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Shrinkage Control and Kinetics Behaviour of Clay-Unsaturated Polyester Nanocomposites

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A B S T R A C T

Recently, it has been shown that the addition of a small quantity of nanoclay can greatly enhance the efficiency of low profile additives (LPAs) on volume shrinkage control of low profiled unsaturated polyester (UP)/styrene/LPA systems. In this study, however it was found that the organically-modified nanoclay (Cloisite 15A) can also affect the volume shrinkage control of non-low profiled UP/styrene systems. The effect of nanoclay on volume shrinkage of UP resin was investigated by an in-house constructed shrinkage measurement apparatus. Experimental results revealed that the nanoclay somewhat decreases the volume change of UP/styrene system. The polymerization kinetics of the nanoclay filled UP systems was studied in a quasi-adiabatic reactor. The quasi-adiabatic exothermic measurements showed that, at higher nanoclay content, the reaction rate increased and the induction time decreased. The reduced viscosity measured by a rheometric dynamic analyzer. The gel time calculated by both quasi-adiabatic reactor and rheometric dynamic analyzer data. Results have showed that adding nanoclay into the UP/styrene mixture makes the onset of the viscosity rise happen much earlier which leads to a higher reaction rate, faster viscosity rise, and earlier gelation. It is clearly observed that measuring the gel time at different level of Cloisite 15A is similar to using rheometry and exothermic experiments.

INTRODUCTION

Unsaturated polyester (UP) resins are the most widely used thermoset resins. It is well known that they are generally utilized in making fibre reinforced thermoset articles. In recent years, low temperature and low pressure moulding processes are developed because of their low cost and ease of handling and processing. The copolymerization of UP resin and styrene leads to a high degree of polymerization shrinkage (7-10%). A technical improvement is the use of low profile additives (LPA)s to reduce shrinkage that occurs during the course of this cure copolymerization reaction [1,2].

Depending on the chemical structure, molecular weight and

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concentration of the LPA used, different degrees of the volume shrinkage may occur [3-8]. This can greatly affect the physical and mechanical properties of the cured systems [9,10].

Among the various standard LPAs, the thermoplastic polyvinyl acetate (PVAc) is most widely used. The effect of LPAs, especially PVAc, on the kinetics [11], thermodynamics [12,13], rheological behaviours, and morphologies [8,14-16] of UP systems have been subjects of extensive studies. However, most LPAs do not work well in low temperature curing conditions.

It is generally agreed that the most important features of LPA for working in high temperature processes are thermal expansion, phase separation, inversion between LPA and reacted UP resin, and microvoid formation along the interface or inside the LPA phase [1,17]. With the development of new manufacturing processes such as resin transfer moulding (RTM), many industries have been recently focused on the low temperature curing operations. When the resin is cured at low temperature, there is a small temperature variation during moulding consequently, the thermal induced shrinkage control often dose not exists.

The shrinkage behaviour of low temperature cured unsaturated polyester resins have been extensively studied by Lee et al. [7,11,15,18-19]. They found that poly vinyl acetates with different molecular weights are effective in shrinkage control only between an upper and a lower concentration limits. High molecular weight poly vinyl acetates and low-PVAc concentration provide a better shrinkage control at low temperature cure, which is totally opposite to that in high temperature processes [15,19].

The formation of a large scale co-continuous structure constructed by LPA- and UP-rich regions, or LPA-rich dominated particulate like structure, is very important for LPA to be effective as a shrinkage control agent [16]. It was shown that volume expansion, during low temperature curing, occurs at very late stage of reaction. With increase of the reaction rate in the LPA-rich phase, an earlier volume expansion and better shrinkage control will occur. The LPA containing carboxy groups tended to attract more cobalt promoter and had a higher reaction rate than the LPA without carboxy groups [7].

Recently, it has been observed that the addition of organically-modified nanoclays can control the shrink-age behaviour in low profiled UP resin systems (i.e.; UP/styrene/LPA/nanoclay systems) [20,21]. It is believed [20] that almost all of clay platelets are located in the LPA-rich phase and there is a tendency to increase the reaction rate in LPA-rich phase. It has been suggested that increasing the reaction rate in LPA-rich phase could result to an earlier microvoid formation in the system for better shrinkage control [7]. It is shown that nanoclay increases the fraction of LPA-rich phase [22]. A more micro-cracking will be arise in the LPA-rich phase or at the interface of the LPA-rich and UP-rich phases by increasing the fraction of LPA-rich phase. Therefore, a major improvement of volume shrinkage control occurs.

