FUNCTIONAL PRODUCTS INC.
A Solution Company

Study on Viscosity Modifiers for Biodegradable Ester-based Lubricants

Functional Products Inc.
www.functionalproducts.com

Purpose of the Study:

- Synthetic esters have excellent low temperature properties, oxidative stability but poor VI character (poor lubricity) – usually more expensive
- Vegetable oils have poor low temperature, poor oxidative stability properties but have a greater VI (good lubricity) – very economical
- Determine the best polymer for a given vegetable oil or synthetic ester that will allow a formulator to prepare any ISO grade oil for their customers

Agenda:

- Review Viscosity Modifier
- Review Base Oils
  - Vegetable Oil
  - Esters
- Discussion of Polymer Structure and Oils
- Experiments
- Results

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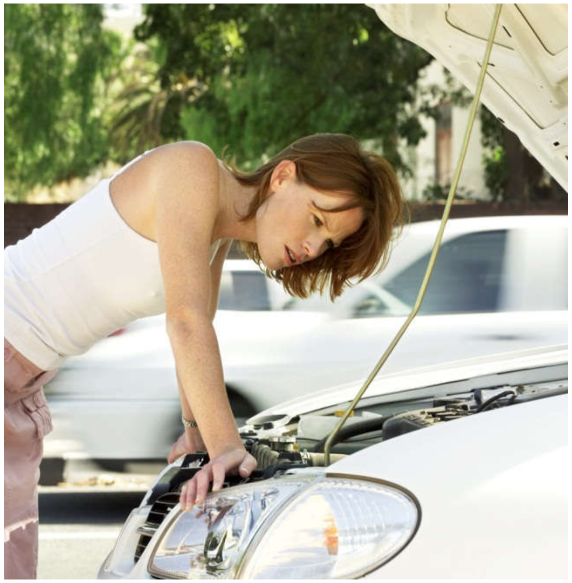
The Formulation of Lubricants

Lubricant Composition

- Base fluid (Mineral or Veg): 70-99%
- Additives: 1-30%



Additives:

- **Stabilizers/Deposit Control**
  - Oxidation Inhibitors/Metal Deactivators
  - Dispersants
  - Detergents
- **Film-forming Agents**
  - Friction Modifiers
  - Anti-wear and Extreme Pressure Agents
  - Rust and Corrosion Inhibitors
- **Polymers**
  - Viscosity Modifiers
  - Tackifiers
  - Pour Point Depressants
- **Miscellaneous**
  - Demulsifiers, Dyes, Biocides, etc.

Viscosity Modifiers:

- Polymers improve the lubricant performance over range of temperatures
- Thermally dependent
- Thickening determined by hydrodynamic volume of polymer chain in oil

Polymer Compatibility with the base oil is critical :

- chemically structural similarities
- polarity similarities, such as double bond, Cis/Trans orientation,
- Similar length of the carbon chain
- presence of similar atoms such as oxygen or nitrogen.

Mineral oil (non-renewable)

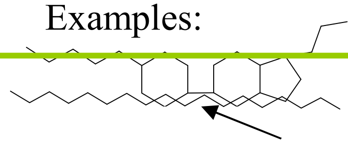
Base oils from difference resources:

- ❑Petroleum-derived (Mineral oil)
- ❑Synthetics (PAO, Synthetic ester, synthetic ether, silicones, etc.)
- ❑Plant or animal based (soybean, rapeseed/canola, castor, palm, sunflower, etc.)

Chemistry of Mineral oil :

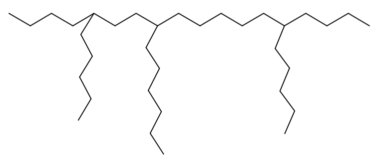
- ❑Paraffinic oils (based on alkanes)
- ❑Naphthenic oils (based on Cycloalkanes)
- ❑Aromatics oils

Examples:



