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Bio-based Thermoset Resins and Their Composites

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Presentation Out-line

- Introduction and motivation
- Bio-based resins, Bio-fibers and Bio-Composites
- Biobased Epoxies and Their Composites
- Biobased Polyurethanes and Their Composites
- Biobased Unsaturated Polyesters and Their Composites
- Conclusions

Acknowledgements

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Motivation

TECHNOLOGY:
To Improve Toughness

ECONOMY:
Economically Viable
HOW ?
Example: Epoxy Resin Costs 126 cents/lb.
Whereas
Epoxidized Oils Costs ~ 60 Cents/lb

BLEND
of Functionalized Oil WITH Thermoset Resins?
(Thermoset Resins: Brittle & Expensive)

ECOLOGICAL BENEFIT:
Incorporation Of Bio-resources To the Maximum Permissible Extent To achieve Required Properties

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NATURAL FIBERS

Natural/Bio-Fiber Composites (Bio-Composites)

Thermoplastic based

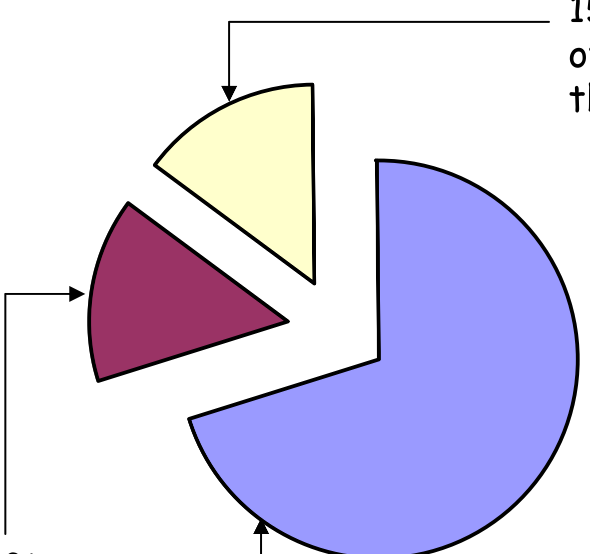
Biofiber- Thermoplastic
(Polypropylene/PVC/PS)
Green: PLA, Cellulose esters etc.

Thermoset based

Biofiber-Thermosets
(Epoxy, Polyesters, Polyurethanes)
Bio-based: Blend with functionalized Vegetable oil

HYBRID BIO-COMPOSITES
(Fiber blending/Matrix blending)

Thermoset vs. thermoplastic composites



Matrix pattern in Polymer Composites

- Use of reinforced thermoset composites: ~doubled in the last decade
- Expected to increase 47% during next 5 years through 2004
- ~ 65% of all composites use glass fiber - polyester composites.
- Natural fiber polyester composites: target is to replace glass-polyester composites

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Bio-based Epoxies and their Composites

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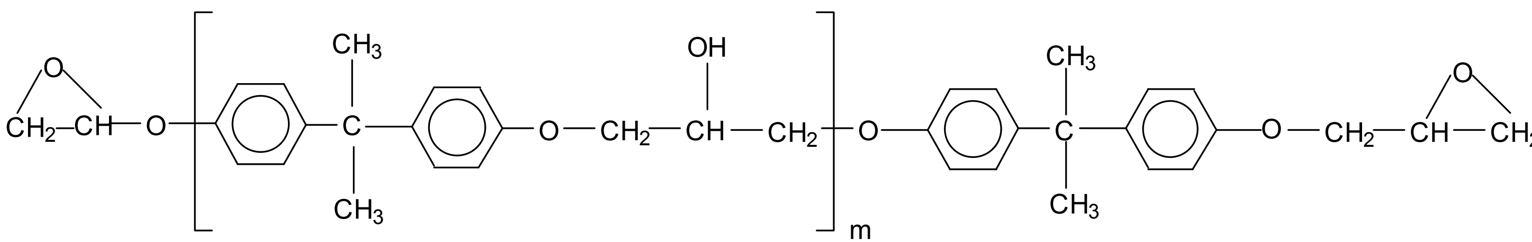
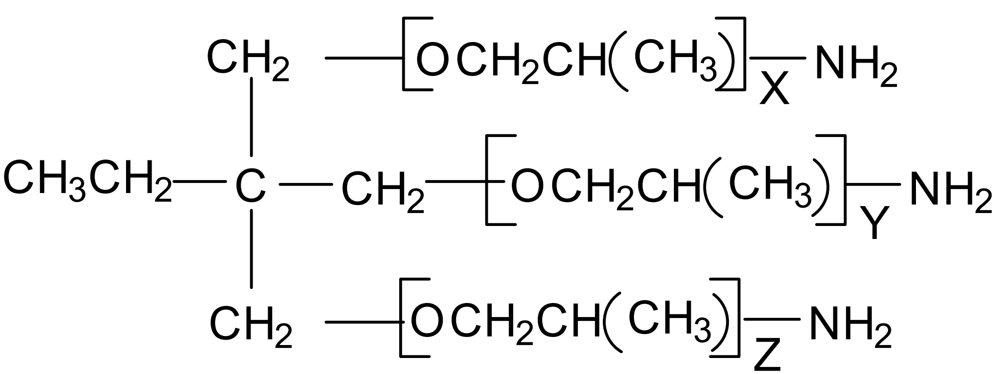
Reagents

DGEBA (Diglycidylether of bisphenol A)

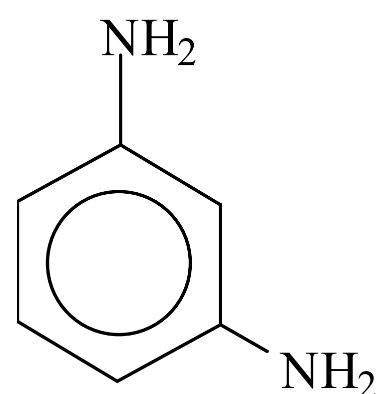


m = 0, 1, 2

J-T403 (Jeffamine T403)



MPDA (m-phenylene diamine)



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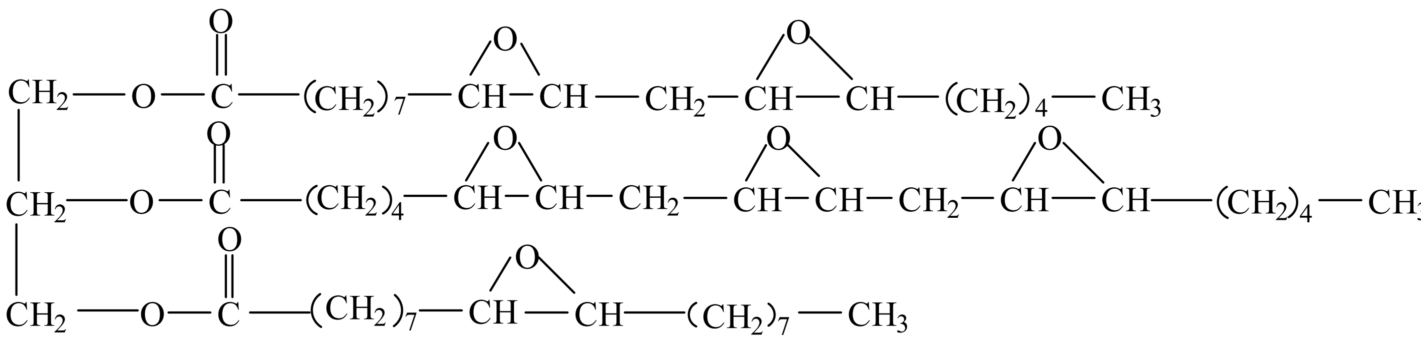
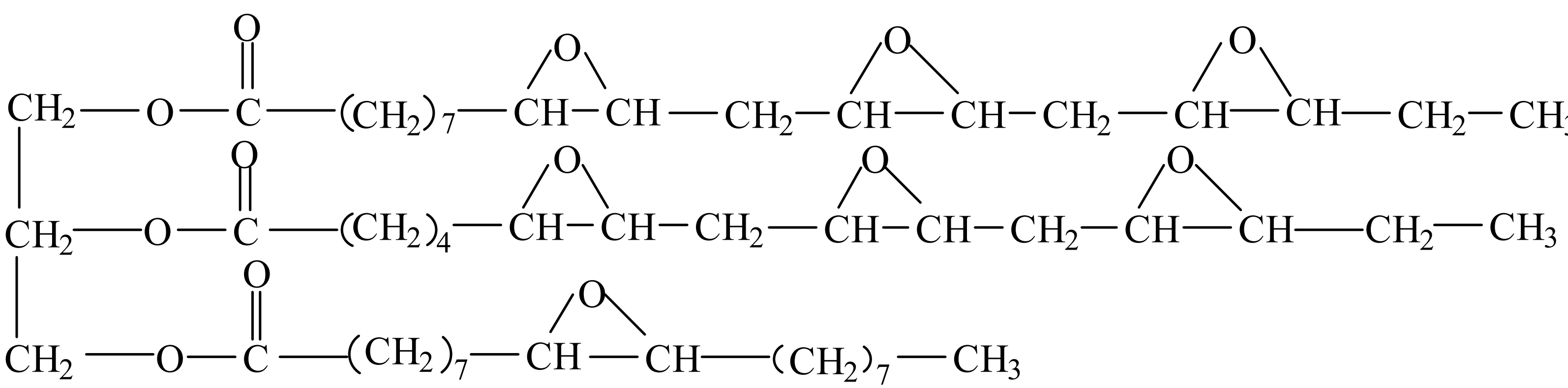
Reagents: Epoxidized Soy(ESO)/Linseed Oils(ELO)

