Validation of Effective Time Translational Invariance and Linear Viscoelasticity of Polymer Undergoing Cross-linking Reaction

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ABSTRACT: In polymeric liquids undergoing cross-linking reactions, rheological properties continuously change as a function of time. Consequently, the materials do not obey the time translational invariance and therefore the principles of linear viscoelasticity. In this work, we propose a methodology in which principles of linear viscoelasticity are transformed from the real time domain to the effective time domain. In the latter, the readjustment of the material clock, which accounts for the time dependency, facilitates validation of the effective time translational invariance. By carrying out experiments on cross-linking PDMS, we show that material that is undergoing time evolution in the real time domain indeed validates the Boltzmann superposition principle and convolution relation relating creep compliance and relaxation modulus in the effective time domain.

I. INTRODUCTION

In a cross-linking reaction, the molecular weight of polymer continuously increases so that a free-flowing polymeric liquid gets transformed to a state that predominantly shows solid like character.1 During this transition viscoelastic properties of a reacting system evolve as a function of time.2 Consequently materials undergoing cross-linking reaction do not obey time translational invariance (TTI), which necessitates properties to remain invariant of time.3 As a result the fundamental law of linear viscoelasticity, the Boltzmann superposition principle, is not applicable to the reacting systems.4 Many applications that involve cross-linking reaction leading to polymer gel formation and processing of thermosetting polymers comprise liquid to solid transition under the application of deformation field.5 However, inherent time dependency that renders TTI inapplicable constrains the rheological analyzability of the same. In this work, we show for the first time that the fundamental relations of linear viscoelasticity such as the Boltzmann superposition principle and convolution relation relating the creep compliance and the relaxation modulus can be successfully applied to the reacting systems in the effective time domain wherein material clock is modified to get rid of the time dependency.

In order to facilitate the linear viscoelastic analysis, two approaches have been used in the literature to address the lack of TTI in the polymeric materials undergoing cross-linking reaction. In the first approach concept of time-resolved rheometry is employed, wherein the polymeric compounds undergoing cross-linking reaction are subjected to small amplitude oscillatory shear with cyclic variation of frequency or superposition of strain waves having different frequencies (ω).6,7 (This method is equivalent to measuring the time evolution of the elastic (G′) and viscous moduli (G″) at different ω in the independent experiments). This method leads to ω dependence of G′ and G″ at different time intervals (different extents of cross-linking), which is further analyzed for linear viscoelasticity. The major limitation of this method is that estimation of both the moduli is not reliable, particularly at low frequencies when viscoelastic properties of the material undergo significant change over the period of a single cycle. In the second approach, time dependency is completely eliminated by terminating the cross-linking reaction at various reaction times.8−12 Since the resultant states of the polymeric material having different extents of cross-linking are observed to demonstrate time−temperature superposition.13 Many studies in the literature have employed this methodology to investigate viscoelastic behavior of a gel at various extents of cure, which is observed to lead to time−cure superposition.8,12,14−17 Although it is, in principle, a full proof methodology, it is very difficult to implement the same experimentally, as terminating a reaction throughout the sample in an instant is practically impossible. Furthermore, this methodology makes the viscoelastic analysis of various states during gelation cumbersome as it necessitates termination of a chemical reaction. Therefore, a methodology which allows viscoelastic analysis without terminating the reaction and also...
addresses time dependency of the reaction process is of great practical importance.

The major focus of various studies in the literature is to investigate linear viscoelasticity associated with the gel point (GP), the point at which polymer forms a space spanning percolated network.10,11 However, a complete linear viscoelastic analysis of different intermediate states of gelation reaction other than the critical state is still lacking. Winter and co-workers1,10,18 in seminal contributions carried out the comprehensive linear viscoelastic analysis of cross-linking material at GP. By terminating a chemical reaction at different states, they observed that at GP the relaxation modulus and creep compliance show a power law dependence on time, while the corresponding tan δ (=G′′/G′) is independent of frequency.10,18 In this work we however employ a completely different approach, which does not require polymeric reaction to be stopped in order to apply the principles of linear viscoelasticity to the same. We also extend the linear viscoelastic analysis to the entire span of gelation and not just the GP.

