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Mechanical Properties of Soya Fatty Acid Based Unsaturated Polyester Resin with Different Glycols

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ABSTRACT

The consumption of different glycols in plant oil based unsaturated polyester resin is discussed and reviewed. The fatty acid used in this research is Soya Fatty Acid. The recent times have seen an ever increasing oil prices, global warming, and many other environmental problems. Since vegetable oils have abundant applications and are readily available, they are commonly considered to be an important class of renewable resources. Of late, polymers from oil have been prepared by free radical, cationic, olefin metathesis, and condensation polymerization. The synthesis of polymers from plant fats and oils is gainingimportance for its industrial applications.

Four different unsaturated polyester resins have been synthesized from purified vegetable oil.Unsaturated Polyester Resin is formed by reacting different glycols with Phthalic Anhydride and Malic Anhydride with fatty acid combination to give orthrophthalic resin. The unreinforced unsaturated polyester resin displays a wide range of mechanical properties. Mechanical properties such as tensile strength, flexural strength, Heat deflection temperature, Barcoal Hardness, and water absorption are tested in this study. The experimental studies revealed that the flexibility of oil based unsaturated resin is higher than pure unsaturated polyester resin. Thus, benefiting us by avoiding cases of cracking.

KEYWORDS: Unsaturated polyester resin, Glycol, Soya Fatty Acid, Tensile properties, Flexural Properties

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INTRODUCTION

Polymers are macromolecules consisting of a large number of units. The units them selfconsist of a number of atoms. They are usually referred as the segments of the polymer. Polymerization is the method of creating synthetic polymers by combining smaller molecules, called monomers, into a chain held together by covalent bonds. In the polymerization of a mixture of two monomers, the structure of each macromolecule contains units of both monomers. Such polymer is called copolymer and the process of its synthesis is called copolymerization. These materials have distinctive properties, subject to the type of molecules being bonded and the structure in which it is bonded. Polymers touch almost every aspect of modern life. Each one of us is always in contact with at least one product containing polymers right from toothbrush, water bottle, gadgets to tiers.

In recent times, the need for replacement of non-renewable resources with natural products to cope with difficulties in the environment has seen an enormous rise; it may be as waste removal or in the reduction of non-renewable resources. Renewable resources become a viable platform to substitute completely to an extent or partially, petroleum-based polymers through the design of bio-based polymers that can compete or outdo the existing petroleum based materials on a cost basis with a beneficial impact on the environment.[1,2,3]

Polyesters are a class of polymers that can be formulated to be hard or soft, brittle or flexible depending on the structure and can, therefore, be used in various applications. Polyesters [4,5,6] are one of the most versatile synthetic copolymers. Polyesters are produced in high volume that exceeds 30 billion pounds a year worldwide.[6] They are widely used commercially as fibers (e. g. polyethylene terephthalate (PET),[7,8,9] plastics, composites and coatings applications,[10,11,12,13] plasticizers,[15]adhesives,[14,15] polyurethane based resins, films,[15] laminates, industrial construction, insulation, molding compounds,[14] etc. Polyesters are used for these applications because of their low cost, ease of process, ease of combination with reinforcements.[16] In addition, these polymers cure rapidly without any volatile products, have excellent dimensional stability,[16] have high impact resistance, transparency, and good weathering resistance.[14]

Plant oils offer many advantages from their renewability, the abundant availability and the relatively low cost make plant oils an industrially attractive and feasible raw material for the industry. Furthermore, diverse chemistry can be applied on them, leading to a large variety of monomers and polymers.[18,19,20]

LITERATURE REVIEW

Carleton Ellis [21] filled a patent in 1922 which laid the foundation of the modern history of the unsaturated polyester resin. This was followed by many publications by H. Dykstra, [22]T. F. Bradley,

E. L. Kropa, W. B. Johnston [23,24] and C. Ellis [25] in the consequent 10 years. Ellis showed for the first time that in the presence of a peroxide catalyst Malic Polyester resin copolymerize with styrene monomer. Thereby, promoting styrene monomer as a drier. This research opened the gates of unsaturated polyester resin being used as a moulding compound. This was the earliest similar type of unsaturated polyester resin that we see today. Further study on this subject was done by I. E. Muskat.[26] He introduced Phthalic Anhydride into the composition mixture to reduce crystallization which in turn improved the compatibility of resin and styrene monomer. This became important after many years when the resin was reinforced with glass fibre. The structural products had high mechanical strength and low density making them the most important matrix of the composite materials even today. [27]

W. Carothers in 1929 introduced the theory of condensation polymers and polyesters. [28, 29]In 1930 and 1936 R. Kienle presented the General Theory of polymer formations based on polyester studies [30, 31]which lead to the commercialization of unsaturated polyester resins in the United States of America in 1941. The basic chemistry of unsaturated polyester resins has remained very much unchanged for the last 40 years.