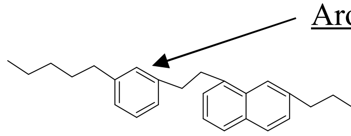
Saturated linear chain

(a) linear alkane



(b) branched alkane

Aromatic ring



Cyclic ring

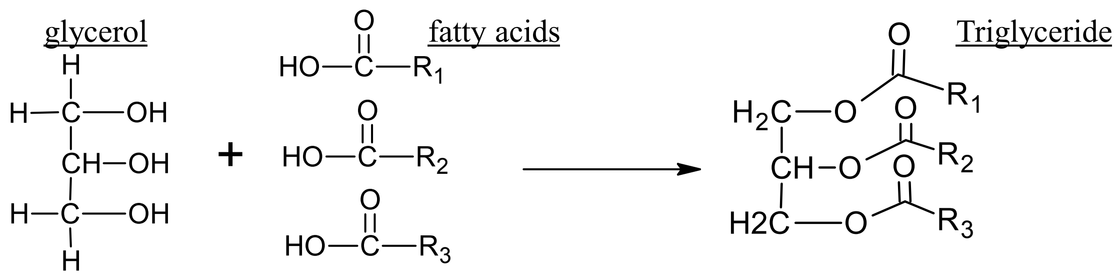
(c) cycloalkanes with alkane chain

(d) aromatics with alkane chain

Vegetable oil (a renewable, varied, natural ester)

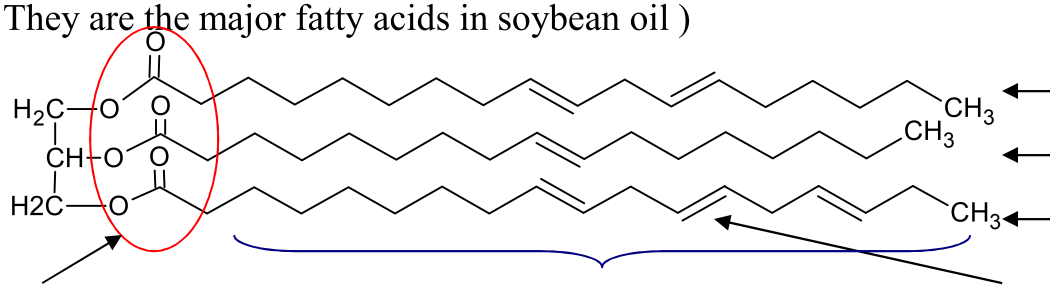
Chemistry of vegetable oil :

The major component in vegetable oil is triglyceride.
(An ester derived from glycerol and fatty acids.)



Triglyceride is formed from glycerol and fatty acids (R1, R2 and R3 represent different unsaturated and saturated hydrocarbon chains)

Example of an unsaturated triglyceride:
Formed from the from esterification of glycerol with linoleic acid, oleic acid and alpha-linoleic acid.
(They are the major fatty acids in soybean oil)



linoleic acid

oleic acid

alpha-linoleic acid

Unsaturated double bond

Polar Ester groups

(different from mineral oil)

Hydrocarbon chain segment in fatty acid (similar to linear paraffinic oil)

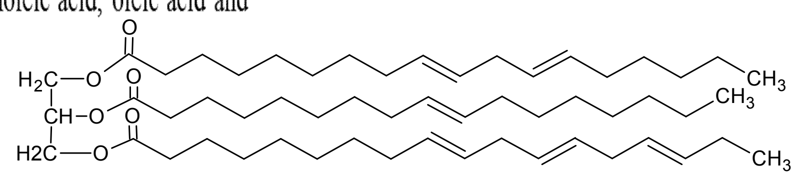
Fatty acids in different refined vegetable oils :