II. THEORY

The materials whose properties are invariant of time, such as polymer melts and solutions, usually follow the Boltzmann superposition principle (BSP). For a stress (σ) controlled field, BSP leads to estimation of strain (γ) induced in the material and is given by

\[ \gamma(t) = \int_{-\infty}^{t} f(t - t_w) \frac{d\sigma}{dt_w} dt_w \]  

(1)

where \( f \) is creep compliance, \( t \) is time and \( t_w \) is time at which deformation field is applied. When the imposed flow field is strain controlled, the stress induced in the material is given by

\[ \sigma(t) = \int_{-\infty}^{t} G(t - t_w) \frac{d\gamma}{dt_w} dt_w \]  

(2)

where \( G \) is the relaxation modulus. Since the material behavior is invariant of time, replacing \( t \) by \( t + \epsilon \), where \( \epsilon \) is a real number preserves the nature of a constitutive relation.5 Consequently \( G \) and \( f \) for the time invariant materials are only functions of \( t - t_w \), so that \( f = f(t - t_w) \) and \( G = G(t - t_w) \), where \( t_w \) is the time at which step stress/strain is applied. Taking Laplace transform of eqs 1 and 2 leads to convolution relation between \( G \) and \( f \) given by

\[ t = \int_{0}^{t} G(s)f(t - s) ds \]  

(3)

which allows estimation of one response function from the other. In the polymer rheology literature, the BSP and the convolution relation form the most fundamental basis to characterize the materials. However, when properties of a material are different at time \( t \) and at \( t + \epsilon \), TTI is no longer applicable.5 Consequently, \( f \) and \( G \) independently depend on time at which a deformation field is applied \( (t_w) \), which leads to \( f = f(t, t_w) \) and \( G = G(t, t_w) \). Accordingly the convolution relation is also not applicable to the time dependent reacting systems. In this work we derive BSP for generalized Maxwell and Kelvin–Voigt models with time dependent springs and dashpots and express the same in the effective time domain. The resultant expression gives a form, which is similar but not identical to, those already available in the literature on aging glasses.19–23 Furthermore, we not only apply the effective time domain approach developed for aging glasses to the reacting systems but also extend the same to incorporate the application of convolution relation.

It is well-known that linear viscoelastic response of any material can be represented by either a generalized Maxwell model or by generalized Kelvin–Voigt model.4 The generalized Maxwell model, which is a parallel combination of large number of single Maxwell elements (a spring and a dashpot in series), is known to be equivalent to generalized Kelvin–Voigt model that is a series combination of large number of single Kelvin–Voigt elements (a spring and a dashpot in parallel).4,24 Since strain is common for all the Maxwell elements in parallel combination, generalized Maxwell model can be easily used to represent Boltzmann superposition principle in strain control mode. In generalized Kelvin–Voigt model, on the other hand, series combination leads to same stress in all the individual Kelvin–Voigt elements. The former leads to relaxation modulus while the latter leads to creep compliance, and when applied to a same material, both can be expressed in terms of each other using a convolution relation.

Consider a multimode Maxwell model formed by placing large number of Maxwell elements in parallel combination. The relaxation time scale \( (\tau_M) \) and modulus \( (G_M) \) associated with each mode are assumed to evolve with time. The total stress in the system is a sum of \( \sigma_p \) contributed by each mode, and is given by

\[ \sigma = \sum_p \sigma_p \]  

(4)

If \( \tau_M = \tau_M(t) \) is the mean value of relaxation times at any time \( t \), then assuming shape of relaxation time spectrum is invariant of time, we can represent each mode in terms of \( \tau_M(t) \) as

\[ \tau_M(p,t) = \frac{\tau_M(t)}{\alpha_p} \]  

(5)

where \( \alpha_p \) is time independent factor which relates \( p \)th mode to the mean value of relaxation time at any time \( t \). If we define the effective time scale in terms of mean relaxation time, we get

\[ \xi(t) = \tau_c \int_0^t dt'/\tau_M(t') \]  

(6)

