Effect of recycled ceramic waste particles on kinetic of curing and thermal degradation of unsaturated polyester resin

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Abstract: In this study, the effect of recycled ceramic waste particles on the curing reaction and thermal degradation of unsaturated polyester resin has been studied kinetically. Methyl ethyl ketone peroxide and cobalt octoate were used as initiator and promoter, respectively. The porcelain powder obtained from ceramic waste was used as filler. The effect of methyl ethyl ketone peroxide and porcelain powder were investigated by measuring the gel time and exotherm behavior. Also, thermal properties have been carried out using TGA at different heating rates in an argon atmosphere, and the results were analyzed by the Friedman method. The results indicate that the curing process is affected by the incorporation of ceramic particles in two ways. Therefore, the use of ceramic particles increases the induction time and decreases the exotherm properties of unsaturated polyester resin. In addition, the results obtained by Friedman method demonstrates that the incorporation of ceramic particles in the resin increases the activation energy, and consequently improves the thermal stability of unsaturated polyester resin.

Keywords: Unsaturated polyester resin; Ceramic particles, Gel time, Curing exotherm, Friedman method, Activation energy.

1. Introduction

Unsaturated polyesters (UPR) are the most widely used polymers in various application such as industrial construction, insulation [1], polymeric composites, etc.. These polymers have excellent dimensional stability [2], high impact resistance, transparency and superior weathering resistance [1]. Unsaturated polyester resins are used for these applications because of their low costs, easy processing, and ease of combination with reinforcement [2]. The curing process of UPR is a free radical chain-growth cross-linkage copolymerization between the double bond of unsaturated polyester and the double bond of styrene (reactive diluent).

The curing kinetics of the UPR system was investigated in recent years by different authors and has proposed various models to predict the curing behavior. Ramis et al. [3] investigated the curing kinetics of unsaturated polyester resin under isothermal (static) and non-isothermal (dynamic) conditions. They established a universal relationship of the type \( \ln(t) = a - b \ln(I) \), between the reaction time \( t \) and the initial initiator concentration \( I \). Cook et al. [4] developed a mathematical expression, which predicts the correlation of the gel time with the level of the three main species (inhibitor, initiator, and accelerator). Also, Yang et al. [5] correlated the curing conditions such as curing temperature, initiator concentration, and acceleration concentration with the gelation of curing of unsaturated polyester resins. Theoretically, the curing process of styrene-UP resins before gelation is expressed by four stages: induction, microgel formation, transition, and macrogelation, based on the microgel formation mechanism.

During the curing process at room temperature, generally the organic peroxides (like methyl ethyl ketone peroxide (MEKP) are mostly used as a catalyst (initiators) while cobalt salt is frequently used as an accelerator. The polyesters are prepared using three types of monomers-unsaturated acids, saturated acids, and glycols. In general purpose grades, these components are often maleic anhydride, phthalic anhydride, and propylene glycol.

The quality of finished products and the economy of the production process depending on the curing reaction. Most fillers are powdered minerals of one type or another, such as silica, alumina, china clay, Calcium carbonate. Fillers affect both the uncured and cured properties of resins. The setting time is modified in two ways. Physically, the exothermic reaction takes place in a larger mass than in unfilled resin, so that the temperature gain and hence the rate of hardening is reduced. Chemically, however, the filler can either accelerate or retard hardening. The addition of organic and inorganic fillers modifies the properties of polymeric articles, also decreasing the total cost of raw materials. However, in service conditions, these materials are
exposed to various stresses, thermal, chemical, and mechanical, which can involve significant losses of properties and compromise the integrity of the structures.

As regard to thermal decomposition kinetics, an alternative approach to kinetic analysis is to use model-free methods that allow for evaluating Arrhenius parameters without choosing the reaction model. Isoconversional methods are the most popular of the methods based on the use of multiple heating programs [6]. These methods yield the effective activation energy (E) as a function of the extent of conversion (α). Knowledge of the dependence E on α assists in both detecting multi-step processes and drawing certain mechanistic conclusions [6,7].

Several studies have been conducted on the kinetics of the thermal decomposition of unsaturated polyester resins. The kinetic analysis technique that was employed in this paper has several advantages [8]. By its use, it was possible to calculate activation energy for the main degradation process without any knowledge of the form of the kinetic equation. In the present work, an attempt has been made to understand the kinetics of curing and thermal degradation behavior in unsaturated polyester resin when ceramic particles were incorporated.