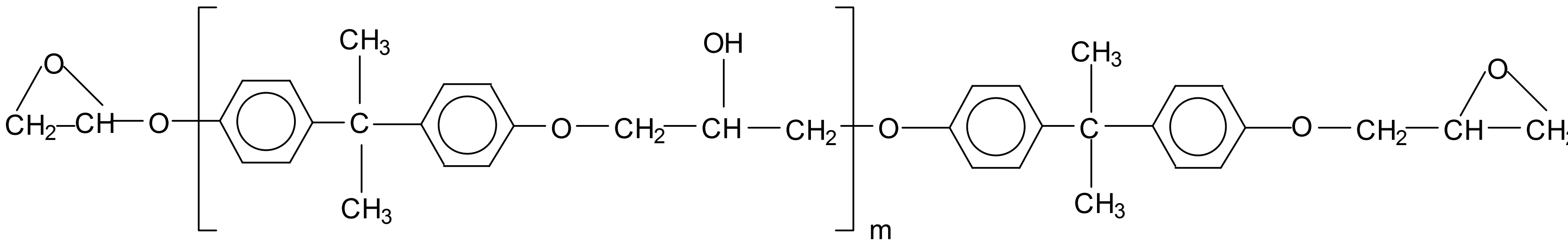


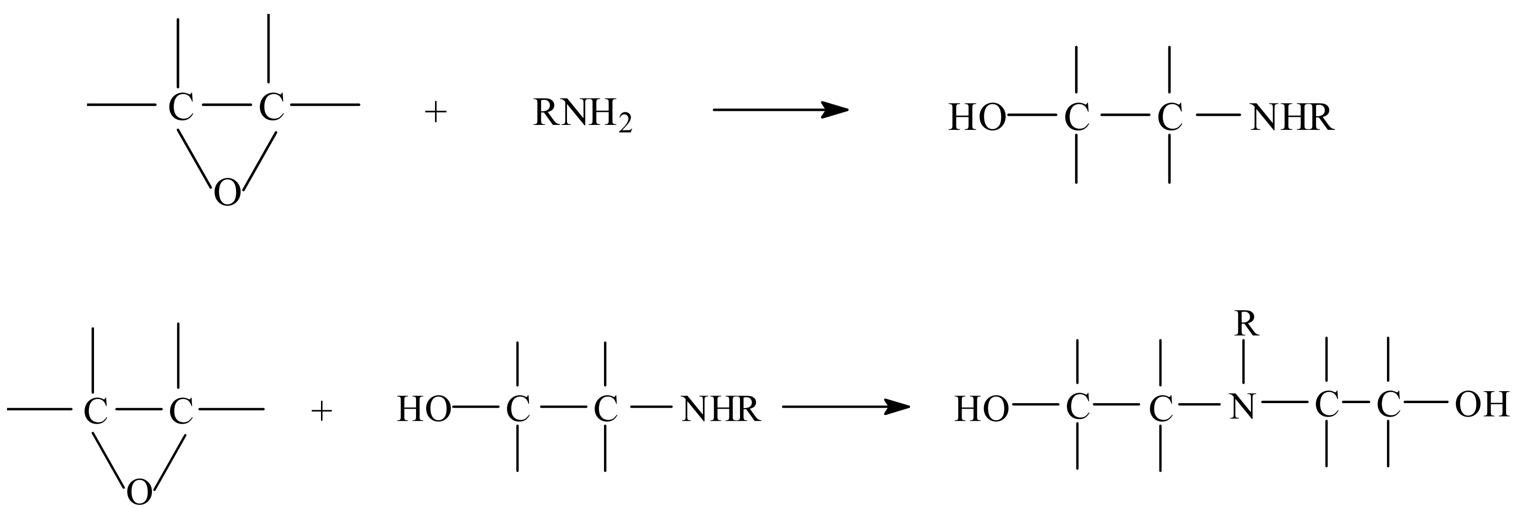
Epoxy equivalent wt. of ESO: 225-230



Epoxy equivalent wt. of ELO: 173-178

Epoxy-Primary Amine Curing Reaction





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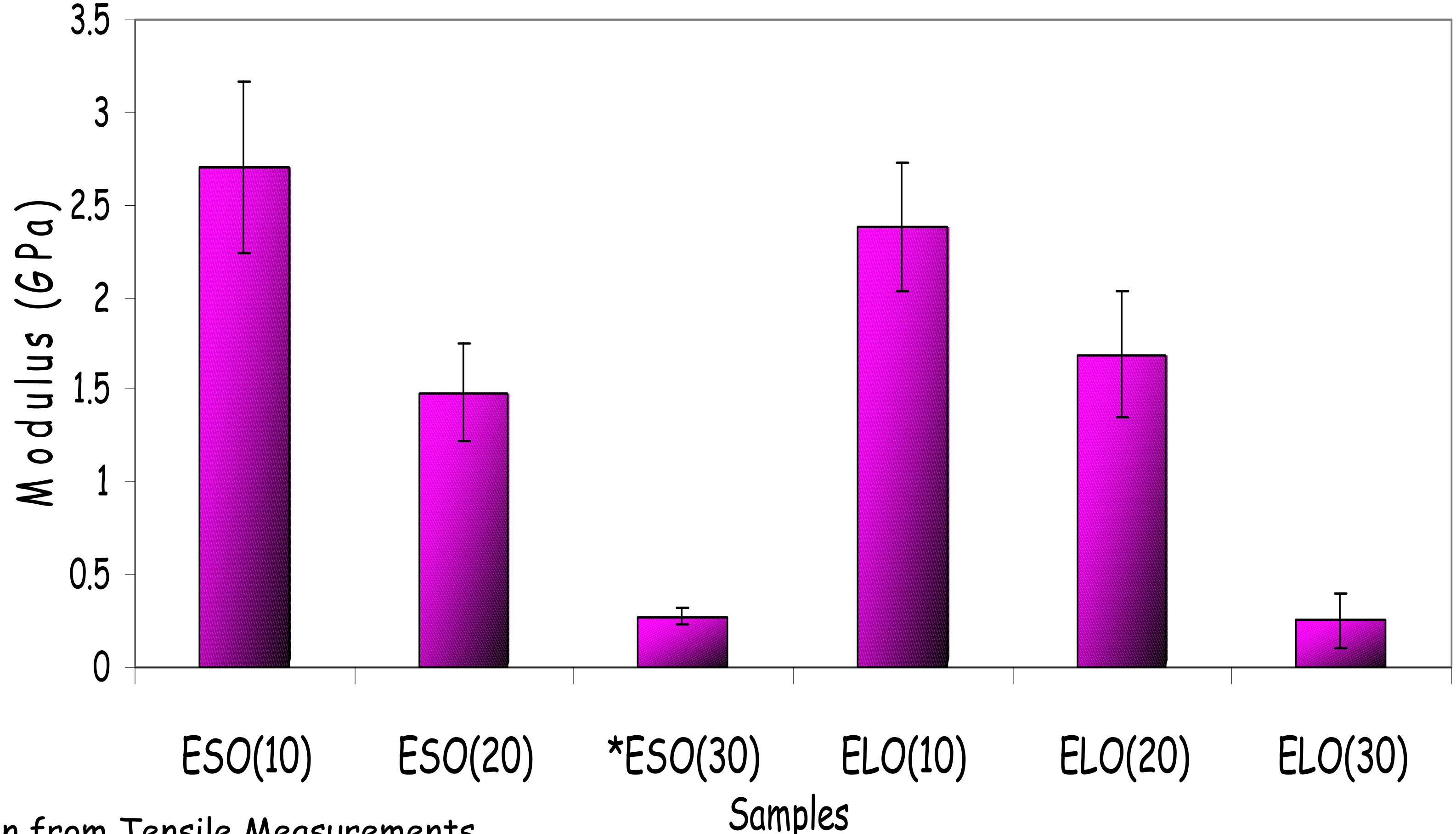
Dynamic Mechanical Analysis of Bio-based Epoxy Resin with Jeffamine T403 at 30°C



