# Effects of Incorporation of Organically Modified Montmorillonite on the Reaction Mechanism of Epoxy/Amine Cure

Camille Alzina, Alice Mija, Luc Vincent, and Nicolas Sbirrazzuoli*

Laboratoire de Physique de la Matière Condensée, Université de Nice − Sophia Antipolis, CNRS UMR 7336, Parc Valrose, 06108 Nice Cedex 2, France

S *Supporting Information*

ABSTRACT: The aim of this study is to understand the effect of nonmodified or different organically modified montmorillonites on the reaction mechanism of epoxy/ amine cure. The reference material consists of diglycidyl ether of bisphenol A (DGEBA) and 1,3-phenylene diamine (*m*PDA) in stoichiometric proportions. The reaction with various organically modified montmorillonites (I28E, I34TCN, and MMTm) is compared to highlight the catalytic effect of MMT water content and of the alkylammonium cations on the epoxy/amine reaction mechanism. In the absence of *m*PDA curing agent, DGEBA develops homopolymerization reactions with I28E, I34TCN, and MMTm. Chemorheological kinetics and advanced isoconversional analysis of epoxy cure are studied by rheometrical measurements and differential scanning calorimetry (DSC). Molecular mobility of the system under curing is modified in the presence of montmorillonites. Finally, the study underlines the role of montmorillonites and the influence of the change in reaction mechanisms on glass transition of the nanocomposites.
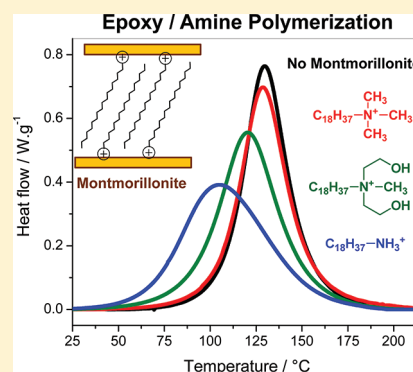
1. INTRODUCTION

Studies of polymer−clay interactions started in the 1960s and significantly expanded when, in 1990, Okada et al.[1] managed to improve the mechanical properties, the barrier effect, and the thermal resistance of polyamide 6 by dispersing only 4% of montmorillonite (MMT). These improvements of properties are related to the form factor of the MMT sheets and are dependent on the state of their dispersion, which also depends on the rate of the incorporation of the MMT.[2−4] The final structure of the materials is directly dependent on complex aspects such as the polymerization conditions and cure kinetics. MMT derivatives have been also dispersed into epoxy amine systems. In particular, the addition of organophilic MMT[5] showed interesting results such as enhancement of the thermal stability,[6] the mechanical properties,[7,8] and the glass transition temperature,[9,10] for example. The modification of the MMT with different alkylammonium cations has an impact on the polymerization mechanisms,[11] and hence on the final properties of the materials. Depending on the nature of the organic ions intercalated into the galleries, the modified MMT can either catalyze reactions or react with the prepolymer or the hardener.

Epoxy resins can be cured via addition reactions or homopolymerizations. For example, Wang et al.[12] highlighted that the homopolymerization of diglycidyl ether of bisphenol A (DGEBA) epoxy prepolymers begins as early as 220 °C in the presence of 5% of montmorillonite modified by HOOC− $(CH_2)_{11}$−NH_3^+, while this reaction occurs at 300 °C for the neat DGEBA. Organophilic montmorillonites can therefore catalyze the polymerization of epoxy prepolymers, leading to

the formation of cross-linked polyethers. Depending on the curing conditions, the homopolymerization could compete with other reactions occurring during the polymerization of an epoxy/amine system. Thus, different structures of nanocomposites will be obtained depending on the curing temperature and on the nature of the organic cations. However, the influence of the nature of these ions on the epoxy-amine curing is still not well-known, and a better understanding of the mechanism involved in the polymerization could allow a better prediction of the final properties of the nanocomposites.

Herein, we propose a study of the chemical and physicochemical effects on the epoxy/amine curing mechanism of different non modified or organically modified MMT. First, to detect the role of MMT water content on the epoxy/amine cure kinetics, two systems containing DGEBA/*m*PDA with no previous dried (wet) or dried MMT were studied and compared to the reference system (DGEBA/1,3-phenylene diamine (*m*PDA)). Next, the influence of MMT modified with octadecylamine moiety-based organic cations on the reaction mechanisms and reactivity is proposed. The curing reaction in the presence of the different organophilic MMT constituents, including the MMT by itself and the different cations used, was studied by using thermal and chemorheological analysis. In the absence of *m*PDA hardener, neat DGEBA has been reacted with various MMT homopolymerization reactions occurring at high temperature. For all of these studies, advanced kinetic
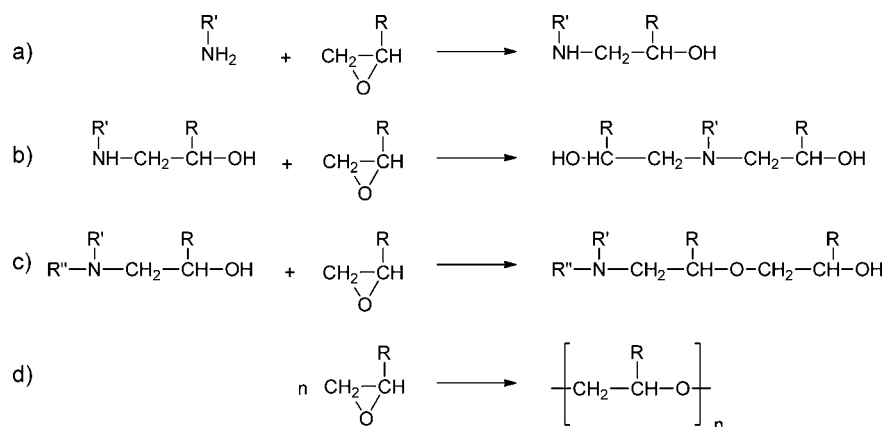
Figure 1. Chemical reactions of epoxy/amine system DGEBA/*m*PDA: (a) primary amine addition; (b) secondary amine addition; (c) etherification; and (d) homopolymerization.

analysis[13−16] allows us to underline the different mechanisms involved during the polymerization process, including both the chemical and the diffusion-controlled stages.

