Rheokinetics of Crosslinkable Poly(vinyl acetate) Emulsion and Diethylene Triamine

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ABSTRACT: The study of the rheological behavior associated with the crosslinking process of epoxy-functionalized poly(vinyl acetate) emulsion and diethylene triamine showed that the system was reactive and very sensitive to temperature. Gelation times and gelation temperatures were determined from the abrupt changes of the viscoelastic material functions G', G'', and η^* in time sweeps and temperature sweeps. Isothermal kinetics models of the crosslinking process based on the isoconversional method predicted the relationship of curing rate, degree of conversion, reaction nature and kinetic parameters, and temperature. The temperature dependence of the rate constants was found to be described by the Arrhenius relationship. The temperature dependencies of G', G'', and η^* were found to be frequency independent at the gel point, T_{gel}, providing a fingerprint for determining T_{gel} of the crosslinkable systems. The variation of G' and G'' with frequency followed the power laws showing $G' = A'\omega^b$ and $G'' = A''\omega^c$ through the frequency sweep. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: adhesives; crosslinking; rheology; emulsion polymerization

INTRODUCTION

Poly(vinyl acetate) (PVAc) latex is one of the most important wood adhesives because of its relatively low cost, low toxicity, ready availability, wide compatibility, and excellent adhesion to cellulosic materials. However, as an adhesive, PVAc has the deficiencies of poor resistance to water and heat and deformation under load over time because of its inherent thermoplastic nature.[1–3] In the current study, we used the strategy of creating core–shell particles comprising PVAc cores and poly(glycidyl methacrylate) (PGMA) shells. The aim was to combine the film-formation properties of PVAc latexes with the ability of PGMA to be crosslinked with amine curing agents. Our expectation was that crosslinking was complete during the film formation, the resulting crosslinked film should have enhanced resistance to water, heat, and creep.

Crosslinking, the postreaction between a crosslinkable latex and a curing agent, is a very important process in film formation, and the structure of the network formed by crosslinking determines the application properties.[4–10] Dynamic rheology is a powerful tool for monitoring crosslinking and microstructural changes, as it allows properties to be probed in conditions without disruption of the microstructure. In addition, it is an effective method for studying the curing process and for the determination of the viscoelastic properties and transition temperatures of the cured products.[11–13] The rheological behavior of aqueous polyurethane dispersions has been systemically studied by Madbouly et al.[14–18] Their experimental determination and prediction of gelation are important for the processing of crosslinking polymers in dispersion, whereas the criticality of the phenomenon and the universality of the properties at the gelation threshold make gelation interesting from a fundamental point of view. The isothermal reaction kinetics were described using a phenomenological equation based on the Malkin and Kulichikhin model.[19,20] The isothermal gelation kinetics were also analyzed using a standard isoconversional method that is based on replicated experimental data and model-free kinetics calculations.[15] Tielemans and Roose[21] carried out a study of the rheology of aqueous radiation-curable polyurethane dispersions modified with associative thickeners. It was suggested that the crosslinking process in the colloids is intrinsically related to the fluid to solid transition that was manifested as a kinetic arrest and was driven by the crowding or clustering of particles. The formation of polymer gels can be monitored from the time evolution of viscoelastic material functions at the gel point, in which the entire network process can be divided into two parts separated by the gel point.[22] It is therefore important to understand the rheological behavior of the latex. To our best knowledge, dynamic

rheological study of crosslinkable PVAc emulsion has not been reported.

EXPERIMENTAL

Materials

Vinyl acetate and vinyl ester of versatic acid (VeoVa10) were supplied by Nuplex Chemicals, Auckland, New Zealand. Inhibitor was removed from VAc by passing the monomer through a column packed with quaternary ammonium anionic exchange resin (Aldrich Chemical, Milwaukee, USA); the first and last 10% fractions being discarded. GMA (supplied by Sigma Aldrich, St Louis, USA) and VeoVa10 were purified by distillation under reduced pressure; the first and last 10% of the distillate being discarded. All monomers were stored in darkness at 2°C for not longer than a week before use. All other reagents were used as received, namely, the initiators ammonium peroxydisulfate (APS; Aldrich Chemical, Heidelbery, Germany) and benzoyl peroxide (BPO; BDH Chemical, Poole, England); sodium dodecylbenzene sulfate (SDBS) surfactant; sodium hydrogen carbonate buffer; and diethylene triamine (Aldrich Chemical, Milwaukee, USA) curing agent.