* taken from Tensile Measurements

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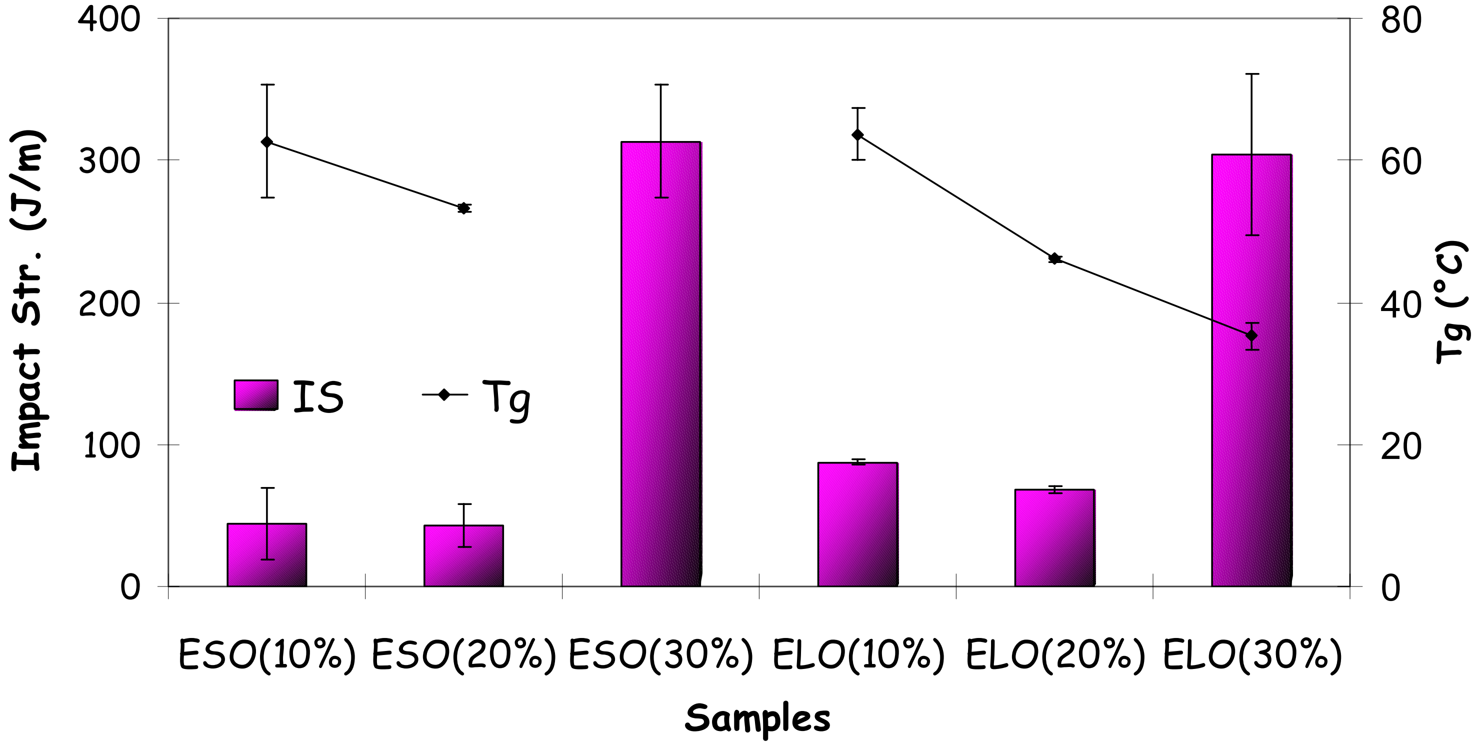
Impact Strength and Glass Transition Temp. of Bio-based Epoxy Resin with T 403



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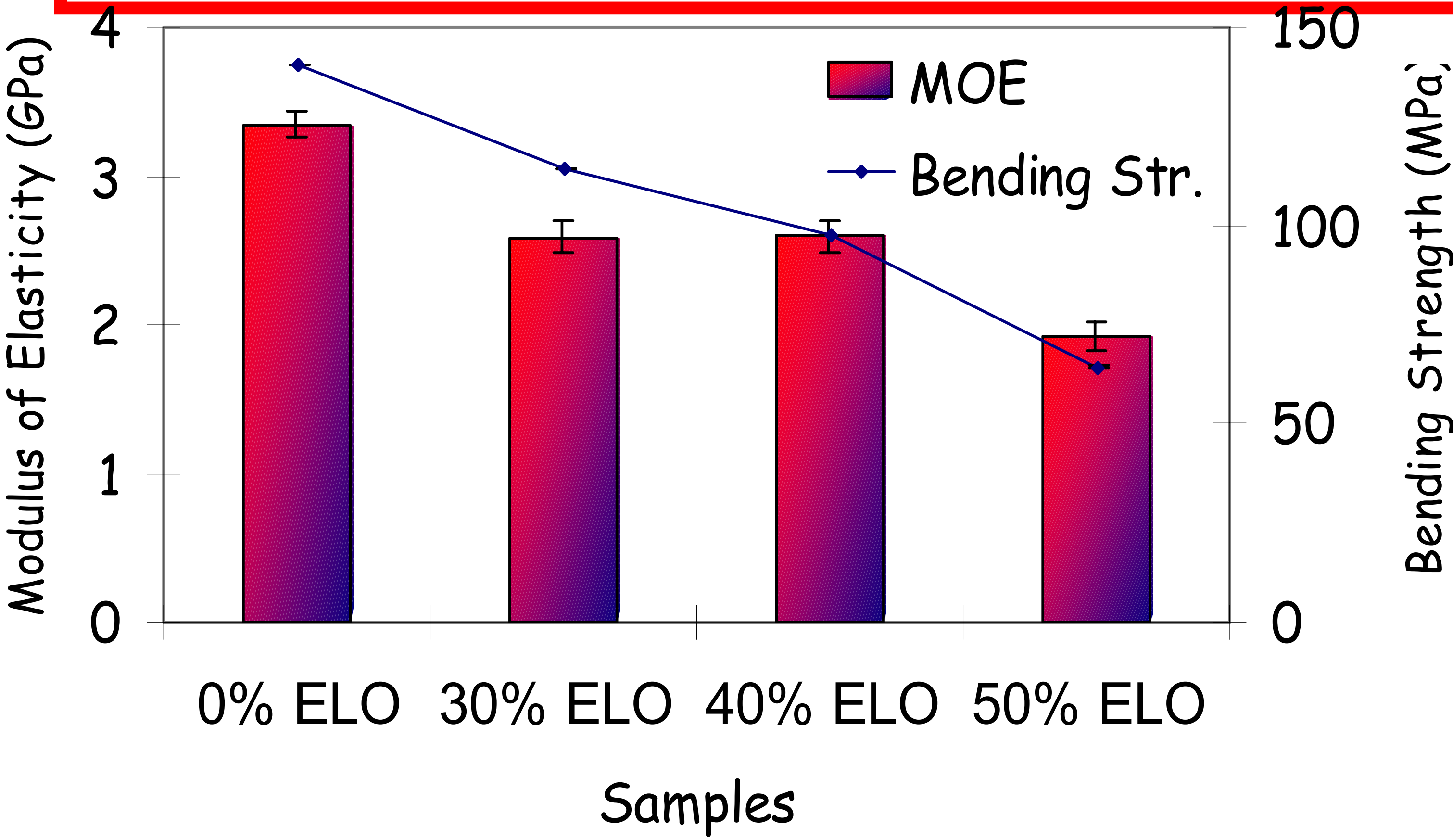
Modulus of Elasticity & Bending Strength of Epoxy Samples containing ELO and MPDA



