



KINETIC STUDIES OF FLAME-RETARDANT UNSATURATED POLYESTER NANOCOMPOSITES: THE EFFECT OF ALUMINUM HYDROXIDE (ATH), AMMONIUM POLYPHOSPHATE (APP) AND NANOCCLAYS

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Abstract

In this work, we study the effect of nanoclay content, aluminum hydroxide and ammonium polyphosphate on the cure of a low-viscosity unsaturated polyester resin, by performing gel-time measurements at 40°C. Results show that, gelation phase decreases with increasing aluminum hydroxide content, ammonium polyphosphate roughly affects gelation and nanoclays have an unexpected effect on gelation. The gelation phase decreases significantly by incorporating 1 wt% of nanoclays, have a slight decrease with 5 wt% and remains roughly unchanged for 10 wt%. The cure rate is faster when nanoclays, ATH and APP are present. For quantities below 10 wt%, the maximum sample attained temperature and nanoclays increase together.

1 Introduction

Unsaturated polyester resins are extensively used in composite industry, because of their good mechanical properties, low cost and low density. Their processing involves a radical polymerization between a pre-polymer that contains unsaturated groups and styrene that serves both as solvent for the pre-polymer and as cross-linking agent. Moreover, the cross-linking process of the resin system significantly affects the physical, chemical, and mechanical properties of the polymer. Therefore, cross-linking changes the performance of the resulting composite: especially some elastic constants, impact behavior, temperature and aging performance. Thus a thorough understanding of the polymerization mechanism is desirable for better

design of, and control over, the properties of unsaturated polyester-based composites [1].

On the other hand, standard unsaturated polyester resins are highly flammable and produce large quantities of smoke and toxic gases [2, 3]. Their increasing commercial utilization may bring these polymers into fire situations at any time, adding urgency to the development of effective and environmental friendly flame retardant systems to reduce fire hazards. Commercially available fire retardants can be highly effective but they have some important disadvantages like, affecting negatively the quality (physical and mechanical properties) and cost of the final product and being harmful [2]. The concept of nanoscale reinforcement provides opportunity for synthesis of new polymer materials with unique properties [4, 5]. Nanoclays could also represent a rational alternative to the conventionally filled polyester because they have distinct advantages over traditional fire retardants on its related problem areas.

However, in spite of the large quantities of inorganic particulate fillers used in the industry, relatively little information is available in the literature discussing how these particulates influence the curing behavior of unsaturated polyester resins.

The gel time is one of the most important kinetic characteristics of curing, because it describes the attainment of a certain critical conversion responsible for the transition from the first to the second stage of the process, and is also a critical point in several composites manufacturing processes [6]. In resin transfer molding (RTM) process, mould filling must occur before gel time: i.e. while the resin remains in the liquid state [1]. One can therefore conclude that as flame retardant and nanoclay filled unsaturated polyester resin becomes

more common, knowledge about cure kinetic of these resin systems is fundamental for process optimization. It follows that composites processing in an RTM machine using filled unsaturated polyester resin can only be optimized if one understands these behaviors.

The purpose of this work is to study the effect of flame retardants as aluminum hydroxide and ammonium polyphosphate, and nanoclays on gel-time of an unsaturated polyester nanocomposite resin. For that, several samples were prepared by an ultrasonic mixing method and gel-time measurements were performed at ambient temperature.

2 Experimental set up

2.1 Materials

The UP resin used in this study was POLYLITE® 275 (REICHHOLD), containing about 45 wt% styrene, with an acid number value between 20 and a viscosity of 80 mPa.s. The nanoclays used for this study were a modified montmorillonite with the commercial name Dellite® 43B (Laviosa Chimica Mineraria Spa). The conventional flame retardants used were Aluminum Hydroxide (ATH) and Ammonium Polyphosphate (APP).

2.2 Preparation of samples

Prior to curing, unsaturated polyester resin was mixed by vigorous stirring with the desired amount (1%, 5% and 10% in resin weight) of nanoclays or (20%, 35% and 50% in resin weight) of ATH for 10 minutes at room temperature. An ultrasonic bath was then used for a period of 15 min to further disperse the clay in the resin. Blanks of pure UP (0% in weight of clay) were also prepared through the same method for reference.