Specimen preparation

Preparation of crosslinkable emulsion

Preparation of seeded latex particles. PVAc-*co*-VeoVa10 seed latex was prepared via semicontinuous emulsion polymerization at 75°C for 4 h using 200 g of deionized water, 85 g of VAc, 15 g of VeoVa10, 0.48 g of APS 0.1 g of $NaHCO_3$, and 0.6 g of SDBS. The synthesis was carried out in a 5-necked glass reactor (500 mL). When the reaction mixture had attained the set temperature, the initial charge of APS solution, dissolved in a small quantity of deionized water, was added, followed immediately by the initial charge of a pre-emulsion of the monomers. The reactor was sealed and stirred for 40 min (avoidance of the polymerization exotherm). Gradual feed of the remaining pre-emulsion of monomers was begun with a feed rate of 70 mL h^{-1}. During the gradual feed of the pre-emulsion of monomers, APS solution was added to the reactor at 30-min intervals. When the feed of pre-emulsion was completed, the reaction was continued for 1 h to allow polymerization of the remaining monomer.

Preparation of crosslinkable core–shell latex particles. Core–shell latexes were prepared as follows: 100 g of the above PVAc emulsion as the seed, 6.7 g of GMA monomer, together with BPO as initiator, were added in a starved process. The seed latex was heated to 50°C, and the GMA monomer was added dropwise to the reactor at a very slow rate

(20 g h^{-1}). BPO (0.2 g) was dissolved in the GMA monomer and added to the reactor with GMA monomer. The reaction was allowed to proceed for 1 h after completion of the monomer feed.

Preparation of curing

The core–shell emulsion with epoxy groups and diethylene triamine were completely mixed at the stoichiometric molar ratio of functional groups by stirring at room temperature until they formed a homogeneous mixture for rheological measurements.

Apparatus and procedures

Rheology was carried out using a Paar Physica Rheometrics system (Physica UDS 200; Anton-Paar, Germany) equipped with a 25-mm plate. The following rheological experiments were performed: (1) time sweeps at different constant temperatures (15, 20, 25, 30, and 35°C) and constant shear frequency in the linear viscoelastic regime (strain amplitude $\leq$ 10%) were used to determine the influence of the gelation process on the viscoelastic characteristic functions (G', G'', and η^*); (2) temperature sweep (2°C min^{-1}) at a range of constant shear frequencies and a strain rate in the linear viscoelastic region to determine the temperature dependence of the linear viscoelastic properties; (3) frequency sweep at various constant temperatures (15, 20, 25, 30, 35, and 40°C) in the linear viscoelastic region to obtain the viscoelastic characteristic functions (G', G'', and η^*) over a wide range of frequencies.

RESULTS AND DISCUSSION

Time dependence of crosslinking process

The isothermal time dependence of G', G'', and η^* at 15, 20, 25, 30, and 35°C and constant shear frequency (10 rad s^{-1}) are shown in Figures 1–3. A dramatic increase in G', G'', and η^* was clearly observed at 25, 30, and 35°C, but not at 15°C, showing that crosslinking did not occur (within the timescale of the experiment) at that temperature. At 20°C, G', G'', and η^* increased relatively slowly over a period of about 75 min, and much more slowly at longer times.

At long times, the values of G', G'', and η^* at 20°C $\leq T \leq$ 35°C became approximately time invariant. The time (t_{onset}) at which G', G'', and η^* started to increase rapidly and the magnitudes of the time invariant values of those parameters were strongly temperature dependent. The elevation in G', G'', and η^* were found to be strongly temperature dependent, that is, the magnitude of the elevation in G', G'', and η^* increased and the onset decreased with increasing temperature. The fact that the magnitude
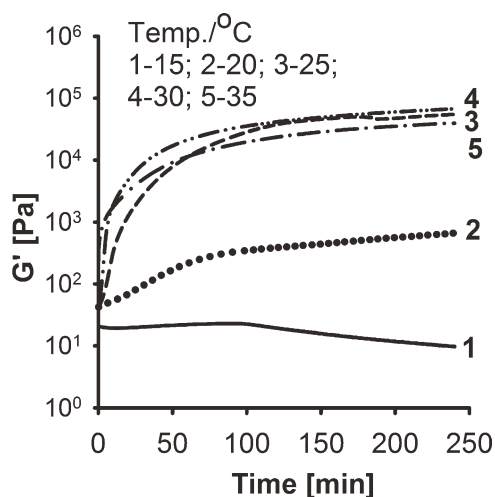
Figure 1 Variation of G' with time.