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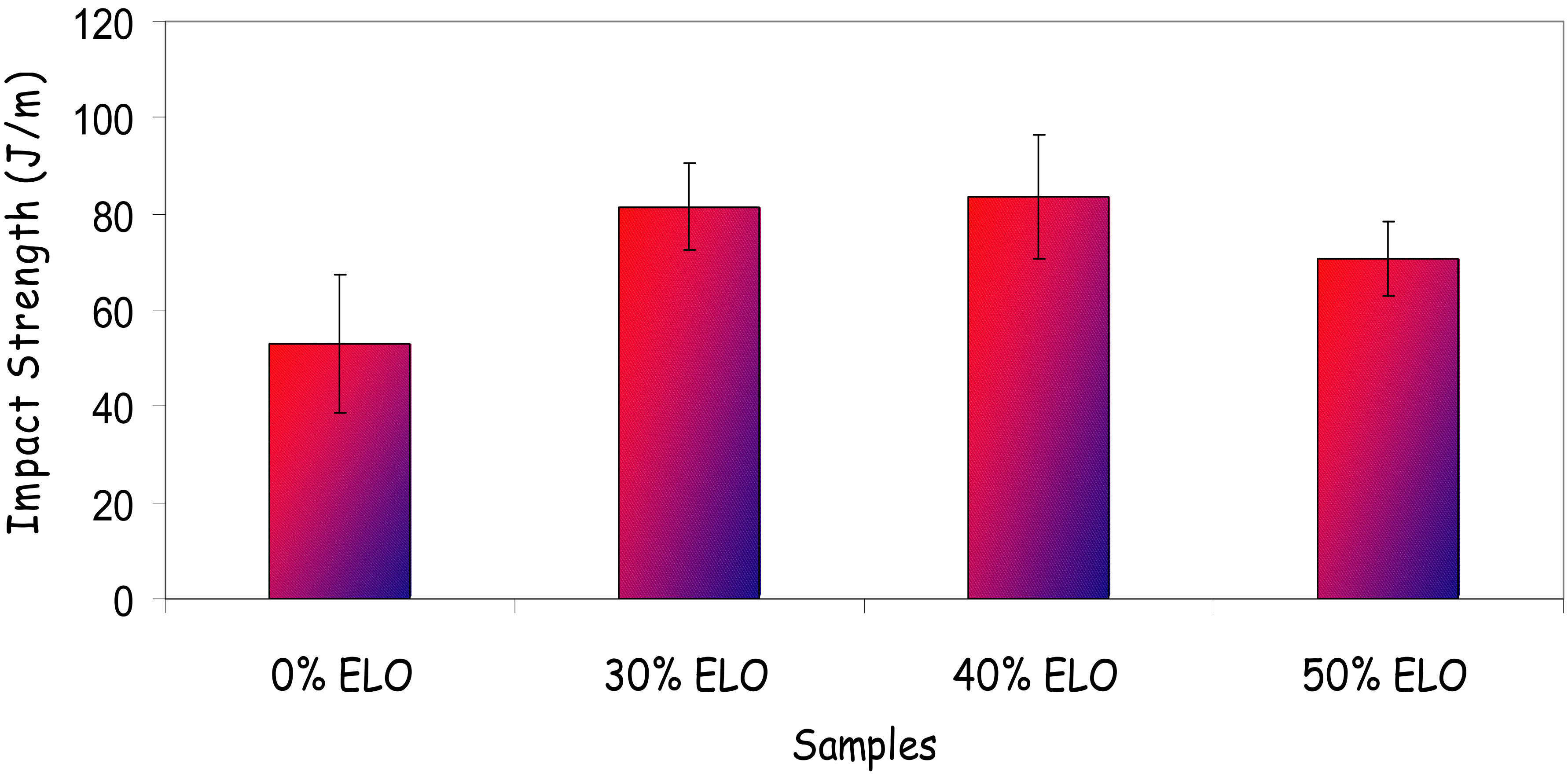
Impact Strength of Epoxy Samples containing MPDA and ELO



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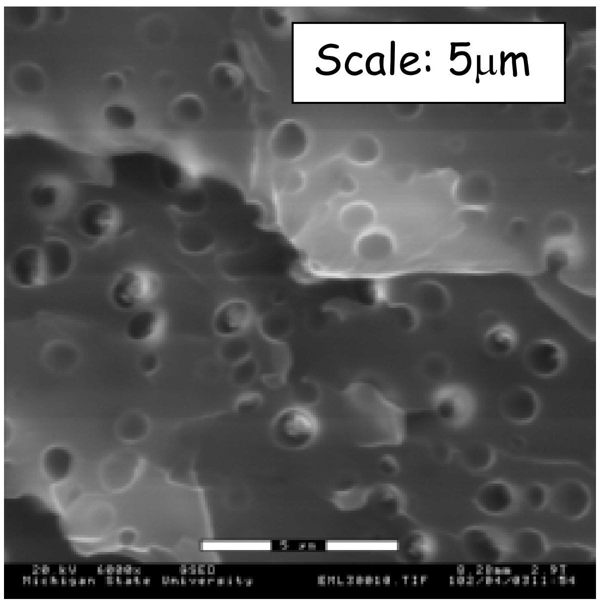
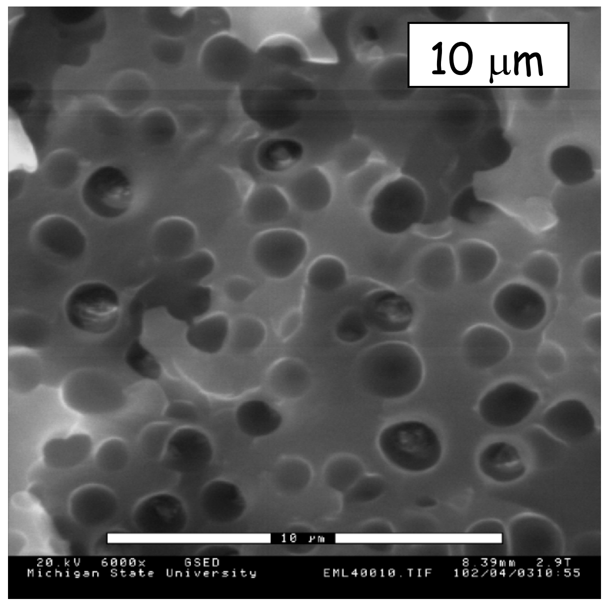
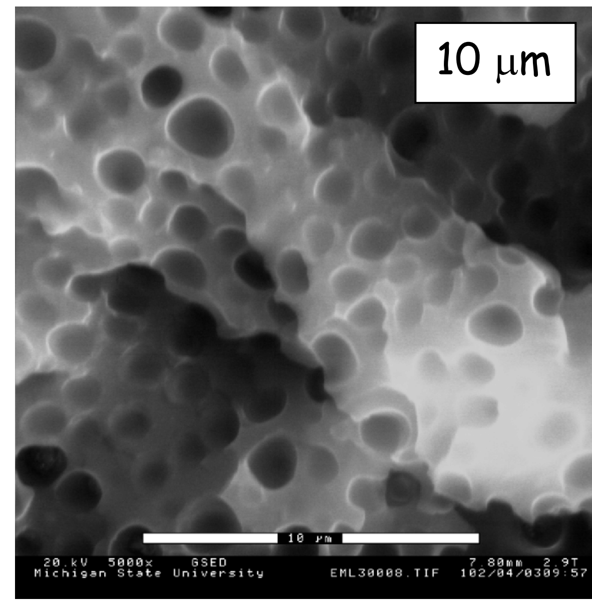
ESEMs of Impact Fractured Epoxy Resin containing MPDA and ELO