2.3 Gel – time measurement

Gel-time measurements were performed in a Gel Timer instrument, model GELNORM®-TC. A test tube with 12g of resin mixed with 2 wt. % of catalyst, was placed into the support of the test unit with the measurement stamper and a thermocouple into the sample. The test tube was then placed in a thermostatic bath at a temperature of 40°C. During experiments, time (s), temperature inside the sample (°C) and temperature (°C) in the bath were registered on-line using computer data acquisition equipment.

3 Results

Polymerization was studied at 40°C with various nanoclays contents: 0, 1, 5 and 10 wt %,

different ATH contents: 20, 35 and 50 wt% and two APP contents: 20 and 35 wt%.

3.1 Evolution of temperature during the cure

All experimental results shown represent an average of two or three replicas. Figure 1 shows the reference experimental results for pure resin. The first slope represents the resin heating rate (heat from the water bath), the second slope of the curve reflects the resin cure rate (heat from the polymerization reaction).

In figure 1, the temperature plot represents the typical curing behavior of a UP resin. Two different polymerization phases have also been identified in the figure: the first phase, corresponding to branching/gelation, concludes in the gel point (t_{gel}), and the second phase (crosslinking) ends when the maximum temperature of the system is reached (T_{max}) and the system is cured. The elapsed time is listed by t_{Tmax} .

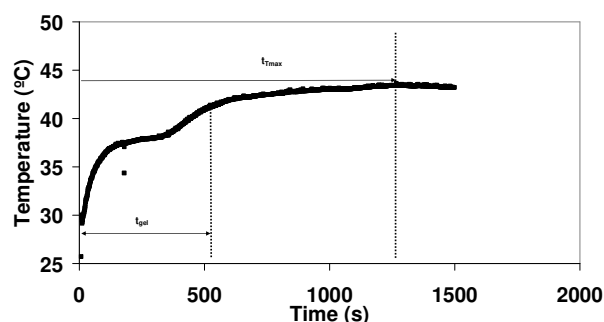


Figure 1 –Evolution of temperature during the cure, at 40°C, of pure resin.

3.2 Effect of ATH, APP and nanoclays on the gel- time and on the time of cure

The results for gel time measurements, maximum temperature and time for polymerization for the different tests performed are presented in Figures 2, 3 and 4.

Figure 2 shows the gel-time data for mixtures of UP resin with different amounts of nanoclays, ATH and APP. These experiments show clearly how ATH, APP and nanoclay content change gel time. As figure demonstrate, gelation phase decreases with increasing ATH content, APP roughly affects gelation and nanoclays have an unexpected effect on gelation. It seems that, ATH influence gel time mainly due to its consequence in resin viscosity: ATH raises resin viscosity and consequently the gel

time data measured by this technique. Apparently, APP does not increase the resin viscosity and is not a promoter of polymerization. These results must be explored by further experiments, namely by Viscometer and DSC measurements

On the other hand, gelation phase decreases significantly by incorporating 1 wt% of nanoclays, have a slight decrease with 5 wt% and remains roughly unchanged for 10%. It appears that, only lower quantities of nanoclays seem to act as promoters of branching. In previous works [7, 8], it was observed that t_{gel} decreases with nanoclays content and this was attributed to the fact that nanoclays act as promoters of polymerization

These results must be explored by further experiments, namely with XRD, TEM, Viscometer and DSC measurements.

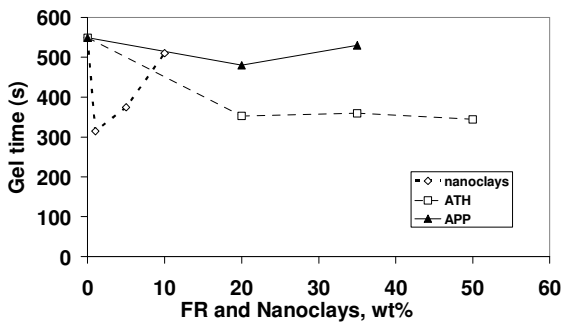


Figure 2 – Gel-time data for mixtures of UP resin with different amounts of nanoclays, ATH and APP.

The maximum temperature (T_{max}) and time of cure (t_{Tmax}) data for mixtures of UP resin with different amounts of nanoclays, ATH and APP are represented in Figure 3 and 4, respectively.

