

# Cure Kinetic Study of Unsaturated Polyester Resin

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## Abstract

An unsaturated polyester resin is one of the principal matrices used in fibres reinforced plastics (FRP) products. Being a pre-polymer the cure kinetics plays an important role in making successful FRP products. Hence, this study deals with the cure kinetics of unsaturated polyester resin. It includes the optimization of gel time, curing time and temperature of it. The gel time, which indicates the formation of cross-linking structure, was studied by varying the weight percentage of the Methyl Ethyl Ketone Peroxide (MEKP) catalyst and Cobalt Octane accelerator. The optimum gel time of 15-16 minutes was found at the 1:1 wt% level of MEKP and Cobalt Octane concentration. A differential scanning calorimetry was used to obtain conversion profiles of the resin at different temperature ranges from 25–45°C. From the DSC study, the suitable curing temperature of unsaturated polyester resin was identified as 45°C. Fourier transform infrared spectroscopy was used to study the effect of time on the curing of unsaturated polyester resin. From FTIR analysis, the major conversion of resin was found at 35 minutes.

## Keywords:

Cure kinetics; curing time; gel time; unsaturated polyester resin

## Citation

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## 1.0 Introduction

Composites are composed of resins, reinforcements, fillers, and additives. Each of these constituent materials or ingredients plays an important role in the processing and final performance of the product [1]. Among these, resins (matrix) are an important constituent of the composite. It is the "glue" that holds the composite together and influences the physical properties of the product [2]. Therefore, these thermoset resins are frequently used as matrix materials in polymer composites such as fibre-reinforced plastic and polymer concretes [3]. The most common thermosetting resin used in the composites industry is unsaturated polyester (USPET). The USPET resins are known as the workhorse of the composites industry as they represent approximately 75% of the total resins used and possess good mechanical properties, excellent thermal stability and weather resistance. Therefore, they are the most versatile, globally used, thermoset polymer [4], [5].

Chemically, USPET resins are nothing but macromolecules with a polyester backbone and belong to the category of thermoset resin. They are broadly defined as condensation products of organic dicarboxylic acids and di-functional alcohols (glycols) [6]. It contains an unsaturated material, such as maleic anhydride or fumaric acid, as part of the dicarboxylic acid component [7]. It is often blended with

vinyl group molecules like styrene (35- 45 wt%) into a reactive resin solution. This styrene acts both as a cross-linking agent and as a viscosity reducer [8]. In addition, during the curing process at room temperature, generally, organic peroxides like methyl ethyl ketone peroxide (MEKP) are mostly used as catalysts while cobalt salt is frequently used as an accelerator to control the gelling time of the resin [8], [9]. The inhibitors such as quinones and phenol are added to react with the initiating or propagating radicals to reduce their reactivity. This gives an induction period before the resin is cured and adds to its storage life [10].

When this resin is cured, the monomer reacts with the unsaturated sites on the polymer converting it to a solid three-dimensional, rigid and hard thermoset polymer structure. However, the curing kinetics of polyester resins is very complex since a free radical chain growth polymerization reaction takes place with the stages of initiation, propagation, and termination. Further, the curing of USPET resin occurs as a combination of chemical kinetics and control by diffusion. In addition, the interaction of chemical kinetics with physical phenomena like gelling makes the curing process more complex [11], [12]. Hence, the success of producing a product by processes like hand lay; resin transfer moulding or resin spraying depends on the cure kinetics as well as the gel time. Hence, the processing of these resins requires an understanding of the polymerization

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reaction kinetics during cure [9],[13]. Therefore, in this present work, the initial gel time of unsaturated polyester resin was studied by varying the wt% of catalyst (MEKP) and accelerator (Co). Then, an optimized recipe was used to study the cure kinetics of the polyester resin by DSC and FTIR spectroscopy analysis.

## 2. Experimental

### 2.1 Materials

The resin transfer moulding (RTM) grade unsaturated polyester resin ESPOLTM containing phthalic anhydride (PA), propylene glycol (PG), diethylene glycol (DEG) and maleic anhydride was procured from Satyan Polymer, Mumbai, India. The peroxy benzoate (MEKP) as a catalyst with cobalt octane (3%) as an accelerator was purchased from Empee Corporation Pvt. Ltd. Bangalore, India.