Figure 3 Variation of η^* with time.

of the elevation in G', G'', and η^* increases greatly with increasing time and temperature is attributed to the proceeding of crosslinking and the significant increase in branching (formation of three-dimensional polymer network).[16] G', G'', and η^* reach near a plateau value at longer time, which is related to the formation of an equilibrium modulus, G'_{eq} and G''_{eq} (a typical criterion for the formation of an elastic, three-dimensional polymer network). The elevation in G', G'', and η^* at 240 min is about three orders of magnitude. The high sensitivity of G', G'', and η^* to the crosslinking process is attributed to the fact that the stress induced in the system by the branching and formation of a three-dimensional polymer network is mostly of elastic origin.[16]

Isothermal Gelation Kinetics

A general objective of the modeling of curing reactions is the derivation of a complete description of the
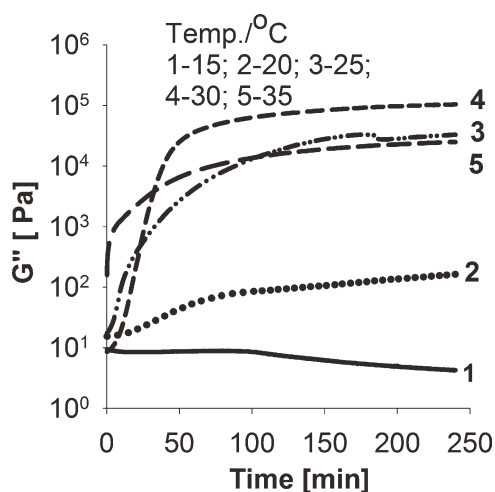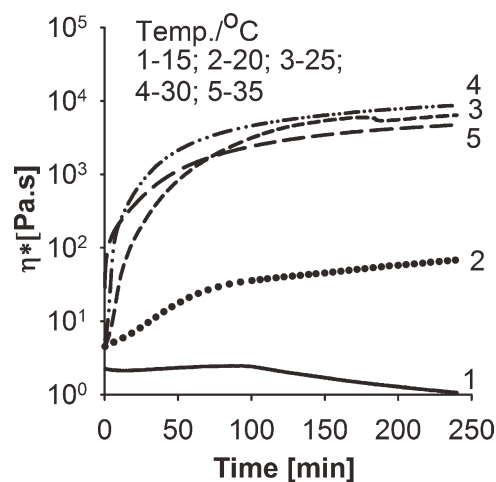

Figure 2 Variation of G'' with time.

progress of the crosslinking process. A basic variable in the case of rheological investigations of curing polymers is the dynamic storage modulus, G', which is proportional to the crosslink density of the network being formed by chemical bonds and physical entanglements.[15,23] Its change with time very often exhibits a transformed crosslinking process. The kinetics of the curing can be evaluated rheologically by applying fundamental rate laws with traditional model-fitting methods.[19,24,25] Another approach used in the study to evaluate the activation energy as a function of the degree of conversion is the so-called isoconversional method that is based on experimental data and model-free kinetics calculations, that is, no assumptions model.[20,26] Isoconversion methods are the most reliable methods for the calculation of activation energies of thermally activated reactions.[20] In this section, the isothermal crosslinking kinetics for the system of the crosslinkable core–shell epoxy-functionalized PVAc emulsion and amine curing agent were studied using model-fitting isoconversional methods.