2. MATERIALS AND METHODS

2.1. Materials. Na⁺-montmorillonite (Optigel EX0255, subsequently called MMT) with a cationic exchange capacity (CEC) of about 100 mequiv/100 g was obtained from Süd Chemie (Germany). The octadecylammonium-treated MMT (subsequently called MMTm) was prepared using a method described in the literature.[17] The intercalation of the octadecylammonium ions into the MMT leaves was verified using powder X-ray diffraction (see Figure S1 in the Supporting Information). The trimethyl stearyl ammonium-treated MMT (I28E) and the methyl dihydroxyethyl hydrogenated tallow ammonium-treated MMT (I34TCN) were supplied by Nanocor (U.S.). Octadecylamine, 1,3-phenylene diamine (*m*PDA), and diglycidyl ether of bisphenol A (DGEBA) were obtained from Sigma-Aldrich and used as received. DGEBA has a glass transition temperature T_g of about −20 °C (midpoint DSC) and an epoxy equivalent weight (determined by ¹H NMR) of about 175 g equiv⁻¹. Octadecylammonium chloride was synthesized from octadecylamine (see the Supporting Information).

2.2. Nanocomposites Preparation. The epoxy DGEBA resin was mixed with montmorillonite (MMTm, I28E, or I34TCN) in the desired proportion (w/w), using a Bioblock 20 kHz-750 W sonifier fitted with a 3 mm titanium probe (two times, 10 min, 50% pulse, intensity 38%).

Thermosetting nanocomposites were obtained by adding the curing agent *m*PDA previously melted to 70 °C to the epoxy/clay mixture to obtain stoichiometric epoxy/amine proportions.

Cross-linking reactions were directly performed in DSC aluminum pans, by simple heating. Thermosetting nanocomposites were obtained by curing the mixtures during 2 h at 75 °C, then 2 h at 125 °C and 2 h at 185 °C, and infinite glass transition temperatures ($T_{g,\infty}$) of these materials were determined by DSC measurements.

2.3. Experimental Techniques. DSC measurements were carried out on a Mettler-Toledo DSC 823ᵉ. This apparatus is equipped with a HSS7 ceramic sensor (heat-flux sensor with 120 thermocouples Au−Au/Pd), which allows very high sensitivity. Temperature and enthalpy calibrations were performed by using indium and zinc standards. Integrations of DSC peaks were done using a line baseline. Samples of about

5−10 mg were placed in 40 μL aluminum crucibles. The different mixtures were cured under nonisothermal conditions. When the studied phenomena exceed 225 °C, the use of high-pressure stainless steel capsules is required. $T_{g,\infty}$ of the materials was measured by simple heating with a scanning rate of 10 °C min⁻¹ after the mixtures have undergone the curing program 2 h at 75 °C, then 2 h at 125 °C, followed by 2 h at 185 °C.

An advanced isoconversional method[18,19] was applied to nonisothermal DSC data of the various systems under cure. The software developed by Sbirrazzuoli et al.[14] was used to compute a value of E_α for each value of α lying between zero and one of 0.02−0.98 with a step of 0.02. Numerical integration was performed using a trapezoidal rule. An interpolation of the integrated $\alpha−T$ curves was performed using a Lagrangian algorithm to find the time $t_{\alpha,i}$ and temperature $T_{\alpha,i}$ that correspond to a given α lying between zero and one of 0.02−0.98 for the i temperature programs used. For each system, the computation was done at the heating rates of 1, 2, 3, and 4 °C min⁻¹.

Thermogravimetric measurements (TGA) were made on a TGA 851ᵉ from Mettler-Toledo. The microbalance has a precision of ±0.1 μg. Samples of about 10 mg were placed into 70 μL alumina pans. The samples were heated from 30 to 800 °C under a nitrogen flow of 50 mL min⁻¹. TGA measurements were performed at the same heating rate as DSC measurements for each system under cure.

The rheological behavior of epoxy/amine mixtures, with and without clay, was measured during curing using a Bohlin C-VOR rheometer. The measurements were conducted on oscillating mode with parallel plate geometries (25 mm diameter and 1 mm gap) with strain convection heating. The tests were carried out by heating the mixtures from 30 to 230 °C with a rate of 1 °C min⁻¹. The frequency was 1 Hz on auto stress mode with a deformation of 0.5%. The gel temperature was taken as the temperature for crossover of the values of storage (G') and loss (G'') moduli. As a first approximation, determination of the temperature of gelification (T_{gel}) during nonisothermal cure was taken as the temperature where $G' = G''$. Chemical extent of conversion at gelification (α_{gel}) was obtained after integration of DSC curve and superimposition with rheometric data obtained under the same conditions (i.e., nonisothermal cure at 1 °C min⁻¹).

3. RESULTS AND DISCUSSION

3.1. Influence of the MMT on the Reaction Mechanisms of Epoxy/Amine Cure. The polymerization of thermosets is a complex mechanism that may include several chemical reactions. Aliphatic or aromatic primary amines are commonly used as curing agents. These active hydrogen compounds undergo an addition reaction with epoxy ring. The polyaddition occurs between epoxy and primary amine, followed by secondary amine addition, and, at latter stages of the reaction or at higher temperature, side reactions such as etherification and/or homopolymerization (Figure 1). A recent study has shown that the presence of MMTm shifts the reaction to lower temperature, and this effect was attributed to an increase in the efficiency of collisions.[20] On the other hand, kinetic analysis seems to indicate that the diffusion control occurring at the latter stages of the reaction (when the system is in the glassy state) is lowered in the presence of MMTm. This previous report has highlighted a change in the overall cure mechanism when MMTm is added.