Fatty Acids		Mustard	Oat	Olive	Palm	Peanut	Rice bran	Safflower	Sesame	Soybean	Sunflower	Walnut	Wheat germ
Common Name	Saturated												
Caproic acid	6:0												
Caprylic acid	8:0												
Capric acid	10:0												
Lauric acid	12:0		0.39		0.1								
Myristic acid	14:0	1.39	0.24		1.0	0.1	0.7			0.1			0.1
Palmitic acid	16:0	3.75	16.67	10.93	43.5	9.5	16.9	4.29	8.9	10.3	5.9	7.0	16.6
Margaric acid	17:0												
Stearic acid	18:0	1.12	1.05	1.98	4.3	2.2	1.6	1.92	4.8	3.8	4.5	2.0	0.5
Arachidic acid	20:0			0.42		1.4							
Behenic acid	22:0			0.13		2.8							
Lignoceric acid	24:0					0.9							
Total		**6.26**	**18.35**	**13.46**	**48.9**	**16.9**	**19.2**	**6.21**	**13.7**	**14.2**	**10.4**	**9**	**17.2**
	Monounsaturated												
Palmitoleic acid	16:1	0.22	0.2	1.16	0.3	0.1	0.2		0.2	0.3		0.1	0.5
111	17:1			0.14									
Oleic acid	18:1	11.61	34.9	72.29	36.6	44.8	39.1	14.36	39.3	22.8	19.5	22.2	14.6
Gadoleic acid	20:1	6.19		0.31	0.1	1.3			0.2	0.2		0.4	
Erucic acid	22:1	41.18											
Total		**59.2**	**35.1**	**73.9**	**37**	**46.2**	**39.3**	**14.36**	**39.7**	**23.2**	**19.5**	**22.7**	**15.1**
	Polyunsaturated												
	Omega 6												
Linoleic acid	18:2n6	15.33	39.08	9.21	9.1	32	33.4	74.6	41.3	51.0	65.7	52.9	54.8
Arachidonic acid	20:4n6												
	Total n6	15.33	39.08	9.21	9.1	32	33.4	74.6	41.3	51	65.7	52.9	54.8
	Omega 3												
Alpha linolenic acid (ALA)	18:3n3	5.90	1.79	0.79	0.2	0	1.6	0	0.3	6.8	0	10.4	6.9
	Total n3	5.9	1.79	0.79	0.2	0	1.6	0	0.3	6.8	0	10.4	6.9
Total Poly		**21.23**	**40.87**	**10**	**9.3**	**32**	**35**	**74.6**	**41.6**	**57.8**	**65.7**	**63.3**	**61.7**
	Ratio n6/n3	**2.6**	**21.8**	**11.7**	**45.5**	**no n3**	**20.9**	**no n3**	**137.7**	**7.5**	**no n3**	**5.1**	**7.9**

<u>Example of an unsaturated triglyceride:</u>

Formed from the from esterification of glycerol with linoleic acid, oleic acid and alpha-linolenic acid.

(They are the major fatty acids in soybean oil)



<u>linoleic acid</u>

<u>oleic acid</u>

<u>alpha-linoleic acid</u>

http://www.thepaleodiet.com/nutritional_tools/oils_table.html

Wide Range of Synthetic Esters

Numerous types of vegetable esters due to large number of alcohols, fatty acids or vegetable oils

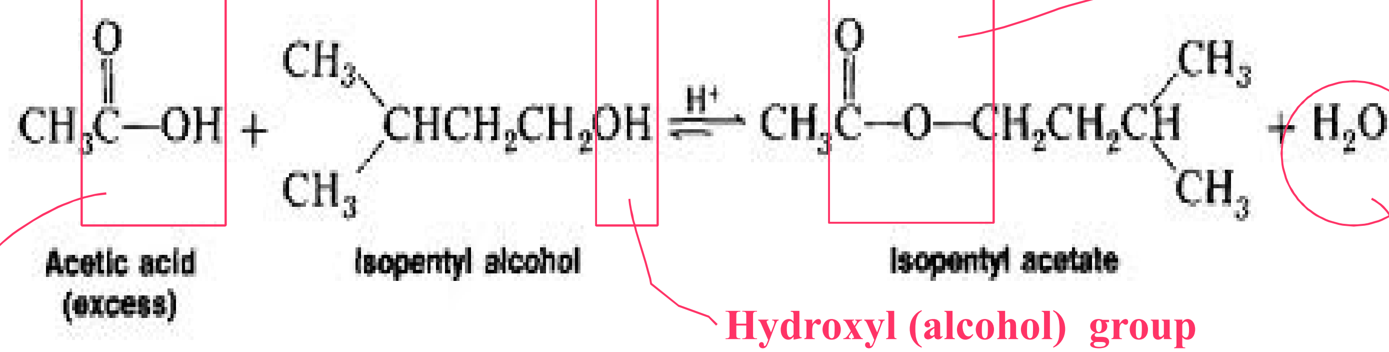
Optimized for lubricity, biodegradability, viscosity, and oxidative stability