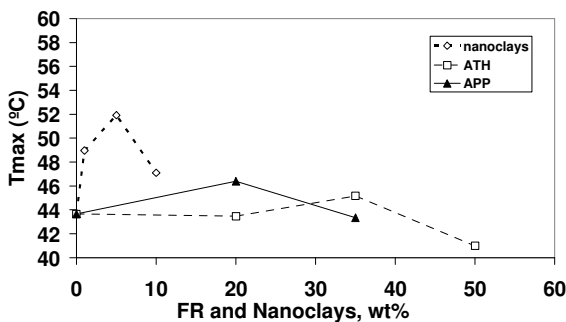


Figure 3 – Maximum temperature (T_{max}) data for mixtures of UP resin with different amounts of nanoclays, ATH and APP.

One observes that the maximum sample attained temperature T_{max} and nanoclays (below 10 wt%) increase together and the cure rate (t_{Tmax}) is

faster when nanoclays are present. Other authors [7, 8] concluded that nanoclay content does not affect the network formation during the course of the reaction and the final conversion at constant temperature. Even so, we are not able to infer a trend on the effect of nanoclay wt. % in cure rate and in T_{max} .

Regarding the effect of ATH and APP in the maximum sample attained temperature T_{max} , one can observe that only amounts of 20 wt% of APP and 35wt% of ATH have a slight positive effect. 50 wt% of ATH have a slight negative effect in maximum sample attained temperature T_{max} .

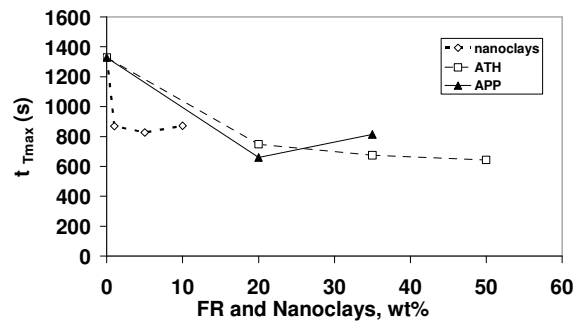


Figure 4 – Time of cure (t_{Tmax}) data for mixtures of UP resin with different amounts of nanoclays, ATH and APP.

One observes that increasing ATH wt. % amounts, faster cure rate happens. However we are not able to infer a trend on the effect in T_{max} . When, one have 20 wt% amount of ATH in the resin we have faster gelation (lower t_{gel}) and cure (lower t_{Tmax}) but generating the same amount of reaction heat (the same T_{max}). It seems that, ATH acts as heat consumer and this could explain what happens for 50 wt% amount of ATH, where, apparently the polymerization reaction do no release heat.

These results must be explored by further experiments, namely with XRD, TEM, Viscometer and DSC measurements.

4 Conclusions

The following main conclusions may be drawn from the present investigation, concerned with the influence on polymerization behavior of an unsaturated polyester network due to the addition of well defined quantities of nanoclay, aluminum hydroxide and ammonium polyphosphate:

- gelation phase decreases with increasing ATH content, APP roughly affects gelation and nanoclays have an unexpected effect on gelation;
- gelation phase decreases significantly by incorporating 1 wt% of nanoclays, have a slight decrease with 5 wt% and remains roughly unchanged for 10%. It appears that, only the lower quantities of nanoclays seem to act as promoters of branching;
- it seems that, ATH influence gel time mainly due to its consequence in resin viscosity: ATH raises resin viscosity and consequently the gel time data measured by this technique;
- apparently, APP does not increase the resin viscosity and is not a promoter of polymerization;
- that the maximum sample attained temperature T_{\max} and nanoclays (below 10 wt%) increase together and the cure rate ($t_{T_{\max}}$) is faster when nanoclays are present;
- one can observe that only amounts of 20 wt% of APP and 35wt% of ATH have a slight positive effect in the maximum sample attained temperature T_{\max} . Amounts of 50 wt% of ATH have a slight negative effect in maximum sample attained temperature T_{\max} ;
- it seems that, ATH acts as heat consumer and this could explain what happens for 50 wt% amount of ATH, where, apparently the polymerization reaction do no release heat.

The results obtained for nanoclays, ATH and APP are under exploration, namely by XRD, TEM, Viscometer and DSC measurements, and will be reported in a future paper.

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