3.1.1. Mechanism of DGEBA/mPDA Cure in the Presence of Nonmodified MMT: Effect of MMT Water Content. MMT was often used as acid catalyst because its structure contains a deficit of charge.[21] TGA analysis has shown that MMT without preliminary drying contains 10% of water (see Figure S2 in the Supporting Information). To highlight the role of natural water MMT content on the epoxy-amine cure kinetics, two systems containing DGEBA/mPDA with no previous drying of MMT (wet MMT) and with dried MMT (dried MMT) were studied under nonisothermal conditions and compared to the reference system DGEBA/mPDA. DSC experiments carried out on these systems show that incorporation of 5% wet MMT in the DGEBA/mPDA mixture shifts the cure to lower temperature. A decrease of about 10 °C of the peak maximum temperature is observed, demonstrating a catalytic effect of wet MMT (Figure 2). This shift is not observed for the system containing dried
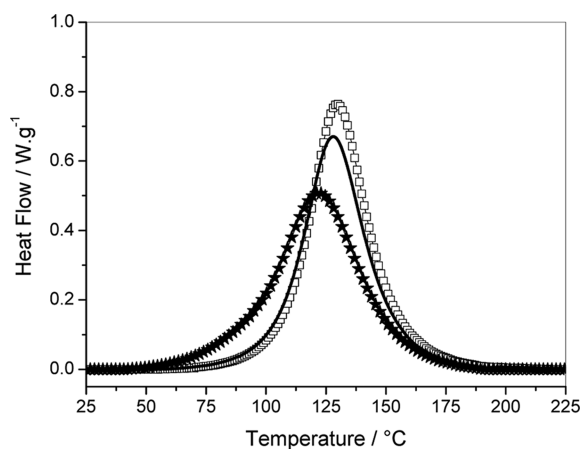

Figure 3. Catalytic effect of the wetMMT on the epoxy group.

3.1.2. Mechanism of DGEBA/mPDA Cure in the Presence of Organically Modified MMT. With the aim to determine the catalytic potential of the different alkylammonium ions, MMTm, I28E, and I34TCN clays were incorporated into the DGEBA/mPDA system. Note that MMTm does not contain water due to the prior cation exchange with alkylammonium ions followed by an intensive drying process. Figure 4 displays

Figure 4. DSC data of the heat release (solid) and conversion (open) versus temperature during nonisothermal cures of different mixtures at 3 °C min^{-1}: DGEBA/mPDA (■, □), DGEBA/I28E/mPDA 95/5 (★, ☆), DGEBA/I34TCN/mPDA 95/5 (▲, △), and DGEBA/MMTm/mPDA 95/5 (●, ○).

that the I28E clay containing ternary ammonium groups has no catalytic effect on the epoxy-amine cure because the DSC data are overlapped with those of the DGEBA/mPDA system. In contrast, the incorporation of I34TCN leads to a shift of the reactions to a lower temperature, indicating a well-marked catalytic effect. This can be explained by the presence of hydroxyl groups in the methyl dihydroxyethyl hydrogenated tallow ammonium located between the sheets of I34TCN clay. These hydroxyl groups catalyze the reactions between DGEBA and mPDA.[22−24] A shift to lower temperature is also observed in the presence of MMTm. The system with MMTm is the system that starts to reacts at lower temperature, displaying higher catalytic effect. The decrease of the peak maximum temperature is approximately 22, 9, and 1 °C for MMTm, I34TCN, and I28E, respectively. This shift of more than 20 °C confirms the high catalytic effect of MMTm on the epoxy ring-opening. In addition, a change of the shape of thermoanalytical curves suggests possible modifications of the kinetic parameters and of the cure mechanism in the presence of MMTm.[20] The primary ammonium NH$_3^+$ plays the role of epoxy ring-opening initiator due to the release of a proton H$^+$. According to this hypothesis, the addition of different amounts of MMTm should lead to different shifts of the chemical reactions. The reactivity of systems with increasing MMTm content (2% and 5%, Figure 5) was compared to that of the reference system (DGEBA/mPDA). As expected, a shift of the exothermic peaks to lower temperature is observed when MMTm is added and increases with the MMTm content. The decrease of the peak maximum

Figure 2. DSC data of the heat release during nonisothermal cures of different mixtures at 3 °C min^{-1}: DGEBA/mPDA (□), DGEBA/wetMMT/mPDA 95/5 (★), and DGEBA/driedMMT/mPDA 95/5 (−).

MMT because the DSC peak is superimposed with the peak of the DGEBA/mPDA mixture. This effect can be explained by the presence of water in the clay layers that may react with epoxy group to form oxonium ions that catalyze the reaction, as explained in the mechanism presented in Figure 3.
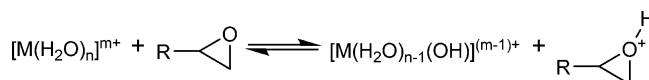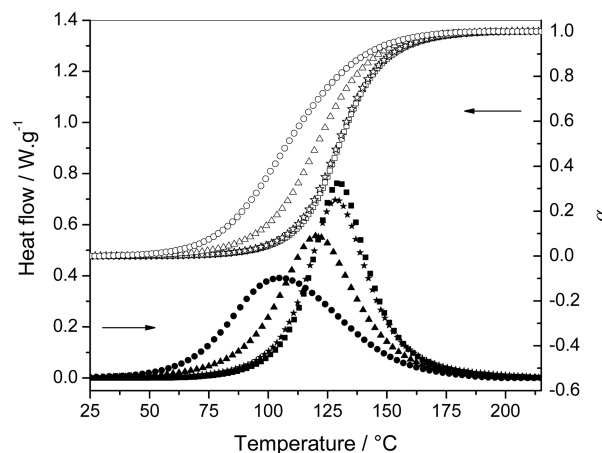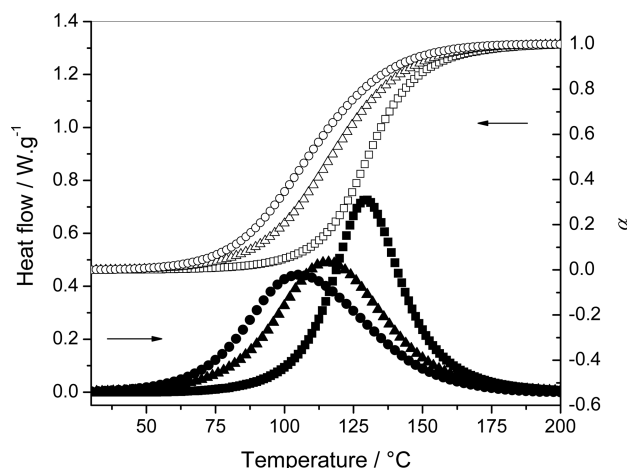
Figure 5. DSC data of the heat release (solid) and conversion (open) versus temperature during nonisothermal cures of different mixtures at 3 °C min^{-1}: DGEBA/mPDA (■, □), DGEBA/MMTm/mPDA 98/2 (▲, △), and DGEBA/MMTm/mPDA 95/5 (●, ○).

