# Epoxy + Montmorillonite Nanocomposite: Effect of Composition on Reaction Kinetics

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The objective of this investigation is to determine the effects of montmorillonite layered silicates on the curing kinetics of an epoxy resin. Differential scanning calorimetry was used to probe the changes in reactivity due to the presence of montmorillonite and due to the diamine hardener. The enthalpy of polymerization was strongly affected at compositions greater than 5% (wt) montmorillonite for epoxy + montmorillonite reactions. On introduction of the hardener, epoxy + amine kinetics dominate the reaction for all compositions except for a montmorillonite concentration of 2.5 wt%. X-ray diffraction was used to determine if the reacted system was exfoliated. The results show a strong montmorillonite composition dependence on the exfoliated state. Transmission electron microscopy of the cured epoxies confirmed a mixed intercalated and exfoliated dispersion at compositions having montmorillonite greater than 2.5 wt%.

## INTRODUCTION

Polymers modified by introduction of smectic clays hold promise for improvement in tensile strength, modulus and heat distortion temperature. Layered silicates belong to the family of 2:1 layered silicites (1, 2). The crystal structure consists of two silica tetrahedra fused to an edge shared octahedral sheet of either alumina or magnesia (1, 2) Stacking of these layers lead to a regular van der Waals gap between them called the interlayer or gallery. Isomorphic substitution within the layers generates negative charges that are normally counterbalanced by cations residing in the interlayer. Pristine layered silicates usually contain hydrated Na+ or K+ cations. These can be replaced by ion exchange reaction with cationic surfactants, including primary, tertiary and quaternary ammonium to render the normally hydrophilic silicate surface organophilic.

Prior research on platelet surface modification of montmorillonite clays for epoxy nanocomposites has shown that ion exchange treatment with onium cations of amine functionality is an effective treatment to encourage intercalation (3). The primary role of the alkyl ammonium cations in the organosilicate is to lower the surface energy of the inorganic layers. More cations might be thought to improve the organic wetting of montmorillonite, but a high charge density clay actually interferes with the spaces available for monomer or polymer intercalation (4). The secondary role of the onium cation is to act as a pillar. In this case the cation length, not the number of cations, defines the intercalation distance that separates the platelets. This was initially demonstrated for epoxy swelling (5); but it also appears to hold true for other systems as shown by polyurethane (6).

Unfortunately, the intercalated state may not be stable in some mixtures. Theoretical analysis by Gianellis (7) did much to help elucidate the nature of the competitive forces at work in terms of phase stability. A change in the volume fraction of the montmorillonite might act to alter the apparent interaction parameter; this can result in a drawing out of the polymer from the gallery interlayer to participate in a

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more favored state outside the gallery. This immiscibility would result in a return of the treated montmorillonite to the status of a simple filler rather than a true nanoscale reinforcement.

Introduction of epoxy into the treated montmorillonite can result in two kinds of morphologies. At first, the montmorillonite swells as the silicate layers move apart, yet regular spaces between layers can still be maintained. This morphology is *intercalation*. Finally, sufficient distortion of the regular structure causes *exfoliation* as individual platelets move far enough apart to form layers that are not parallel with each other. Mass transport of polymer into the gallery is the rate determining step of intercalation (8).

A new strategy was required to keep the epoxy monomer or polymer between the silicate layers. The first practical solution was found by Messersmith and Giannelis (9), who thought to directly bond montmorillonite to reactive epoxy monomer. They thought this would improve the strength of the montmorillonite-polymer interface. This was an effective procedure to help induce and keep intercalation of the montmorillonite, as well as produce large amounts of the exfoliated state (10). It was later clarified (11) that the ion-exchanged cations at the surface of the treated clay facilitate opening of the strained epoxide ring.

The mechanical properties of later consolidated epoxy nanocomposites have shown mixed results to date. For an Epon 828 resin cured with m-phenylenediamine marginal improvement in mechanical properties was reported (12). The limited improvement was tied to the high $T_g$ of the epoxy matrix. Subsequent work that targeted a low $T_g$ epoxy used Jeffamine D2000 polyether amine to obtain a sub-ambient $T_g$ (13). For each of these studies, montmorillonite was added to a mixture of resin and hardener. Tensile modulus was increased from 2.5 MPa for the base epoxy resin to 7.5 MPa for 5% montmorillonite. The increase in strength for low $T_g$ epoxy was partly attributed to a natural increase in plasticity due to the presence of nanoclay, and partly due to an ability of the nanoclay platelets to reorient further as well as more quickly above the $T_g$. It was thought that the mechanism of platelet orientation at large strain provides improved platelet alignment in the direction of the strain field for reinforcement.

Three methods are available to prepare nanocomposites for two part reactive systems. Mechanical mixing of nanoclay into the curing agent can permit a room temperature dispersion. For the system reported here, agglomeration was observed by light microscope to indicate nanoclay dispersion in the amine hardener curing agent was not a favorable method. The second preparation method is a resin dispersion at elevated temperature. This method has three potential drawbacks. The first is deactivation of nanoclay reactive sites with monomer. The second is early exfoliation that affects workability by an undesired increase of viscosity. The third is reduction in pot life with the hardener. Identification of the upper temperature and time limit for preparation with allowance for expected variability can address the first two issues. The reduced pot life may actually be desirable provided that nanoclay dispersion can be assured. The third method combines the mixture of all three components at once. This technique suffers a major limitation at greater than 7% concentration by weight of nanoclay. Premature uncontrolled exotherm or "runaway reaction" will start at local clumps in the mixture typically found at high concentrations of nanoclay. The cure reaction increases and results in an uncontrolled exotherm runaway reaction unless subambient mix precautions are taken. The required extent of cooling can result in undesired high viscosity that impacts workability at high nanoclay concentration. Therefore use of the three part mixture preparation is limited to low concentrations of nanoclay.

