# New Class of Unsaturated Polyester Resins for Eco friendly Coatings for Automotive Composites

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**ABSTRACT SUMMARY**:

A new class of unsaturated polyester resins was designed and developed as the basis of a fast curing and zero emissions powder gel coat for automotive composites. The resins were characterized with wet chemistry techniques, DSC and gel times measurements in order to evaluate the reactivity of the binder. Additionally, experiments were carried out in order to unearth the appropriate components of the binder for the powder gel coat. Finally, two unsaturated polyester resin formulations were scaled-up to semi-industrial scale.

**INTRODUCTION**:

In the last decades, composites have surfaced as a lightweight alternative to metallic parts and have found applications in several business segments, such as the automotive, aviation, aerospace, boat manufacturing and others.[1] More specifically, the automotive industry faces significant challenges due to increasingly stringent regulations in order to reduce emissions to the environment. One way to reduce emissions to the environment is to reduce the weight of vehicles. Composites are materials that can effectively enhance weight reduction in vehicles and are being used currently, but are cost intensive and existing production methods do not have the production rates that are required by manufacturers for mass production of vehicles. Furthermore, liquid powder gel coats that contain regulated substances such as styrene, are being utilized in the manufacturing of composites, further hindering the penetration to potential markets due to environmental, health and safety regulations. A lot of scientific effort has been dedicated to suppressing or even eliminating VOC emissions that are produced during the manufacturing of composites.[2,3,4,5] In the present work, novel unsaturated polyester resins (UP resins) were developed and characterised as the key building block of a powder gel coat. The powder gel coat can be utilized in a Resin Transfer Molding Process (RTM) for composites manufacturing. In order to comply with the environmental requirements, the powder gel coat should have zero emissions and in order to achieve the production rate requirements it should be fast curing. Further to the development of the UP resin, the appropriate mixture of components for the binder of the powder gel coat was identified and optimised with regard to percentage of each ingredient, namely the resin, hardener, peroxide initiator and inhibitor. The curing of the gel coat should occur rapidly (within a minute) at low temperatures (below 150°C), something that can not be achieved with conventional polyester systems. For this reason the free radical polymerization method of the resin and hardener was chosen in order to achieve a low bake system instead of the high temperature (180-200ºC) curing method aided by a catalyst which is used in conventional powder coatings. Experiments were carried out in the lab in order to evaluate and tune the gel time of the binder. After optimisation of the formulations, two UP resins were selected for up-scaling at semi-industrial scale.

**EXPERIMENTAL METHODS**:

The materials were used as received and without further purification. The synthesized unsaturated polyesters were characterized with wet chemistry techniques (Titrimetric Acid Value determination), Differential Scanning Calorimetry (DSC) for the determination of glass transition temperature of the resins and gel time measurements according to ASTM D4217 at 130, 140 and 150 degrees Celsius for reactivity assessment. The UP resins were prepared utilizing polycondensation reactions, under inert atmosphere (nitrogen flow). The cross-linking of the mixture of resin with the hardener was achieved with free radical polymerization. The processing of powders was done with a twin-screw extruder which was used to blend, mix and homogenize the binder.

**RESULTS AND DISCUSSION**:

In table 1 a selection of building blocks that were used for formulating UP resins, are presented. Each monomer influences the final properties of the polyester, and thus the formulator should pay attention to the final application in order to achieve the desired requirements.

Table. 1: *Building blocks for formulating UP resins*

| *Di-carboxylic acids* | *Diols* |
|---|---|
| Terepthalic Acid<br>Cost effectiveness | Neopentyl Glycol,<br>Outdoor resistance |
| Isopthalic Acid<br>Outdoor resistance | Mono Ethylene Glycol,<br>Enhanced storage stability |
| Maleic Anhydride,<br>Unsaturation content | Trimethylol Propane,<br>Improved mechanical resistance |

As a result of the investigation, UP resins with enhanced reactivity, good storage stability and process-ability were pursued. The results of the characterization for selected UP resins are shown in Table 2.