Figure 6. Comparison of thermograms obtained by DSC (open) and thermogravimetry (solid) during nonisothermal cures at 8 °C min^{-1} of DGEBA/I28E 95/5 system (○, ●) and DGEBA/I34TCN 95/5 system (☆, ★).

temperature is approximately 22 and 14 °C for 5% and 2% MMTm, respectively. In addition to this, the slope of the first part of the curves decreases with the MMTm content. Generally, it can be reasonably assumed that this slope is proportional to the reaction rate and so directly linked to the overall reaction kinetics. This indicates that the presence of MMTm allows the reticulation to start earlier, but the reaction rate is slower. The shape of the curves is modified by the addition of MMTm, which supports the hypothesis of a change in the reaction mechanism, facilitating the epoxy ring-opening. Moreover, the modified shapes are not related, according to TGA analyses, to a mass loss during the reaction (see Figure S3 in the Supporting Information). Similar results have been reported in the literature on the effect of MMTm on the reaction kinetics of polymers produced by a free radical polymerization mechanism.[25−27] In this case, it was shown that the reaction starts earlier in the nanocomposite system with the alkylammonium organic modifier, but it was reported that MMTm enhances the reaction rate.

3.2. Effect of Organically Modified MMT on Homopolymerization Reactions. In the absence of mPDA hardener, DGEBA can react on itself by homopolymerization at high temperature (Figure 1d). This reaction can be studied by comparing the reactivity of various MMT with neat epoxy (DGEBA). Figures 6 and 7 show that all of the montmorillonites react with neat DGEBA, but these reactions occur at different temperatures. In perfect agreement with the previously mentioned hypotheses, the system that reacts at lower temperature is DGEBA/MMTm (Figure 7), followed by DGEBA/I34TCN and then DGEBA/I28E (Figure 6). This highlights the possibility of alkylammonium cations to react with epoxide groups and the various catalytic powers of these alkylammonium cations on the homopolymerization of DGEBA prepolymer.

3.2.1. DGEBA/I28E and DGEBA/I34TCN Systems. The thermograms of the DGEBA/I28E and DGEBA/I34TCN systems (Figure 6) are characterized by very steep exothermic peaks, indicating fast reaction between the prepolymer and the modified clays. The exothermic peak of the reaction between DGEBA and I28E is located in the same temperature range as that of the reaction between DGEBA and a tertiary amine DMBA that allows etherification type reactions to occur.[28]
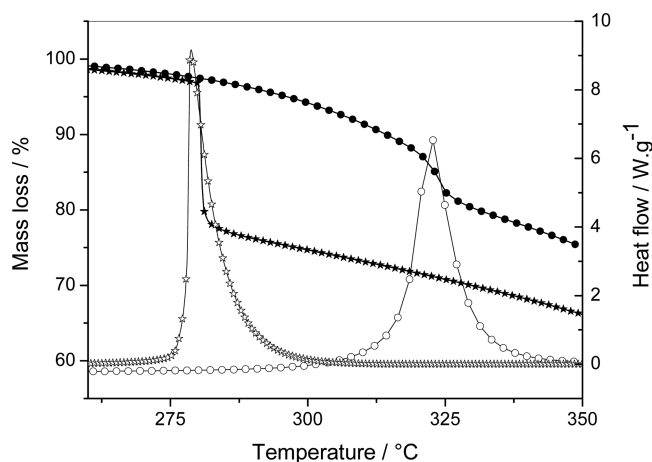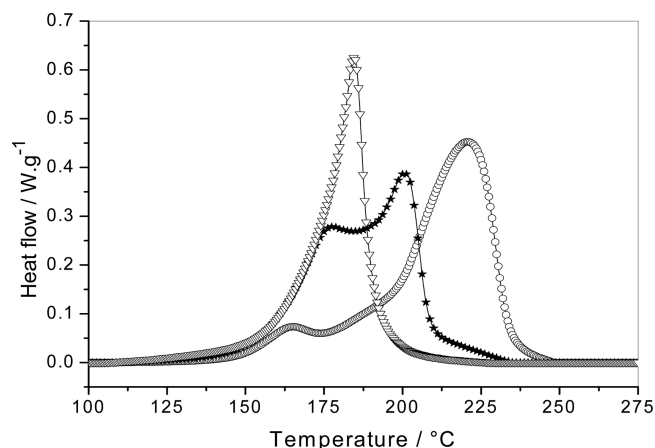

Figure 7. DSC data of the heat release during nonisothermal cures of different mixtures at 3 °C min^{-1}: DGEBA/MMTm 98/2 (○), DGEBA/MMTm 95/5 (★), and DGEBA/MMTm 85/15 (▽).

The mass loss in TGA for the DGEBA/I28E system is in the area of exothermic peak temperature obtained by DSC (Figure 6). In addition, the inflection point of the mass loss (25%) corresponds to the maximum of the peak obtained by DSC that is consistent with a degradation of the material. However, the shape of the exothermic peak in DSC is not as abrupt as it should be in the case of degradation. Several studies[29−32] demonstrate the formation of tertiary amines at 200 °C during the degradation of trimethyl stearyl ammonium contained in the modified montmorillonite. Therefore, the peak could correspond to degradation superimposed with homopolymerization of DGEBA catalyzed by tertiary amines produced by degradation.