In each of the above preparation techniques, any aid to speed diffusion of polymer into the nanoclay is desirable. Ultrasonic treatment has been widely recognized. Treatment by vacuum degas is also widely recommended to permit better wetting of the nanoclay by removal of gas inclusions (14).

## EXPERIMENTAL

The epoxy resin used was a Bis-phenol A diglycidylether Epon 828 from Shell Chemical Company. The hardener was an amine curative hardener, Jeffamine D-230 provided by Huntsman Chemical Corporation whose chemical formula is Poly(oxy-(methyl-1,2-ethanediyl)), alpha-(2-methylethyl) omega- (2-aminomethylethoxy)-amine. The nanoclay provided by Nanocor is octadecylammonium salt of Montmorillonite, a derivitized form of bentonite clay designated I30.E, formula $[CH_3\ (CH_2)\ 17NH_3(+)(-)[Mg_{0.54}\ Al_{3.38}](Si_{7.64}\ Al_{0.36})\ O_{20}\ (OH)_4]$.

Epoxy resin was mixed with silicate nanoclay for 1 hour at 80°C and degassed at this temperature. The pre-mix was then allowed to cool to room temperature. Samples of the resin and nanoclay premix were set aside for test. Jeffamine hardener was then added in stoichiometric proportion to the epoxy resin. This three component mixture of nanoclay, hardener, and epoxy resin shall be designated as the "three-part mixture." Epoxy–nanoclay three-part mixtures were prepared containing 1, 2, 2.5, 3, 5, 7, 10 and 15% nanoclay by weight. Samples from each of these preparations were stored at −65°C for the later DSC test.

A second degassing of each of the three part mixture was required prior to curing. Panels were then cast from each three-part mixture in open top rectangular solid molds prepared with a (DuPont) Teflon release. The mixture was then cured for twelve hours at 60°C. These panels were then post-cured at 105°C for twelve hours to ensure complete curing. That portion of the two-part mixture of epoxy and nanoclay prior to the addition of hardener shall be referred to in this work as the "resin premix." X-ray samples were prepared from rectangular thin section slices cut from each resin panel with a water-cooled carbide saw.

Differential Scanning Calorimetry was conducted on a Rheometrics High Temperature Model PL-DSC. The resin premix was tested at a constant heat rate of 5°C/minute from 25°C to 300°C. Unreacted three part mixtures of epoxy, hardener, and nanoclay were tested at a constant heat rate of 2, 5, and 10°C/minute from 25 to 290°C to determine reaction kinetics. Prior to testing, the epoxy + montmorillonite mixture was sheared at 80°C for 1 hour. The mixture was cooled and hardener introduced. Following the curing test, these samples were cooled to 25°C with liquid nitrogen, equilibrated for 15 minutes at room temperature, and tested again at a heat rate of 10°C/minute and over the same temperature range to determine the glass transition temperature and to confirm cure completion. The glass transition temperature was determined by the midpoint method for each nanoclay concentration in the three-part mixture.

X-ray diffraction was conducted with a Siemens D-500 diffractometer using CuKα radiation (λ = 1.54056 Å). The tube source was operated at 40 kV and 30 mA. Scans were run between 2 and 35 degrees 2θ at a scan rate of 0.01°/sec and a 0.05 sec dwell time. A divergent slit width of 1° was chosen after testing various size divergent slits to minimize scattering from the sample holder at low angles.

## RESULTS AND DISCUSSION

Reaction between just the montmorillonite and the epoxy was used to clarify the chemical effect of the montmorillonite presence prior to the addition of the hardener. The oxyrane ring is the active functional group in epoxy. This ring becomes unstable and hydrolyzes at elevated temperatures. Epoxy ring-opening reaction in resin-montmorillonite premix may be affected as a result of nanoclay dispersion. Two distinct DSC peaks in the reaction of epoxy in montmorillonite clay reported in (11) were attributed to a difference in the concentration of reactive acidic onium protons inside the nanoclay gallery as compared with the chemical environment outside the gallery.

The single peak observed for 2°C/minute for a 1% and 5% by wt nanocomposite is shown in *Fig. 1* indicates the acid protons from inside or outside the nanoclay galleries behaved no differently in the attack of the epoxide ring. It was therefore concluded that the gallery environment in the premix was not sufficiently different to cause the peak splitting effect observed in (11). The preparation used here was 80°C with a 1 hour shear, whereas the preparation reported in (11) was 75°C with a 1-hour shear. A better dispersion at elevated temperature may explain the desirable single peak results. Enthalpy as a function of composition for the resin premix is shown in *Fig. 2*. As can be seen, minimal change in enthalpy is observed for compositions having less than 5 wt% montmorillonite. This is related to the incidence of platelet aggregation above 5 wt% montmorillonite through increased turbidity of the mixture. When hardener is introduced into the epoxy + montmorillonite mixture, there is a significant change in the concentration effect of the montmorillonite on the epoxy (*Fig. 3*). Introduction of 1% montmorillonite by weight decreases the reaction enthalpy but after that there is little change in enthalpy except for a peak value at 2.5% montmorillonite by weight. We note that above 2.5 wt% montmorillonite a critical concentration is established analogous to the critical micelle concentration in surfactant sols. This is shown in the scanning electron micrograph in *Fig. 4*.