Table 2: *Results for selected UP resins*

| Sample | AV (mgKOH/g) | Melt Viscosity (P, 200°C) | Tg (°C) |
|---|---|---|---|
| ECPE7b4 | 53 | 265 | 54 |
| ECPE8b1N | 24 | 49 | 62 |
| ECPE10b1 | 20 | 78 | 63 |

Storage stability of the resins was evaluated via measurement of the glass transition temperature. A high glass transition temperature (>54°C) usually ensures that the resin will remain intact during shipping and storage. Additionally, the components (hardener, initiator, additives, fillers etc.) of the powder gel coat further decrease the Tg of the powder and thus it is extremely important for the formulator to have a resin with high enough Tg to work with. In figure 1, DSC graphs for selected UP resins are shown. Depending on the formulation, a wide variety of glass transition temperatures were recorded and the UP resins exhibiting Tg values higher than 54ºC were selected for further studies. Further, a measure to evaluate the process-ability of the UP resins is their melt viscosity.

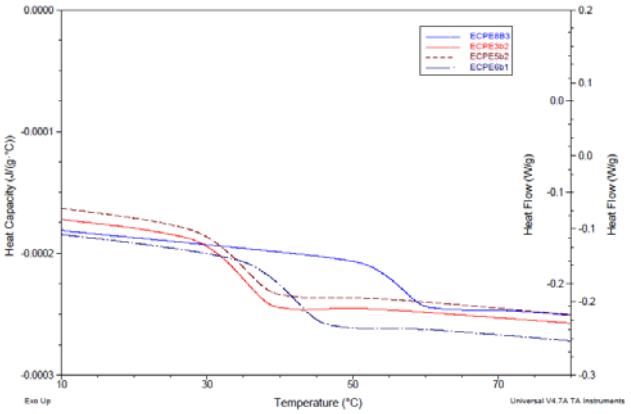


Fig. 1: *DSC graphs for selected UP resins ECPE8b3, ECPE3b2, ECPE5b2, ECPE6b1*

High viscosities result in slower processing times, insufficient mixing of the components of the curing system during extrusion and may lead to undesired premature crosslinking and network formation, i.e. premature gelation, inside the machinery. Reactivity of the powders was evaluated with gel time measurements according to ASTM D4217. Two types of hardeners (Tert-Butyl Acrylamide (TBAA) and Triallyl Isocyanurate (TAIC)) as well as two types of peroxide initiators (Benzoyl Peroxide and Lauroyl Peroxide, and an inhibitor (Tert-butyl Hydroquinone) were selected for evaluation. The ratio of UP resin to hardener was calculated in order to be equimolar with respect to double bonds of each. The mixture of components was blended and gel times were measured prior to further processing of the powders to determine their reactivity so as to avoid gelation in the extruder. Results of indicative gel time values are shown in table 3. It is observed that, as temperature rises, gel time of the binder drops significantly. The binders exhibited formation of gel in short time period and according to the technical requirements of the intended application.

Table 3: Indicative gel times for selected UP resins

| *Sample* | *Ratio* | *Gel time (s)* | | |
|---|---|---|---|---|
| | *UP/Hardener* | *130°C* | *140°C* | *150°C* |
| ECPE8b1N + TBAA | 94/6 | 121 | 58 | 34 |
| ECPE8b1N + TAIC | 96/4 | 87 | 61 | 31 |
| ECPE10b1 + TBAA | 95/5 | 111 | 64 | 36 |
| ECPE10b1 + TAIC | 96/4 | 79 | 57 | 43 |

After evaluating a plethora of resins, two formulations (ECPE8b1N and ECPE10b1), that fulfilled the technical requirements, were selected for up-scaling to semi-industrial scale.

**CONCLUSIONS**:

A new class of UP resins was developed as the basis for a powder gel coat for automotive applications. Properties of the resins were tuned in order to fulfill the desired requirements, namely reactivity, process-ability and storage stability. Further, the appropriate components for the binder were selected, tested and their ratio that allows sufficient curing of the powders was defined and optimized. Results show that a fast curing binder, based on novel UP resins, can be achieved utilizing a free radical curing reaction. Furthermore, the versatility of the system, both in terms of UP resin and other components of the binder, provides an excellent opportunity for its exploitation in additional applications such as low bake powders for plastic and wood, SMC powder coatings etc.

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