In spite of the fact that unsaturated polyester resins contain thermoplastic LPAs and nanofillers have been studied [20-22], no information is available in the literature, which discusses about UPs contain only nanofillers as low profile additives. The presence of nanoclay particles as reinforcement fillers, auxiliary promoters, heat resistance materials and fire retardants in UP systems (without LPAs) have been investigated, but their shrinkage control behaviours have not been studied.

In this work, reactive shrinkage measurement method was used to study the volume change of UP/styrene/nanoclay systems cured at room temperature. The kinetics behaviour of UP/styrene system at presence of nanoclay was investigated by measurement of quasi-adiabatic exotherm behaviour. Quasi-adiabatic reactor and rheometric dynamic analyzer were used to measure the gel time of the UP/styrene/nanoclay systems.

EXPERIMENTAL

Materials

The unsaturated polyester resin used in this study was an ortho UP resin containing 38% by weight styrene (Bushepol 81715, Bushehr Chemical Industry, Iran), with an average of 3.4 vinylene groups per unsaturated polyester molecules. The average molecular weight of the unsaturated polyester resin is 1589 g/mol and the equivalent molecular weight (mole of C=C) is 464 g/mol. The molar ratio of styrene/unsaturated poly-

ester resin is 2.7 [3]. The initiator was methyl ethyl ketone peroxide (MEKP) (50% in phthalate plasticizer) containing 9.9% active oxygen supplied by Pamokale Co., Tehran, Iran.

The promoter used was cobalt naphthanate, CoN (10% in White spirits, Chekad Co., Tehran, Iran). Hydroquinone (HQ, Merck) was used as inhibitor. Cloisite 15A (15A) is a natural montmorillonite modified with 2M2HT (dimethyl dihydrogenatedtallow quaternary ammonium chloride) used as nanoclay and was purchased from Southern Clay Co., USA.

Instrumentation

The volume change of the resin during curing was measured by an in-house constructed apparatus designed based on Watts method [23]. The volume change was detected by linear variable displacement transducer (LVDT) through the movement of a lamella, which placed on the sample. Figure 1 shows schematic configuration of the shrinkage measurement apparatus.

The cure exotherm was measured according to ASTM D-2471. Approximately 80 g of the resin mixture was poured into a paper cup (4 cm diameter and 7 cm deep) at room temperature. The height of mixture in the paper cup was 5.5 cm. The time-temperature data were measured by placing a thermocouple connected to a digital thermometer in the center of the isolated paper cup.

A rheometric dynamic analyzer (RDA) model MCR300 (Paar Physica; Germany-Austria) was used to evaluate the rheological changes that occurs during the copolymerization of UP and styrene. Viscosity was measured under isothermal conditions (26ºC) and at a shear rate $0.1 \ s^{-1}$. The diameter of plates was 25 mm, and the gap between them was on the order of 1 mm.

A Haake viscometer model ViscoStar-R (Selecta; Spania) was used to measure the viscosity of uncured mixtures before addition of MEKP at room temperature.

For the X-ray diffraction (XRD) analysis a Miniflex diffractometer using CuK_{α} radiation with a dwell time of 1º/min, in the θ-2θ Bragg- Brentano (0-10º) geometry was employed.

Preparation Method

Five-step procedure was employed for preparation of Bushepol 81715/15A sample, that 15A content was 4 parts per one hundred parts (phr) of Bushepol 81715 by weight. In the first step, Bushepol 81715 and 15A powder were mixed by using a mechanical mixer and an impeller speed of 2000 rpm for 2 h at room temperature, until a homogeneous mixture was obtained. Then the homogeneous mixture stored for 48 h at room temperature. In the third step, the mixture mixed again at 2000 rpm for 2 h at room temperature.

In the forth step, the mixture stored for 4 weeks at room temperature. Finally, it mixed at 2000 rpm for 2 h at room temperature. In order to prepare the test samples with 0-3 phr Cloisite15A, this homogeneous mixture was degassed and mixed with the appropriate amount of Bushepol 81715, CoN, HQ, and MEKP.