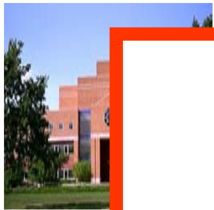




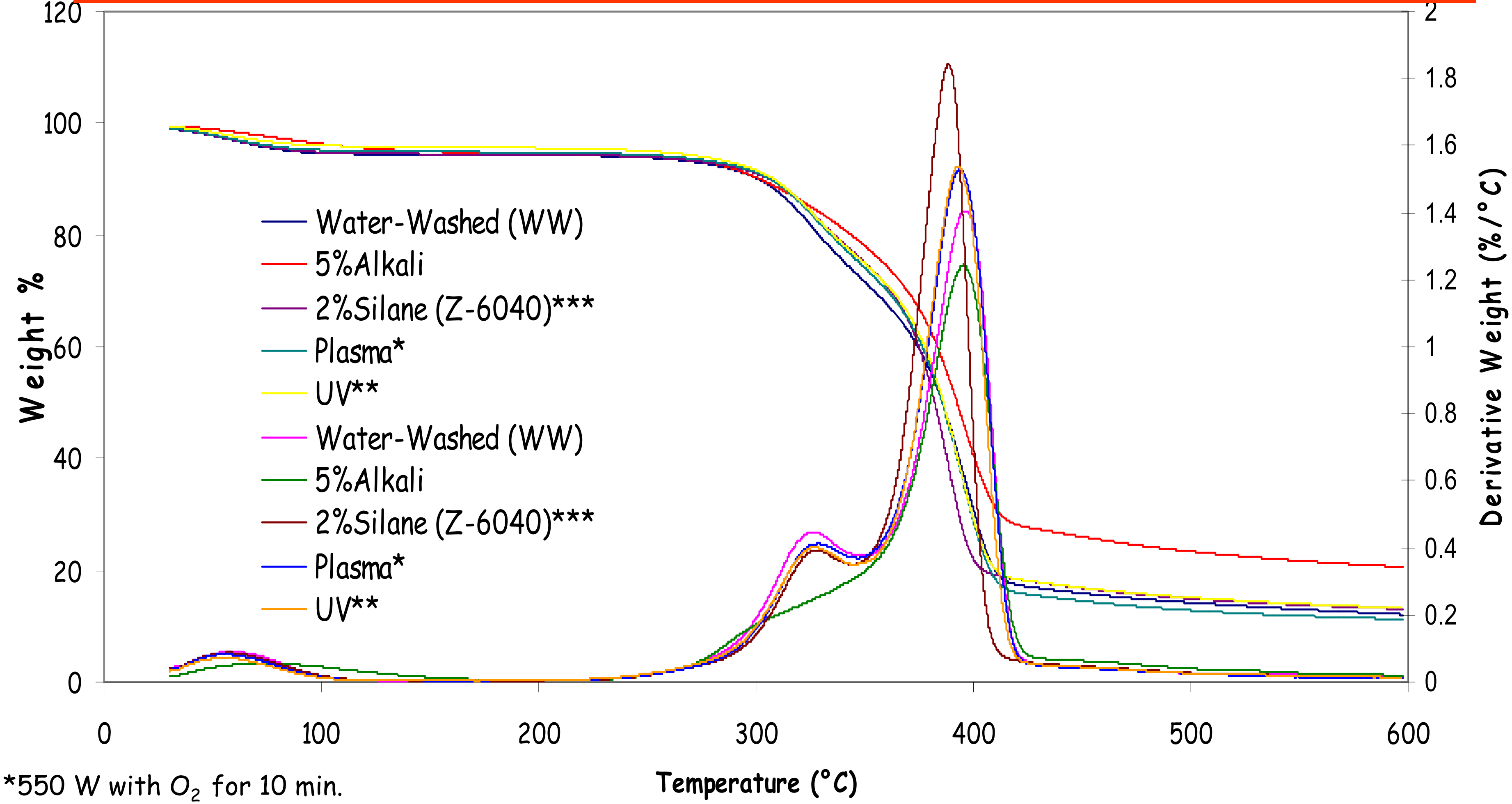


30%ELO X 6000 | 40%ELO X 6000 | 50% ELO X 5000

Phase separation between epoxy-rich phase and ELO-rich phase



Thermogravimetric Analysis of Surface Modified Henequen (HQ)



*550 W with O_2 for 10 min.

**120 sec. of UV at 60 °C

***Epoxy compatible silane

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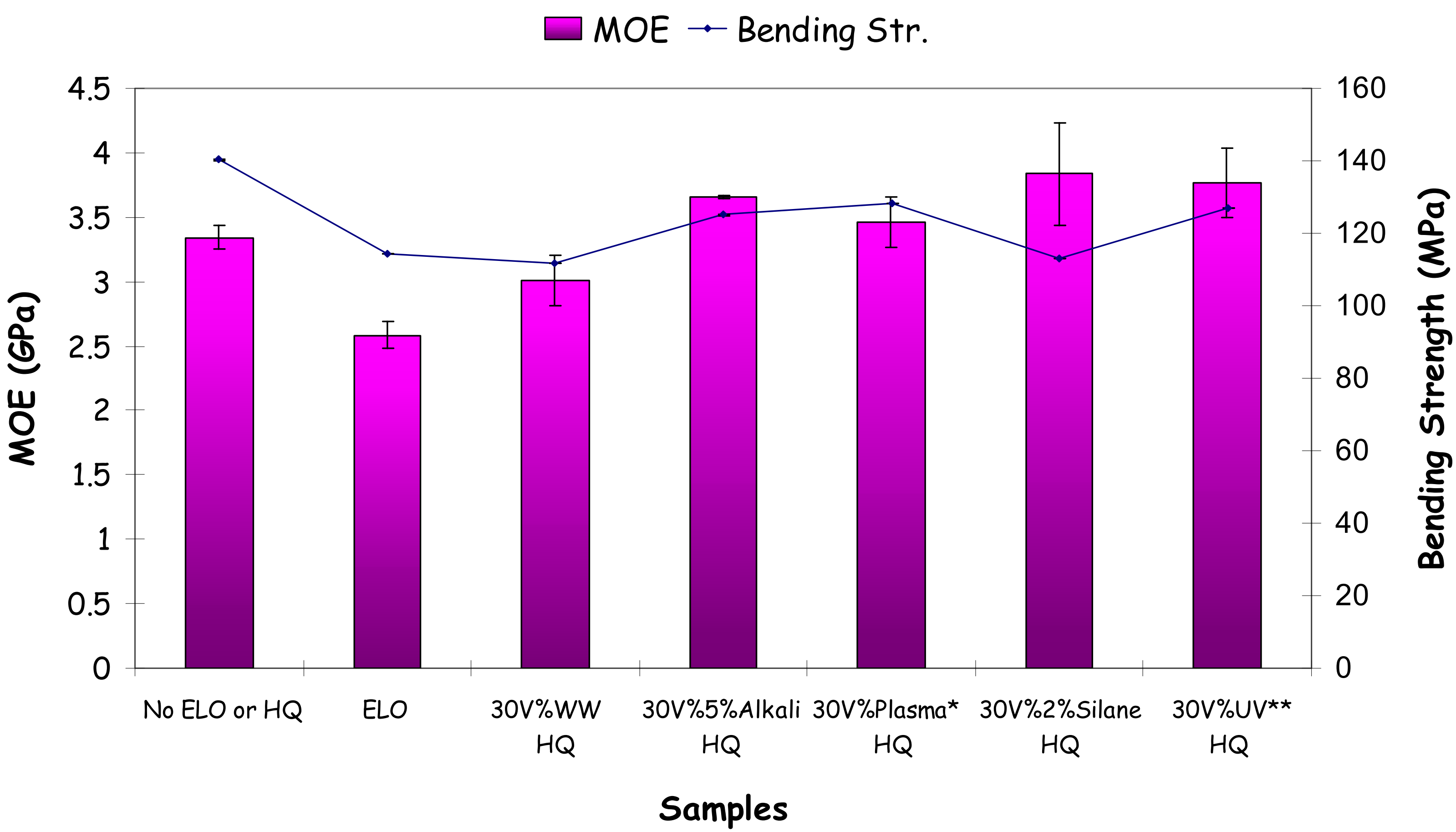
Modulus of Elasticity (MOE) & Bending Strength of - Epoxy Composites containing 30% ELO and 30V% HQ



Conclusion

- The impact strength was directly proportional to the concentration of the epoxidized oils when using J-T403.
- The modulus, bending strength, and Tg were inversely proportional to the concentration of the epoxidized oils when using J-T403.
- The impact strength was directly proportional to the concentration of the ELO when using 30 or 40% ELO and MPDA.

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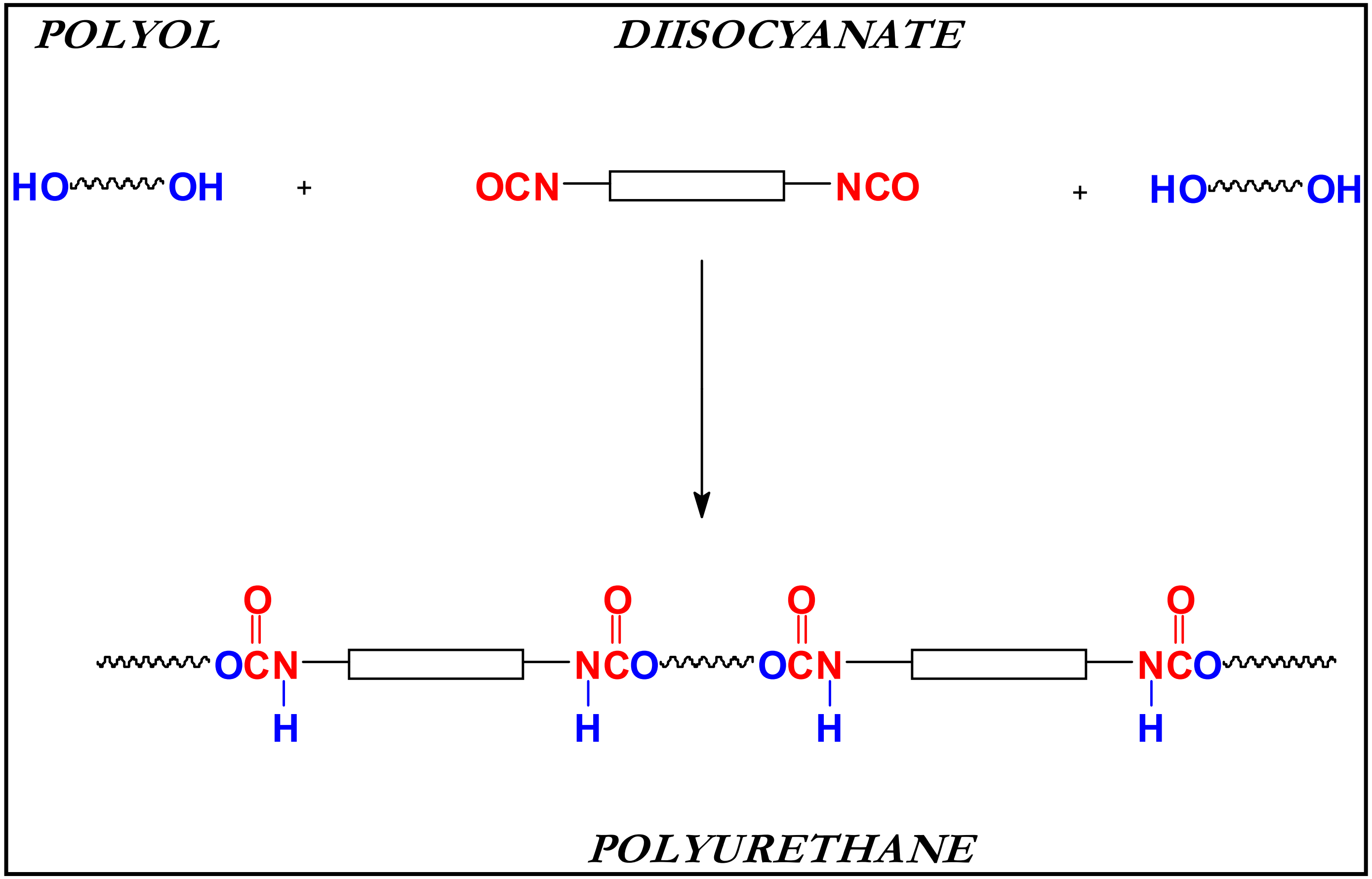
Bio-based Polyurethanes & their Composites