Cost is variable depending on alcohol and fatty acid choice

Synthetic Esters

Synthesis of Synthetic Esters :

Ester group

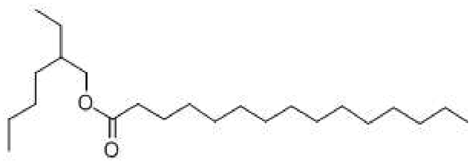


Hydroxyl (alcohol) group

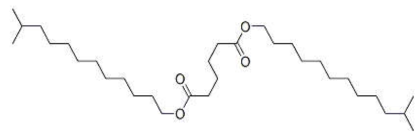
Acid group

Water is also a product of the reaction which is removed by distillation.

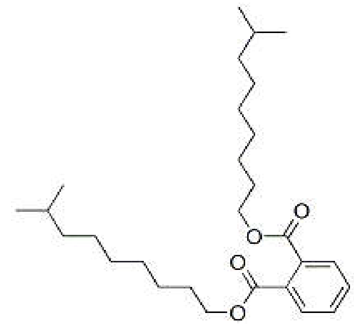
Synthetic Esters Used in this Paper



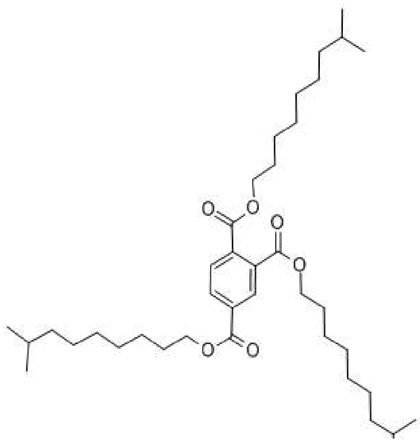
Monoester: 2-ethylhexyl stearate



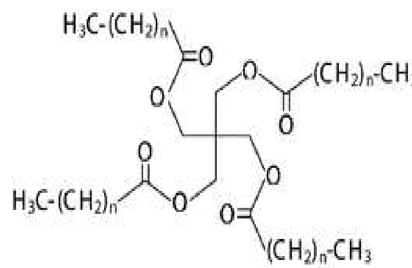
Diester: Di-tridecyl adipate



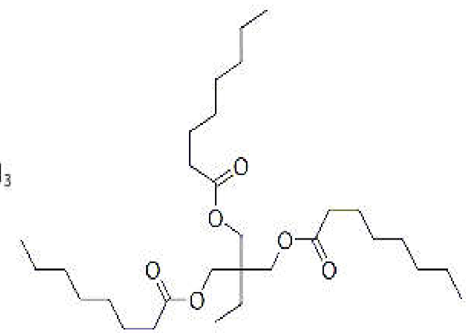
Di-isodecyl phthalate



Timellitate ester: Tri-isodecyl trimellitate



Polyol ester, n=C_6 to C_8



TMP ester:
trimethylopropane
tricaprylate

Properties of esters and vegetable oils

Sorted according to VI

Oil		Chemical name	Synthetic ester type	Molecule description				VI	Pour point ° C
				Chains	Length	Double bonds	Aromatic		
#I	Vegetable oils	Soybean oil	triglycerides	3	C18	>3	No	218	-9
#J		Canola oil	triglycerides	3	C18	>3	No	216	-21
#A	Synthetic esters	2-ethyl hexyl stearate	Monoester	1	C18	0	No	170	5
#E		Trimethylol propane tricaprylate	Trimethylol propane ester (TMP)	3	C8	0	No	140	-51
#C		Di-tridecyl adipate	Adipate diester	2	C13	0	No	136	-57
#D		C6 to C8 polyol ester	Polyol ester	3	C6-C8	0	No	130	-60
#B		Di-octyl adipate	Adipate diester	2	C8	0	No	88	-67
#G		Tri-octyl trimellitate	Trimellitate ester	3	C8	0	Yes	84	-35
#F		Tri-isodecyl trimellitate	Trimellitate ester	3	C10	0	Yes	81	-36
#H		Di-isodecyl phthalate	Phthalate ester	2	C10	0	Yes	62	-42
#K		Castor oil	triglycerides	3	C18	3	No, 3 hydroxyl	51	-24