The resin mixtures used in this study contain 1.5, 0.2, 0.02, and 0-3 phr of MEKP, CoN, HQ, and Cloisite15A, respectively. Four samples of N0, N1, N2 and N3 were prepared which their amounts of nanocaly were 0, 1, 2, and 3 phr, respectively.
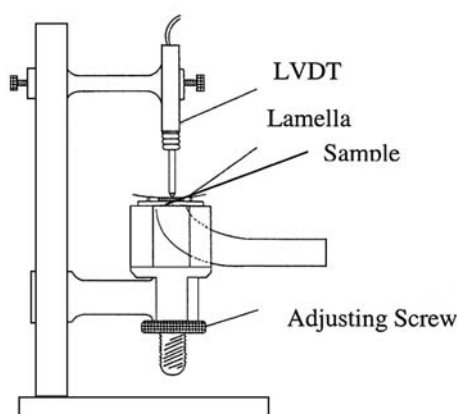
RESULTS AND DISCUSSION

X-ray Analysis

The X-ray diffraction patterns of the organically modified clay, 15A, and N3 (nanoclay filled UP/Styrene mixture contain 3 phr 15A) are depicted in Figure 2. The XRD curve for 15A shows a strong X-ray diffraction peak, with characteristic gallery spacing of about 3.1 nm. For N3, the characteristic peak has nearly disappeared and the gallery spacing increases from 3.1 to 3.8 nm. Hence, intercalation has occurred and a highly unordered intercalated structure has been formed.
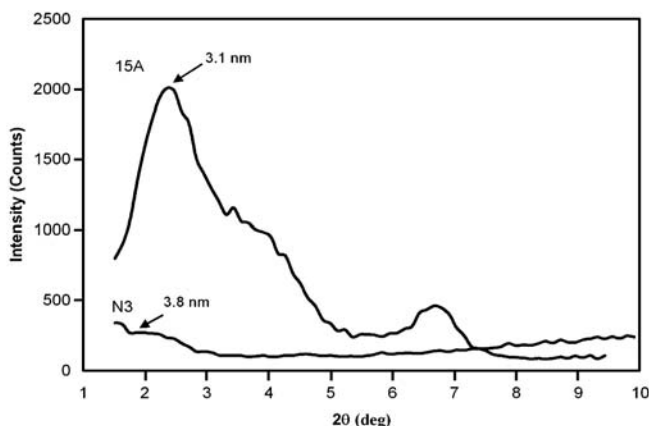

Figure 1. Schematic of shrinkage measurement apparatus.

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Figure 2. XRD Patterns of 15A powder and N3 sample.

Figure 4. Schematic of the nanoclay filled UP/styrene mixture after curing.

Volume Shrinkage Behaviour of UP/Styrene/15A Mixtures

Figure 3 is a plot that compares the volume change of UP/styrene/15A mixtures, which were examined by the shrinkage measurement apparatus at 26ºC. For all the cases, the samples showed sharp polymerization shrinkage before flattening. The volume change curves in these region show differences, probably due to their different reaction kinetics. Unlike mixtures containing conventional low profile additives (e.g., PVAc), these mixtures did not exhibit an expansion at the further stage of cure. It has been found that microvoid formation in the further stage of curing is a critical factor for shrinkage control [19].

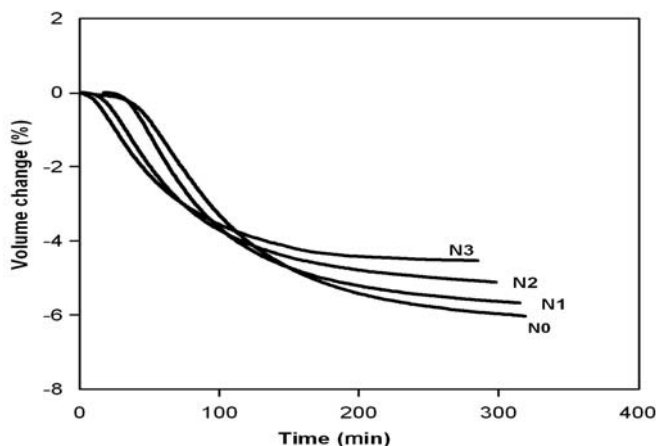The appearance of N1, N2 and N3 samples was opaque, whereas the appearance of N0 (the sample without 15A) was translucent. There was not any LPA-rich phase consequently, any microvoid was not formed. The opaque appearance may be due to the intercalated clay platelets clusters that dispersed through the cured UP/styrene/15A mixture (Figure 4).