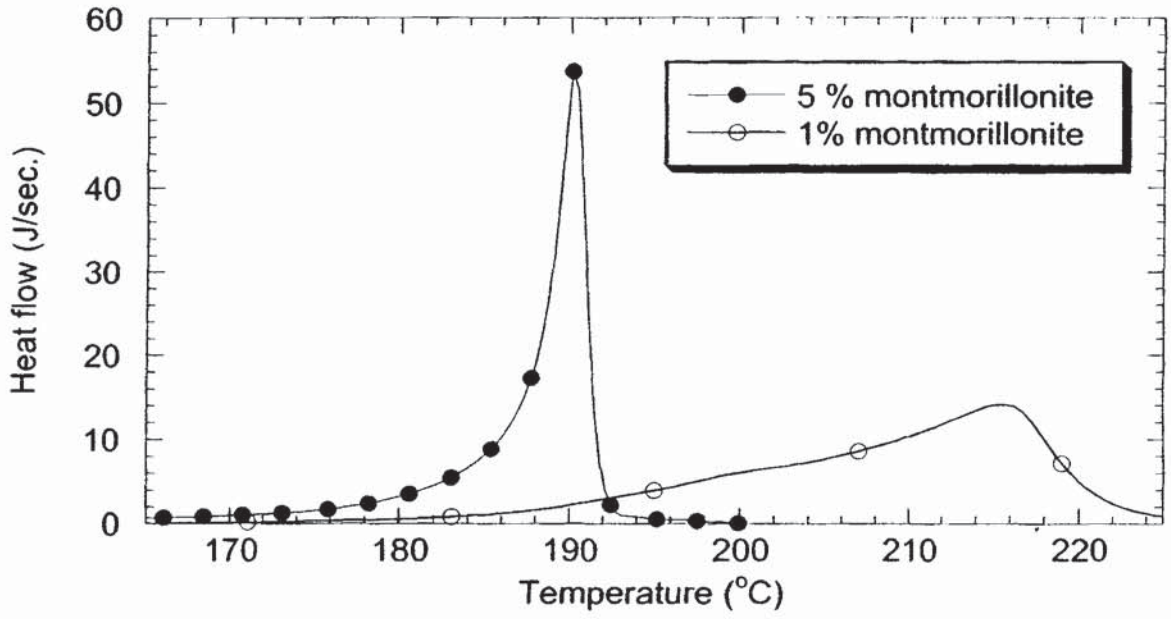



*Fig. 1. DSC results for epoxy monomer with 1% and with 5% montmorillonite at 2°C/minute.*

