{max} [a] (^oC)	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 modu lus

[c] Break strength

[d] Elongation at break

[e] A typical elastomer

[f] A ductile plastic

[g] A rigid plastic

Unique Properties of Soybean Oil Polymers

- Damping properties
  - Damping materials are capable of reducing unwanted noise and preventing vibration fatigue failure.
  - Good damping polymeric materials should exhibit a high loss factor (tan $\delta > 0.3$) over a wide temperature range of at least 60-80 ^{o}C.

Damping Properties of Soybean Oil Polymers

Table. Damping results of soy bioplastics measured by DMA at 1 Hz

Polymer	Tg (°C)	$(\tan\delta)_{max}$	$(\tan\delta)_{rt}$	ΔT at tan δ > 0.3 (°C)	tan δ area TA (K) [a]
PU-based IPN[b]	–50-40	0.53-0.70	0.44-0.69	90-120	41-66
SOY45-ST42-DVB5-(NFO5-BFE3)	36	3.90	1.36	83	124
SOY45-ST37-DVB10-(NFO5-BFE3)	44	1.46	0.60	110	57
SOY45-ST32-DVB15-(NFO5-BFE3)	68	0.85	0.32	90	48
LSS55-ST25-DVB12-(NFO5-BFE3)	32	1.00	0.96	89	50
LSS45-ST37-DVB10-(NFO5-BFE3)	48	1.51	0.74	91	75
CLS45-ST37-DVB10-(NFO5-BFE3)	60	1.50	0.30	93	77

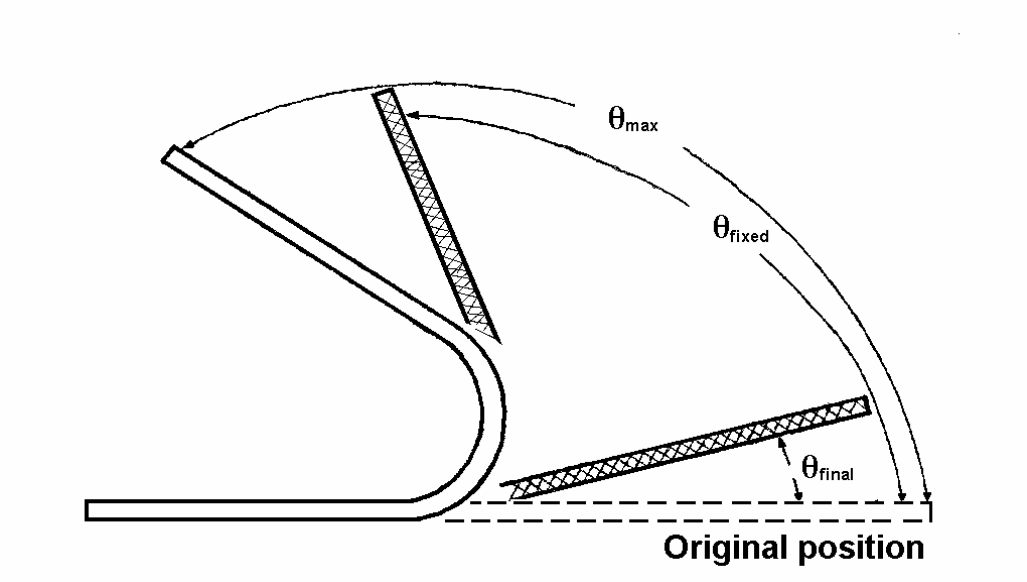
[a] The background was corrected.

[b] Data for typical polyurethane damping materials [*J. Appl. Polym. Sci.* **74**, 28 (1999)].