EXPERIMENTAL

Materials

The materials required can be classified into two major categories:Equipmentand Chemicals.

Equipment

A 3F 5litre round bottom flask, half feet by half inch glass column, 1 feet by 2 inch condenser, receiver, heating mantle, ¼ HP Vacuum pump, Electric Thermometer, stirrer, thermometer, pipettes, burette, Electronic Tensometer, Heat Deflection Temperature Machine (HDTM), Barcoal Hardness Tester, Brookfield Viscometer, Hydrometer (Range: 1.0 – 1.2).

Chemicals

Propylene Glycol (PG), Soya Fatty `Acid (SOFA), Phthalic Anhydride, Malic Anhydride, Styrene Monomer, Diethylene glycol (DEG), Mono ethylene glycol (MEG),Neopentyl Glycol (NPG), Hydroquinone (HQ), Methyl Ethyl Ketone Peroxide (MEKP), Cobalt (Concentration:6%),Triphenyl phosphate (TPP), Potassium Hydroxide (0.1N), Phenolphthalein, Acetone. All reagents used are of commercial grade.

Process

In a weighted 3F round bottom flask of capacity 5 liters a known quantity of Soya fatty acid, Phthalic Anhydride, Malic Anhydride, Glycol is added. Tri Phenyl Phosphate is added according to the desired percentage. The glass column is attached to one of the openings, and to another,a thermometer is inserted. Further, the glass column is connected to a condenser which leads to the receiver. Continuous flow of water is kept around the condenser for easy removal of water. The round bottom flask is kept in the heating mantle and stirring is started.

The temperature of the reaction mixture is increased under a controlled environment and simultaneously removal of water is done. Acid Value of the mixture is kept in checkfrom time to time. Temperature is increased upto 220°C gradually.[32] Once the discharge of water stops, the acid value is checked and vacuum is applied, which helps to build in viscosity and removes any excess traces of water. If the Acid value of solid is found to be between 35- 45mg KOH/gm Hydroquinone is added and it is left to cool. At 80°C Styrene monomer is added.

Poly condensation reaction takes place:

Poly carboxylic acids + Poly alcohols + Fatty acids, Vegetable oils → Unsaturated Polyester Resin + H_2O

CHEMICALS	SAMPLE NO.1	SAMPLE NO.2	SAMPLE NO. 3	SAMPLE NO. 4
Phthalic Anhydride	134	134	134	134
Malic Anhydride	95	95	95	95
Propylene Glycol	-	-	176	-
Mono Ethylene Glycol	-	143		-
Di Ethylene Glycol	220	-		-
Neopentyl Glycol	-	-		222
Soya Fatty Acid	60	60	60	60
Styrene Monomer	262	216	232.5	263

TABLE 1: Composition of Samples (in grams)

Percentage of Hydroquinone- 0.064%

Percentage of TPP- 0.064%

CHARACTERIZATION OF UNREINFORCED CAST RESIN

Tensile Test: [33]

Tensile strength is a measure of the force required to pull something such as rope, wire or a structural beam to the point where it breaks. [34]

Size of specimen – 16 X 1.25cm and 3 mm thickness. Tensile strength of unreinforced cast resin was done by an electronic tensometer, where the lower load limit was 1900 Newton and the upper load limit was 19000 Newton.

Tensile strength= load/area N/mm^2

Flexural test:[35]

Maximum flexural stress sustained by the test specimen during a bending test. [36]

Size of Specimen-10 X 2.5 cm and 3 mm thickness. Flexural strength of unreinforced cast resin was done by an electronic tensometer, where the lower load limit was 1900 Newton and the upper load limit was 19000 Newton. The load vs deflection values were recorded.

Flexural Strength= $PL/bd^2 N/mm^2$

Where,

P= peak load

L= Length

b = width

d = thickness

RESULTS AND DISCUSSION

Properties of Liquid State of Resin

The results given below are of the Properties of liquid state of four different unsaturated polyester resins.