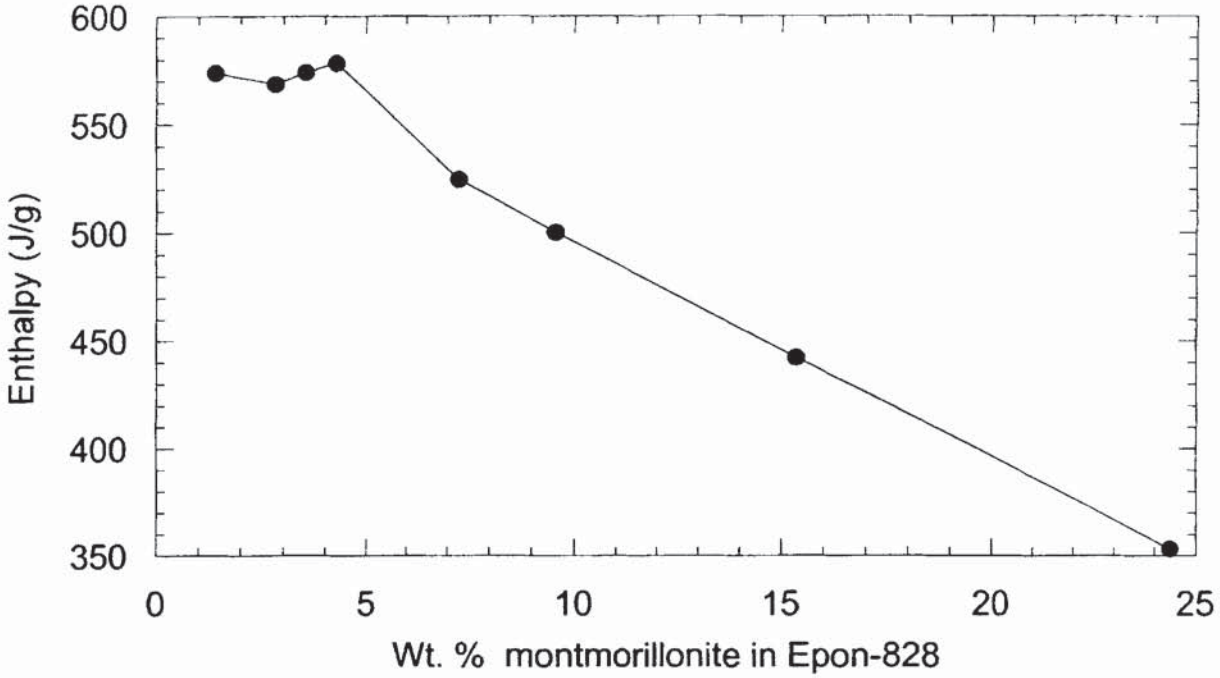



*Fig. 2. Enthalpy of self-polymerization of epoxy at 5°C/minute.*

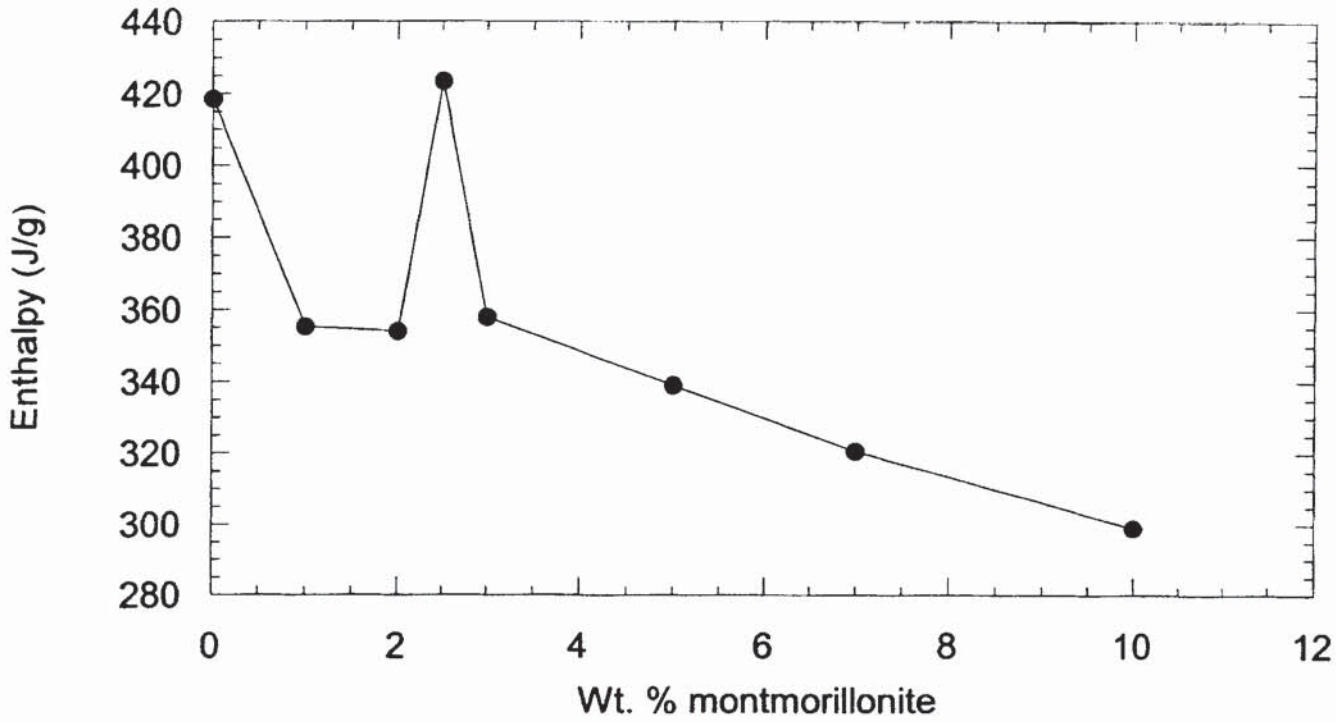



*Fig. 3. Concentration effects of montmorillonite on the enthalpy of three-part mixtures.*

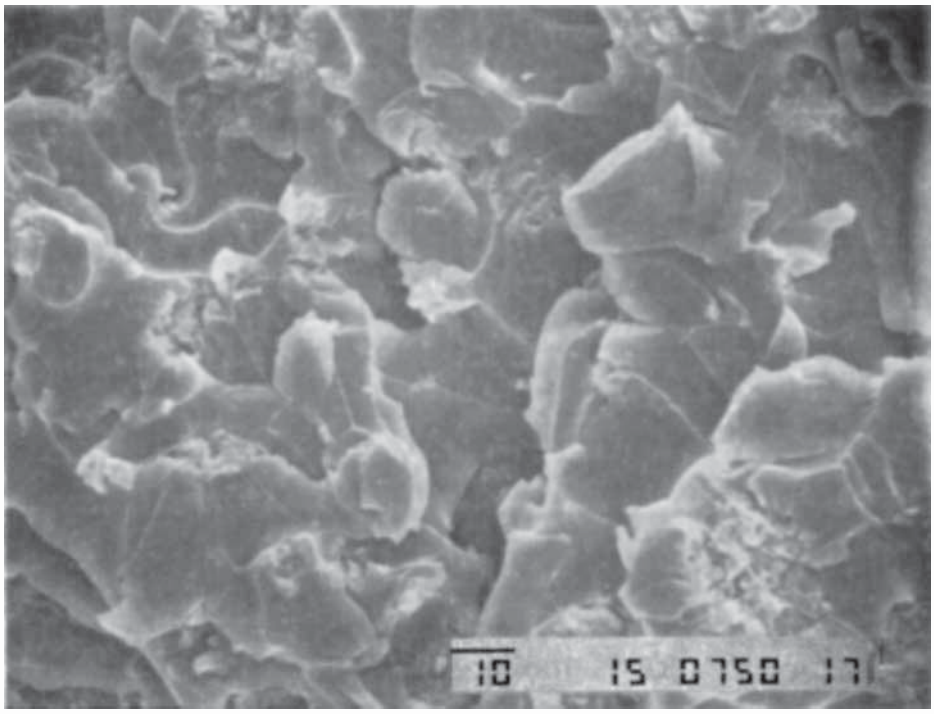



*Fig. 4. Scanning electron micrograph of platelet aggregation at 2.5% montmorillonite by weight.*

Reaction kinetics were analyzed from the dynamic scans using *Eq 1*.

$$k = Ae^{\left(\frac{-E_a}{RT}\right)^n} \quad (1)$$

Where:

$A$ = pre-exponential factor; $E_a$ = activation energy in J/mole; $R$ = 8.3144 ideal gas constant in J/(mole K), $T$ = Temperature in degrees Kelvin, $n$ = reaction order.

Activation energy of the reaction and pre-exponential factors were calculated. For the activation energy, the temperature ($T_{max}$) where the maximum reaction rate was observed at each of four constant heat rates was used to construct straight line plots of ln(heat rate/$T_{max}^2$) versus ($1/T_{max}$). The slope of this line is the activation energy. The activation energy is plotted as a function of nanoclay content in *Fig. 5*. A detailed review of the basic relationships for kinetic studies of cure has been written by Yousefi *et al.* (15).