Incorporating eq 5 in eq 4, and representing the same in the effective time domain we get:

\[ \sigma[\xi(t)] = \int_{-\infty}^{\xi(t)} \left[ \sum_p G_{M_p}(\xi) \exp\left(-\alpha_p \frac{\xi - \xi_p}{\tau_c}\right) \right] \frac{d\gamma}{d\xi_w} d\xi_w \]  

(7)

where \( \xi_w = \xi(t_w) \). We further assume that modulus of every Maxwell element shows identical time dependence, which allows us to express \( G_{M_p}(\xi) \) as a product of time dependent and mode dependent term given by

\[ G_{M_p}(\xi) = g(\xi)G_{M_p} \]  

(8)

Consequently, eq 7 can be written as

\[ \frac{\sigma[\xi(t)]}{g[\xi(t)\xi]} = \int_{-\infty}^{\xi(t)} G(\xi - \xi_w) \frac{d\gamma}{d\xi_w} d\xi_w \]  

(9)

where
We next consider the generalized Kelvin–Voight model. Let us assume that \( \eta_{Kp}(t) \) and \( \tau_{Kp}(t) \) are respectively the time dependent viscosity and retardation time of \( p \)th mode. The total strain in the system is a sum of strain induced in each mode, given by

\[
\gamma = \sum_p \gamma_p = \int_{-\infty}^{t} \left\{ \sum_p \frac{1}{\eta_{Kp}(t_w)} \exp \left( -\int_{t_w}^{t} \frac{dt'}{\tau_{Kp}(t')} \right) \right\} \sigma(t_w) \, dt_w
\]

Figure 1. (a) Temporal evolution of elastic \( (G', \text{closed symbols}) \) and viscous modulus \( (G'', \text{open symbols}) \) during cyclic frequency sweep measurement. (b) Evolution of \( \tan \delta \) as a function of time at different frequencies. It can be seen that all the curves intersect each other at GP (indicated by plus sign).

The very fact that the relaxation time spectrum and the retardation time spectrum are related to each other, the assumption that shape of relaxation time spectrum is invariant of time compels shape of retardation time spectrum also to be independent of time. Consequently we can relax each mode of retardation time spectrum to the mean value of relaxation time using a time independent factor \( \beta_p \), as

\[
\tau_{Kp}(t) = \frac{\tau_p(t)}{\beta_p}
\]

Consequently eq 11 can be expressed in terms of effective time domain as

\[
\gamma(\xi(t)) = \int_{-\infty}^{t} \left\{ \sum_p \frac{1}{\eta_{Kp}(\xi_w)} \exp \left( -\beta_p \frac{(\xi - \xi_w)}{\tau_p} \right) \right\} \sigma(\xi_w) \, d\xi_w
\]

If we assume the dashpot viscosity of each Kelvin–Voigt element shows identical time dependence, we get:

\[
\eta_{Kp}(\xi) = h(\xi) \eta_{Kp}
\]

Integrating eq 13 by parts and using eq 14 we get:

\[
\gamma(\xi) = \int_{-\infty}^{t} J(\xi - \xi_w) \frac{d}{d\xi_w} \left( \frac{\sigma(\xi_w)}{h(\xi_w)} \right) \, d\xi_w
\]

where

\[
\mathcal{J}(\xi - \xi_w) = \sum_p \frac{\tau_p}{\eta_{Kp} \beta_p} \left[ 1 - \exp \left( -\beta_p \frac{(\xi - \xi_w)}{\tau_p} \right) \right]
\]

Equation 9 in the strain controlled and eq 15 in the stress controlled form are the expressions of Boltzmann superposition principle in the effective time domain. Furthermore, if we assume \( g(t) = h(t) \), Laplace transform of eqs 9 and 15 can be equated to obtain \( \mathcal{L}(J(\xi)) \mathcal{L}(G(\xi)) = 1/s^2 \), whose Laplace inverse produces the convolution relation in the \( \xi \) - domain given by

\[
\xi = \int_{0}^{t} \tilde{G}(\zeta) J(\xi - \zeta) \, d\zeta
\]

It should be noted that although eqs 3 and 17 appear to be mathematically identical, the time dependent material obeys convolution relation only in the \( \xi \)-domain described by eq 17.