### 2.2 Methods

#### 2.2.1 Gel time study

The effect of amounts of catalyst and reaction accelerator on the gel time of USPET resin was studied to understand the time, and temperature superposition required for curing. The gel time was determined by manual methods based on “by eye” evaluation of the rheological behaviour of the resin during stirring, the pattern of resin fibre drawing or adhesion to the probe.

#### 2.2.2 Cure kinetic measurements by DSC analysis

The reaction kinetics (curing temperature) of USPET resin mixed with catalyst and reaction accelerator were measured by a DSC-30 Mettler Toledo instrument. A dynamic curing reaction scan was conducted from 25 to 300°C at a heating rate of 10°C/min in a nitrogen flow rate of 10 mL/min. The isothermal runs were carried out for 60 minutes at 25, 30, 40 and 45°C temperatures. The samples are then heated to 350°C in the non-isothermal scanning mode with a heating rate of 10°C/min to determine the residual heat of the reaction ( $\Delta H_{res}$ ). All the reactions were conducted in hermetically sealed aluminium sample pans. The weight of the samples taken for the study ranged between 5 to 10 mg.

#### 2.2.3 Cure kinetic measurements by FTIR spectroscopy

The reaction kinetics (curing time) of styrene monomer and polyester vinyl groups was determined by FTIR spectrometer (Perkin Elmer 2000, USA). Before acquiring a spectrum, initially, the reactants were thoroughly mixed and then one drop of the mixture was pasted between two KBR plates and mounted on a sample holder. The FTIR spectrum for each sample was acquired after 10 scans in the range of 4000 to 400  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$  in the absorbance mode.

## 3. Results and discussion

### 3.1 Determination of styrene content and gel time

Initially, it was necessary to determine the content of styrene present in the USPET resin. Here, the weight loss method

was used to find out the amount of styrene used in the USPET resin. For that, the purchased USPET resin was kept in an oven under vacuum at 120°C for 2 h followed by a measurement of weight loss. This procedure was continued several times until the complete evacuation of styrene took place. The styrene content in the USPET resin was calculated by Equation 1 and it was found to be 41% (wt/wt).

$$\text{Styrene content} = \frac{\text{Initial Weight} - \text{Final Weight}}{\text{Initial Weight}} \times 100 \dots \dots \dots \text{Eq. 1)}$$

After the quantification of the styrene content, the gel time (Tgel) of USPET resin for making composites was studied “by eye” evaluation of the rheological behavior of the resin during stirring, the pattern of resin fibre drawing or adhesion to the probe as mentioned in the experimental section. The effect of the differential concentration of catalyst and accelerator on the gel time was studied at 23°C  $\pm$  3°C and RH: 50%  $\pm$  5% atmospheric conditions. The corresponding gel time is tabulated in Table 1.

**Table 1. Gel time (Tgel) of unsaturated USPET at various concentrations of catalyst and accelerator**

Experiment	Cobalt Octane (wt%)	MEKP (wt%)	Gel time (Tgel)
1	2	2	3-5 min
2	1.75	1.75	7 min
3	1.5	1.5	10-11 min
4	1.25	1.25	13-14 min
5	1	1	15-16 min
6	0.75	0.75	23 min
7	0.5	0.5	36 min
8	0.25	0.5	58 min
9	0.5	0.25	Above 1 h
10	0.25	0.25	Above 1 h
11	0.1	0.1	Above 1 week

From Table 1, it was observed that as the amount of both reactants decreases, the gel time proportionately increases. The value of Tgel was approximately above one week at the lowest level (0.1, 0.1) of the catalyst and accelerator, whereas it was found to be reduced significantly to 3-5 min at the highest level (2, 2) of reactants. The increase in gel time is primarily because of less number of available free radicals during the free radical polymerization reaction of USPET resin. The crosslinking reaction of USPET is shown in Figure 1.