2. Experimental

2.1. Materials and specimen’s preparation

A commercial general-purpose orthophthalic polyester resin was employed. The specific gravity of the resin was 1.3, Viscosity at 25°C was 7.5-9 poises, the acid value was 20-30 mgKOH/g, and the styrene content was 34%. The porcelain powder (PP) (CP means equal mass percentages of UPR and PP) was obtained from ceramics waste of Settat city in Morocco. The average particle size as 180 µm with a density of 2.43 g.cm⁻³.

The resin (UPR) or resin filler (CP) was mixed with the appropriate amount of the peroxide initiator at 25°C. Then, the requested amount of cobalt accelerator was added and the mixture rapidly mixed. The gel time was determined manually by stirring from time to time. At the same time, the curing exotherm was measured by placing a thermocouple in the center of an appropriate amount of catalyzed resin or resin filler contained within a glass test-tube and initially maintained at 25°C. The exotherm rise (Texp) was corrected for heat loss to the environment using the heat balance method of Rojas et al. [9]. The following equations calculate the conversion values at each time:

$$T_{ad} = T_{exp} + \int_0^\alpha U' (T_{exp} - T_0) dt$$

$$\alpha = \frac{T_{ad} - T_0}{T_{ad,max} - T_0}$$

where $T_{ad}$ is the corrected temperature for adiabatic conditions, $T_0$ is the ambient temperature, $\alpha$ is the degree of conversion, and $U'$ is the ratio of the global heat transfer coefficient per unit mass to the specific heat, and assumed to be constant.

A plot of ln($T_{exp} - T_0$) vs. time gives a straight line from a certain time after the experimental maximum temperature. The $U'$ value is obtained by calculating the gradient of this line.

2.2. Thermogravimetric analysis

The thermal behavior of the UPR and CP was examined using the TA instruments (labsys TM Evo TGA-DTA 1600°C). The test samples, each weighing 20 mg, were heated in a platinum pan from 25 to 650°C with different heating rates of 10, 15 and 20°C.min⁻¹. The thermal decomposition temperature of each sample was examined under argon atmosphere with a 30 mL.min⁻¹ flow rate.

3. Results and discussion

3.1. Curing analysis

In general, the decomposition of the initiator MEKP with the aid of a metallic promoter may be expressed by the following equations:

$$ROOH + Co^{2+} K_{d1} \rightarrow RO + OH^- + Co^{3+}$$

$$ROOH + Co^{3+} K_{d2} \rightarrow ROO^\cdot + H^+ + Co^{2+}$$

where ROOH and Co represent the MEKP and cobalt species, $k_{d1}$ and $k_{d2}$ represent the rate constants for the formation of the alkoxy (RO•) and peroxy (ROO•) radicals, respectively.

The decomposition of ROOH is the rate controlling step in free radical polymerization. Beaunez et al. [10] have noted that the peroxy radical is much less reactive to the ethylenic monomers than the alkoxy radical and therefore, Eq.3 determines the initiation rate. Eq.4 is important, however, because in this case step, the $Co^{2+}$ is regenerated, giving a pseudo-stable state for the concentration of $Co^{2+}$. As a result, the rate of formation of alkoxy radicals is predicted to be approximately constant until the MEKP concentration is severely depleted as indicated by the reaction kinetics:

$$-\frac{d[ROOH]}{dt} = \frac{d[RO]}{dt} = K_{d1} [Co^{2+}][ROOH]$$

To investigate the curing behavior, the exotherm of UPR at three different content of MEKP of 2, 1.5 and 1 was measured at ambient temperature and constant content of cobalt octoate.

The effect of MEKP concentration on the exotherm behavior of the unsaturated polyester resin containing 0.5 wt% cobalt naphthenate solution is shown in Fig.1. It is observed that the induction time rapidly decreases with increasing of MEKP concentration. This is due to increases of decomposition of MEKP molecules and quickly produces alkoxy and peroxy radicals which initiate the polymerization reactions as described in the kinetic scheme and the Eq.5.
The time for gelation is critical to the resin application because it indicates the working time of the resin, which in turn, can be manipulated by variation in the concentration of the initiator.