The pre-exponential or frequency factor (A) was found from the activation energy and the temperatures of the maximum reaction rate according to *Eq 2* and adjusted by a factor of 1.052 to correct for non-isothermal kinetics. This correction is according to the general method for polymeric reactions (16, 17) and has been applied to reactive polymers with nanoclay (18):

$$A = \frac{\frac{dT}{dt} E_a e^{(E_a/RT)}}{RT^2} \quad (2)$$

Where: $dT/dt$ = heat rate, in °K / minute.

The corresponding activation energy and pre-exponential factor are shown in *Figs. 6* and *7*, where peak values are found again at 2.5% montmorillonite by weight. Independence of the Arrhenius frequency factor at all other compositions plotted from the heat rate of test shows the rate of cure was not limited by diffusion of epoxy and hardener through the nanoclay on a molecular level. This indicates each reactant was labile, or had sufficient energy to be free to move at each test temperature. The frequency factor used to calculate this effect can be explained by quantum mechanics. A time lag for the reaction might be observed even though the energy to go from products to reactants has not been altered. At any given constant temperature, a given population has a distribution of reactants that have a certain level of energy. Only those molecules that express sufficient energy at a given moment can overcome the activation energy barrier to react. When only a small amount of reactant molecules possess this energy in a given population, then the probability is that it will take a long time for some of them to attain the correct energy state. If the temperature is increased, this increases the probability of finding more reactants in the desired reactive state. The frequency factor is therefore a constant that expresses that population of reactants ready to react.

The consistent occurrence of a peak in kinetics, especially activation energies, show that at 2.5% a critical concentration of montmorillonite is achieved. This behavior was evident for all heating rates. Confirmation of a change in the reactivity as a function of concentration is shown in *Fig. 7* by the trend in

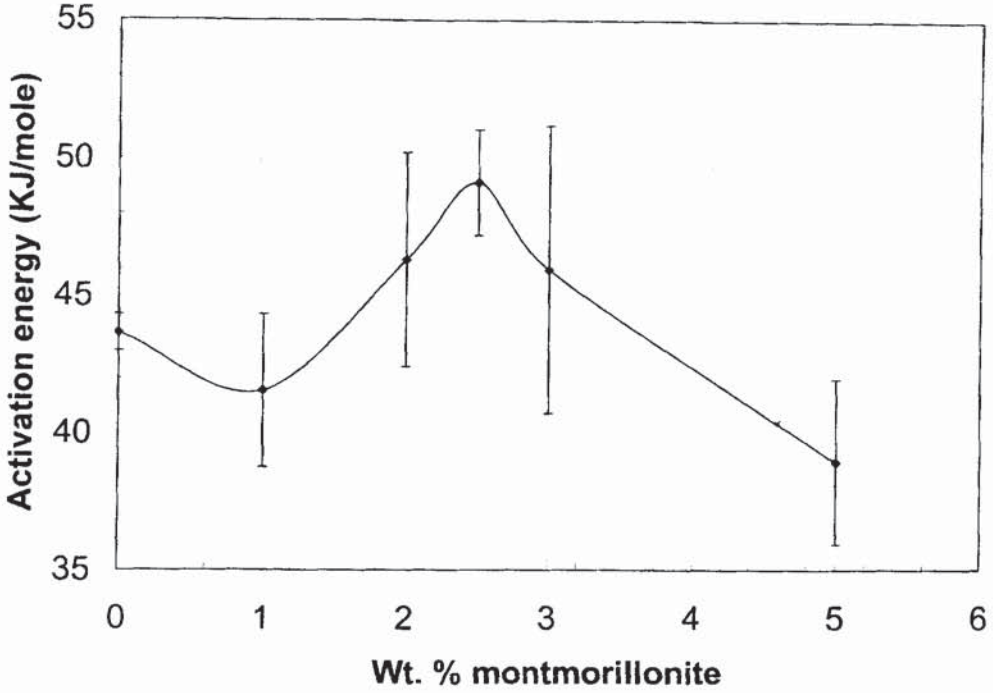



*Fig. 5. Activation energy for cure of Epon 828, nanoclay, and amine hardener.*

the temperature of the maximum reaction rate as a function of montmorillonite concentration as shown for 5°C and 10°C per minute.

X-ray diffraction patterns for the nanoclay and composites are shown in *Fig. 8*. The X-ray pattern of the treated montmorillonite clay shows a strong 001 reflection at $2\theta = 3.72°$, corresponding to the interlayer spacing of the regular stacked nanoclay structure, and the 002 reflection at $2\theta = 8.02°$. Since the chemical formula for the nanoclay is not that for an ideal