Sr. No.	PARAMETER	Specification[37, 38]	Value
1	Appearance	Clear pale yellow	Clear pale yellow
2	Specific Gravity at 25 ^{0}C	1.00 -1.20	1.15
3	Viscosity at 25 ^{0}C (brook field) [Centipoise]*	700– 1500	460
4	Volatile contents [Weight%]	30– 35	29
5	Gel time at 25 ^{0}C, (1.5% MEKP of 50% & 1.5% Accelerator of 3%) [minutes]	20– 30	16

TABLE 2: Properties of Sample 1 [Soya Fatty Acid and Di ethylene Glycol (DEG)] in liquid state

Sr. No.	PARAMETER	Specification	Value
1	Appearance	Clear pale yellow	Clear pale yellow
2	Specific Gravity at 25 ^{0}C	1.10 -1.20	1.12
3	Viscosity at 25 ^{0}C (brook field) [Centipoise]*	700 – 1500	550
4	Volatile contents [Weight%]	30 – 35	33
5	Gel time at 25 ^{0}C, (1.5% MEKP of 50% & 1.5% Accelerator of 3%) [minutes]	20 – 30	23

TABLE 3: Properties of Sample 2 [Soya Fatty Acid and Mono ethylene Glycol (MEG)] in liquid state

Sr. No.	PARAMETER	Specification	Value
1	Appearance	Clear pale yellow	Clear pale yellow
2	Specific Gravity at 25 ^{0}C	1.10 -1.20	1.20
3	Viscosity at 25 ^{0}C (brook field) [Centipoise]*	700 -1500	900
4	Volatile contents [Weight%]	30 – 35	32
5	Gel time at 25 ^{0}C, (1.5% MEKP of 50% & 1.5% Accelerator of 3%) [minutes]	20 – 30	23

TABLE 4: Properties of Sample 3 [Soya fatty Acid and Propylene Glycol (PG)] in liquid state

Sr. No.	PARAMETER	Specification	Value
1	Appearance	Clear pale yellow	Clear pale yellow
2	Specific Gravity at 25 ^{0}C	1.00 -1.20	1.20
3	Viscosity at 25 ^{0}C (brook field) [Centipoise] *	700 -1500	1450
4	Volatile contents [Weight%]	30 – 35	33
5	Gel time at 25 ^{0}C, (1.5% MEKP of 50% & 1.5% Accelerator of 3%) [minutes]	20 – 30	27

TABLE 5: Properties of Sample 4 [Soya Fatty Acid and Neopentyl Glycol (NPG)] in liquid state

* Using Brookfield LVF viscometer, spindle 2, 60 rpm.

GRAPHICAL REPRESENTATION OF PROPERTIES OF LIQUID STATE RESIN

Four samples of Unsaturated Polyester Resin were tested for Acid value and Peak Exotherm.[37,38] For peak Exotherm1.5% of 50% MEKP and 1.5% of 6% Cobalt was used. The following table shows the results.

	ACID VALUE [mg KOH/gm]	PEAK EXOTHERM [^{o}C]
Specification	10- 25	170-190
Sample NO. 1	31.8	110
Sample NO. 2	29.8	138
Sample NO. 3	18	170
Sample NO. 4	13	185

