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Effect of ammonium and aminosilane montmorillonites organo-clays on the curing kinetics of unsaturated polyester (UP) resin nanocomposites

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ABSTRACT

The curing kinetics of UP nanocomposites prepared by incorporating different amounts of two kinds of organo-montmorillonite (organo-MMT): trimethyloctadecacylammonium chloride (TMOA) and aminopropyl-triethoxysilane (APTES) were studied by non-isothermal differential scanning calorimetry (DSC) experiments. small angle X-ray scattering (SAXS) was used for measuring the *d*-spacings in the modified organo-clays, and no intercalation UP into these clays was observed for the nanocomposites. HRTEM images showed dispersed and agglomerated platelets in UP/APTES 2 and 10 wt%. DSC analysis showed two peaks in UP resins and UP/organo-MMT, and a decrease in the exothermal peaks temperature (T_{p1} and T_{p2}) for nanocomposites with the heating rate as compared with those of neat UP system; thus, the higher the heating rate, the higher the curing reaction rate. This effect was more clearly on the UP/MMT-APTES nanocomposites. The effective activation energies (E_a) were determined with the mode-free isoconversional Starik's method. Sesták–Berggren model was chosen to simulate the reaction rate with a good match achieved. Thermal gravimetric analysis showed that the cured UP/APTES at high concentration were slightly more stable than UP and TMOA.

1. Introduction

Unsaturated polyesters (UPS) are economical thermoset materials extensively used due to their excellent processability and good mechanical properties when cured [1]. Unsaturated polyesters are commonly reinforced with inorganic particles, such as talc, mica, carbon black, and fused silica [2–15]. Montmorillonite (MMT) is a crystal structure showing two-dimensional layers formed by fusing two silica tetrahedral sheets with an edge-shared octahedral sheet of either alumina or magnesia (T–O–T). Stacking of these layers leads to van der Waals gaps or galleries [2,16,17]. The galleries (alternatively referred to as interlayers) are occupied by cations, typically Na^+, Li^+ and/or Ca^{2+}, which balance the charge deficiency resulting from isomorphous substitution within the layers (e.g., tetrahedral Si^{4+} by Al^{3+} or octahedral Al^{3+} by Mg^{2+}). Layered clay can be intercalated or exfoliated by organic polymers to form nanocomposites [18–20]. Both intercalated and exfoliated nanocomposites exhibit significantly enhanced properties when compared to the neat polymers or conventional composites at concentrations of 1–10 wt% [18–20]. Generally, the hydrophilic pristine layered silicates would be intercalated using organic ammonium or phosphonium salts via cation exchange reaction to improve the affinity of inorganic layered silicates with organic polymers [8,18–25]. However, there is always the possibility of degradation of the quaternary ammonium salt through the well-known Hofmann's process (β-elimination), which depends on the basicity of the anion, the steric environment around the ammonium, and temperature [18,22,26]. The multiple pathways are attributed to a fraction of excess (unexchanged) surfactant and the chemically heterogeneous morphology of the layered silicate. Catalytic sites on the aluminosilicate layer reduce the thermal stability of a fraction of the surfactants by an average of 15–25 °C [18]. Thus, organoclays prepared by using quaternary alkyl ammonium salts are less suitable for most engineering plastics with high processing temperature (above 250 °C) [17,19,22,27]. For this reason, the silylation approach involving direct grafting reaction by using a coupling agent has recently attracted much attention, and represents a viable method to make compatible inorganic platelets and organic matrices [20–23,28–33]. The presence of broken bonds on the platelet edges are common for layered silicates, and leads to the formation of hydroxyl groups, which are suitable for chemical modification by silylation reaction [17,30]. By using an organosilane, it is then

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possible to covalently bond the organic functional groups onto the layer surface at three different sites: the interlayer space, the external surface, and the edges [17,30,34,35]. In addition, the organic tail of each aminosilane molecule can have not only $-CH_2$ groups, which are hydrophobic, but also one or more $-NH_2$/NH-groups, which are endowed with hydrophilic character, and capable to originate both intra- and inter-molecular hydrogen bonds [17].

On the other hand, the kinetics study of UP/St systems has shown that the presence of nanoclay greatly enhances the reaction rate. The long chain alkylammonium-modified silicates can act as auxiliary accelerators in the redox reaction of UP/St systems [1]. One of the most widely used techniques for studying the kinetics of the cure reaction of thermosetting resins is differential scanning calorimetry (DSC) in dynamic mode followed by kinetic analysis using isoconversional method [35–40].

The aim of this study was to investigate the effect of two commercial organoclay (trimethyloctadecacylammonium chloride and 3-aminopropyltriethoxysilane) on the cure kinetics, intercalation or exfoliation process and thermal stability of the UP resin. For this purpose, non-isothermal DSC measurements have been carried out to reveal the cure behavior of these UP systems and the isoconversional approaches are used to model the kinetics of the curing reactions. Small angle X-ray scattering (SAXS), transmission electron microscopy (HRTEM) and thermal gravimetric analysis (TGA) were used to check if exfoliation or intercalation of the organo-MMT in the UP resin systems took place.