By the nonlinear curve fitting, the following equation was found that was the best one to fit the experimental rheological data of the crosslinking process:

$$d\beta/dt = y_0 + \{A/w(\pi/2)^{0.5}\} \exp\{-2(\beta - x_c)^2/w^2\} \quad (1)$$

where β is the rheological conversion degree. Equation 1 describes the overall kinetics in both the early and late stages of a reaction. The rheological degree of conversion, β, can be evaluated at a constant temperature from the time dependence of G' (Fig. 1) using the following relation[14,15,27]:

$$\beta = (G'_t - G'_0)/(G'_\infty - G'_0), \quad (2)$$

where G'_t is the value of the storage modulus at time t; and G'_0 and G'_∞ are the values of storage modulus at the beginning of the experiment and at
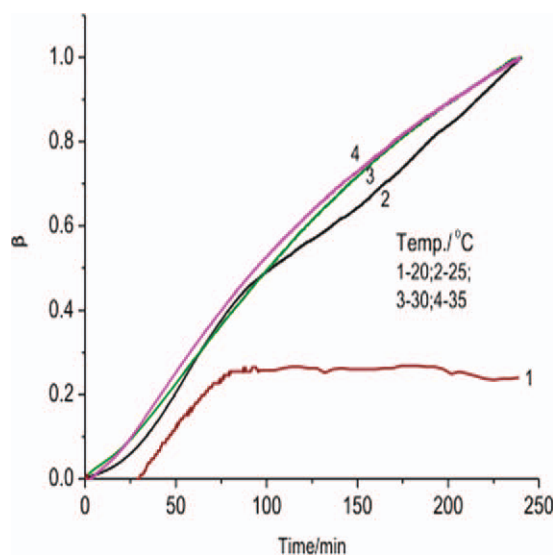
Figure 4 Rheological degree of conversion, β, as a function of gelation time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the maximum crosslinking time, respectively. Figure 4 shows the rheological degree of conversion [calculated from eq. (2)] as a function of crosslinking time at constant temperatures. Obviously, the degree of conversion was almost zero before the onset of crosslinking process and then increased strongly with crosslinking time. The maximum degree of conversion was almost unity at 30 and 35°C; however, it was very small at 20°C due to the very slow crosslinking process at this temperature over the time scale of the measurements (see Fig. 4).

It can be seen that at 35 and 30°C, the curing rate preceded relatively rapidly; however, on the other hand, it was slower at 20°C, requiring and needing a
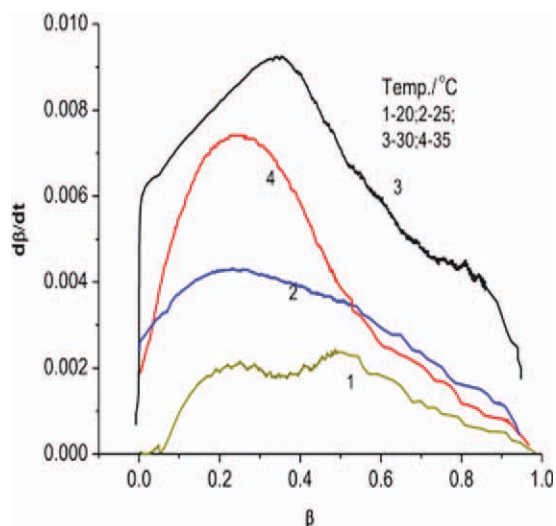
TABLE I
Kinetic Parameters of Crosslinking Process of PVAc Emulsion with Diethylene Triiamine Given by Eq. (1)

Temperature (°C)	A	m	w	y_0
20	0.00241	0.37028	0.72524	0.0041
25	0.00845	0.28747	0.86641	0.0023
30	0.01654	0.36217	1.09361	0.0035
35	0.03216	0.26675	0.84166	0.0022

longer crosslinking time to reach to the plateau. The maximum point shifted to longer time with decreasing temperature as the reaction at lower temperature took longer time to kinetically proceed to completion.

Figure 5 shows the rate of rheological degree of conversion ($d\beta/dt$) as a function of β for different isothermal temperatures. The cure rate increased with the degree of conversion, and reaches to the maximum at the degree of conversion 0.1, and decreased with the degree of conversion. By using the nonlinear regression analysis to fit the experimental data, eq. (1) was the best fitting to the experiment data. The obtained parameters for eq. (1) are listed in Table I.

