# Determination of Styrene Compatibility of Polyester Resin and Influence of Raw Materials - An overview

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*Abstract:-*Styrene compatibility of orthophthalic polyester resin and it's variation with respect to nature and type of ingredients was investigated. A useful method for manufacturing industry to predict the styrene compatibility of resin at room temperature was proposed. It will be useful to predict very common styrene flotation problem during the storage time especially in economical general purpose polyester resin.

*Keywords:- Orthophthalic polyester resin, Raw material, Styrene compatibility*

## INTRODUCTION

Unsaturated polyester resins (UPR) is widely used for a variety of industrial and consumer applications. The consumption can be split into two major categories of applications viz., reinforced and non-reinforced. In reinforced applications, resin and reinforcement (usually fibreglass) are used together to produce a composite with improved physical properties. Typical reinforced applications are boats, cars, shower stalls, building panels, and corrosion- resistant tanks and pipes. Non-fibre reinforced applications generally have a mineral filler incorporated into the composite for property modification. Some typical non-fibre reinforced applications are sinks, bowling balls, and coatings. Polyester resin composites are cost effective because they require minimal setup costs and the physical properties can be tailored to specific applications. Another advantage of polyester resin composites is that it can be cured in a variety of ways without altering the physical properties of the finished part. Consequently, polyester resin composites compete favourably in custom markets [2, 3].

Polyester resins are mainly classified into two classes based on the chemical structure of the ingredients viz., orthophthalic and isophthalic resins. The orthophthalic resin is used for general purpose applications of low cost without compromising quality. Likewise, isophthalic resins preferred for situations such as weather and chemical resistant environment, better mechanical properties and higher heat deflection temperature (HDT) [1,3].UPR is condensation polymer formed by the reaction of diols and dicarboxylic acid with water as the by-product normally. Ethylene glycol (EG), diethylene glycol (DEG), propylene glycol (PG), methyl propane diol (MPD), dipropylene glycol (DPG) and neopentyl glycol (NPG) are well-known members in polyols family. Phthalic anhydride (PA), isophthalic acid (IPA), terephthalic acid (TPA), adipic acid (AA), maleic anhydride (MA) and fumaric acid (FA) are normal industrial favourable members in dicarboxylic acid molecules. For an unsaturated polyester resin, it is necessary to add olefinic unsaturation in the backbone to crosslink with a monomer such as styrene. Usually maleic anhydride and fumaric acid provide the unsaturation in the polymer chain. UPR with maleic/fumaric and any polyols normally result a hard and brittle product of poor mechanical properties.

To overcome these demerits, higher reactive aliphatic unsaturated dicarboxylic acid/anhydride is partially replaced with aromatic saturated dicarboxylic acid/anhydride (phthalic anhydride, isophthalic acid, terephthalic acid etc.) and aliphatic dicarboxylic acid (adipic acid) [1-3]. The nature and the percentage of substitution in the main backbone define properties of the end product. Partial substitution results in decreased reactivity, reduced brittleness, lower exotherm during the polymerization and increased mechanical properties, toughness etc. An economical general purpose resin, phthalic and maleic anhydrides are preferred.

Propylene glycol (PG) enhances maximum isomerisation of lower reactive maleate to highly reactive fumarate and better solubility in styrene monomer [1]. But a neat propylene glycol batch is expensive due to the higher cost of PG when compare with EG and DEG. In the UPR industry, cost of the product has an important role to compete with other brands. There is a possibility for the partial replacement of propylene glycol (PG) with cheaper ethylene glycol (EG) and diethylene glycol (DEG). DEG have seldom used because of the poor hydrolytic stability and higher flexibility. Also, EG conjunction is restricted due to the poor styrene compatibility. However, many of the manufacturers extensively incorporate EG and DEG in their formulation to reduce the cost. The main drawback of this primary glycols conjunction is the styrene separation during the storage time. Hence, it is very important to find out the maximum limit of EG and DEG in the formulation. This paper describes a useful method to measure the exact styrene compatibility of economical orthophthalic resin and influence of raw material in styrene compatibility

## MATERIALS AND METHODS

All the raw materials procured were industrial grade with purity of above 99.00%. Propylene glycol from Manali petrochemical, Chennai, ethylene and diethylene glycol from Reliance, adipic acid and maleic anhydride from JP Dyechem Pvt Ltd, Mumbai, and phthalic anhydride from Aekyung Petrochemical Co. Ltd, Korea.

*Experimental preparation of Orthophthalic Resin*

A four-necked five liters round bottom on a heating mantle with a thermometer, condenser, Nitrogen stream flow and a mechanical agitator was designed as a glass reactor for the preparation of UPRs. Mol % composition various raw materials to prepare UPRs are given the following Table: 1.