Raising the 15A content to 3 phr increased the opacity. If there is no LPA-rich phase, then how does shrinkage control take place? The shrinkage control behaviour of UP/styrene/15A mixtures cured at room temperature can be explained by two competing factors: (i) shrinkage caused by polymerization and (ii) expansion induced by microvoid formation. Another factor probably is the formation of a fixed stable structure which the clusters of intercalated clay platelets are its fixed elements. If entanglements occur between UP chains and clay platelets, the fixed structure will prevent the shrinkage.

After adding MEKP, the sample without 15A (N0)

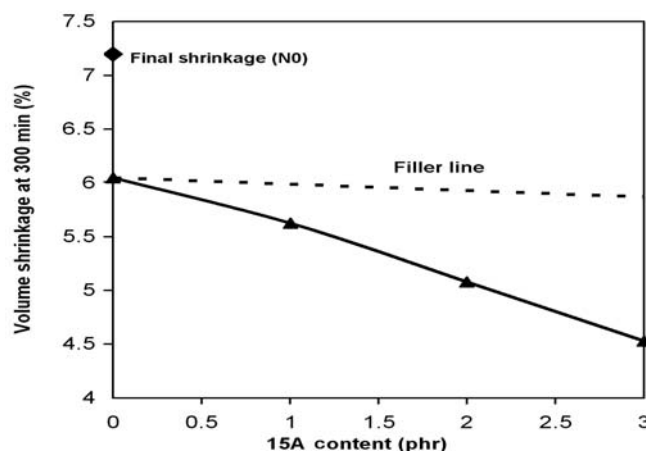**Figure 3**. Volume change profile of nanoclay filled UP/styrene mixture cured at 26ºC.

Figure 5. Volume shrinkage at 300 min vs. the 15A contents of UP/styrene/15A mixtures cured at room temperature.

was cured at room temperature for 24 h and then post-cured isothermally in an oven at 100°C for 2 h. Density measurement [11] of the post-cured sample was employed to calculate the final volume shrinkage of the resin system. The sample without 15A has the final volume shrinkage of 7.2%.

Figure 5 summarizes the volume shrinkage results at 300 min as a function of 15A contents. The shrinkage at 300 min and the final shrinkage of N0 are also compared in Figure 5. The final shrinkage of sample contaning 0 phr of 15A is only 1.2% greater than the value of that at 300 min. This difference is even smaller for the samples containing 15A, because it nearly increases reaction rate and a higher conversion percentage will obtain at 300 min. The filler line that plotted in Figure 5 shows the effect of nanoclay, if it simply acts as a filler without any low profile (i.e., shrinkage control) effect.

It has been demonstrated [15] that there are an upper and a lower concentration limits for the thermoplastic LPAs to be effective for shrinkage control. However, Figure 5 shows that, the shrinkage at 300 min decreases gradually and results to 4.55% at 3 phr 15A content. There is not a sharp drop in final shrinkage that generally observes in thermoplastic LPAs. When nanoclay acts as a low profile additive, there is not a LPA-rich phase and co-continuous particulate structure. It is suggested that with increasing of 15A content, the number of clusters that disperse through the mixture, will also increase. More clusters cause more entanglements and therefore, it lowers shrinkage.

Reaction Kinetics of UP/Styrene/15A Mixtures

Study of highly exothermic polymerizations is possible by quasi-adiabatic exothermic measurements without the use of expensive equipments (e.g., DSC) [24]. This method, which is often applied to very fast reactions is very suitable for mixtures containing nanoclay that really rising reaction rate. An n-order kinetics was proposed by Rojas [24]:

$$dx/dt = A (1-x)^n \exp(-E/RT) \qquad (1)$$

where x, A, E, and T are the conversion, the Arrhenius pre-exponential factor, the activation energy and the adiabatic temperature (K), respectively. The adiabatic temperature and the conversion values at each time are cal-

culated by the following equations:

$$T = T_{exp} + \int_0^t \frac{U}{c_\rho} (T_{exp} - T_o) dt \qquad (2)$$

$$x = \frac{T - T_o}{T_{max} - T_o} \qquad (3)$$

where T_o, U, and C_p are the room temperature, the global heat transfer coefficient per unit mass, and the specific heat, respectively which the latter is assumed to be constant. The ratio of U/C_p was calculated from the cooling curve when the polymerization reaction had ceased.