Polyurethanes: Synthesis and Uses



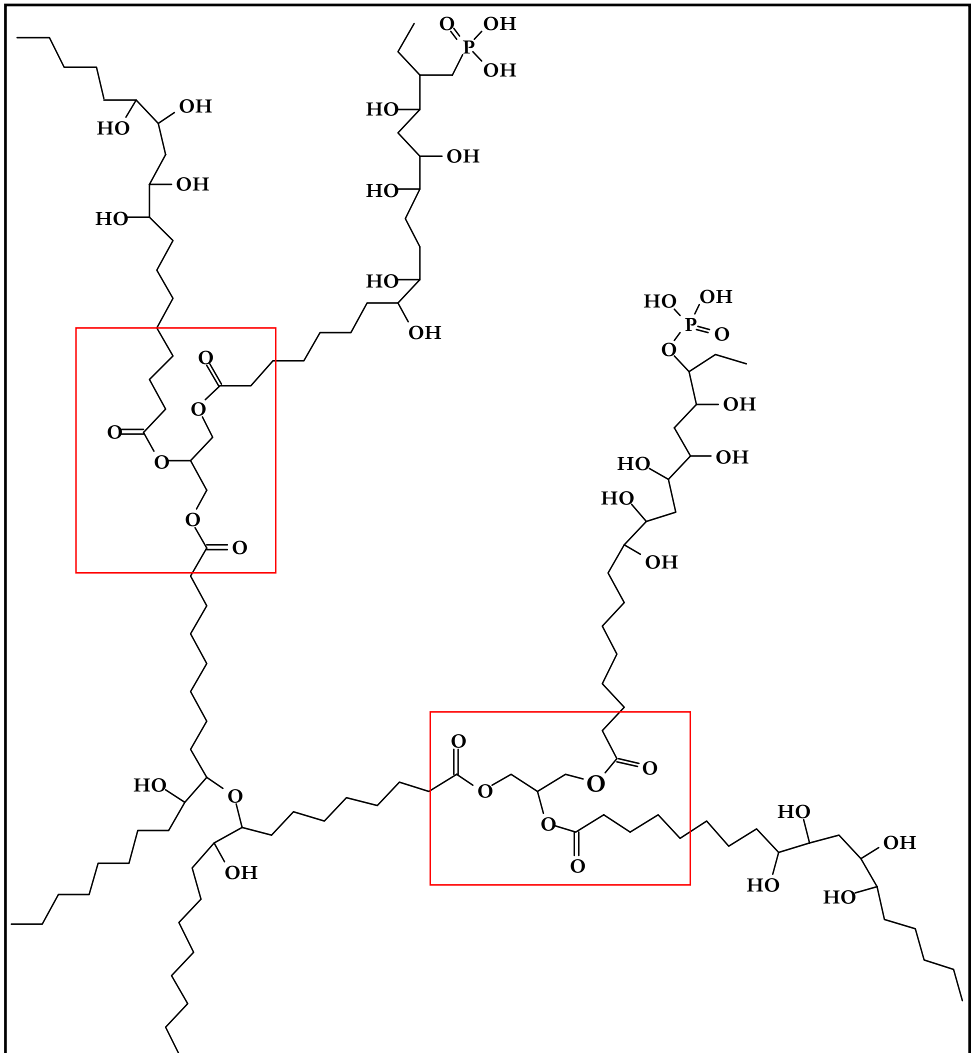
- Fast reaction, no by-product
- Wide range of polyols and isocyanates ⇒ *numerous uses*

Distinguishing Characteristics of Polyols

Characteristics	Elastomers, Coatings, Flexible foams	Rigid coatings, Rigid foams
Molecular weight	**1,000** to **6,500**	**150 – 1,000**
Functionality	**2.0** to **3.0**	**3.0** to **8.0**
Hydroxyl number	**28** to **160**	**250** to **1,000**

(SZYCHER'S HANDBOOK OF PURs), CRC Press (1999).

Soy phosphate ester polyol



Mw **= 2304 g/mol**
Functionality **= 20**

↓

492 mg KOH/g

Properties of Biobased Polyurethane's

Entry	Polyol OH ratio (JEFFOL / SOPEP)	Tg (°C) (DMA)	G' (30°C) (MPa)	Density (g/cm^3)
1	100 / 0	167	2100	1.072
2	90 / 10	154	1431	0.855
3	75 / 25	142	1427	1.051
4	50 / 50	111	1200	1.088
5	25 / 75	71	518	1.069
6	0 / 100	52	202	1.064

Isocyanate / OH ratio = 1.1. ***Jeffol 495 polyol***: polyether polyol (495 mg KOH /g) and ***SOPEP*** (154 mg KOH /g). Isocyanate: *polymeric diphenylmethane diisocyanate* (MDI).

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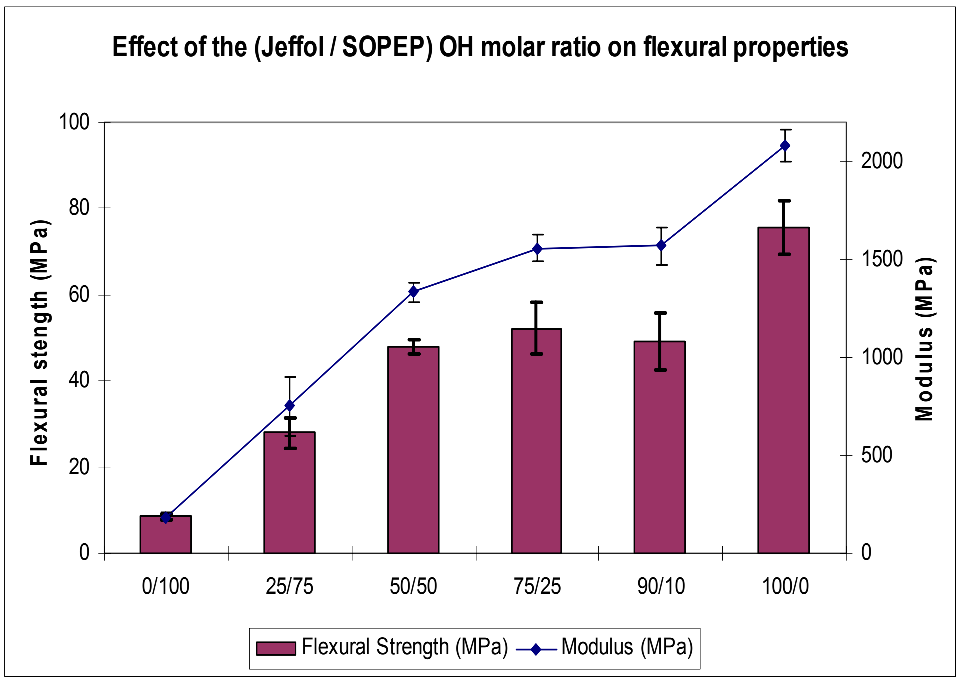
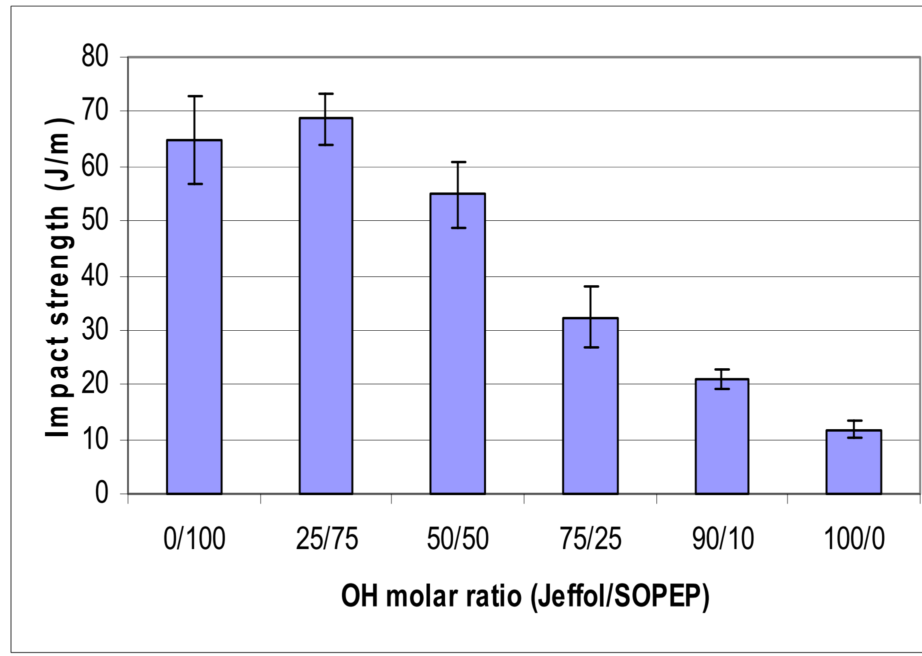
"Polyol" Hybridization ⇒ Biobased PURs with acceptable properties (thermal, mechanical performances) and effective cost