Unique Properties of Soybean Oil Polymers

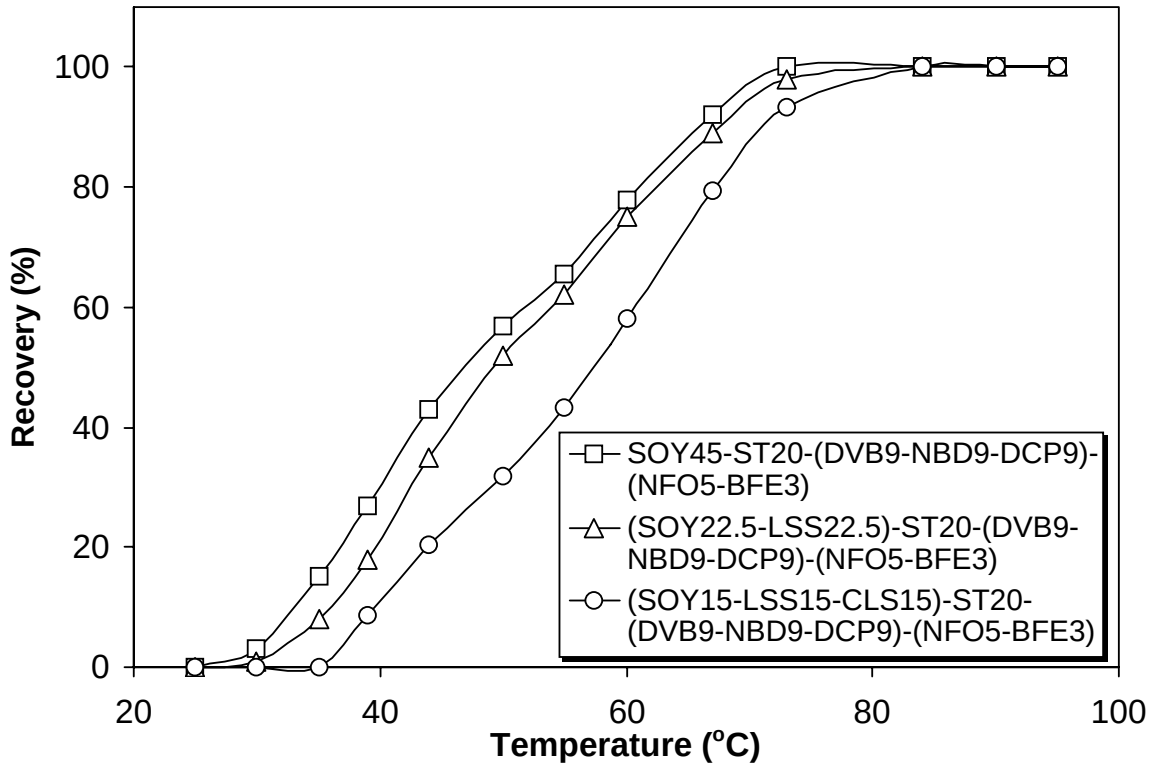
- Shape Memory Properties
  - Shape memory refers to the ability of certain materials to remember a specific shape, on demand, even after rather severe deformations.
  - Shape memory herein refers to thermally stimulated shape memory.

Structure Design of Shape Memory Polymers



- A bending test for shape memory properties has been employed.
- The soybean oil polymers should be hard plastics at room temperature (Tg > room temperature□).
- The soybean oil polymers should behave like good elastomers at temperatures higher than their Tg's (stable chemical crosslinks).