The curves of experimental temperature (T_{exp}) - reaction time are shown in Figure 6. After the maximum, temperature decreased with a varying rate. Although, value of this rate was very low (for N0 its greatest value was of the order of 1.7 K/min), the effect of heat losses has been corrected by eqn(2). In deed, adiabatic temperature (T) is the corrected temperature. The adiabatic temperature was calculated from the experimental curves, but has not shown in Figure 6. The induction time is reduced by addition of 15A (N0 : 54.8, N1: 30.1, N2: 25.1, and N3: 22.3 min). It has also been revealed [21] that nanoclay acts as a co-promoter in the copolymerization between UP and styrene. On the other hand, the maximum experimental temperature (exotherm peak) is increased from 176°C (N0) to 196°C (N3). This indicates that the reaction had gone to completion with increasing the level of 15A. However, Xu [21] has showed that the nanoclay content does not
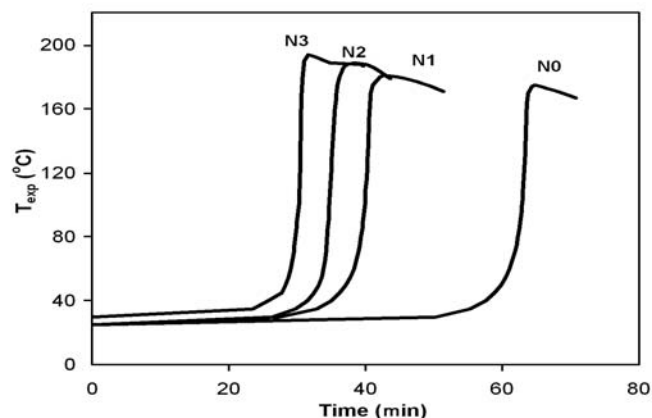

Figure 6. Experimental cure exotherm temperature vs. reaction time in the quasi-adiabatic reactor.

Table 1. Kinetic parameters of UP/nanoclay systems for runs carried out in a quasi-adiabatic reactor.
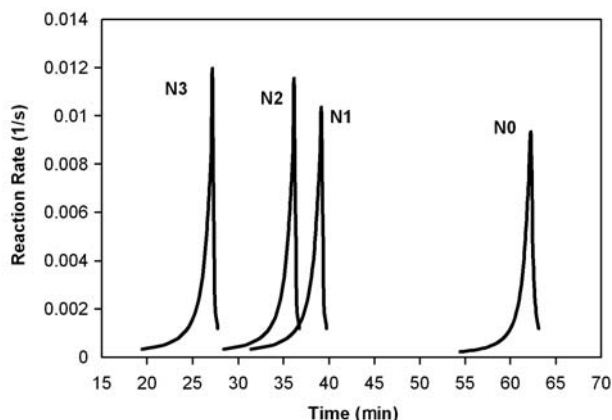
Kinetic parameter	N0	N1	N2	N3
$U/C_p \times 10^{-2}$ (min^{-1})	2.53	1.93	1.75	1.03
A (min^{-1})	2.81×10^6	5.44×10^8	5.75×10^9	0.94×10^{11}
E (kJ/mol)	49.4	55.9	68.0	71.2
n	1.9	2.4	3.7	4.1

affect the network formation during the course of reaction and the final conversion at a constant temperature. But, there is a difference between Xu's experiments and what has been obtained in this study. Sample amount in DSC is very small but in quasi-adiabatic testing it is nearly 80 g. When sample amount is small, most of the initiation is due to the catalyzed decomposition of the peroxide by cobalt, which is true at moderated temperatures. But all the experiments that are used to identify the kinetic effects are quasi-adiabatic, and take place at temperatures up to 170°C. In such conditions, the thermal initiation (direct decomposition of the peroxide) can not be neglected (and become even predominant) thus, the network formation is affected.