It should be noted that the expression of BSP in the effective time domain (eqs 9 and 15) and resulting convolution relation are not applicable to every reacting (or time dependent) system. For example, consider a solution polymerization reaction, wherein a step strain is applied at such an instance where the polymer molecules are only partly grown. Application of step strain results in deforming such partly grown molecules. However, during subsequent relaxation, which is also accompanied by polymerization reaction, the growing part of the molecule will be randomly oriented. Consequently, enhanced relaxation time due to increased molecular weight will not primarily affect the relaxation of the already deformed chain. Such case is more complicated and the effective time domain approach cannot be applied to such situations. On the other hand, in a gelation reaction, deformed chains react (cross-link) with each other so that their relaxation gets affected due to cross-linking. In such case if enhancement in relaxation time occurs in such fashion that preserves the shape of spectrum of relaxation times, the BSP in the effective time domain expressed by eqs 9 and 15 can be used.

**III. MATERIALS AND EXPERIMENTAL PROCEDURE**

In this work, we study the cross-linking reaction of vinyl terminated Polydimethylsiloxane elastomer (PDMS) having brand name Sylgard 184 supplied by the Dow Chemical Company. We mix Sylgard 184 base elastomer with Sylgard 184 curing agent in the ratio of 7:1 weight by weight. The mixing is carried out at 0 \(^\circ\)C to prevent any chemical reaction. To perform rheological experiments we use a rotational rheometer (Anton Paar MCR 501) with concentric cylinder geometry.
(inside diameter of 5 mm and gap of 0.2 mm). For each experiment, a sample preserved at 0 °C is loaded in a shear cell maintained at 0 °C. At certain time, the temperature is raised to 35 °C at which the cross-linking reaction occurs. The temperature is raised by applying a temperature step jump from 0° to 35 °C, from which a reaction time (ω or waiting time) \( t_w \) is measured. A thermocouple takes about 1 min to stabilize the temperature at a final value after giving the step-jump. In this work we carry out oscillatory shear experiments with stress amplitude 0.5 Pa and frequencies in the range 0.1 to 3.16 Hz. We also carry out creep and step strain experiments wherein constant magnitude of stress (1 Pa) and strain (1%) is applied to the samples at predetermined reaction times.

IV. RESULTS AND DISCUSSION

As reaction proceeds, the molecular weight of the polymer increases. The corresponding evolution of \( G' \) and \( G'' \) as a function of reaction time under application of oscillatory stress field having different magnitudes of \( \omega \) is plotted in Figure 1a. We observe that up to nearly 2 h, \( G' \) remains constant; while \( G'' \), which is greater that \( G' \), shows a noticeable increase as a function of time. However, after 2 h, both the moduli rapidly increase as a function of time with \( G' \) increasing at a faster rate than \( G'' \). Eventually \( G' \) crosses over \( G'' \), but the time at which they cross, increases with increase in \( \omega \). The point of gelation transition, which is independent of \( \omega \), is obtained by plotting \( tan \delta \) as a function of time at different \( \omega \) in Figure 1b. It can be seen that sample undergoes gelation transition around a reaction time of 188 min \( (tan \delta \approx 2.1) \). The phase lag \( (\delta) \) at the point of gelation is given by \( \delta = n \pi/2 \), where \( n \) is the relaxation exponent having a value of \( n \approx 0.72 \). This suggests that the \( G'(t) \) and \( f(t) \) should demonstrate a power law dependence at the gelation point given by \( G'(t) \propto t^m \) and \( f(t) \propto t^\nu \).

In Figure 2a, we plot \( J \) induced in the material due to application of \( \sigma \) while in Figure 2(b) we plot decay of \( G' \) as a function of \( t - t_w \) upon applying \( \gamma \) at different reaction times \( t_w \). It can be seen that \( J \) induced in the material decreases, while decay in \( G' \) becomes progressively sluggish for experiments carried out at higher \( t_w \). Since every sample undergoes gelation irrespective of \( t_w \), \( J \) eventually reaches a plateau in the creep experiments. On the other hand, \( G' \) decays to zero, when \( \gamma \) is applied before \( \sigma \), while before \( \sigma \) \( G' \) remains constant.