Shape Memory Effect of Soybean Oil Polymers

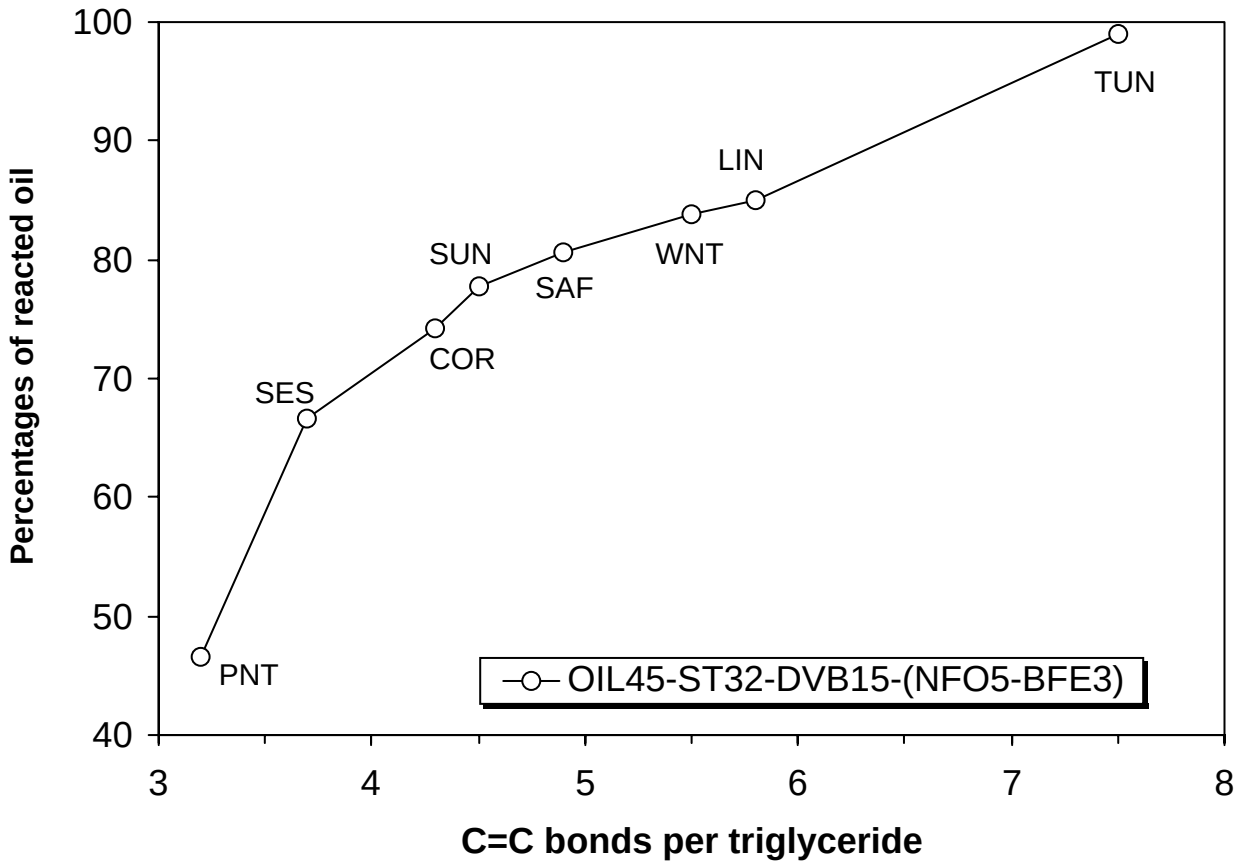


Polymer	Shape memory results (%)[a]		
	D	FD	R
SOY45-ST20-(DVB9+NBD9+DCP9)-(NFO5-BFE3)	100	97	100
(SOY22.5+LSS22.5)-ST20-(DVB9+NBD9+DCP9)-(NFO5-BFE3)	100	98	100
(SOY15+LSS15+CLS15)-ST20-(DVB9+NBD9+DCP9)-(NFO5-BFE3)	100	99	100

[a] D: deformability of the polymer at a temperature higher than T_g

FD: fixed deformation at room temperature, R: recovery

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.