TABLE 6: – Peak Exotherm and Acid Value

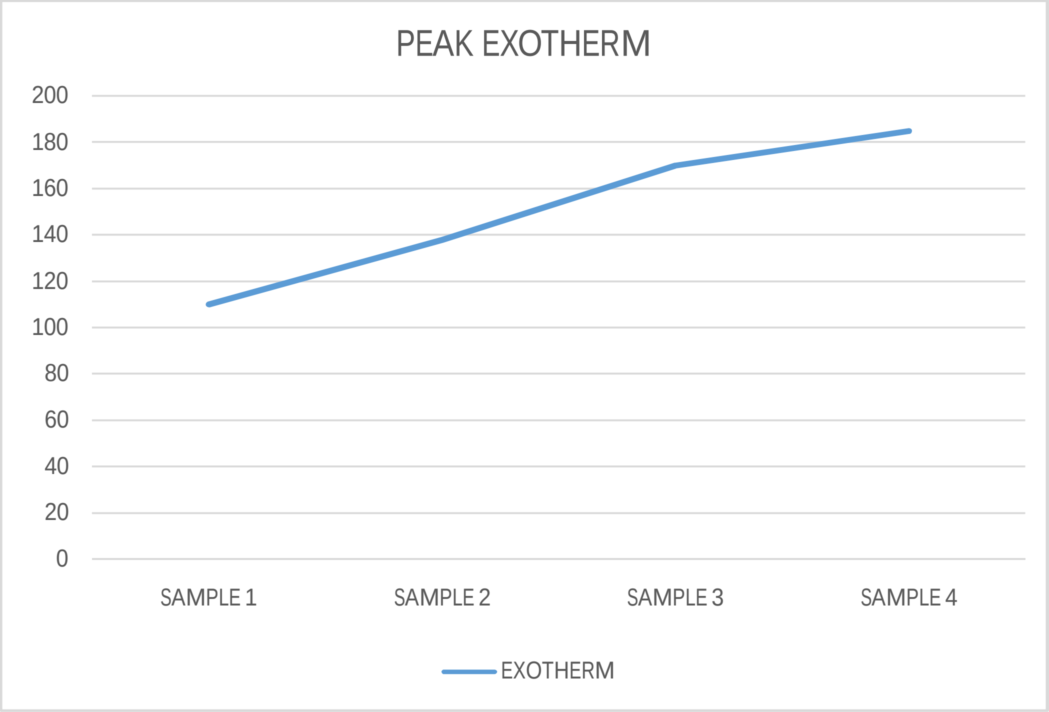

Figure 1 The above figure shows the gradual rise in Peak Exotherm as a higher glycol is used.

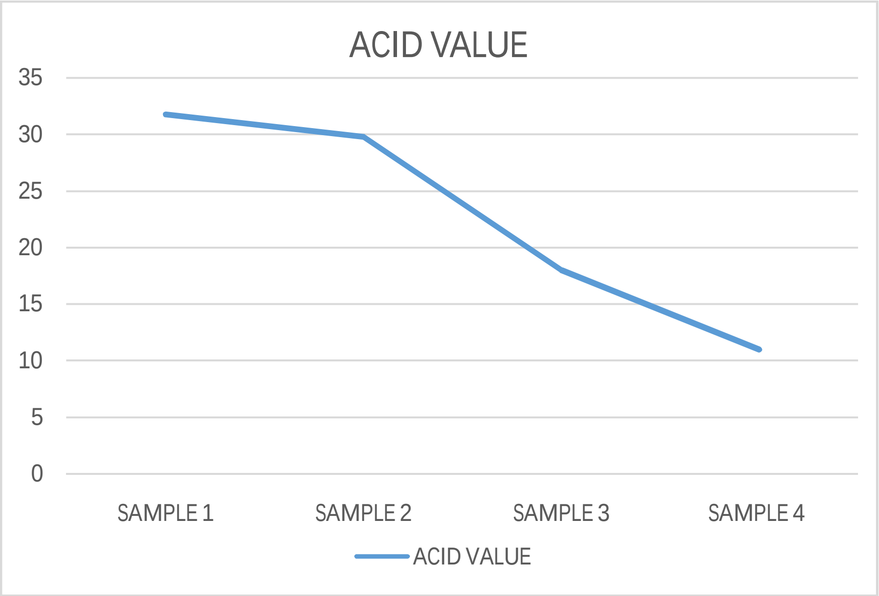

Figure 2 The above figure shows the gradual decrease in Acid Value as a higher glycol is used.

From Figure 1 and Figure 2, it is clear that a gradual increase in the Peak Exotherm is seen. Whereas, a gradual decrease in Acid Value is observed.

Acid Value indicates completion of reaction thus, it is vital that it falls within the range. It ensures tack-free cured resin. Peak Exotherm ensures that the mass of resin is completely cured.

From the above results, it is clear that Neopentyl glycol is the best suited glycol when used with Soya Fatty Acid but as the values of Propylene Glycol also fall in range it can be used.

MECHANICAL PROPERTIES IN A TYPICAL UNSATURATED UNREINFORCED POLYESTER RESIN

Tensile Strength	65 N/mm^2
Flexural Strength	97 N/mm^2
Barcoal Hardness	40 BHU
Temperature of Deflecion under 18.5 kg/cm2 load of cast resin	95^{o}C
Water adsorption when cast resin is immersed in distilled water for 24 hours	0.10%

TABLE 7: Mechanical Properties of Solid UnreinforcedResin Sample 4 are shown below

CONCLUSIONS

Neopentyl glycol is the best suited glycol when used with soya fatty acid but Propyl Glycol may also be used to give close results.

The flexibility of a plant oil based unsaturated resin is higher than Pure unsaturated polyester resin, thus benefiting us by avoiding cases of cracking.

As seen, the exotherm of liquid resin increases gradually as we use a higher glycol, the temperature ensures that thecomplete curing of the Unsaturated Polyester Resin is achieved which is not seen when lower glycols are used. If complete curing is not achieved the mechanical and chemical properties of the product are hindered.

SCOPE OF FUTURE WORK

In this study, only mechanical properties have been considered. This work can be extended by considering the thermal, chemical or molecular properties.

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