2. Theoretical section

DSC is an analytical method convenient for investigating exothermic reactions of UP resins due to its great accuracy and easy sample preparation. Reaction heat measured with DSC could be correlated with fractional conversion and reaction rate, as expressed by Eqs. (1) and (2), respectively [37–40]:

$$\alpha = \frac{\Delta H_t}{\Delta H_T} \tag{1}$$

α is the conversion at time t, ΔH_t is the reaction heat at time t, and ΔH_T is the total reaction heat.

$$\frac{d\alpha}{dt} = \frac{d\Delta H_t/dt}{\Delta H_T} \tag{2}$$

where $d\alpha/dt$ is the conversion rate at time t, and can be expressed as:

$$\frac{d\alpha}{dt} = \frac{d\Delta H_t/dt}{\Delta H_T} = k(T)f(\alpha) \tag{3}$$

where $f(\alpha)$ represents a function of α as independent variable, while $k(T)$ represents temperature-related reaction rate constant, and could be acquired according to the Arrhenius equation [39]:

$$k(T) = A \ \exp\left(-\frac{E_a}{RT}\right) \tag{4}$$

where A is the frequency factor, E_a represents the activation energy, and R is the universal gas constant (8.314 J/molK). Combining Eqs. (3) and (4) yields:

$$\frac{d\alpha}{dt} = A \ \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \tag{5}$$

The temperature program can be isothermal (at fixed T) or non-isothermal, $T = T(t)$. The most common non-isothermal program is the one in which the temperature changes linearly with time, so that [39]:

$$\beta = \frac{dT}{dt} = \text{const} \tag{6}$$

where β is the heating rate.

For constant heating rate non-isothermal conditions, Eq. (6) is frequently rearranged as:

$$\beta\frac{dT}{dt} = A \ \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \tag{7}$$

For better understanding of the kinetics of non-isothermal UP curing reactions, iso-conversional technique, such as Starink's [39] method is widely used due to its simplicity and accurate estimates of E_a are achieved when setting $B = 1.92$ and $C = 1.0008$ according to:

$$\ln\left(\frac{\beta_i}{T_{\alpha,i}^{1.92}}\right) = \text{const} - 1.0008\left(\frac{E_a}{RT_\alpha}\right) \tag{8}$$

where T_α is the absolute temperature at a certain conversion α obtained in the DSC curve at a particular heating rate.

Eq. (3) describes the rate of a single-step process. The overall transformation can generally involve more than a single reaction or, in other words, multiple steps each of which has its specific extent of conversion. For example, the rate of the overall transformation process that involves two parallel reactions can be described by the following equation [37,38]:

$$\frac{d\alpha}{dt} = k_1(T)f_1(\alpha_1) + k_2(T)f_2(\alpha_2) \tag{9}$$

In Eq. (9), α_1 and α_2 correspond to specific extents of conversion of two individual reactions (steps), and their sum yields the overall extent of conversion: $\alpha = \alpha_1 + \alpha_2$.

The steps should be separate (e.g., by using deconvolution methods) to analyze their kinetics individually. The principle continues to work as a reasonable approximation because iso-conversional methods describe the process kinetics by using multiple single step kinetic equations in a narrow temperature range (ΔT) related to this conversion. As a matter of fact, the E_a dependencies evaluated by an isoconversional method allow for meaningful mechanistic and kinetic analyses as well as for reliable kinetic predictions [39].

According to the Malek's method, apparent activation energy E_a for a non-isothermal process must be known previously (Eq. (8)), and then the two special functions $y(\alpha)$ and $z(\alpha)$, Eqs. (10) and (11), can be defined as the diagnostic signatures for determination of reaction models and for calculation of model parameters [36,39,40].

$$y(\alpha) = \left(\frac{d\alpha}{dt}\right) \exp(x) \tag{10}$$

$$z(\alpha) = \pi(x)\left(\frac{d\alpha}{dt}\right)\frac{T}{\beta} \tag{11}$$

In Eqs. (10) and (11), x is the reduced activation energy E_a/RT and $\pi(x)$ is the function of temperature integral, which can be numerically approximated with sufficient accuracy using a fourth-order rational equation derived by Senum and Yang [36,40]:

$$\pi(x) = \frac{x^3 + 18x^2 + 88x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120} \tag{12}$$

Then, they examine the conversion peaks (α_M, α_p^∞) of the normalized $y(\alpha)$ and $z(\alpha)$ functions and conversion α_p corresponding to maximum experimental rates satisfying a set of specific conditions proposed by Malek [36,39,40]. Thus, one can probably confirm an appropriate kinetics model and further obtain a method to calculate model parameters.