The mass loss of 25% in TGA of the DGEBA/I34TCN system is also located in the area of exothermic peak temperature obtained by DSC (Figure 6). The inflection point of the mass loss corresponds to the maximum of the peak obtained by DSC. The shape of this peak has a characteristic rise following a right angle with the baseline, suggesting a degradation of the material. Unlike with organoclay I28E, no tertiary amine that could induce homopolymerization reaction is produced by the degradation of the mixture in the case of

montmorillonite I34TCN. However, the hydroxyl group could catalyze the degradation of DGEBA that occurs at lower temperature.[33,34]

3.2.2. DGEBA/MMTm System. In the case of DGEBA/MMTm system, the shape of the exothermic peak obtained by DSC is more complex, and the reactions occur at much lower temperatures (Figures 7 and 8). The shift to lower temperature
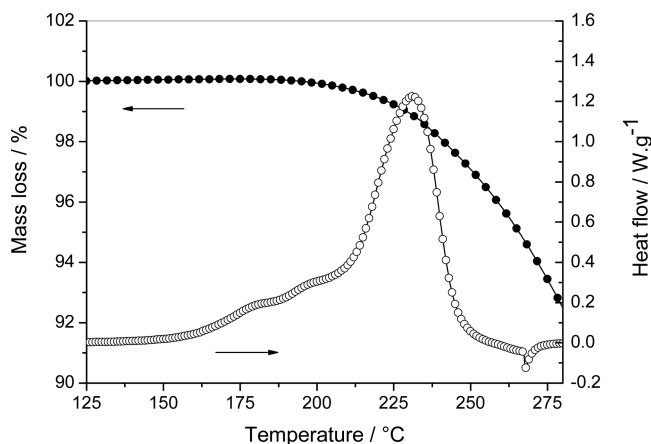

Figure 8. Comparison of thermograms obtained by DSC (○) and thermogravimetry (●) during nonisothermal cures at 4 °C min⁻¹ of DGEBA/MMTm 98/2.

increases with MMTm content (Figure 7, 2%, 5%, and 15%). This shift is about 36 °C between the peak maximum temperature at 2% and 15% of MMTm. This demonstrates the high catalytic effect of the octadecylammonium ions on the polymerization of DGEBA. The thermograms show two distinct exothermic peaks for the reaction of neat DGEBA with MMTm by varying the MMTm content. These two exothermic peaks were attributed to two polymerization processes by Lan et al.[35] The first peak, which increases with the MMTm content, was attributed to the reaction of the DGEBA monomers preintercalated between the galleries where the octadecylammonium concentration is important. The second peak at higher temperature, which decreases with the MMTm content, was attributed to the extra-gallery polymerization of the DGEBA. For Hutchinson et al.,[36] these two exothermic peaks are the result of the overlap of one exothermic and one endothermic peak due to the degradation of ammonium ions. Nevertheless, TGA analysis of DGEBA/MMTm 98/2 shows that the percentage of weight loss is less than 3% at the end of the reaction (250 °C) (Figure 8), so that this last hypothesis does not seem to be fully applicable for the system of the present study and the two exothermic DSC peaks may be predominantly attributed to two polymerization processes.

To confirm the existence of a chemical reaction between the octadecylammonium ions present in the MMTm and DGEBA, the reactivity of the mixture DGEBA/CH$_3$(CH$_2$)$_{17}$NH$_3^+$Cl$^-$ (system without clay) was compared to that of DGEBA/MMTm (Figure 9). The ratios of the mixtures DGEBA/CH$_3$(CH$_2$)$_{17}$NH$_3^+$Cl$^-$ (21/1) and DGEBA/MMTm (85/15) were chosen so that the ratio between the epoxy prepolymer and octadecylammonium ions is identical in both mixtures. In the case of the DGEBA/CH$_3$(CH$_2$)$_{17}$NH$_3^+$Cl$^-$ system, two exothermic peaks are present. The first peak is between 60 and 120 °C, and the second peak is between 170 and 230 °C. After
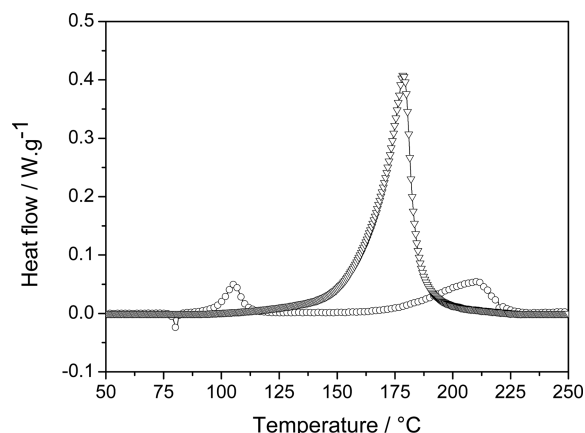

Figure 9. DSC data of the heat release during nonisothermal cures of different mixtures at 6 °C min⁻¹: DGEBA/C$_{18}$H$_{37}$NH$_3^+$Cl$^-$ 21/1 (○) and DGEBA/MMTm 85/15 (▽).

the melting point of octadecylammonium chloride (endothermic peak at 60 °C), the polymerization could be initiated by the proton H$^+$ of octadecylammonium ion that is captured by the epoxy ring (Figure 10). This activated form can react with the generated octadecylamine, allowing the epoxy-amine polymerization reactions to take place (from 60 to 120 °C). In a second stage, this activated form possibly present because the proton H$^+$ acts as a catalyst could react with a hydroxyl group or another epoxide group, allowing the etherification and homopolymerization reactions to occur (from 170 to 230 °C).[20]

For the mixture DGEBA/MMTm, the exothermic peak includes all of the reactions. It is known that epoxy-amine reactions begin approximately at 20 °C and start to be significant at 60 °C, and then they are followed by etherification and homopolymerization reactions that occur at higher temperature (~150 °C). The epoxy-amine reactions of the DGEBA/CH$_3$(CH$_2$)$_{17}$NH$_3^+$Cl$^-$ system are in a temperature range narrower than for the DGEBA/MMTm system. This could be explained by the fact that the counterion Cl$^-$ is much less bulky than the montmorillonite, and the access of the octadecylammonium ions to epoxy prepolymers is thus facilitated. As for the etherification and homopolymerization reactions, they occur at higher temperatures for the DGEBA/CH$_3$(CH$_2$)$_{17}$NH$_3^+$Cl$^-$ system. It is possible that HCl gas is formed and evaporates at these temperatures so very little protonated epoxy groups catalyze the etherification and homopolymerization reactions. This could explain the different reactivity of the systems containing MMTm where all protonated epoxy groups transmit their proton during the etherification and homopolymerization reactions. Thus, the catalytic effect continues until the end of the reaction, explaining the large enthalpy of exothermic peak for this mixture.