It was very obvious that the kinetic parameter A was mostly dependent on temperature and was involved with the instinct nature of the chemical reaction. On the other hand, other parameters such as m and w were not sensitive to the temperature, and slight changes were not regular with temperatures. The temperature dependence of the apparent rate constants, A, of eq. (1) obtained from the above regression (Table I) can be described by the following Arrhenius relationship equation[27]:

$$k(T) = A \exp(-E_a/RT), \qquad (3)$$

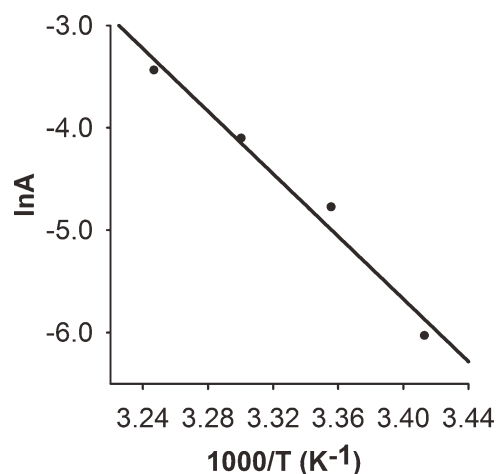where E_a is the apparent activation energy, R is the universal gas constant, and T is the absolute

Figure 5 Variation of $d\beta/dt$ as a function of β. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 6 Arrhenius treatment of the temperature dependence of the rate constants and A of eq. (3).

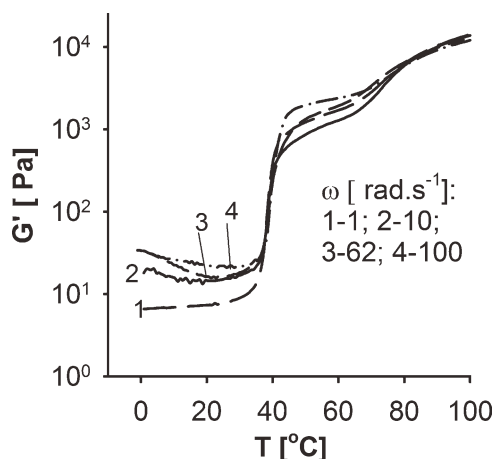**Figure 7** Temperature dependence of G'.

Figure 9 Temperature dependence of η^*.

temperature. One can determine the value of E_a from the slope of the linear relationship between $\ln(A)$ and the inverse of absolute temperature, as demonstrated in Figure 6.

It was found that E_a equaled 126 kJ mol^{-1} for the temperature dependence of A. The value of E_a for the present system ascribed was properly due to the activities of functional groups, and latex nature which lead to the formation of a network structure. The crosslinking reaction is diffusion controlled depending on the structure of the molecules or the diffusivities of the molecules. The diffusion control not only depends on the size and shape of the molecules but also on the viscosity of the system.

Temperature dependence of crosslinking process

Figures 7–9 revealed the temperature dependence of G', G'', and η^* at 2°C min^{-1} heating rate and at different constant shear frequencies for the epoxy-functionalized PVAc emulsion with diethylene triamine.

As shown in Figure 7, the value of G' was almost constant with increasing temperature at a tempera-
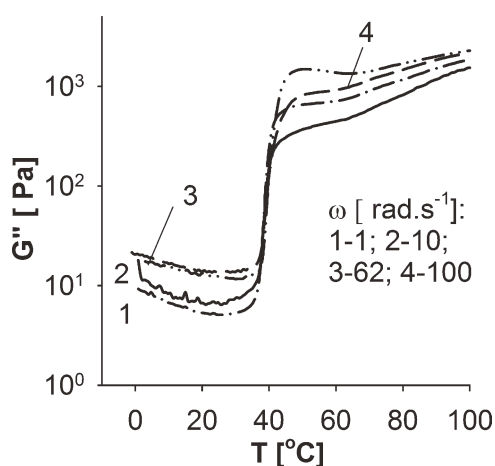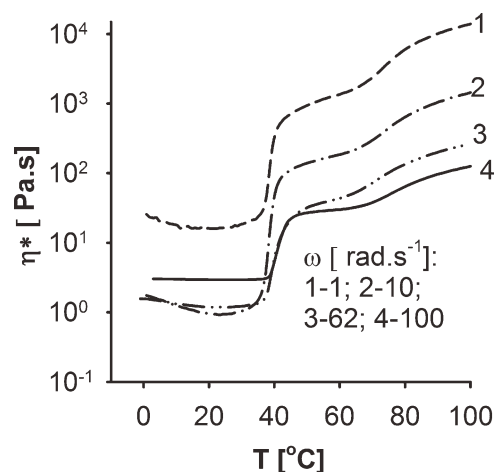
ture range lower than the gel temperature (i.e., T_{gel} around 39°C). A sudden increase in the G' at around 39°C (T_{gel}) was observed at all values of frequencies due to the formation of network. The temperature dependencies of G' were found to be frequency independent at the gel point, T_{gel}, providing a fingerprint for determining T_{gel} of the system. The magnitude of the elevation in G' increased greatly with the increasing temperature due to the evolution of the crosslinking process and the significant increase in branching (formation of gel). In addition, G' was no longer frequency dependent at the high temperature range due to the formation of an equilibrium storage modulus, G'_{eq}, which was a typical criterion for the formation of an elastic fractal gel.[15]