The relaxation modulus \( G' \) and \( G'' \) are obtained by plotting the data very well. The relaxation time \( (\tau) \) is related to the KWW function parameters by relation: \( \tau = \tau_{\text{KWW}} \Gamma(1/\beta)/\beta \), where \( \Gamma(1/\beta) \) represents the Euler gamma function. As described in Figure 3, before the GP, the relaxation time obtained from these fits can be seen to be following a power law dependence given by \( \tau(t') = A \tau_m(t'/\tau_m)^\mu \) (18) where \( A, \tau_m \) and \( \mu \) are constants. After GP, however, \( \tau \) is observed to follow an exponential dependence on time given by \( \tau(t') = \tau_0 \exp(\alpha t') \) (19) where \( \tau_0 \) and \( \alpha \) are constants. In the literature, \( \tau \) of cross-linking polymeric systems has been observed to demonstrate various functional forms including power law and exponential for pre and post GP scenarios. In this work we observe different functional dependences of \( \tau(t) \) for pre and post GP states represented by eqs 18 and 19 respectively.

For a pre GP state, substituting eq 18 into eq 6 and setting \( \tau_m = \tau_w \) effective time elapsed since application of deformation field can be written as

\[
\xi - \xi_w = \tau \int_{t_w}^t \frac{dt'}{\tau(t')} = \frac{\tau_0^\mu}{A} \left[ \frac{t^\mu - t_w^\mu}{1 - \mu} \right]
\]

On the other hand, for a post GP state incorporating eq 19 into eq 6 and fixing \( \tau_0 = \tau_\psi \) we get

\[
G' = G_0 \exp \left( -\left( [t/\tau_{\text{KWW}}]^\beta \right) \right), \quad G'' = G_0 \exp \left( -\left( [t/\tau_{\text{KWW}}]^{\beta/2} \right) \right)
\]
On one hand, eqs 20 and 21 describe the effective time domain for pre and post gel point states, respectively. On the other hand, eqs 10 and 16 respectively suggest $G = \tilde{G}(\xi - \xi_w)$ and $J = \tilde{J}(\xi - \xi_w)$, which are obtained by normalizing $G$ and $J$ by respective time evolving components. In Figures 4a and 4b, we plot vertically shifted $G$ and $J$ as a function of $\xi - \xi_w$ respectively (vertical shifting is equivalent to normalizing the respective variables by their time evolving contribution). For the pre GP states compliance and relaxation modulus are termed as $J_1$ and $G_1$ respectively and are plotted as a function of $(\xi - \xi_w)A/\tau_\mu$ with $A/\tau_\mu=10^{-7}$. For the post GP states compliance and relaxation modulus are respectively termed as $J_2$ and $G_2$ are plotted with respect to $\xi - \xi_w$. The corresponding vertical shift factors $a$ and $b$ are plotted in Figure 5. As indicated by eqs 9 and 15, $a \approx h(t_w)/h(t_{wR})$ while $b \approx g(t_w)/g(t_{wR})$, where subscript $R$ refers to the reference state. It can be seen that $J$ and $G$ lead to remarkable superposition in the $\xi$ - domain. For $J_1$ and $G_1$ (before GP) the superpositions are obtained for the same value for $\mu = 2.96 \pm 0.02$ and $\alpha=(6.30 \pm 0.19) \times 10^{-4}$. It is, however, important to note that $J$ and $G$ curves at GP (188 min) do not participate in either of the respective superpositions. For samples subjected to the deformation field before GP, although $G_1$ decays to zero before sample attains GP, $J_1$ reported in Figure 2 includes data before and after GP. We have, however, considered only the data before GP in the superposition shown in Figure 4. The creep data after GP has been shown using gray scale, which can be seen to be not superposing very well, as expected.

Figure 3. (a) Short-term relaxation modulus data for pregel and postgel conditions. Solid lines are the KWW function fit ($G - G_e = G_0 \exp(-(t/\tau_{KWW})^\beta)$) with $\beta = 0.25 \pm 0.007$ for the pregel and $\beta = 0.26 \pm 0.011$ for the postgel data. Relaxation time ($\tau$) is plotted as a function of $t_w$ for the pregel states (b) and for the postgel states (c).