3.3. Advanced Kinetic Analysis of Epoxy Cure in the Presence of Organically Modified MMT. *3.3.1. DGEBA/Organically Modified MMT/mPDA Systems.* An advanced isoconversional method was applied to tend to elucidate the complex reactivity of the four systems DGEBA/mPDA, DGEBA/MMTm/mPDA 95/5, DGEBA/I28E/mPDA 95/5, and DGEBA/I34TCN/mPDA 95/5 using the DSC data (Figure 11). Here, it should be reminded that epoxy-amine reactions are chemically controlled for $\alpha < 0.55$ and diffusion controlled for $\alpha > 0.55$.[37] At the beginning of the reaction ($\alpha <$
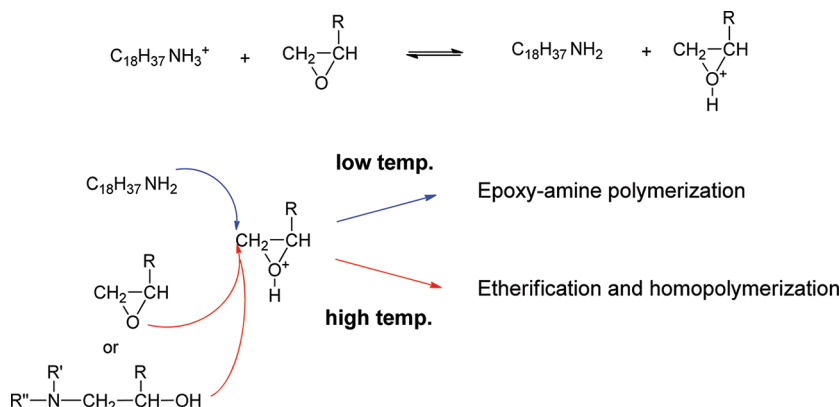
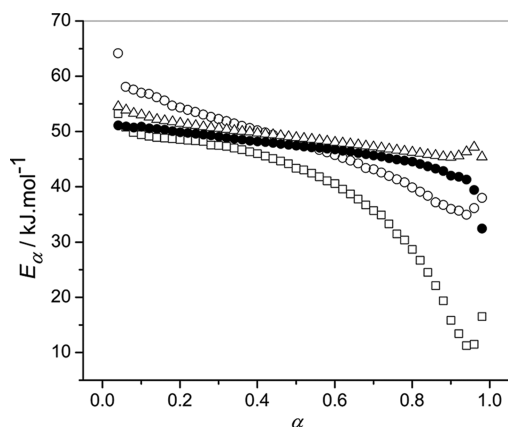**Figure 10.** Chemical reactions of octadecylammonium ion and epoxy group.

Figure 11. E_{α}-dependency versus conversion of DGEBA/mPDA ($\square$), DGEBA/I28E/mPDA 95/5 ($\bullet$), DGEBA/I34TCN/mPDA 95/5 ($\triangle$), and DGEBA/MMTm/mPDA 95/5 ($\bigcirc$) systems.

0.55), the E_{α}-dependency shows relatively close values for the various systems. The system with MMTm has the higher activation energy, followed by I34TCN and I28E respectively. These energy barriers are in perfect agreement with the hypotheses formulated in light of Figures 4, 6, and 7. Hence, the characteristic E_{α} decrease at low α values reported for catalytic effect is more pronounced for the system with MMTm, than for those with I34TCN and I28E, respectively. The E_{α}-dependency of the system containing I28E is very similar to that found for the reference system for $\alpha < 0.30$.

Greater differences are observed in the second part of the reaction, as seen in Figure 11, where it is known that the cure comes to be diffusion controlled ($\alpha > 0.55$). An opposite trend is observed here: the system with MMTm has the lower activation energy, followed by I28E and I34TCN, respectively. The E_{α} decrease of the end of the reaction ($\alpha \rightarrow 1$), observed for the reference system and characteristic of a diffusion control, is less marked in the presence of any montmorillonites (Figure 11). The diffusion control seems to be suppressed or very low for nanocomposites. This could indicate that the molecular mobility is higher, leaving the opportunity for chemical reactions to complete. These results suggest that the nature of the alkylammonium ions present between the clay layers has a little influence on the E_{α}-dependencies at the end of the reaction, but indicates that the physical structure and the shape factor of the montmorillonite are responsible for this behavior at the end of reaction.

3.3.2. DGEBA/MMTm System.
To obtain additional mechanistic information on the reactivity between DGEBA and MMTm, an advanced isoconversional method was applied for three DGEBA/MMTm systems 98/2, 95/5, and 85/15. The resulting E_{α}-dependencies are presented in Figure 12. At
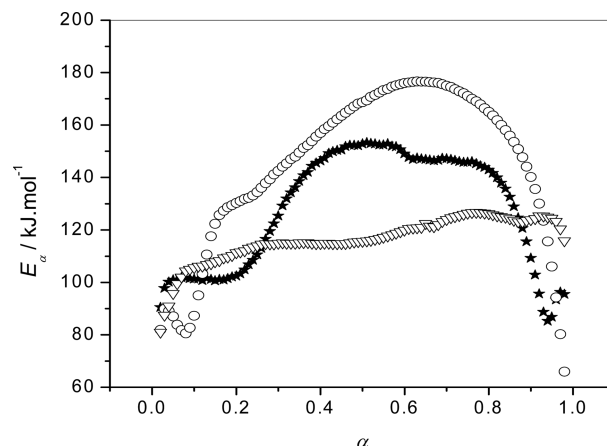

Figure 12. E_{α}-dependency versus extent of conversion of DGEBA/MMTm 98/2 ($\bigcirc$), DGEBA/MMTm 95/5 ($\bigstar$), and DGEBA/MMTm 85/15 ($\triangledown$).