The dynamic temperature ramps of the loss modulus, G'', at different constant shear frequencies are shown in Figure 8. Similar to Figure 7, G'' abruptly increased at the onset of the crosslinking process and became almost frequency independent at the high temperature range due to the formation of an
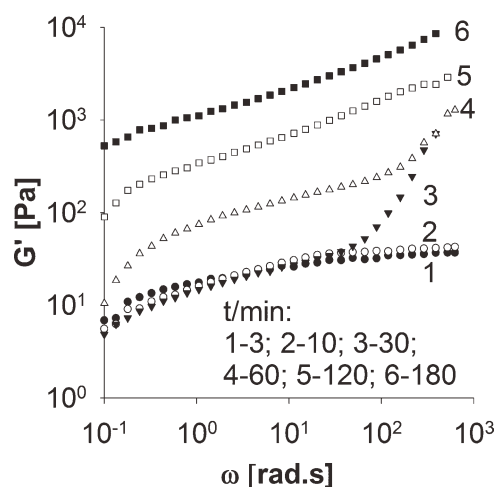

Figure 8 Temperature dependence of G''.

Figure 10 Variation of G' as a function of shear frequency.

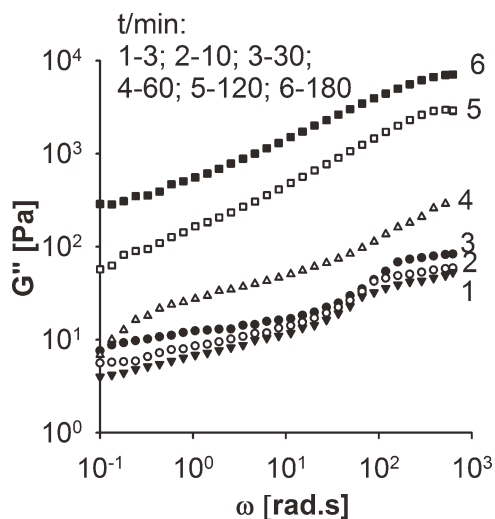**Figure 11** Variation of G'' as a function of shear frequency.

Figure 12 Variation of η^* as a function of shear.

equilibrium loss modulus, G''_{eq}. Similarly, the value of η^*, as shown in Figure 9, was almost constant at a temperature range lower than the gel temperature (i.e., T_{gel} around 39°C). In fact, the viscosity slightly decreased with frequency and temperature in this temperature range ($T < 40$°C). A sudden increase in the η^* at about 39°C (T_{gel}) was observed at all values of frequencies due to the onset of the formation of gel. The temperature dependencies of G'' and η^* were found to be frequency independent at the gel point, T_{gel}, providing a fingerprint for determining T_{gel} of the system. At T_{gel}, the crosslinking system changed from liquid-like to solid-like structure, and consequently, the η^* became frequency independent as the crosslinking process evolved into the formation of network.

Frequency dependence of crosslinking process

Figures 10 and 11 show the frequency dependence of G' and G'' for the system of epoxy-functionalized PVAc emulsion with diethylene triamine at different time intervals at 25°C.