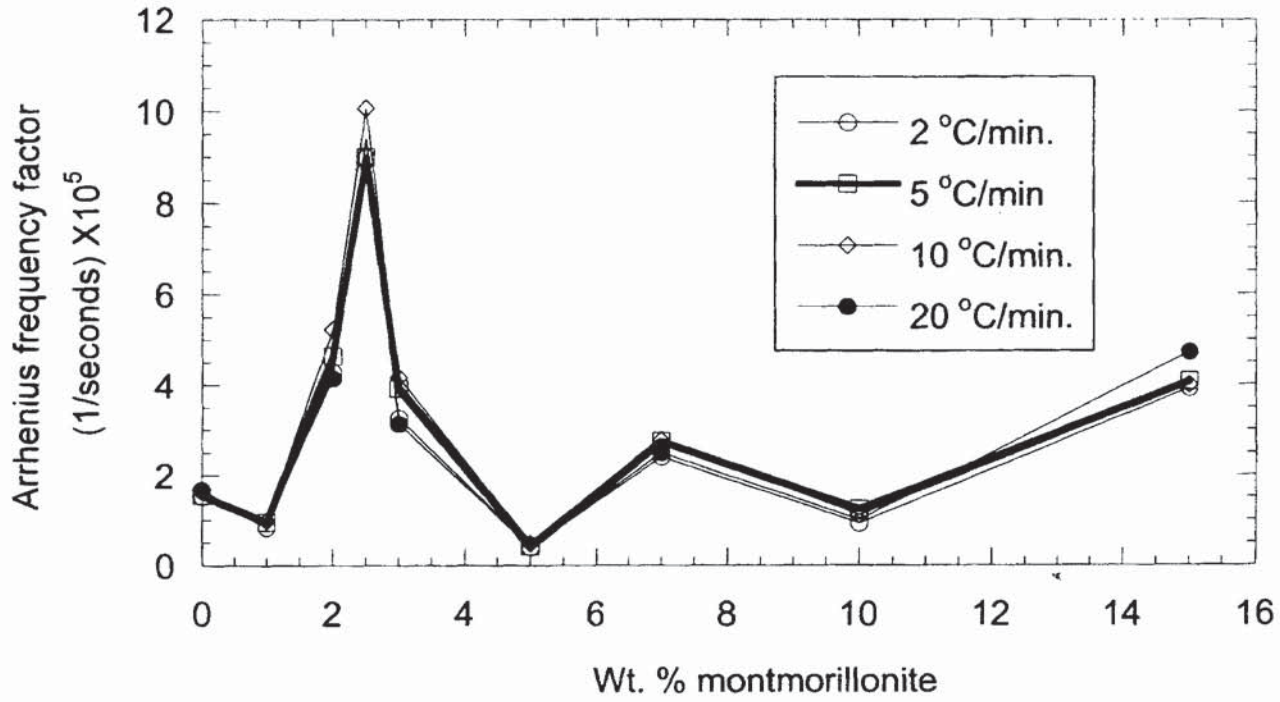



*Fig. 6. Arrhenius frequency factor for the cure of three-part mixtures.*

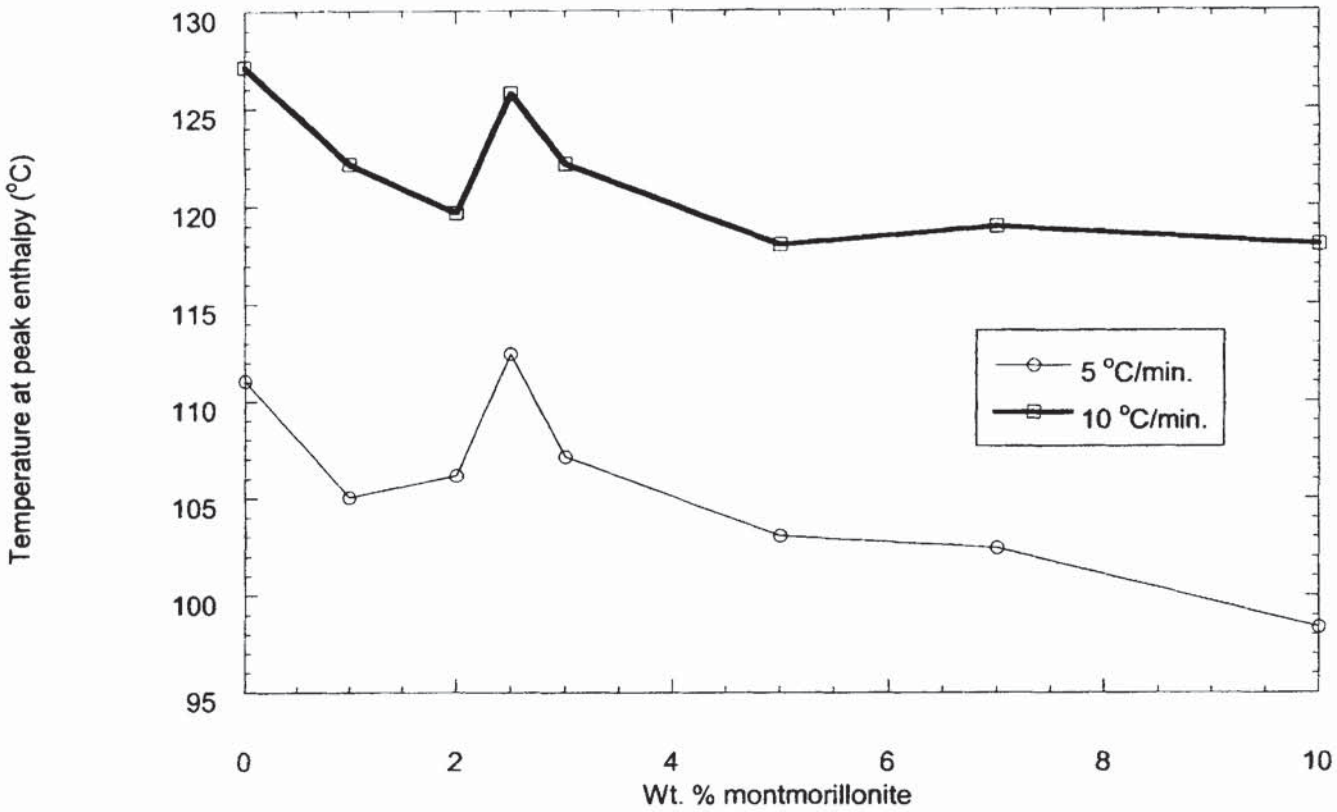



*Fig. 7. Concentration effect on peak exotherm temperature for cure of three-part mixtures.*