Figure 4. Superposed creep curves $J_1$ and $J_2$ (a), and the superposed relaxation curves $G_1$ and $G_2$ (b) are plotted in the effective time domain for $\mu = 2.96 \pm 0.02$ and $\alpha = (6.30 \pm 0.19) \times 10^{-4}$ for the data shown in Figure 2. Subscripts 1 and 2 represent pregel and postgel data, respectively. For the pregel superposition ($J_1$ and $G_1$), abscissa is $(\xi - \xi_w)A/\tau_\mu$ however in order to represent the data clearly we have used $A/\tau_\mu=10^{-7}$. The solid lines shown in part a are the predictions of creep compliance from the superposition of stress relaxation modulus shown in part b using convolution relation (eq 17) in the effective time domain. Similarly, solid lines shown in part b are the prediction of stress relaxation modulus obtained from the superposition of creep compliance shown in part a using eq 17.

Figure 5. Vertical shift-factors ($a$ for compliance, $b$ for relaxation modulus), needed to obtain time-reaction time superposition in the $\xi$ -domain, are plotted as a function of reaction time (filled symbols represent the pre-GP data while the open symbols represent the post-GP data).
It should be noted that even though functional forms of the dependences of relaxation time on time obtained by the procedure shown in Figure 3 and that gotten from superposition shown in Figure 4 are identical, the values of various coefficients are very close but not identical. This is because, the relation obtained from the procedure shown in Figure 3 is merely indicative as it utilizes only the short time data. The dependences obtained from Figure 4 on the other hand are more accurate as those are obtained for superpositions of compliance as well as relaxation modulus and that also for the long time data.

Existence of superposition in the pre GP states suggests that shape of relaxation time spectrum remains unaffected by the evolution of relaxation time before GP. Similarly the existence of superposition in the post GP states also indicates that the shape of the relaxation time spectrum (apart from the equilibrium modulus $G_{eq}$) is independent of reaction time after GP is crossed. The mean value of relaxation time undergoes evolution following relations given by eqs 18 and 19 for pre and post GP states, respectively. Independence of $\tan \delta$ at GP, produces a power law dependence of the relaxation time spectrum $H(\tau)$ given by $H(\tau) \propto \tau^{-n}$.

As shown in Figure 2, before GP, $G(t)$ decays to zero within finite time indicating the spectrum to be truncated for the slow modes. On the other hand, after GP, the very fact that $G(t)$ shows a plateau suggests that spectrum is strongly influenced by the slow modes. This suggests that the shape of the spectrum undergoes a change at GP, where power law dependence is observed. The self–similarity of relaxation time spectrum in a cross-linking polymeric system before and after GP has been reported in the literature, wherein time–cure superposition of viscoelastic properties at different extents of reactions is observed.9,12,14–17

The present work however allows the manifestation of this observation in terms of linear viscoelasticity. The demonstration of superpositions of both, $J$ as well as $G$ in the $\xi$ - domain in pre and post GP states validates BSP in the $\xi$ - domain expressed by eqs 9 and 15. Moreover this result also implies that the material obeys effective time translational invariance (eTTI) in $\xi$ - domain. Furthermore, Figure 5 clearly shows that the shift factors employed for $J$ and $G$ are practically identical suggesting $g(t) \approx h(t)$, which leads to convolution relation given by eq 17. As mentioned before convolution relation facilitates estimation of either of the response functions from the experimental data of the other. However, eq 17, which is a Volterra integral of the first kind, is extremely tedious to solve numerically as even small noise in the experimental data leads to significant errors and fluctuations in the prediction as discussed in the literature.24,31–34 In this work we implement a numerical methodology suggested by Zhu and co-workers and obtain a prediction of each of the response functions from the other response function using the superposed experimental data in the $\xi$ - domain shown in Figure 4. The predictions of $G_1$ and $G_2$ (using respectively the experimental data of $J_1$ and $J_2$ shown in Figure 4a) are shown by lines in Figures 4b. Similarly predictions of $J_1$ and $J_2$ (using respectively the experimental data of $G_1$ and $G_2$ shown in Figure 4b) are described by lines in Figure 4a. It can be seen that the solution of convolution integral leads to an excellent prediction of the superimposed experimental data of both $J$ and $G$ in the $\xi$ -domain.