Table 1. Experiments based on different raw materials at different molar ratios

| No | Ref | Mol in % | | | | | |
|---|---|---|---|---|---|---|---|
| | | PA | AA | PG | EG | DEG | MA |
| 1 | UPR 1 | 23.4 | - | 31.9 | 14.3 | 7.0 | 23.4 |
| 2 | UPR 2 | 23.8 | - | 13.1 | 28.8 | 10.5 | 23.8 |
| 3 | UPR 3 | 31.0 | - | 13.1 | 32.2 | 7.0 | 16.7 |
| 4 | UPR 4 | 31.0 | - | 31.5 | 13.8 | 7.0 | 16.7 |
| 5 | UPR 5 | - | 23.8 | - | - | 52.4 | 23.8 |
| 6 | UPR 6* | 23.4 | - | 31.9 | 14.3 | 7.0 | 23.4 |

*same formula of UPR 1, but the maximum batch temperature was limited as 199°C. [PA-Phthalic anhydride; AA-Adipic acid; PG-Propylene glycol; EG-Ethylene glycol; DEG-Diethylene glycol; and MA-Maleic anhydride
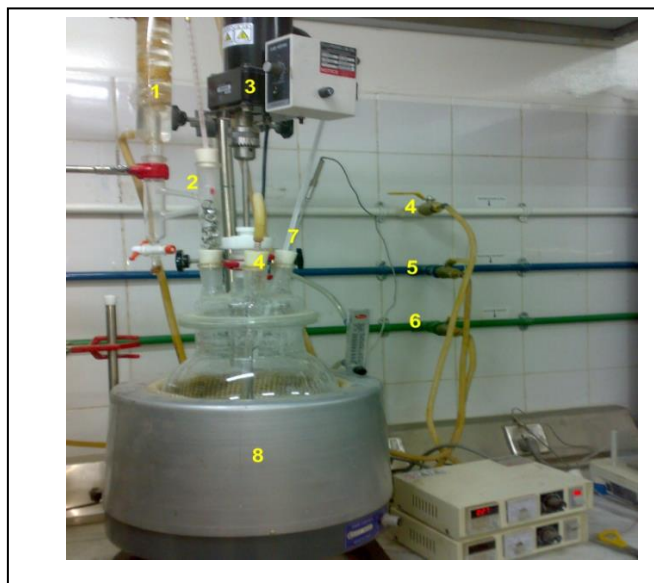


Figure: 1, Glass reactor set up for UPR Processing [1] Total condenser, 2) Partial condenser, 3) Motor with a stirrer, 4) Nitrogen, 5) water inlet, 6) water outlet, 7) Thermometer and 8) Heating mantle

The experiment was conducted in a nitrogen stream and the temperature was gradually increased to 100 °C and kept constant. (The experimental set up shown in the Figure: 1). As a consequence of exothermic reaction by the ring opening of maleic anhydride, the temperature is raised up to the maximum. Cook the batch for an hour at 180 °C when the exothermic reaction becomes stabilised. Heat the solution up to 215-220 °C and maintain until the acid value of about 30 mg KOH/g, then cool it to 185 °C and add mono-t-butyl hydroquinone to prevent pre-mature polymerisation. Further cool to 150 °C and blend with enough cold styrene so as to get 60 % solid content in the final solution then reduce blenders'

temperature to the room temperature as soon as possible to get UPR [12].

## RESULTS AND DISCUSSIONS

*Styrene Compatibility of the UPR*

The solid percentage of a UPR is tried to reduce by careful addition of styrene monomer, at a particular solid level the resin becomes cloudy at room temperature. The solid percentage at this cloudy state is defined as styrene cloud point (SCP). The solid percentage at which styrene starts to separate and reach as a constant safe solid level which is free from any further separation is considered as an optimum solid percentage (OS%)". If the manufacturer keeps the solid level in their resin as the exact OS %, will not face any separation problem during the shelf life period. Styrene compatibility of the UPR was defined by the parameters styrene cloud point (SCP) and Optimum Solid Percentage (OS %) and was obtained as follows,

Styrene at 25± 1 °C forms a burette slowly and gradually added to 250 ml beaker contains 25 to 50 g of resin with a known % of solid. Stir well and check for the change in transparency or cloudiness after every 1 ml of addition. Continue the styrene addition until the solution becomes cloudy.