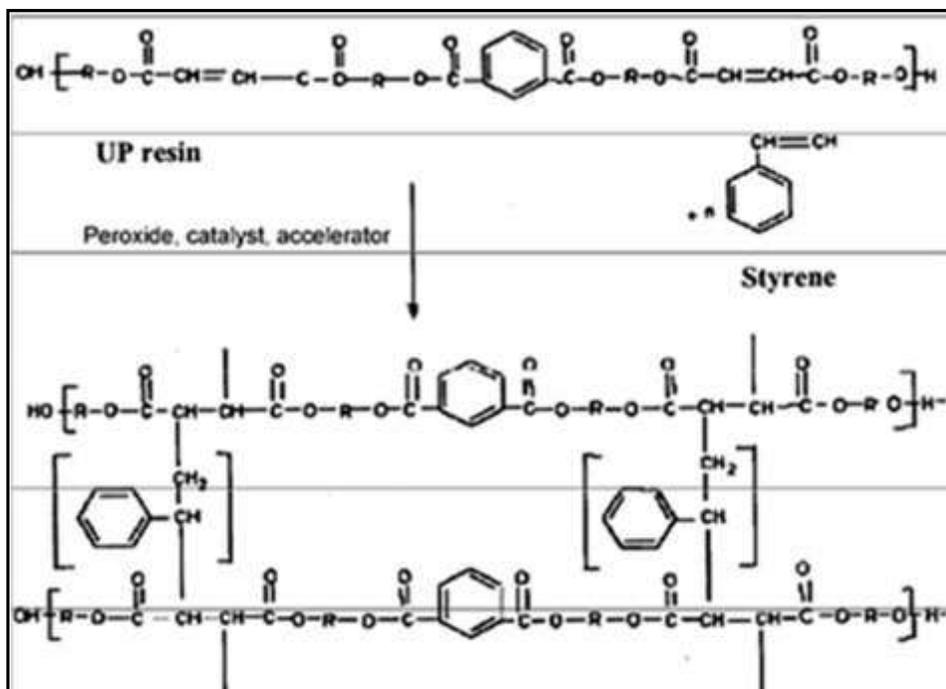


Figure 1. Cross-linking or gelling mechanism of USPET resin

During the reaction, the free radicals initiate the exothermic copolymerization reaction. Due to this, the formation of macromolecules takes place which continues to grow resulting in a gel form which is a phenomenon describing the transition of a material from a viscous liquid to an elastic solid during curing. From the chemical point of view, gelation implies the formation of a continuous network of covalent bonds in the system (i.e., the formation of a molecule with an infinitely high molecular weight). However, this transition does not occur instantaneously; rather, the viscosity of the system increases gradually, which makes it very difficult to precisely determine the gel time [11]. In addition, a certain problem is presented by the differentiation of gelation from vitrification that also leads to a solid but is not characterized by the formation of a continuous network of covalent bonds. Finally, this makes the reaction mass a semi-viscous state [11]. Further, it is also known that the lower  $T_{gel}$  can result in the formation of incomplete mould-filling defects because of the restriction of molecular chain mobility in the polymer. Whereas, a higher  $T_{gel}$  value can increase the cycle time and reduce productivity. Therefore, the value of  $T_{gel}$  should be neither too less nor too high. Hence, a (1, 1) level was selected as the optimum where the difference in gel time was not too much with the level of (2, 2).

### 3.2 Differential scanning calorimetry (DSC) analysis

The working temperature also has a significant role in the gel and curing time. Therefore, to understand the effect of temperature on the conversion of unsaturated polyester into gel formation during curing, a difference in heat of reaction was measured during a series of isothermal scans at 25, 30, 40, and 45°C and after it, as shown in Figure 2.