Polymers from Other Vegetable Oils

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

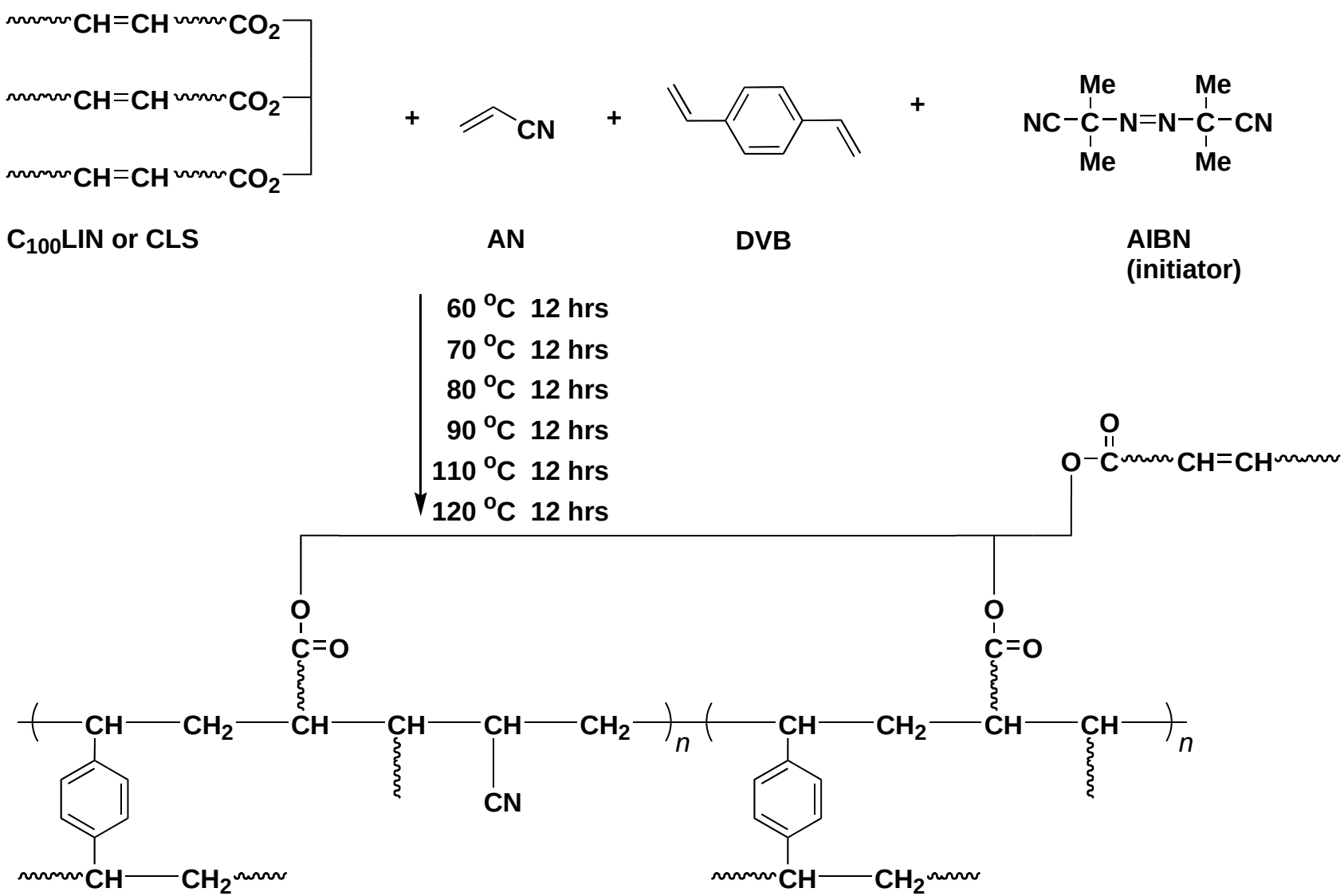
Samples	E (MPa)	σ_b (MPa)	ε_b (%)	Toughness (MPa)
PNT45-ST32-DVB15-(NFO5-BFE3)	32	2.5	20.0	0.27
SES45-ST32-DVB15-(NFO5-BFE3)	48	3.8	48.1	1.46
COR45-ST32-DVB15-(NFO5-BFE3)	48	4.0	51.7	1.64
SUN45-ST32-DVB15-(NFO5-BFE3)	49	5.1	55.7	1.78
SAF45-ST32-DVB15-(NFO5-BFE3)	76	4.5	48.1	1.79
WNT45-ST32-DVB15-(NFO5-BFE3)	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.

Thermal and Mechanical Properties

Copolymers	T_g (¼C)	ν_e[a] (mol/cm^3)	Tan Delta Maximum	Damping Capacity	TGA Data (¼C) T_{10}	T_{50}	T_{max}	Extractions (%) Insoluble	Soluble
SOY50-DCP42-(NFO5-BFE3)	39.9	1405	0.69	7.44	333	549	569	73.7	26.3
SOY55-DCP37-(NFO5-BFE3)	16.5	299	0.87	9.90	332	539	565	73.2	26.8
SOY60-DCP32-(NFO5-BFE3)	2.9	380	0.93	8.52	323	537	564	73.0	27.0
SOY65-DCP27-(NFO5-BFE3)	-6.9	132	1.15	10.23	331	541	564	72.5	27.5
SOY70-DCP22-(NFO5-BFE3)	-13.0	152	1.11	7.59	334	535	560	72.0	28.0
SOY75-DCP17-(NFO5-BFE3)	-17.7	119	1.02	7.49	330	530	548	69.7	30.3
C_{100}SOY55-DCP37-(NFO5-BFE3)	21.3	963	0.81	6.56	337	548	581	84.2	15.8
C_{100}SOY60-DCP32-(NFO5-BFE3)	6.0	742	0.87	6.58	330	529	561	83.5	16.5
C_{100}SOY65-DCP27-(NFO5-BFE3)	-7.9	830	1.02	6.93	338	548	553	83.0	17.0
C_{100}SOY70-DCP22-(NFO5-BFE3)	-8.8	1028	0.96	5.28	325	511	538	82.8	17.2
C_{100}SOY75-DCP17-(NFO5-BFE3)	-10.1	621	0.82	2.38	340	530	550	82.4	17.6
C_{100}SOY80-DCP12-(NFO5-BFE3)	-18.6	751	0.89	4.00	332	532	547	82.4	17.6