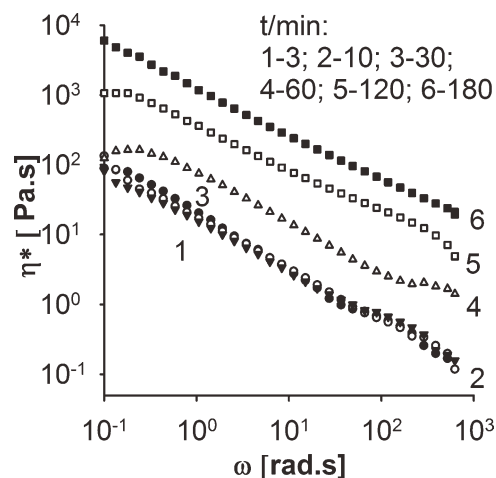We can see from Figures 8 and 9 that at all time intervals, the values of G' and G'' increased with increasing frequency. The values of G' and G'' increased with both frequency and curing time. At $t = 3$, 10, and 30 min, the values of G' and G'' increase slightly with increasing frequency. After 60 min, both values of G' and G'' increased greatly with increasing frequency and time. According to Winter-Chambon criterion,[17] the storage and loss moduli should show the following power law behavior:

$$G' \sim G'' \sim \omega^n \qquad (4)$$

The exponent n was called the relaxation exponent and can be linked to microstructural parameters.[15]

The equations showing the relationship between storage or loss moduli and shear frequency are summarized in Table II. From Table II, it was observed that all the curves representing the relationship between moduli and shear frequency at different time followed the power law relationship. When curing time was 3 and 10 min, the value of G'' was higher than G', indicating a classical liquid behavior. It was apparent that both of the front factors A' and A'' increase gradually with increasing time, and $A' > A''$ indicates that the storage modulus grew faster than the loss modulus. Therefore, at 30 min, the G' was becoming to overweight the G''. Both the front factors A' and A'' might be related with the structure of the polymer chains and their entanglements. Both the exponents b and c were smaller than 0.5, indicating

TABLE II
Power-Law Fitting Equations of G' and G'' Moduli

Curing time (min)	$G' = A'\omega^b$	R^2	$G'' = A''\omega^c$	R^2	
3	$G' = 14.65\omega^{0.2135}$	0.8921	$G'' = 6.17\omega^{0.3126}$	0.9768	$G' < G''$
10	$G' = 15.86\omega^{0.1649}$	0.8852	$G'' = 8.5326\omega^{0.3004}$	0.9640	$G' < G''$
30	$G' = 12.88\omega^{0.4552}$	0.8735	$G'' = 11.86\omega^{0.0.2791}$	0.9197	$G' > G''$
60	$G' = 56.38\omega^{0.3993}$	0.9326	$G'' = 21.13\omega^{0.3676}$	0.9752	$G' > G''$
120	$G' = 296.52\omega^{0.3852}$	0.9894	$G'' = 142.29\omega^{0.3813}$	0.9931	$G' > G''$
180	$G' = 998.51\omega^{0.3981}$	0.9978	$G'' = 498.36\omega^{0.3982}$	0.9836	$G' > G''$

the flexible precursor molecules.[28] The crosslinkable systems underwent an instant transition when the largest molecular cluster diverged to network structure in term of the huge growth of G' and G'', and finally, $G' > G''$.

The frequency dependence of η^* for different crosslinking times is depicted in Figure 12. Obviously, η^* entire curves were strongly frequency dependent and decrease with increasing frequency. The three curves of η^* at 3, 10, and 30 min almost overlapped, indicating that the η^* behavior did not vary too much before the gel point. After 30 min, the value of η^* increased greatly with increasing curing time.

CONCLUSIONS

The study on the rheological behavior of crosslinking process of the system with the core–shell latex composites and diethylene triamine demonstrated that these systems were reactive and very sensitive to the temperature. It was found that the crosslinking time of crosslinking temperatures could be determined by the abrupt variation of viscoelastic material functions, G', G'', and η^* across the time sweep and temperature sweep. The isothermal kinetics models of the crosslinking process based on the isoconversional method predicted more accurately the relationship of curing rate, conversion degree, reaction nature, kinetic parameters, and temperature. The temperature dependence of the rate constants was found to be well described by the Arrhenius relationship. The temperature dependencies of G', G'', and η^* were found to be frequency independent at the gel point, T_{gel}, providing a fingerprint for determining T_{gel} of the crosslinkable systems. The variation of G' and G'' with frequency well followed the power law showing $G' = A'\omega^b$ and $G'' = A''\omega^c$.

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