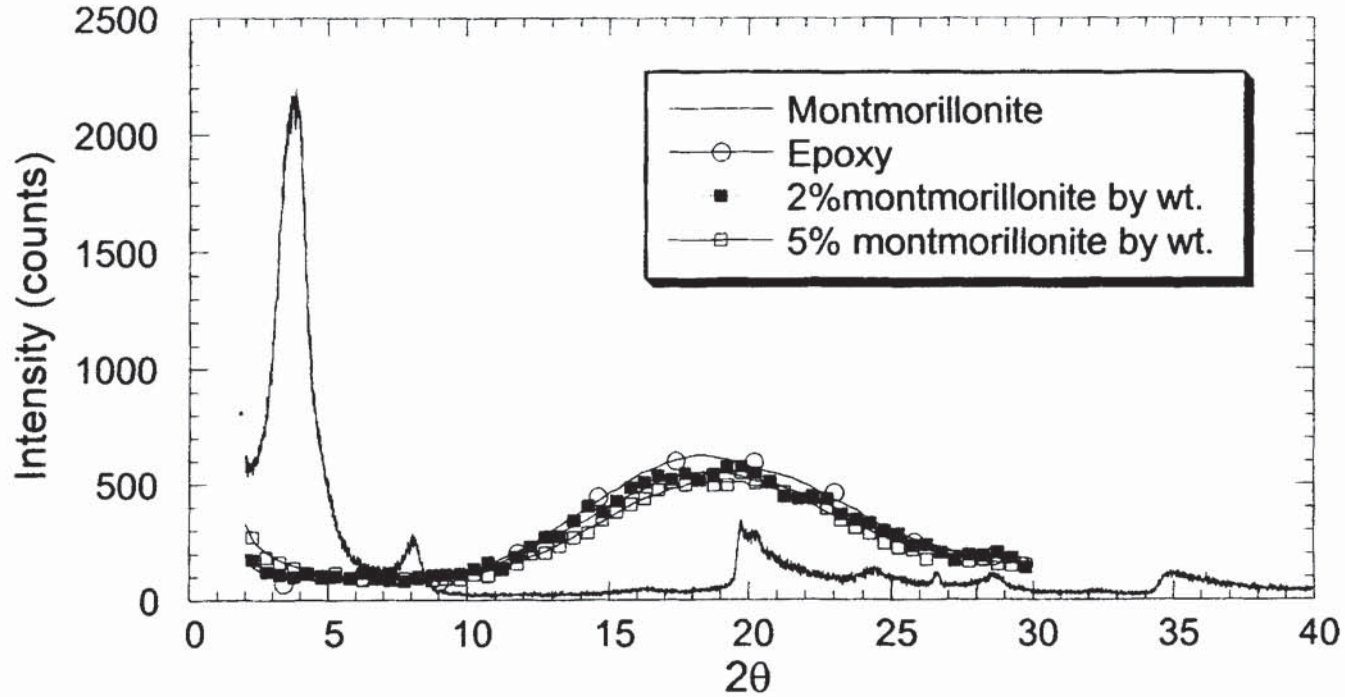



*Fig. 8. X-ray of the treated montmorillonite and epoxy + montmorillonite nanocomposites.*

montmorillonite, the 003 ($2\theta = 12.01°$) and 004 ($2\theta = 16.25°$) reflections are weak for the treated nanoclay (19). Slower scan speeds reveal that the 005 ($2\theta = 20.16°$) reflection overlaps a 02;11 band at $2\theta = 19.72°$. This band at $2\theta = 19.72°$ corresponds to a turbostratic stacking disorder common in smectite minerals and is confirmed by a 20;13 asymmetrical band at $2\theta = 34.84°$ (20).

Once the clay is introduced into the epoxy (see *Fig. 8*, 2% and 5%), there is an absence of the 001 reflection corresponding to an increase in d-spacing between the basal planes. The broad peak between $2\theta$ of 10° to 25° corresponds to the amorphous epoxy component present in the nanocomposite. Evidence to support the interpretation of increased d-spacing, or swelling, of the silicate platelets in the epoxy nanocomposites is shown by the TEM pictures in *Fig. 9* for the 2.5% montmorillonite. It would be reasonable to conclude that the ends of the card-like structures are attracted to each other because they could contain charge polarized regions. The observation of the 45° angle appears to support an argument for platelet attraction based on an edge to edge association. Charge nonuniformity due to different layer spacing of adjacent platelet stacks, or tactoids, may be a mechanism for aggregate formation.

The 5% nanoclay was also examined by TEM in *Fig. 10* to determine why there might be no large-scale structures. This micrograph indicates a change to a much more compact parallel arrangement of the intercalated regions of nanoclay. Little or no space between these was left for individual exfoliated platelets. This structure is short range, not long range. It is clearly illustrated in this *Figure* that some regions of parallel cards, or intercalated montmorillonite plates have their grains oriented at right angles to others. No flocs or micelle-like structures were observed. Flocs might therefore form only when the density of plates does not exceed the percolation threshhold, where this would force the bulk alignment of montmorillonite particles into dense structures of parallel and perpendicular sheets. If there is a charge polarization balance at work for this concentration, then this orientation is not a herringbone end on association, but instead an edge to face type of platelet orientation.