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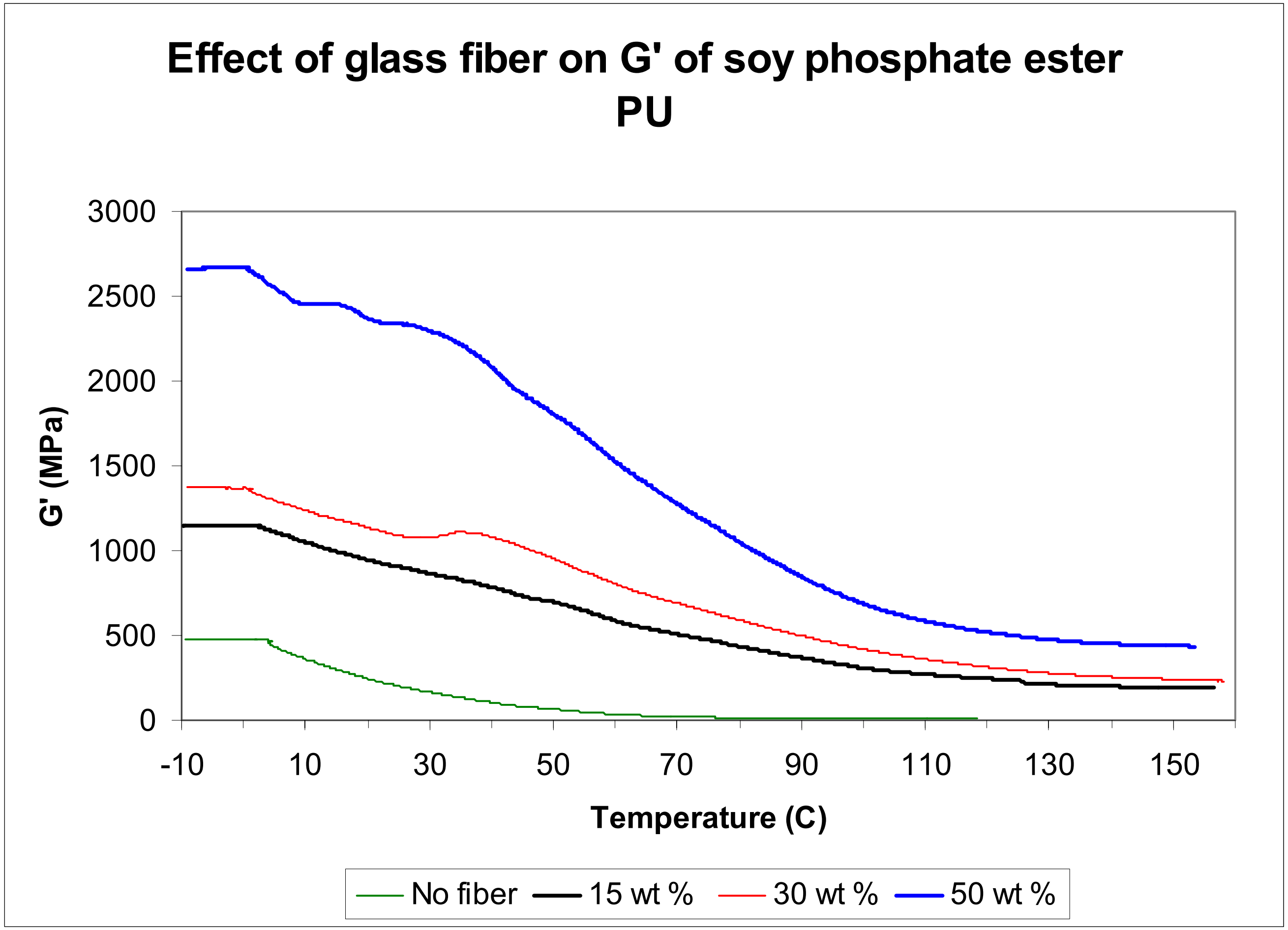
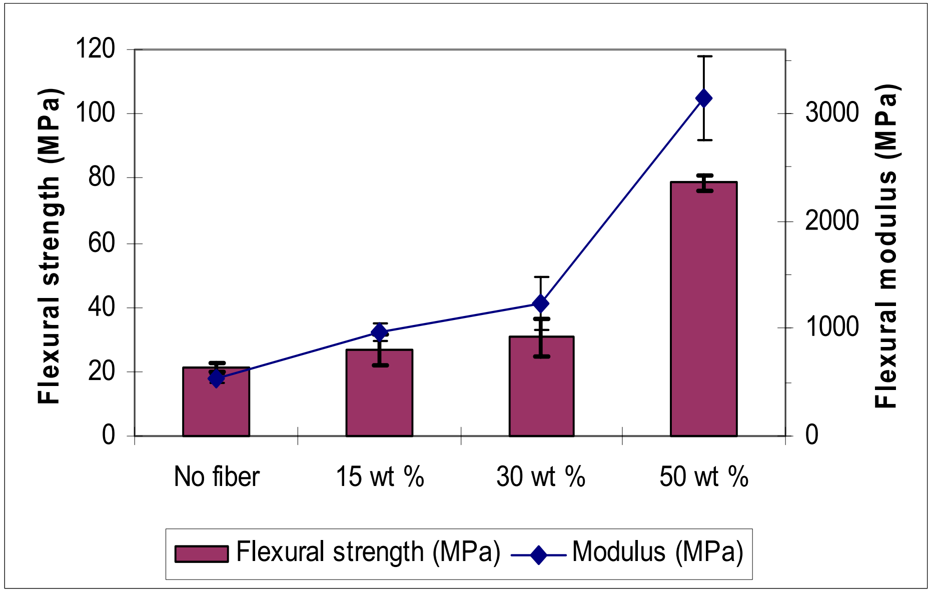
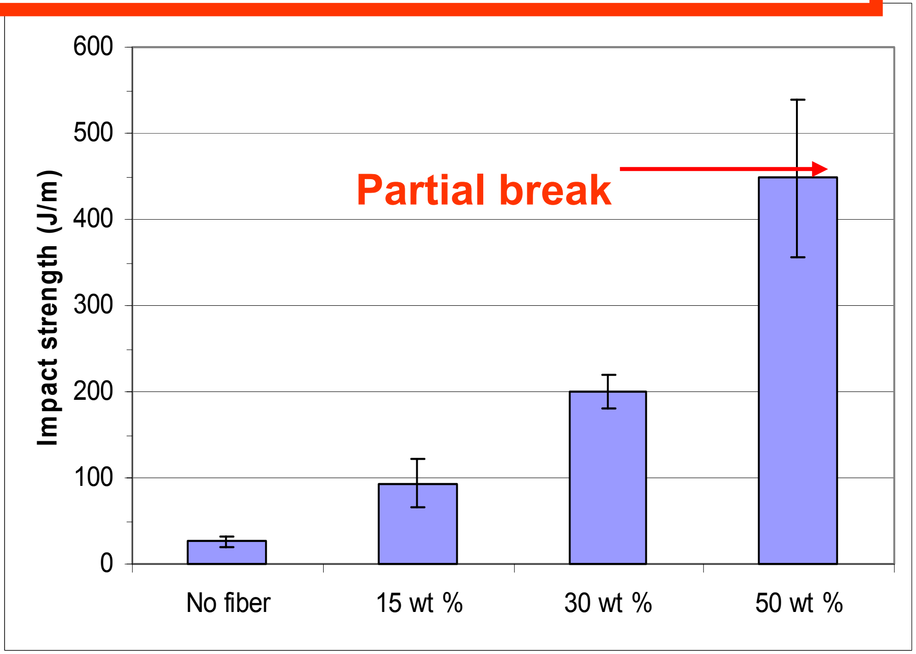
Glass reinforced Polyurethanes from soy phosphate ester polyol: DMA Study