the beginning of the polymerization ($\alpha \rightarrow 0$), the activation energies for the different mixtures are in the range of 80−100 kJ mol^{-1}. Next, the activation energy increases. This phase corresponds to a competition between two types of homopolymerization reaction, that is, catalyzed and uncatalyzed homopolymerization. This increase is more pronounced for the mixture containing 2% of MMTm, while the mixture with 15% shows a slight increase. According to Figure 8, the thermogram of the mixture with 15% of MMTm (DGEBA/MMTm 85/15) exhibits a single DSC peak between 100 and 230 °C. This mixture contains a large amount of octadecylammonium ions present in the MMTm that can initiate homopolymerization through oxonium species formation or that can react directly with DGEBA by nucleophilic attack of the amine group on the epoxy ring.[20] It was shown that the activation energy of homopolymerization reactions is in the range of ∼100−110 kJ mol^{-1}.[28] This value corresponds to the value obtained at the beginning of the reaction ($0.10 < \alpha < 0.50$) for the mixture containing 15% of MMTm (Figure 12). A slight increase in E_{α} to 125 kJ mol^{-1} is then observed for $\alpha > 0.50$. This increase is more pronounced for the mixture containing 2% MMTm. The

thermogram of this mixture in Figure 7 indicates the presence of two peaks. The activation energy of chemical reactions mainly corresponding to the first DSC peak is about ~90 kJ mol^{-1} (Figure 12). These reactions can be attributed to catalyzed homopolymerization reactions. The activation energy of chemical reactions mainly corresponding to the second DSC peak is about ~180 kJ mol^{-1}. These reactions could correspond to uncatalyzed homopolymerization reactions. Because the mixture with 2% of MMTm contains less alkylammonium ions, therefore less tertiary amines and protons H$^+$ that act as initiators of oxirane ring-opening are present. In addition, there is an inhibition of catalysis because the few tertiary amines and H$^+$ present are trapped when the network is formed. Thus, the catalytic effect is lower, which results in an increase of the apparent activation energy E_α of homopolymerization reactions.

In the case of the DGEBA/MMTm 95/5 mixture, the thermogram obtained by DSC (Figure 7) presents also two peaks. In Figure 12, there are two levels for each of the peaks. The first level observed for $0.05 < \alpha < 0.20$ with $E_\alpha \approx 100$ kJ mol^{-1} could correspond to the catalyzed homopolymerization reactions. Next, an increase of E_α to ~150 kJ mol^{-1} is observed for $0.20 < \alpha < 0.50$. This increase is lower when more MMTm is added. This can be explained because more octadecylammonium ions are present in the mixture when MMTm content increases from 2%, 5%, until 15%. Catalyzed homopolymerization reactions with lower energetic barrier are more pronounced than the noncatalyzed one. In the case of the DGEBA/MMTm 85/15 mixture, the proportion of octadecylammonium ions is so important that the homopolymerization reactions are mostly catalyzed (~100 kJ mol^{-1}), hence leading to a small increase of E_α (100 → 125 kJ mol^{-1}) and the presence of a single peak on the DSC thermogram.

At the end of the reaction, a decrease of E_α, characteristic of the transition from a chemically controlled reaction to a reaction controlled by diffusion[37,38] of unreacted monomers, is observed.

3.4. Viscoelastic Properties. Rheometric measurements of DGEBA/mPDA, DGEBA/MMTm/mPDA 98/2, and DGEBA/MMTm/mPDA 95/5 systems are shown in Figure 13. The characteristic values are summarized in Table 1. The analysis of rheometric data indicates a decrease of T_{gel} with the increase of
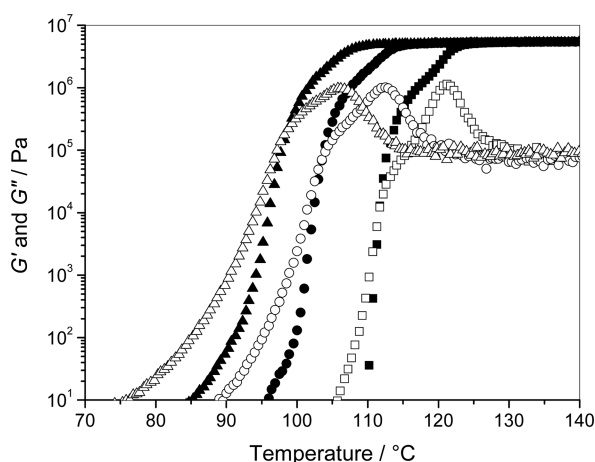
Table 1. T_{gel} and α_{gel} Values for Different Systems at 1°C min^{-1}

	DGEBA/mPDA	DGEBA/MMTm/mPDA 98/2	DGEBA/MMTm/mPDA 95/5
T_{gel}/°C	111.6 ± 0.3	103.5 ± 0.3	98.7 ± 0.3
$\alpha_{gel}{}^a$/%	66.0 ± 1.0	68.7 ± 1.0	70.4 ± 1.0

^{a}Obtained after integration of DSC data.

MMTm content. This is consistent with conclusions previously drawn from DSC data. Because MMT acts as a catalyst, a higher content of MMTm shifts the reaction to lower temperature. The values of α_{gel} are given in Table 1. According to these results, α_{gel} seems to slightly increase with the MMTm content and T_{gel} decreases. Surprisingly, the incorporation of MMTm in the DGEBA/mPDA system delays the gelification. These results are in agreement with earlier works that reported an earlier start of the gel effect and higher conversion values at the gel-effect period.[25−27]

3.5. Analysis of the Glass Transition. Several mixtures DGEBA/mPDA, DGEBA/MMTm/mPDA 95/5, DGEBA/I28E/mPDA 95/5, and DGEBA/I34TCN/mPDA 95/5 were prepared and cured. The $T_{g,\infty}$ values of these materials are given in Table 2. The highest $T_{g,\infty}$ is obtained for the reference

Table 2. $T_{g,\infty}$ of Thermoset Materials Determined by DSC

materials	$T_{g,\infty}$ (°C)
DGEBA/mPDA	178 ± 0.2
DGEBA/I28E/mPDA 95/5	176 ± 0.2
DGEBA/I34TCN/mPDA 95/5	176 ± 0.2
DGEBA/MMTm/mPDA 95/5	175 ± 0.2

material DGEBA/mPDA ($T_{g,\infty}$ = 178 °C). Addition of modified montmorillonites into the material slightly decreases the $T_{g,\infty}$. The materials containing I28E and I34TCN showed an identical value of $T_{g,\infty}$ (176 °C), while the lowest $T_{g,\infty}$ (175 °C) was obtained for the material with MMTm. Regardless of the organically modified montmorillonite added to the material, the $T_{g,\infty}$ value obtained is always lower than the reference material. This indicates that the structure of the clay could be responsible for this decrease.