## CONCLUSIONS

The montmorillonite concentration strongly affects the reaction kinetics of epoxy nanocomposites. At concentrations below 5% there is no significant contribution to the enthalpy of reaction for the epoxy + montmorillonite two part mixtures. However, higher concentrations of montmorillonite substantially decrease the enthalpy. With the addition of hardener to the epoxy + montmorillonite mix a peak in activation energy and frequency factor occurs at 2.5% by weight. Depression of the temperature of the maximum rate of the reaction of epoxy and amine hardener was significant for all montmorillonite concentrations tested with the recurrent exception of 2.5% montmorillonite. This anomaly was observed at all heating rates tested. In the x-ray spectrographs, the absence of the 001 reflection peaks corresponding to the interlayerd-spacing of the montmorillonite showed that for all concentrations the intergallery order was disturbed. This conclusion was validated through the TEM micrographs

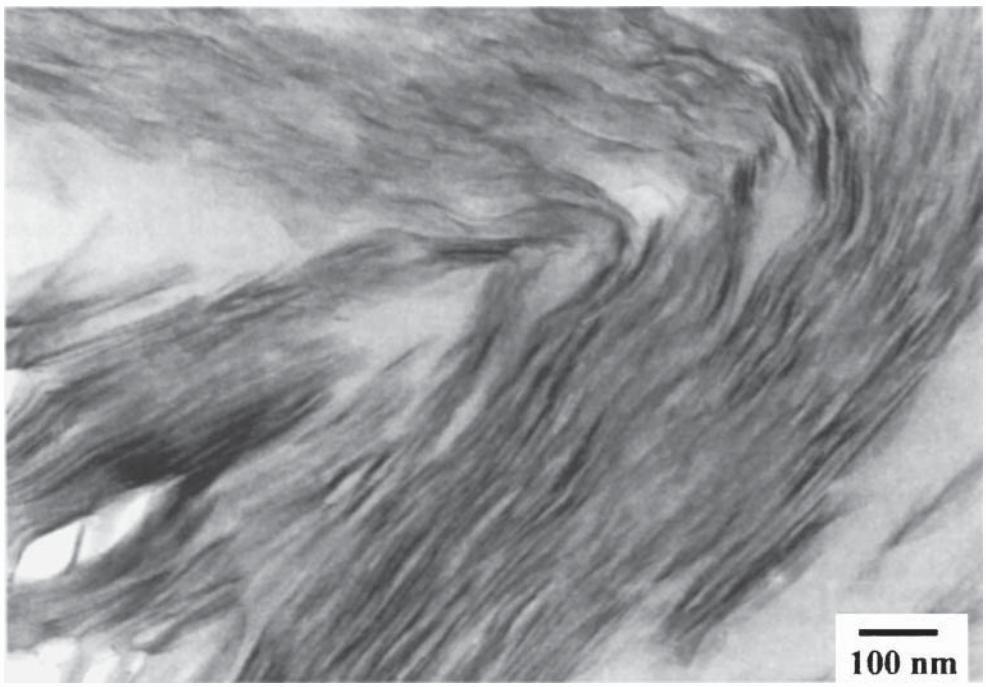



*Fig. 9. TEM of platelet edge association for 2.5% montmorillonite by weight.*

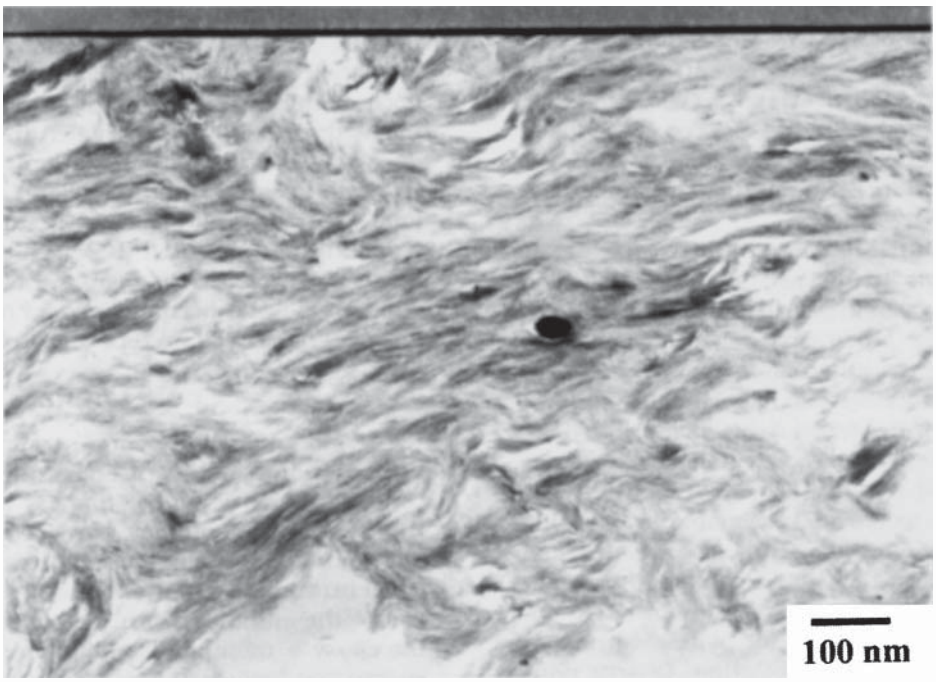



*Fig. 10. TEM of platelet edge to face association at 5% montmorillonite by weight.*

where interlayer spacing observed to range between 3 and 6 nm for different montmorillonite concentrations.

TEM results indicate a loosely packed herringbone pattern of the partly intercalated platelets that are oriented end to end at 2.5% concentration, and a tightly packed right angle pattern in platelets that are oriented edge to face at 5% concentration. Even though the montmorillonite was both exfoliated and partially intercalated at both concentrations, X-ray results correlated well with the micrographs indicating limits to the degree of exfoliation above 2.5% montmorillonite. Extensive micrographs of the concentration effect on dispersion are given in (21).

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