Biodegradability of Common Base Oils

Lubricant type by base stock	**Biodegradability range as evaluated by CEC-L-33-A-93 (% loss at 21 days)**
Mineral oil	25-45
Hydrocracked Mineral oils	25-80
Bright stock	5-15
Polyalpha Olefins	20-80
Diesters	50-100
Aromatic esters	0-95
Polyols	5-100
Vegetable oils	75-100
Polyethylene glycols	10-30
Polypropylene glycols	10-70

MICROBES ATTACK DOUBLE BONDS OR ESTER GROUP

Vegetable oils – unsaturated fatty chains

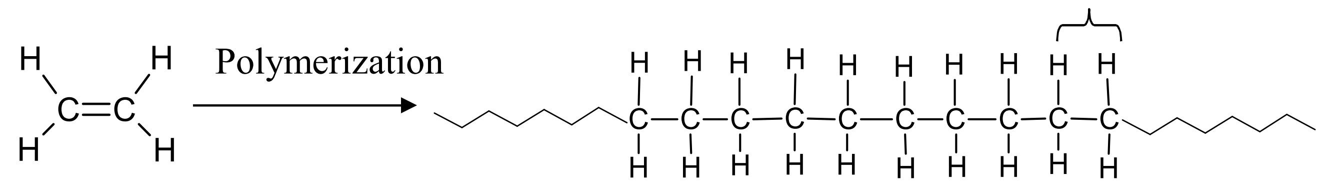
Esters double bonds for chemical cleavage

Polymer Structure

What is a polyolefin?

❑Polyolefin is a group of polymers from the polymerization of alkene monomers (alkenes have chemical formula as C_nH_{2n}). (e.g. polyethylene, polybutadeine, polyisobutylene)

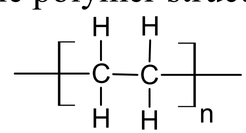
Repeat unit



Ethylene monomer

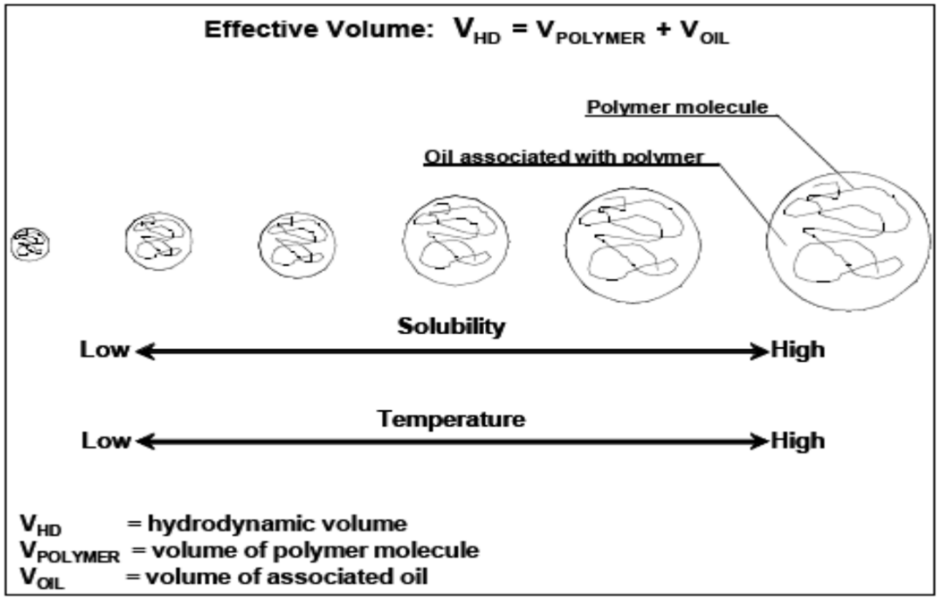
Polyethylene polymer

For simplicity, the polymer structure is expressed as:



where n is the repeat number of monomer units

The Solubility of Polymers in both mineral and vegetable oil



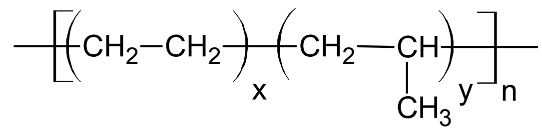
- Factors contributing to hydrodynamic volume:
  - Van der Waals forces
  - Steric affects
  - Entanglement

Polymers Studied

Polyolefin:

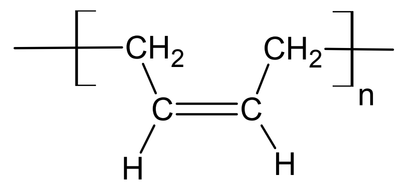
Ethylene-propylene copolymer (EPM)

(Saturated hydrocarbon)



Polybutadiene (PB)

(unsaturated hydrocarbon)

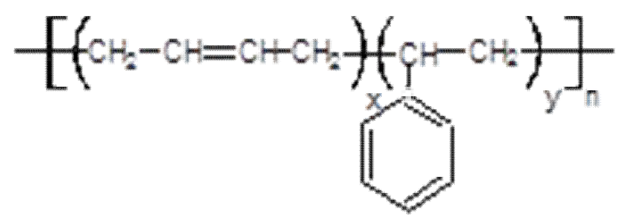


Cis configuration

Modified Polyolefin:

Styrene-butadiene copolymer (SBR)

(unsaturated hydrocarbon)



Alkyl-diester copolymer (AD)

(Proprietary)

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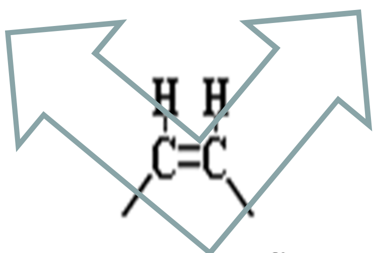
Polymer PB

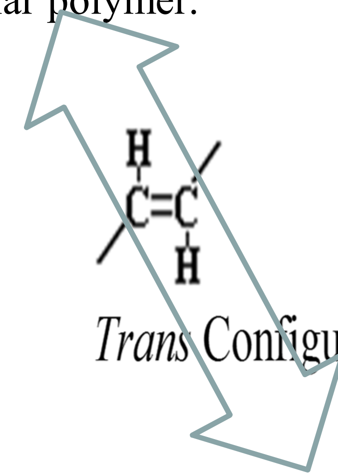
Cis and *Trans* Configuration Affects Solubility of PB

- A polymer is a high molecular weight molecule composed of repeating monomeric units. The repeating units are connected by covalent chemical bonds formed from polymerization of monomers.

- The chemical structure of the repeating unit, the number of repeating units in the polymer, and the stereochemistry, i.e., cis and trans configurations, of the molecule are several factors that determine the physical properties of a particular polymer.



Cis Configuration



Trans Configuration

Like polymers tend to dissolve more readily in like oils

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Polymer EPM

Linear hydrocarbon-like structure affects solubility of EPM polymer

EPM polymer:

- Saturated without double bonds in the repeating units.
- Copolymer from ethylene and propylene monomers.
- Soluble in paraffinic oils.
- Insoluble in vegetable oil or synthetic esters other then 2-ethylhexyl stearate.
- Soluble in paraffinic due to similarity of the polymer's hydrocarbon chains with the long C18 chain in the ester.

Like polymers tend to dissolve more readily in like oils

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Polymer SBR and AD

Aromatic group and double bond affects solubility of SBR

Styrene-butadiene (SBR) and Alkyl-diester polymers:

- Unsaturated with double bonds in the repeating units.
- Soluble in vegetable oil
- Insoluble in paraffinic
- The aromatic group in the polymer helps it to solubilize in aromatic type ester oils.