The values of E/R, A, and n (eqn 1) are calculated by plotting of $Ln(\frac{\Delta T/_{\Delta t}}{\Delta T_{max}(1-x)^n})$ versus 1/T (eqn 4).

$$Ln(\frac{\Delta T/_{\Delta t}}{\Delta T_{max}(1-x)^n}) = LnA - (E/R)(1/T) \qquad (4)$$

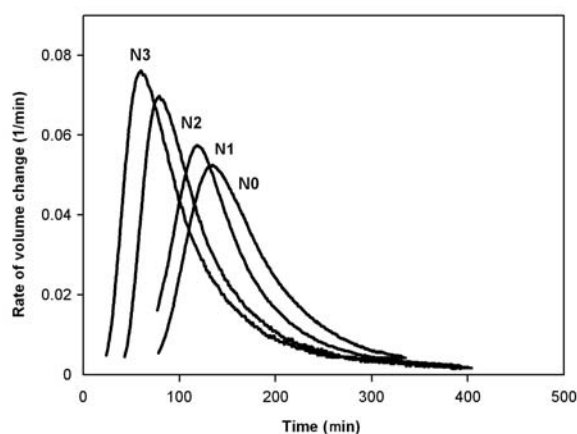The values of A and E are sensitive to changes in value of n. Therefore, the best values of LnA and E/R were

calculated for a certain value of n [24]. The values of U/C_p, A, E, and n are listed in Table 1.
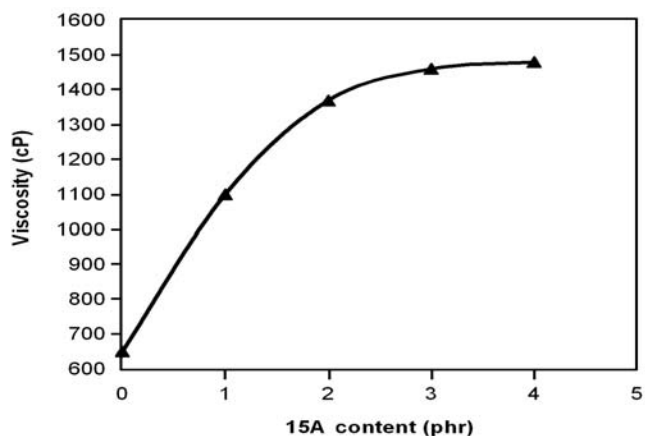
Figure 7 shows the reaction rates of the resin system at different 15A contents, which were calculated by eqn 1. At higher clay content, the reaction rate increased and the induction time decreased. This observation is clearly confirmed by the rates of volume change curves that had been calculated by the dynamic shrinkage experimental results (Figure 8).

Figure 9 shows the effect of nanoclay loading on the viscosity of the UP/styrene/15A mixtures at 26°C without reaction. The addition of 1-2 phr 15A into the UP/styrene mixture dramatically increases the viscosity. Further increase of the 15A content (2-4 phr) also increase the viscosity, however, the influence is not very significant.

The effect of 15A loadings on the rheokinetics of the samples cured at 25°C is shown in Figure 10. Introducing 1 phr 15A into the UP/styrene mixture (N1) makes the onset of the viscosity rise happen much earlier, and it led to a higher reaction rate, faster viscosity rise, and earlier gelation. Further increase of the 15A

Figure 7. Reaction rate profiles calculated by Rojas method [24] for nanoclay filled UP/styrene systems in a quasi-adiabatic reactor.

Figure 8. Rate of volume change profiles of UP/styrene/15A mixtures.

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Figure 9. Viscosity of nanoclay filled UP/styrene mixture without reaction at 26°C.

content (1-3 phr) also reduces the gel time; however, the influence is not very significant.

At the gel point, the curing system transforms suddenly from a viscous liquid to an elastic gel. A well-accepted indicator for the occurrence of gelation is the rapid increase in viscosity. When the viscosity increases to infinity, the gel point is considered to be achieved. However, it is not practical to measure they infinite viscosity. An accepted but not scientifically a well defined method is to obtain the gel time when the reduced viscosity $\eta_r = \frac{\eta}{\eta_o}$ (where η : instantaneous viscosity and η_o : initial system viscosity) equals 10^3 [25].