The equation derived by Cook et al. [4] predicts the correlation of the gel time with the concentration of the three main species (inhibitor, initiator and accelerator). Cook et al.’s equation is written as:

\[ t_\text{gel} = \frac{[X]_0}{k_\text{gel}[ROOH][Co^{2+}]} \] (6)

This equation is similar to that derived by other workers [11]. For times larger than \( t_\text{gel} \), there are free radicals available to react with monomers and generate heat.

The gel-time results shown in Fig.3 confirm the acceleration of the reaction by increased levels of peroxide. As predicted by Eq.6, the gel time is reciprocally related to the initiator concentration over most of the initiator range investigated, which is in agreement with gel time results of other workers [4,12]. On the other hand, \( \Delta T_{\text{ad,max}} \) did not remain constant for MEKP values ranging from 1.0 to 2.0 wt% so that the initiator may be depleted before the completion of the reaction, and the reaction had not gone to completion as noted by Tang et al. [4]. In the measured exotherm data, the temperature then decreases due to heat loss to the environment: this stage is virtually eliminated in the heat loss corrected exotherm curves, which allow for this effect [4].

The times obtained by isothermal measurements for the UPR at different levels of MEKP are transformed according to the equation of Ramis et al. [3]. In Fig.2, the \( \ln(t) \) is plotted against the logarithm of initial concentration at different conversion. From the slope of the fitted curve, one obtains the kinetic parameters, \( b \), which indicates that \( b \) varies between 0.821 and 0.86. The values are very similar, suggesting no change in reaction mechanism. Vafayan et al. [12] found that the kinetic parameter, \( b \), for MEKP was increased from 0.8401 to 1.0047 when the degree of conversion risen from 8% to 80%.

Fig.2 shows that the relationship between \( \ln(t) \) and \( \ln(\text{MEKP}) \) was linear for all conversion and the regression coefficients between 0.994 and 0.999. This result demonstrates that the relationship established by Ramis et al. was valid for describing the curing of UPR with MEKP when the initial concentration varies between 1.0 and 2.0 wt%.

The effect of porcelain powder on the curing of unsaturated polyester resin is illustrated in Fig.4. It can be seen that adding a PP to the resin resulted in a delay in the cure reaction for free radical initiators systems. Besides, the temperature decreases significantly as the PP incorporates. For UPR, the decomposition of free radicals contributes to an increase in heat accumulation. Then, these results justify the effect of PP in the absorption of the heat of reaction, as suggested by other workers when using CaCO\(_3\) and glass fibers [13]. The incorporation of PP showed a decrease in temperature of reaction and therefore, a retardation effect on the cure reaction. The rise in gel time in the presence of PP can be
attributed to the retardation of the cross-linkage of the UPR and the absorption of the heat generated in the exotherm reaction. Other authors have suggested the same behavior. Rheological measurements carried out by Simitzis et al. [14] showed that the inorganic fillers, talc, and quartz, lead to an increase in the gel time delaying the crosslinking of the unsaturated polyester. The authors reported that the microgels formed cannot come close because they are impeded by the presence of the filler, with the consequence that the transition stage and then the macrogelation are retarded.

Reduction of the heat of the reaction was already described in the literature. Harsh et al. [15] investigated the effect of the quartz on the cure kinetics of an epoxy/anhydride resin. They found that the total heat of reaction decreases with the incorporation of the fillers. Therefore, the reduction of the total heat of reaction should be traced to the fact that the fillers adsorb the reacting monomers at their surfaces and thus affecting the stoichiometry and creating some sterical hindrance in respect to the forming network.

The Friedman method [8] utilizes the following logarithmic differential expression:

\[ \ln \left( \frac{da}{dt} \right) = \ln \left( \frac{\beta d\alpha}{dT} \right) = \ln(Af(\alpha) - \frac{E}{RT}) \]  

(8)

The activation energy, \( E \), over a wide range of \( \alpha \) can be determined by plotting \( \ln(\beta d\alpha/dT) \) against \( 1/T \) for a constant \( \alpha \). \( E \) represents the minimum energy required to transform a substance from a steady state to an activated state; it is a good description of how easily a material can be decomposed.

The above-mentioned thermal stabilities have been evaluating using TGA at three heating rates (10, 15, and 20°C min\(^{-1}\)). The obtained results are shown in Figs.5 and 6, which represent the mass loss and change of \( \beta d\alpha/dT \) respectively as a function of temperature. It’s shown that the behavior of both materials presents two steps of degradation between 130°C and 400°C. Similar behavior was reported in the literature [16]. The mass curves were shifted to high-temperature regions as the heating rate increased from 10 to 15, and 20°C min\(^{-1}\).