Like polymers tend to dissolve more readily in like oils

Experiment

Procedure:

Mineral or Vegetable Base oil + Polymer $\xrightarrow{\text{Mixing at 230°F for 2 days max or until dissolved}}$ Oil Solution of polymer

Test:

D2270 Viscosity at 40°C and 100°C, VI

The solubility of polymers in base oil

Polymer	Paraffinic oil (Mineral oil)	Canola oil (vegetable oil)
Ethylene/propylene copolymer (EPM)	good	poor
Polybutadiene (PB)	poor	good
Styrene-butadiene copolymer (SBR)	poor	good
Alkyl Diester copolymer (AD)	poor	good

In the solubility test, polymer was mixed in oil at 180°F for 2 days.

- **The solubility of polymers in base oils varies with the chemical structure of the oil.**
- **The double bonds and polar groups in polymers make it more soluble in vegetable oil.**

Compatibility between Polymers and Synthetic Esters

	Ester	EPM	PB	SBR	AD
#A	2-ethyl hexyl stearate	yes	yes	yes	yes
#B	Di-octyl adipate	no	yes	yes	yes
#C	Di-tridecyl adipate	no	yes	yes	yes
#D	C6, C7, C8 polyol ester	no	no	no	yes
#E	trimethylolpropane tricaprylate	no	yes	yes	yes
#F	Tri-isodecyl trimellitate	yes	yes	yes	yes
#G	TriOctyl trimellitate	no	yes; no at high conc.	yes; no at high conc.	yes
#H	Di-isodecyl phthalate	no	yes	yes	yes

General Compatibility between Polymers and Vegetable oils

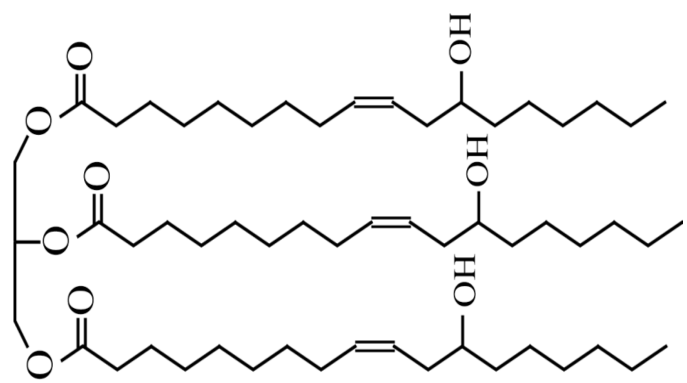
	Vegetable Oil	EPM	PB	SBR	AD
#I	Soybean oil	no	yes	no	yes
#J	Canola oil	no	yes	yes	yes
#K	Castor oil	no	no	no	yes

Castor oil is unique- a third functional or hydroxyl group- more polar

General compatibility between polymers and vegetable oils

	Vegetable Oil	EPM	PB	SBR	AD
#I	Soybean oil	no	yes	no	yes
#J	Canola oil	no	yes	yes	yes
#K	Castor oil	no	no	no	yes

Castor oil is unique- a third functional or hydroxyl group- more polar



Viscosity Data of Synthetic Esters with 1% and 5% PB

Oil	Chemical name	0% PB			1% PB			5% PB		
		40° C	100° C	**VI**	**40° C**	**100° C**	**VI**	**40° C**	**100° C**	**VI**
#A	2-ethyl hexyl stearate	10.0	3.0	171	19.3	5.7	271	491.0	122.5	337
#B	Di-octyl adipate	7.0	2.3	157	15.3	4.5	235	41.6	11.0	270
#C	Di-tridecyl adipate	27.0	5.4	139	42.3	8.8	194	221.4	39.4	231
#D	C6, C7, C8 polyol ester	25.0	5.0	129	N/S	N/S		N/S	N/S	
#E	trimethylopropane tricaprylate	20.	4.0	92	38.2	8.5	209	142.2	28.5	240
#F	Tri-isodecyl trimellitate	124.0	11.9	81	222.5	20.3	106	3796.	315.6	234
#G	TriOctyl trimellitate	88.3	9.4	78	123.0	14.1	114	N/S	N/S	
#H	Di-isodecyl phthalate	38.0	5.4	62	64.0	9.2	121	501.0	62.5	198