Free Radical Polymerization



Free Radical Polymerization of Conjugated Linseed Oil

Sample	T_g (ºC)	Tan Delta	T_{10} (ºC)	T_{50} (ºC)	T_{max} (ºC)	% Sol	% Insol
C_{100}LIN40-AN54-DVB6-AIBN1	107	0.399	397	462	472	4	96
C_{100}LIN45-AN49.5-DVB5.5-AIBN1	94	0.409	391	462	456	4	96
C_{100}LIN50-AN45-DVB5-AIBN1	87	0.417	397	452	445	8	92
C_{100}LIN55-AN40.5-DVB4.5-AIBN1	67	0.408	398	456	460	20	80
C_{100}LIN60-AN36-DVB4-AIBN1	-	-	403	461	459	39	61

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

Thermal Polymerization of Conjugated Linseed Oil

Copolymer Composition	T_g (¼C)	ν_e (10^4 mol/m^3)	E[a] (Mpa)	σ_b[b] (Mpa)	ε_b[c] (%)	Toughness (Mpa)
(C_{87}LIN30-ST28-DVB42)	hump & 120	2.41	26.6	8.2	21.5	438.1
(C_{87}LIN40-ST24-DVB36)	-50 & 72	1.16	16.4	9.7	16.4	237.1
(C_{87}LIN50-ST20-DVB30)	-49 & 74	0.94	13.3	14.9	9.9	121.8
(C_{87}LIN60-ST12-DVB28)	-49 & 76	0.50	5.6	9.8	5.6	58.1
(C_{87}LIN70-ST08-DVB22)	-49 & 77	0.15	2.0	16.0	0.2	11.7
(C_{87}LIN50- ST00-DVB50)	-49 & hump	1.32	12.2	8.4	12.2	157.6
(C_{87}LIN50-ST10-DVB40)	-50 & hump	0.87	9.3	6.8	9.3	145.5
(C_{87}LIN50-ST20-DVB30)	-49 & 74	0.94	13.3	14.9	9.9	121.8
(C_{87}LIN50-ST30-DVB20)	-50 & 120	0.37	11.0	23.6	7.4	64.5

[a] YoungÕs Modulus in compression. [b] Ultimate strength in compression. [c] Elongation at break in compression.

Market Opportunity Analysis

Omni Tech International, December 15, 2001.

- Polymers ranging from tough elastomers to rigid composites.
- At least 50% of the raw materials are natural and renewable.
- Polymerization at relatively low temperature and pressures.
- Capital-intensive manufacturing process not required.
- Raw material costs competitive with commercial polymers.
- Crosslinking and properties can be controlled over a broad range.
- Polymers have good thermal stability below 200 ^{o}C.
- Polymers have excellent damping and shape memory properties.

Future Research Plans

- Explore additional properties of the bioplastics.
- Examine their biodegradation.
- Find a less expensive replacement for DVB.
- Develop the elastomers.
- Prepare a wide variety of composites.
- Examine real life applications.
- Utilize other comonomers.
- More work on other natural oils.
- Explore other polymerization processes.

Summary

- Industrially promising biopolymers ranging from elastomers to rigid plastics have been prepared.
- These plastics have excellent thermal and mechanical properties, and unique damping and shape memory properties.
- Considerable work with composites and other comonomers, oils and processes lies ahead.

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