The existence of superposition shown in Figure 4 implies that the creep or the stress relaxation behavior of material undergoing cross-linking reaction will follow the respective superpositions in the $\xi$ -domain. The prediction of the experimental data using convolution relation showed by lines in Figure 4, therefore can be transformed from the $\xi$ -domain to the real time domain. For a power law dependence of $\tau$ we get:

$$ t - \tau_w = \left[ \left( A_1 \xi^{1 - N/2} \xi_{w_0} \right) \left( 1 - \mu \right) + \tau_w^{1 - N/2} \right]^{1/(1 - \mu)} - \tau_w $$

(22)

which is obtained by inverting eq 20; while for exponential dependence of $\tau$ we have

$$ t - \tau_w = \ln \left( \left( e^{\alpha \xi_{w_0} - \alpha (\xi - \xi_{w_0})} \right)^{-1/\alpha} \right) - \tau_w $$

(23)

which is obtained by inverting eq 21. In eqs 22 and 23 the term in braces $\ldots$ is the abscissa of Figure 4. We describe the transformed prediction of $J$ and $G$ in the real time domain by lines in Figure SI-1, parts a and b, respectively, in the Supporting Information. It can be seen that the predictions fit the experimental data very well.

We believe that the validation of Boltzmann superposition principle and the convolution relation for the polymeric material undergoing cross-linking reaction is a very important step forward. This work is the first that extends both the mentioned principles of linear viscoelasticity to this class of materials. Complementary to many reports in the literature that apply linear viscoelastic principles to time invariant critical gel state, this work applies linear viscoelastic principles to the entire span of gelation reaction, and not just the critical state, without terminating the reaction. For an unknown material undergoing cross-linking reaction the following steps can be followed in order to represent the effective time domain. For a reaction started at $\tau_w = 0$, the material is subjected to step strain at different reaction times in the independent experiments. The subsequent stress relaxation in each experiment is carried out over a period longer than the reaction time $(t - \tau_w \gg \tau_w)$. An appropriate form (such as KWW) for the stress relaxation is fitted to the experimental data in a short time limit $(t - \tau_w \ll \tau_w)$ to obtain relaxation time at different reaction times, which leads to $\tau = \tau(t)$. The effective time scale can then be obtained by $\xi(t) - \xi_{w_0} = \tau_{\xi_{w_0}} \int_{\tau_{x}}^{\tau(t)} df/df$, which directly allows representation of the constitutive equation for that material in terms of eq 9 or 15. With availability of a constitutive relation in the effective time domain in the form of BSP, this work practically allows estimation of stress, strain or any other response function for an arbitrary flow field in the limit of linear viscoelasticity irrespective of the fact that the material is time dependent. Furthermore, very importantly, this work also opens up the possibility that, with suitable computational tools, mere measurements of the relaxation modulus or the creep compliance as a function of time while the reaction is underway can be used to obtain complete information about the elastic and viscous moduli as a function of frequency.

V. CONCLUSIONS

The major finding of the present work is the validation of effective time–translational invariance (eTTI) for reacting systems over the entire span of gelation. Such validation is facilitated through adjusting the material clock by normalizing the real time with the time dependent relaxation time, thus taking the reaction induced time dependency into account. For reacting systems applicability of eTTI allows not just conformation of the Boltzmann superposition principle but also the successful prediction of creep compliance (relaxation modulus) from the knowledge of relaxation modulus (creep compliance) in the $\xi$ - domain. This is the first report wherein
both these fundamental principles of linear viscoelasticity have been validated for a polymer undergoing cross-linking reaction. Importantly, characterization of the material behavior using this methodology does not require stopping the cross-linking reaction to oblate the time dependency. We believe that this methodology can be applied to different kinds reacting systems wherein shape of relaxation time spectrum is preserved, and the resultant rheological behavior can be analyzed as a bridge between the microstructural evolution and the reaction kinetics.

**ASSOCIATED CONTENT**

**Supporting Information**

Predictions of creep compliance ($J$) and relaxation modulus ($G$) using experimental data in the real time domain, Figure S1, parts a and b. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

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