The montmorillonite MMTm contains octadecylammonium ions that can integrate the three-dimensional network according to the reactions presented earlier. The number n of active hydrogen of octadecylamine is 2, and this molecule has a long alkyl chain while the hardener mPDA is a small molecule with $n = 4$. Thus, the three-dimensional network is less rigid, and the cooperative motion of the chain segments, characteristic of the glass transition, takes place at a lower temperature for the material DGEBA/MMTm/mPDA 95/5, which is expressed by the lowest $T_{g,\infty}$. If considering that the alkylammonium ions have reacted, the decrease in $T_{g,\infty}$ could also be explained by a plasticizing effect of the hardener mPDA in excess. Regarding the $T_{g,\infty}$ values of the materials containing montmorillonites I34TCN or I28E, the very slight decreases of the $T_{g,\infty}$ values can be explained because clays are modified by alkylammonium ions that are not involved in the three-dimensional network of the material.

The homopolymerization/etherification reactions at high temperature could lead to the formation of cross-linked polyethers, resulting also in lower $T_{g,\infty}$ values. As we have previously shown, the polymerization of different DGEBA/

Figure 13. Rheometric data during nonisothermal cures of different mixtures at 1 °C min^{-1}: DGEBA/mPDA (■, □), DGEBA/MMTm/mPDA 98/2 (●, ○), and DGEBA/MMTm/mPDA 95/5 (▲, △) (G′, solid; and G″, open).

organically modified MMT/mPDA systems is complete at 200 °C (Figure 4). On another hand, the study in the absence of hardener, which can highlight the presence of homopolymerization/etherification reactions, had showed that in the case of I28E and I34TCN these reactions are not present before ∼280 °C (Figure 6). On the contrary, for the DGEBA/MMTm system, the homopolymerization/etherification reactions starts at lower temperature (∼150 °C, paragraph 3.2.2, and Figures 7, 8, and 9), therefore before the completion of the epoxy/amine polymerization. Nevertheless, these homopolymerization/etherification reactions would be very limited in this case as evidenced by the slight decrease (1 °C) observed in $T_{g,\infty}$ values between the material with MMTm and the materials with I28E and I34TCN.

However, the study shows that 5% of nanoclay has been successfully introduced into the epoxy/amine matrix without significantly decrease the $T_{g,\infty}$ of the DGEBA/mPDA reference material, which is currently very high.

4. CONCLUSIONS

Organically modified montmorillonites influence the kinetics of epoxy-amine polymerization and change the reaction mechanisms. According to the alkylammonium ions introduced in the clay, the reactions pathways in the epoxy-amine system are different. The modified clay may simply catalyze chemical reactions (case of I34TCN) or else react during the polymerization and integrate the three-dimensional network as in the case of clay MMTm that cannot be considered as a simple inert filler.

The rheological study showed that the T_{gel} decreases with increasing MMTm content. This is consistent with the conclusion that the cross-linking starts earlier in temperature with higher contents of MMTm as shown with DSC data and confirms the catalytic role of MMTm.

The study in the absence of the mPDA hardener also highlights the importance of homopolymerization/etherification reactions at high temperature, while kinetic analysis applied to DGEBA with various MMTm contents shows the role of MMTm for the catalyzed and uncatalyzed homopolymerization.

The use of kinetic analysis applied to the system DGEBA/mPDA containing montmorillonites I34TCN, I28E, and MMTm also demonstrated that control by the diffusion of monomers at the end of the reaction was considerably reduced as compared to the reference system DGEBA/mPDA. The molecular mobility could be higher at the end of the reaction (α > 0.55) for mixtures containing clay, allowing the different chemical reactions to complete. These results do not depend on the nature of the alkylammonium ions present in the galleries of the clay but show that the physical structure of the montmorillonite could play a predominant role for this behavior at the end of reaction.

Measurements of $T_{g,\infty}$ by DSC of several materials displayed that montmorillonite is responsible for the slight decrease of $T_{g,\infty}$ of the nanocomposite as compared to the reference system DGEBA/mPDA. This result is consistent with the conclusions drawn from kinetic analysis demonstrating that the presence of clay caused an increase of molecular mobility in the glassy state. In the case of the montmorillonite containing alkylammonium ions that react with the epoxy matrix, the slight decrease of $T_{g,\infty}$ can be also explained by a plasticizing effect of the hardener mPDA in excess. Measurements of $T_{g,\infty}$ with modified montmorillonite with inert alkylammonium ions (case of I28E) showed a slight decrease of $T_{g,\infty}$, which implies that the structure of montmorillonite is also responsible of the decrease. In all cases, the $T_{g,\infty}$ values of the various systems remain very high as required for high performance composites.

As highlighted in the present study, an additional advantage of organically modified montmorillonites is their catalytic effect on the oxirane ring-opening reaction associated with a decrease of the overall reaction rate. This leads to the possibility of replacing common less eco-friendly and expensive initiators used in industry with organically modified clays.

■ ASSOCIATED CONTENT

⑤ Supporting Information

X-ray diffraction of MMT and MMTm, synthesis of octadecylammonium chloride, TGA of the MMT, and DSC and TGA of DGEBA/MMTm/mPDA 95/5. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Tel.: +33 4 92 07 61 79. Fax: +33 4 92 07 61 19. E-mail: nicolas.sbirrazzuoli@unice.fr.

Notes

The authors declare no competing financial interest.

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