Viscosity Data of Synthetic Esters with 1% and 5% SBR

Oil	Chemical name	0% SBR			1% SBR			5% SBR		
		40° C	100° C	VI	40° C	100° C	VI	40° C	100° C	VI
#A	2-ethyl hexyl stearate	10.0	3.0	171	19.8	5.7	261	651.2	125.6	294
#B	Di-octyl adipate	6.7	2.3	157	12.5	3.6	189	55.3	13.9	263
#C	Di-tridecyl adipate	27.0	5.4	139	32.7	6.4	152	61.4	10.9	171
#D	C6, C7, C8 polyol ester	25.0	5.0	129	N/S	N/S		N/S	N/S	
#E	trimethylopropane tricaprylate	20.	4.0	92	24.2	6.5	245	147.3	26.2	215
#F	Tri-isodecyl trimellitate	124.	11.9	81	177.7	17.4	106	921.2	75.4	157
#G	TriOctyl trimellitate	88.3	9.4	78	121.9	13.3	104	N/S	N/S	
#H	Di-isodecyl phthalate	38.0	5.4	62	70.2	9.4	111	581.0	54.0	155

Viscosity Data of Synthetic Esters with 1% and 5% AD

Oil	Chemical name	0% AD			1% AD			5% AD		
		40° C	100° C	VI	40° C	100° C	VI	40° C	100° C	VI
#A	2-ethyl hexyl stearate	10.0	3.0	171	14.2	4.6	283	66.5	19.6	316
#B	Di-octyl adipate	7.0	2.3	157	14.5	4.1	204	103.0	21.6	238
#C	Di-tridecyl adipate	27	5.4	139	46.6	8.2	151	286.7	39.0	189
#D	C6, C7, C8 polyol ester	2.5	5.0	129	44.3	7.8	147	304.5	58.0	259
#E	trimethylopropane tricaprylate	20	4	92	33.7	7.4	195	268.2	48.4	242
#F	Tri-isodecyl trimellitate	124	11.9	81	241.2	19.8	94	1488.	97.2	147
#G	TriOctyl trimellitate	88.3	9.4	78	149.3	15.9	111	1147.	82.8	149
#H	Di-isodecyl phthalate	38	5.4	62	81.7	9.5	92	543.5	48.4	146

Viscosity: Vegetable oil + Polymer 5.0% wt.

Oil	Vegetable Oil	PB			SBR			AD		
		40° C	100° C	VI	40° C	100° C	VI	40° C	100° C	VI
#I	Soybean oil	827.7	150.6	294	N/S	N/S		115.5	21.7	216
#J	Canola oil	2069.	341.4	326	508	88.7	262	327	49.2	214
#K	Castor oil	N/S	N/S		N/S	N/S		410.7	29.9	102

Conclusions

- Oils are biodegradable due to the ester structure and unsaturation (double bonds). These functional groups also help explain why PB and AD polymers are soluble in vegetable oils, and EPM polymers are not.
- All compatible polymers increase the VI of base oil
- Natural vegetable oils are predominantly of cis configuration around a double bond.
- Polybutadiene where the double bonds are a minimum of 40% in the cis conformation is compatible with vegetable oils.

Conclusions (Continued)

- When blended with polymer, the highest viscosity index achieved with 2-ethylhexyl stearate and di-octyl adipate ester base fluids.

- Of the vegetable ester base fluids studied. Soybean oil and canola oil are effective at solubilizing PB and AD polymers and giving high VI blends. SBR was minimally soluble and unable to determine VI. Castor oil is not effective at solubilizing polymers except AD and then only providing a nominal VI.

- EPM polymers are not soluble in vegetable oils and only partially soluble in a few synthetic esters such as 2-ethylhexyl stearate and tri-isodecyl trimellitate as shown in Table 5.