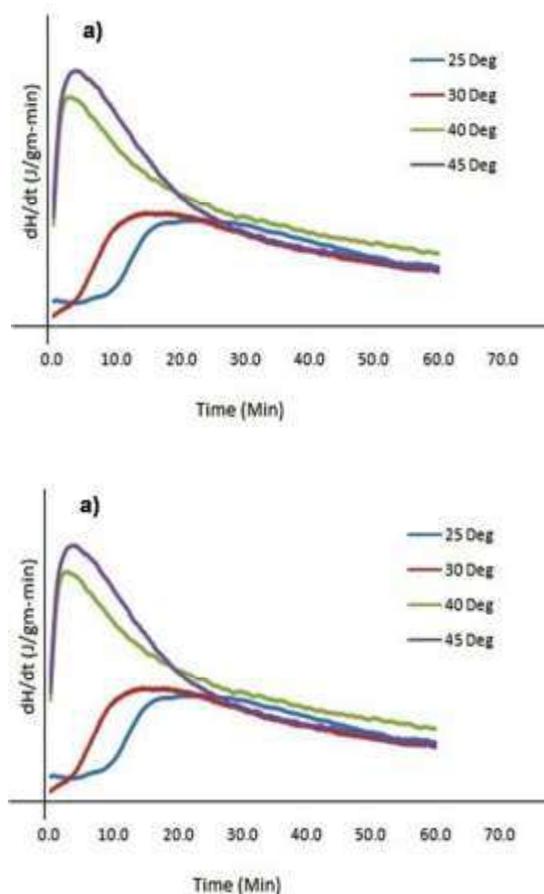


Figure 2. DSC dynamic curves obtained (a) during and (b) after isothermal scans

From Figure 2(a), it was observed that at the lower isothermal time, as isothermal temperature increases, the heat of the reaction also increases and thereafter no significant change was observed in it at higher isothermal time. In other words, the greater Tiso value, the ΔHiso value is also higher which is reflected in an increase in the conversion of the unsaturated polyester resin into the gel with an increase in reaction temperature. This is because of the styrene homo-polymerisation and its copolymerization with the C=C bond of the unsaturated polyester resin chain via the heat of the reaction involved during the isothermal period. Due to this, the molecular chains of the polymer become more mobile and the resin can further react at a higher temperature, resulting in higher final conversion and lower styrene residue. However, a total conversion was not reached at any temperature employed in this study [13]. Hence, the non-isothermal scan was carried out of the same isothermally cured sample, and a residual heat ΔHres appeared, which is the result of the reactivity of the residual functions that have not reacted during the isothermal period. The variation of this heat of reaction (ΔHres) with Tiso is shown in Figure 2(b). Therefore, the value of heat generated during the isothermal scans ΔHiso, together with the residual heat values ΔHres, are shown in Table 2.

It can be seen that the heat generated during the isothermal scan increased as the temperature increased, while the residual heat decreased. This is because of the higher mobility of double bonds and the vitrification process, which occurred at higher conversions as the temperature increased. Thus, the concentration of unreacted double bonds is reduced [14]. On the other hand, it is supposed that the quantity of (ΔHiso+ΔHres) must remain constant [15]. However, we did not find this observation, except for the greater value of Tiso. This is because of the known fact that evaporation of styrene appeared during the experiments. This leads to experimental errors in the determination of the different enthalpy values. However, 45°C was found as the optimum temperature where maximum conversion and low level of styrene residue exist.

**Table 2. The heat generated during and after an isothermal scan of unsaturated polyester resin**

Temperature (°C)	ΔHiso (Jg <sup>-1</sup> )	ΔHres (Jg <sup>-1</sup> )	ΔHiso + ΔHres (Jg <sup>-1</sup> )
25	99.38	173.18	272.56
30	182.43	142.69	325.12
40	260.56	66.08	326.64
45	268.86	61.83	330.69