Styrene Cloud Point, $S_{CP}$ =

$$\frac{\text{Actual Solid in Sample, } g \times 100}{\text{Wt. of Resin, } g + (\text{Amount of Styrene, } ml \times 0.910) \, g}$$ (1)

The styrene cloud point value of deferent experiments are given in the following Table: 2

At this clouding point or extra 1-2 ml addition of styrene can observe small micro ball like suspended solid resin particle-rich solution in the beaker at a closer observation in front of a light source.

*Determination of Optimum Solid Percentage (OS %)*

The solid content of resin was reduced to its $S_{CP}$ by adding extra styrene monomer and fill up to the mark of 100 ml in a measuring cylinder of accuracy of 0.1 ml. The separation of styrene on the top of the mixture was gradually checked until the separation got stabilized (3 days to 1 week may it will take at room temperature 26 ± 2 °C). The final amount of separated styrene and the OS% were calculated as follows;

Optimum Solid Percentage (OS%) =

$$\frac{S_{CP} \times (A_1 \times d_1)}{(A_1 \times d_1) - (A_1 \times 0.910)}$$ (2)

where $A_1$ and $d_1$ are the amounts and the density of mixture was taken respectively, $A_2$ is the amount of styrene separated of density 0.910, and $S_{CP}$ is Styrene Cloud Point.

The calculated OS % results of different UPR are given in following table 3.

Table 2: Styrene Cloud Point, (SCP) of different resins prepared as given in Table: 1

| No | Ref | Mol % | | | | | | |
|----|-----|------|------|------|------|------|------|---------|
| | | PA | AA | PG | EG | DEG | MA | $S_{CP}$ |
| 1 | UPR 1 | 23.4 | - | 31.9 | 14.3 | 7.0 | 23.4 | 13.9 |
| 2 | UPR 2 | 23.8 | - | 13.1 | 28.8 | 10.5 | 23.8 | 52.7 |
| 3 | UPR 3 | 31.0 | - | 13.1 | 32.2 | 7.0 | 16.7 | 49.6 |
| 4 | UPR 4 | 31.0 | - | 31.5 | 13.8 | 7.0 | 16.7 | < 5 |
| 5 | UPR 5 | - | 23.8 | - | - | 52.4 | 23.8 | 16.9 |
| 6 | UPR 6 | 23.4 | - | 31.9 | 14.3 | 7.0 | 23.4 | 35.5 |

*PA-Phthalic anhydride; AA-Adipic acid; PG-Propylene glycol; EG-Ethylene glycol; DEG-Diethylene glycol; and MA-Maleic anhydride*

Table 3: Optimum Solid Percentage (OS %) of the UPRs

| No | Ref | $S_{CP}$ | OS% |
|----|-----|----------|-----|
| 1 | UPR 1 | 13.9 | 13.9 |
| 2 | UPR 2 | 52.7 | 54.9 |
| 3 | UPR 3 | 49.6 | 52.2 |
| 4 | UPR 6 | 35.5 | 41.1 |
| 5 | UPR 7* | 41.2 | 47.2 |

*UPR 7 is a commercial UPR – Qupol 142 UO (a known brand of Sulaiman Al-Qudaibi Co. for Resin production, Kuwait)

*Non-separation tendency of styrene from $S_{CP}$*

If go lower $S_{CP}$, say below 20%, the separation tendency of styrene minimized or never happen and at this moment OS% becomes equal to $S_{CP}$ and it has not any particular application or any logical value in the industrial segment. This is because; the industrial UPR's solid level usually starts at 40 %. The compatibility issue and separation tendency are more when the $S_{CP}$ above at 40; hence it has an important role in the UPR industry.

Apart from the raw materials and it's different compositions, there are two more factors which make an influence in the styrene cloud point and hence optimum solid percentage also,

*a) The temperature during the SCP experiment:*

It is found that there is a significant change in lowering the $S_{CP}$ of UPR 1, 2, 3, 6 and 7 when the $S_{CP}$ experiment conducted at room temperature 45° C. But this is a temporary observation. The solution becomes cloudy and start to separate styrene when it returns to room temperature 25° C. So the influence of the room and material temperature on the $S_{CP}$ is temporary during the experiment that shown in Table 4,

Table 4: Styrene cloud point at different temperatures

| No | Ref | $S_{CP}$ at 25° C | $S_{CP}$ at 45° C |
|----|-----|-------------------|-------------------|
| 1 | UPR 1 | 13.9 | < 5 |
| 2 | UPR 2 | 52.7 | 37.2 |
| 3 | UPR 3 | 49.6 | 31.0 |
| 4 | UPR 6 | 35.5 | 20.7 |
| 5 | UPR 7 | 41.2 | 30.1 |