Kinetic parameters were calculated according to ICTAC recommendations [17]. Decomposition of cross-linked polymers in an inert atmosphere occurs in such a way that they tend to conserve the structure of their matrix. Thus, bond breaking inside the polymer matrix requires a large amount of energy.

The model-free approach to kinetic analysis rests upon the isoconversional principle, according to which the reaction rate at a constant extent of conversion is only a function of temperature. This fact implies that curves plotted at different heating rates cannot intersect. Therefore, an interval of temperatures 200-420°C was chosen for model-free kinetics calculations. To determine the kinetic parameters for the thermal degradation, we take out of 10 “\( \alpha \)’’ values from the samples at different heating rates and read the corresponding temperature from the original data in Fig.6.

According to Eq.8, the apparent activation energy can be evaluated from the slope of these linear relationships, and the results are shown in Fig.7. The obtained results from the applied Friedman isoconversional method suggest that the correlation of the regression lines is very good and the magnitude of correlation coefficient varies between 0.86 and 0.99, which shows that the isoconversional method Friedman is appropriate.

For UPR, an initial value of \( E \) about 105 kJ mol\(^{-1}\) at \( \alpha=0.05 \), slightly increases up to 126 kJ mol\(^{-1}\) at \( \alpha=0.10 \) and remain constant between 0.1 and 0.6. Afterward, a significant change follows, and the activation energy increases from 128 to 236 at 0.95. As regards the composites, an initial value of about 80 kJ mol\(^{-1}\) at \( \alpha=0.05 \), slightly increases up to 119 kJ mol\(^{-1}\) at \( \alpha=0.10 \) and remain constant between 0.1 and 0.55. Afterward, a significant increase follows, and the activation energy rises from 152 to 237 at 0.95.
Fig. 5 shows the apparent activation energy versus conversion obtained by the Friedman kinetic methodology. However, the E profile obtained indicates that the decomposition mechanism is a function of the conversion degree.

Baudry et al. [18] used the Ozawa method to calculate kinetic parameters for different phases of degradation. They reported that the low-value E typically correspond to depolymerization of styrene that constitutes the microcondules formed in the gelation process. They indicated that the value of E in intermediary degradation phase, which equal 170 kJ.mol\(^{-1}\) could be associated with the proper polyester network.

It is difficult to make comparisons between these results on single polymers and those found in similar studies carried out on the same unsaturated polyester resins, due to different operating conditions adopted (type of carrier gas, flow rate, heating rate), the method used for kinetic computations, various characteristics of polymers, such as additives, structure and molecular weight composition.

All these remarkable differences may be responsible for the wide range of E values reported in the literature. As an example, Mortaigne et al. [19] used using invariant kinetic parameter method for The degradation of unsaturated polyester. They found even significantly different E values for the degradation of two different samples of UPR (118 and 138 kJ.mol\(^{-1}\)), due to their different average molecular weights. In any case, the average E values calculated for degradation of UPR by the Friedman method in this study falls within the wide range reported in the literature, and the agreement is better with those derived by isoconversional methods. Similar founding was obtained by Tribelli et al. [20], they calculated activation energy by the invariant method of Lyon. The obtained results indicate that the E change with the conversion degree and the values are 50, 100, 133, ..., 206 at the conversion degree of 5, 5, 30, ..., 98%, respectively.
The E values of CP are higher than those of UPR. These results revealed that the presence of ceramic particles improved the thermal stability of composite, which was attributed to the physical barrier effect to prevent the transport of volatile decomposed products in the polymer composite as well as the excellent thermal stability of the PP particles.

In the case of composite, TGA kinetic analysis demonstrates that the introduction of ceramics particles into the UPR matrix could increase the E values of Unsaturated polyester resin, which was related to the improvement in the thermal stability of composite with the incorporation of porcelain powder.

4. Conclusion

The addition of ceramic particles powdered modifies the properties of curing and thermal degradation for unsaturated polyester resin, also decreasing the total cost of raw materials. Incorporation of ceramic particles in the formulation of unsaturated polyester resin reduces the temperature of reaction and consequently retarding the polymerization of free radical. The TGA data were analyzed kinetically by Friedman method indicating that the incorporation of ceramic particles increases the apparent activation energy. To understand these effects in depth, however, further investigation, like IR measurements, are needed.

References