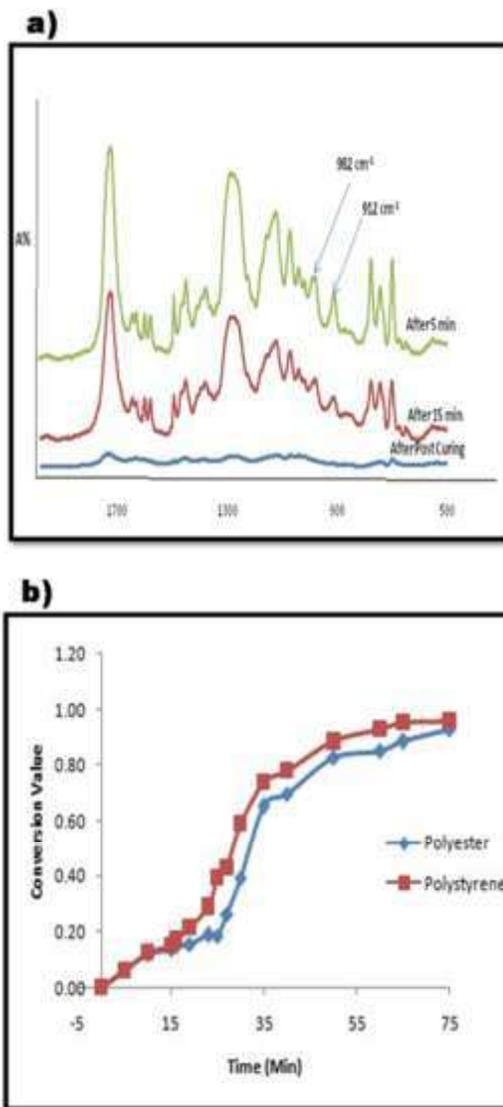
**3.3 FTIR analysis**

Based on the optimum reactant concentration from gel study and temperature by DSC analysis, to optimize the curing time, the changes that occurred in the ATR-FTIR spectra at different curing times (0–35 min) were analyzed and shown in Figure 3. It has also been correlated with conversion

fraction as tabulated in Table 3. The reaction kinetics of styrene monomer and polyester vinyl groups were determined by Equations 2 and 3 in terms of changes that occurred in the characteristic peak of the C=C bond at 982 cm<sup>-1</sup> and 912 cm<sup>-1</sup> before the reaction starts (A0) and after at different times (At) for USPET and styrene respectively.

$$X_{usp\text{et}} = 1 - \frac{A_t(982)}{A_o(982)} \dots\dots\dots (Eq. 2)$$

$$X_{st} = 1 - \frac{A_t(912)}{A_o(912)} \dots\dots\dots (Eq. 3)$$



**Figure 3. (a) FTIR spectra and (b) conversion fraction of unsaturated polyester resin at different curing times**

From Figure 3(a), as the curing time increased, the magnitude of the characteristic peaks 982 cm<sup>-1</sup> and 912 cm<sup>-1</sup> was found to decrease. The changes obtained in the magnitude of peaks (Xup and Xst) were quantified in terms of conversion fraction and shown in Figure 3(b).

**Table 3. Conversion of unsaturated polyester and styrene at different curing times**

Time (min)	USPET	Styrene	USPET %	Styrene%
0	0.279	0.115	27.9	11.5
5	0.421	0.432	42.1	43.2
10	0.508	0.612	50.8	61.2
15	0.721	0.734	72.1	73.4
20	0.725	0.839	72.5	83.9
25	0.742	0.873	74.2	87.3
30	0.815	0.919	81.5	91.9
35	0.901	0.931	90.1	93.1

From Table 3, the conversion of styrene and USPET was found to be less at the beginning of the reaction. This first stage was termed before the gel point was reached. This is because, at low conversions, the cross-linking density of the reacting system would not be sufficiently high to appreciably influence the propagation mechanism of the styrene and C=C bonds of unsaturated polyester resin. At the later stages of curing, the conversion of styrene steadily increases with time, while the conversion of polyester C=C bonds slows down. This fact is due to the formation of a highly cross-linked network, so propagation reactions become diffusion controlled [16]. Hence, the mobility of small styrene molecules is less affected by the increase of cross-linking density than that of C=C units in larger polyester molecules. The major reaction was found to be completed at the curing time of 35 minutes.

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## 4. Conclusions

The cure kinetics of USPET resin was studied in terms of gel time, curing temperature and curing time. The gel time study shows that (1, 1) wt % of MEKP and Co-octane in unsaturated polyester resin is favourable for the preparation of composites on the RTM machines. The variation with the curing temperature (Tiso) and the heat of reaction ( $\Delta H_{iso}$ ) characterizing the styrene homo-polymerisation and its copolymerization with the polyester chains were determined from isothermal DSC investigation, while the residual heat of reaction ( $\Delta H_{res}$ ) was revealed from non-isothermal measurements. The optimum curing temperature of USPET resin was found as 45°C. From FTIR investigation the conversion C=C bonds of polyester and styrene are determined and it shows that initially, the conversion was less while in a later stage the conversion of styrene C=C bonds increases. The optimum conversion of both reactants was found at a curing time of 35 minutes.

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## Declaration of conflicting interests

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