The gel time is plotted as a function of 15A contents in Figure 11. The gel time values measured with RDA and the quasi-adiabatic reactor show the same trends. Introducing 1 phr 15A into the UP/styrene mixture (N1) leads to the gel time decreases to about 17 min. A com-
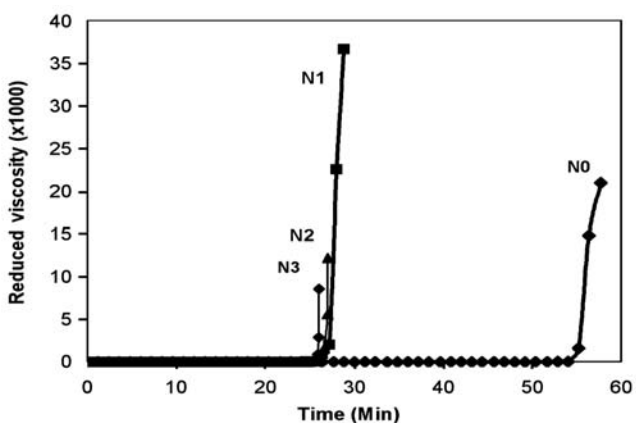
Figure 10. Reduced viscosity rise vs. reaction time as a function of nanoclay content at 25°C.
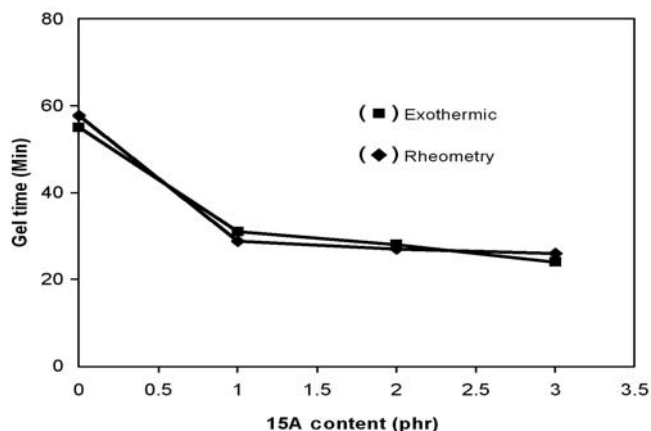
Figure 11. Dependence of gel time on 15A contents of UP/styrene/15A systems.

parison of rheometry and quasi-adiabatic exothermic measurements shows that gel time values are nearly constant when 15A content is more than 1 phr.

It is worth mentioning that the polymer-clay nanocomposites show outstanding improvements in tensile strength and modulus, heat distortion temperature, gas and liquid permeability, biodegradability, ionic conductivity, etc. [26,27] but, it was not the objective of this study to investigate these properties. Anti-shrinkage effect of nanoclay is an important issue that was investigated in this work.

CONCLUSION

In this study, it is found that the unsaturated polyester resin with a nanoclay content of 1-3 phr dose not exhibit an expansion at the last stages of cure. There is no LPA and consequently no LPA-rich phase, then how does shrinkage control take place? It is suggested that formation of a fixed stable structure where the clusters of intercalated clay platelets are its fixed elements, is probably the reason of this behaviour. When entanglements occur between UP chains and clay platelets, the fixed structure will prevent from shrinkage. It seems that with increasing of 15A content, the number of clusters that dispersed through the mixture will also increase. More clusters cause more entanglements and therefore lower shrinkage.

The experimental temperature (T_{exp}) - reaction time (t) results from the quasi-adiabatic reactor showed that

the induction time is reduced by addition of 15A content. On the other hand, the maximum experimental temperature (exothermic peak) is increased from 176°C (without nanoclay) to 196°C (with 3 phr nanoclay). Both the reaction rate calculated by eqn 1 and the rate of volume change percentage calculated by the shrinkage measurements confirmed that at the higher clay content, the reaction rate increases and the induction time decreases.

Introducing 1 phr nanoclay into the UP/styrene mixture makes the onset of the viscosity rise happen much earlier which led to a higher reaction rate, faster viscosity rise, and earlier gelation. Further increase of the nanoclay content (1-3 phr) reduces the gel time; however, the influence is not very significant. Finally it is clearly observed that the effect of increasing the level of 15A on the gel time is the same for rheometry and exothermic results.

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