Modulus of Elasticity (MOE), Bending Strength and Impact Strength of Glass reinforced Polyurethanes





$\Rightarrow$ Improvement of mechanical properties (dynamic, flexural and impact)

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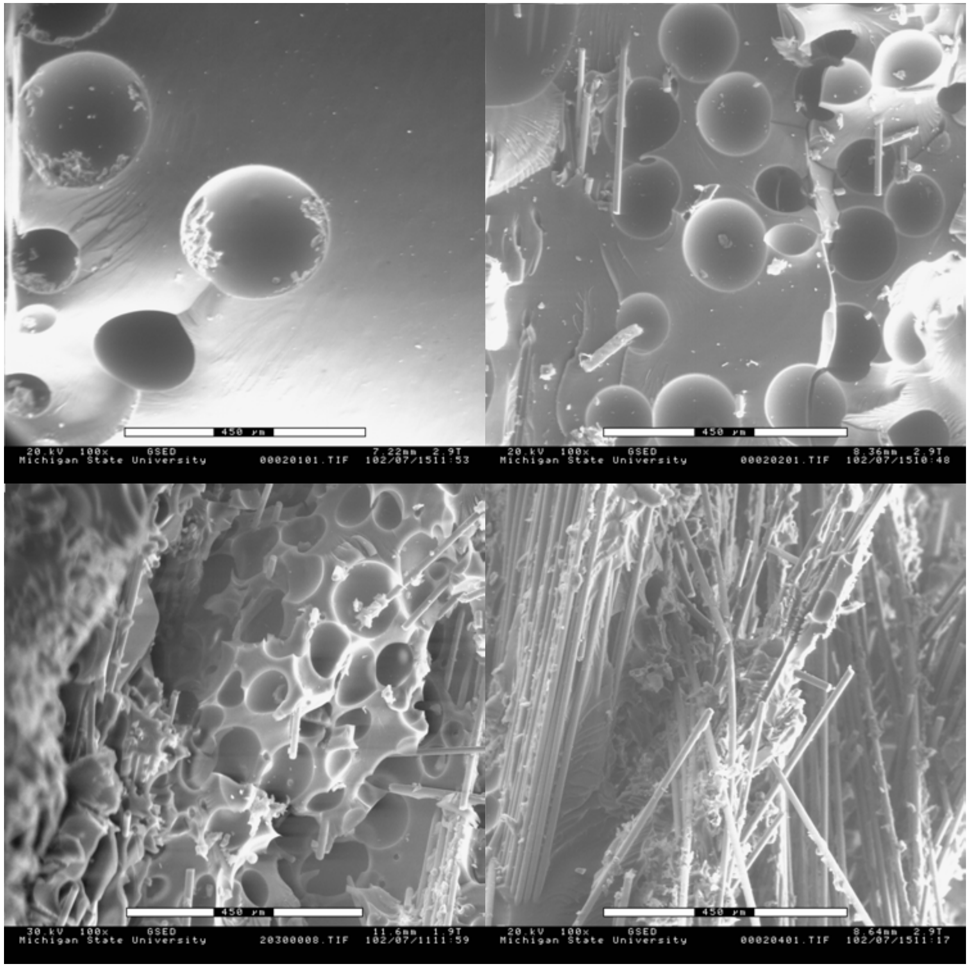
Impact Fractured surfaces of Glass reinforced Polyurethanes



No fiber

10 wt %

100X

30 wt %

50 wt %

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Conclusions

➢ **Preparation of PURs from soy phosphate ester combined with petroleum-based polyol** *(tuning of properties).*

➢ **Commercially available plant-based polyols**: low OH content for preparation of RIGID polyurethanes $\Rightarrow$ ***Glass reinforced PURs from SOPEP.***

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Unsaturated Polyester Resins and their Composites

Exterior (Natural Fiber-Polyester): Under- floor panels, engine & transmission covers

Ref.: DaimlerChrysler High Tech Report 1999

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Classification

Unsaturated Polyester Resins

- Ortho resins
- Isoresins
- Bisphenol-A fumarates
- Chlorendics
- Vinyl ester resins

Ortho resins → General purpose polyester resins (Cheapest resin)

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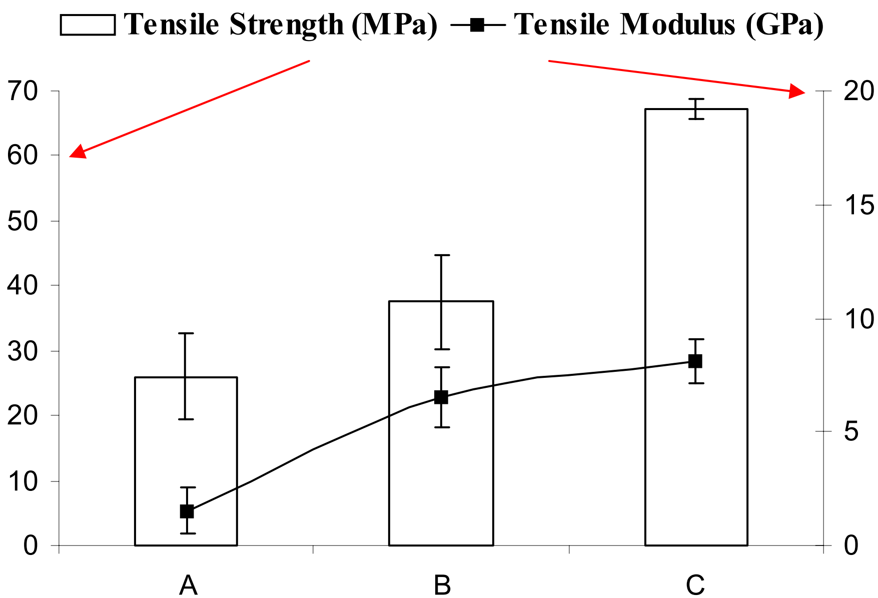
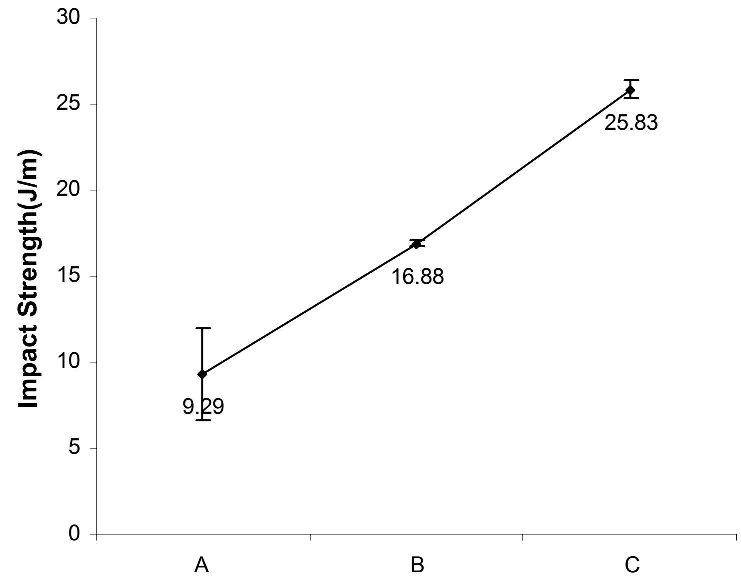
Nonwoven Hemp – Unsaturated Polyester Composites





A: Neat polyester, B: Raw Hemp (30 vol.%)-polyester, C: Surface treated Hemp-polyester

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CONCLUSIONS

- **Thermoset resins can be effectively blended with functionalized vegetable oil (Stiffness-toughness balance)**
- **Different Bio-based polyurethanes can be designed and engineered - - Reinforment with bio-fiber/glass fiber result superior physico-mechanical properties.**
- **Bio-Composites can Replace/Substitute Glass Fiber Composites**
  - Energy benefit
  - Renewability, biodegradability, CO_2 sequestration
  - Independent of dwindling petro-sources
  - Value-Added Opportunity for Agriculture Industry

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