*b) Process condition of resin preparation:*

In general, polyester resins are processing in a controlled manner as stated early in this paper. The batch cooked at higher temperature of 215 to 220°C and targeting for an acid value of approximately 30 mg KOH/g [1,10]. All resin prepared in this invention is followed the said statement except UPR 6. In the case of UPR 6, the maximum temperature of the reaction limited as 199°C and blending started at an acid value at 55mg KOH/g. Consider the $S_{CP}$ and OS% result of UPR1 and UPR 6 in the Table: 3. The UPR 1 which is followed the exact process procedure show $S_{CP}$ and OS% as 13.9. UPR 6 with lower process temperature and higher acid value exhibit lesser styrene compatibility than UPR 1 and the $S_{CP}$ & OS% as 35.5% and 41.1 % respectively. These two experiments are same in formulation wise but their process condition was different. Now experimentally it is cleared that, process condition can also affect the styrene compatibility in the same formulation. The change in styrene cloud point and optimum solid level by the process condition is permanent and it will not deviate like the influence of room and material temperature during the $S_{CP}$ experiment.

CONCLUSION

Methods to determine the styrene compatibility of polyester resin and influence of raw material and its percentage in the compatibility is presented. The styrene compatibility is mainly affected by the change in the percentage of secondary diol – Propylene glycol. Also, Phthalic anhydride has a role to increase in the compatibility but the effect is minor like diethylene glycol. A huge dramatic variation we can observe by playing with PG to EG ratio. The styrene separation from the clouding point can't observe at lower $S_{CP}$ say below 20, but as per industrial concept the solid level starts from 40 % hence can ignore the importance of styrene cloud point behind 20%. These experiments are prepared in the laboratory to explain the methods to determine the styrene compatibility only. Because of the process condition, volume and other factors, the mentioned formulations may exhibit different values in bulk commercial batches.

The simplest experimental methods to determine SCP and OS% described in this invention is very useful to identify the styrene compatibility of UPR and predict the styrene separation problem happen or not. This invention is also an index for the process history of the resin batch produced. We confidently believe that this invention is acceptable for UPR industry because of the above-said application fields.

## ACKNOWLEDGEMENT

## REFERENCES

[1] Sidney H Goodman, Hand Book of Thermoset Plastic, 2nd edition, (Noyes Publication, New Jersey, USA), 1998

[2] H Hansmann and Hochschule, Composites, ASM handbook/Extraction, Vol: 2021, October.2003

[3] Johannes Karl Fink, Reactive Polymers Fundamentals and Application –A concise guide to industrial polymers, (William Andrew Publishing, Norwich, USA), 2005

[4] Debdatta Ratna, Hand Book of Thermoset Resins, (Ismith strawberry, SY4 4NR, UK), 2009

[5] Ken L Forsdyke and Trevor F Starr, Thermoset Resin Market Report, (Rapra Technology Limited, Shropshire, SY4 4NR, UK), 2002

[6] R Mildenberg, MZander and G Collin, Hydrocarbon resins, (published jointly by; VCH Verlag Gesellschaft mbH, Weinberg, Federal Republic of Germany and VCH publishers, Inc New York, USA), 1997

[7] D Braun, H Cherdron, M Rehahn, H Ritter and B Voit, Polymer Synthesis: Theory and Practice- Fundamentals, Methods, Equipments, Fourth Edition, (Springer-Verlag Berlin Heidelberg, Germany), 2005

[8] George Odian, Principles of Polymerization, Fourth Edition, (Wiley Interscience, A John Wiley & Son's Inc, Publication, USA), 2004

[9] Piotr Penczek, Piotr Czub and Jan Pielichowski, Adv Polym Sci (2005) 184: 1–95, (Springer-Verlag Berlin Heidelberg 2005), July 26, 2005

[10] P. Oldring, G Hayward and C. Chom, Resin for Surface Coatings, Vol: III, ( SITA Technologies, London, England), 1987

[11] Lennart A Lundberg, Stannford, and Conn, Process for the Preparation of High Molecular Weight Polymerizable Orthophthalate Polyester, US Patent: 3,079,368, February 1963

[12] Lawrence J, Karas, Paul M Pucket, Lake Jackson, Polyester resin base on terephthalic acid and 2,methyl-1,3 propane diol and process for the preparation, US Patent: 6,414,085 B1, July. 2, 2002

[13] Bayer Aktiengesellschaft, Germany, Free Flowing Unsaturated Polyester Moulding Compositions Hardenable with Very Little Shrinkage, US Patent: 4,079,024, March 14, 1978

[14] Carl J Sullivan, 48th Annual Conference, Composites Institute, The Society of Plastic Industry, Inc, Feb-8-11, 1993