Effect of Colloidal Fillers on the Cross-Linking of a UV-Curable Polymer: Gel Point Rheology and the Winter–Chambon Criterion

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ABSTRACT: The effect of colloidal silica fillers on the cross-linking behavior of a model UV-curable polymer system (thiol–ene) is studied using in situ rheology and real-time FTIR spectroscopy. The validity of the Winter–Chambon criterion (convergence of the loss tangents at the gel point) is examined for the cross-linking of these filled polymers, some of which are strongly flocculated dispersions (physical gels) prior to chemical cross-linking. Two different types of colloidal silica particles are studied: one with octyl chains tethered to the surface and the other with methyl surface groups. The Winter–Chambon criterion is satisfied for all samples containing the methyl-terminated silica. However, the criterion breaks down for samples containing the octyl-modified silica, with the loss tangents not converging at any single point. This suggests the absence of a self-similar critical gel at the gel point in the latter case. Neither type of silica particles alters the mechanism of the cross-linking reaction, as revealed by FTIR spectroscopy, but they do retard the cross-linking kinetics. An alternate method is suggested for determining the chemical gel point of filled systems that fail to obey the Winter–Chambon criterion. This method involves monitoring the critical strain (limit of the linear viscoelastic region) at various UV exposure times. A dramatic increase is observed in the critical strain at the gel point, indicating a transition from weak, physical bonds to strong, covalent cross-links.

Introduction

Polymeric systems used for industrial applications frequently employ fillers to control their rheological properties. Fillers such as fumed silica and carbon black find wide application in systems ranging from elastomers to coatings. In the case of UV-curable adhesives and coatings, fillers serve multiple purposes: they act as thickening agents, imparting high viscosity and viscoelasticity to the formulation, and at the same time render the system thixotropic and shear thinning. In the absence of fillers, formulations containing just the pure monomers have low viscosities and tend to run off the substrate surface or sag after being applied to a substrate. Thus, fillers play a vital role in typical photopolymer formulations.

One important aspect of UV-curable polymer systems is their gelation behavior, in particular, the kinetics of gelation as well as the instant of incipient gelation or gel point. Recently, we have systematically elucidated the gelation behavior of a neat thiol–ene photopolymer system using a combination of in situ rheology and real-time FTIR spectroscopy.1 We monitored the rheological properties, such as the elastic (G') and viscous (G'') moduli, of the system as it underwent UV curing. We demonstrated the validity of the Winter–Chambon criterion2,3 for accurately determining the gel point from the rheological data. According to this criterion, the gel point is identified as the instant in time when the moduli scale in an identical fashion with frequency, such that G' ∼ ω^n. The exponent n is called the relaxation exponent and can be linked to microstructural parameters. The above relationship implies that the loss tangent, tan δ (=G''/G'), is independent of frequency at the gel point. Through independent studies using real-time FTIR spectroscopy, we also confirmed that the intersection point of the tan δ is indeed occurs at the chemical gelation time.

In recent years, the validity of the Winter–Chambon criterion has been extended to a variety of polymeric as well as physically cross-linking systems. Most of the polymeric systems studied so far have been neat polymers. A pertinent question, therefore, is whether the Winter–Chambon criterion would be applicable even for the cross-linking of polymers in the presence of added fillers. This becomes particularly important for filled systems that can exist either in a flocculated state or as a physical gel prior to cross-linking. In such cases, the colloidal fillers may interfere with the chemical gelation, or there may be a competition between physical and chemical cross-linking.

Motivated by the above issues, we examine the effects of adding colloidal fumed silica fillers to a thiol–ene photopolymer system. We use the thiol–ene system on which we have gained expertise through our previous work1,4,5 and which we know to be a model UV-curable system. We choose fumed silica because it represents a filler that is used widely in a number of industrially relevant systems (e.g., epoxies, silicones, polyurethanes, and acrylic polymers) to improve and control their rheological properties. The surface chemistry of fumed silica can be readily tailored, making it a versatile colloidal system as well. In addition, we have accumulated an extensive database and understanding on the rheology of fumed silica dispersions through independent studies in our laboratory over the past few years.6–9 Fumed silica is a pure form of silicon dioxide (SiO2) prepared by a flame hydrolysis process.10 The fundamental structure of fumed silica consists of branched aggregates (~100 nm) formed by the fusion of primary
spherical particles (~10 nm). Fumed silica is amorphous, nonporous, and hydrophilic in its native form, with a surface covered by silanol (Si–OH) groups. Hydrophobic fumed silicas are obtained by replacing the silanols by nonpolar (e.g., alkyl) groups. The silica surface chemistry determines the extent of aggregation of silica units in a given dispersion, and the microstructure, in turn, determines the rheological properties of the dispersion.

The effects of introducing fumed silica fillers on the kinetics and gelation behavior of photocurable polymers have not been rigorously investigated. Studies on filled systems have primarily focused on other types of fillers in thermoset polymers. For example, kinetic studies had been done on systems such as CaCO3 in polyester resins, SiO2 in epoxy resins, and fiberglass in polyester resins. Various techniques, such as differential scanning calorimetry, FTIR spectroscopy, rheology, and a dynamic torsional vibration method, have been employed to obtain reaction rates or cure profiles. The different fillers had a wide range of effects on the reaction rates of the resins studied. The reaction rates were found to increase, decrease, or remain the same as that of the unfilled resins, depending on the fillers and resins studied. Therefore, there seems to be no general rule that can be applied to predict how particular fillers may affect the kinetics of a curing system. Moreover, no effort has been made to analyze the gel point and the role of chemical vs physical cross-links in such systems.

In this study, we utilize in situ rheology and real-time FTIR spectroscopy to characterize the effects of fumed silica on the UV-curing kinetics and gelation behavior of a thiol–ene system. We add two hydrophobic fumed silicas to our thiol–ene system: one silica having methyl surface groups (R974) and the other with octyl surface groups (R805). We chose the two fumed silicas because they exert a pronounced effect on the rheology of the precure formulations. We focus primarily on whether the Winter–Chambon criterion holds for filled systems and examine the relationship between physical and chemical cross-links in UV curing.

**Experimental Section**

**Sample Preparation.** The thiol–ene formulation consisted of a trifunctional thiol, trimethylolpropane tris(2-mercaptoacetate), and a difunctional allyl monomer, trimethylolpropane diallyl ether. The chemical structures of these monomers are shown in Figure 1a. Both monomers were purchased from Aldrich Chemicals and were used as received. Each formulation was prepared by first placing the two monomers in separate vials. Esacure T7T (Sartomer Inc.), a photoinitiator that consists of a blend of methyl benzophenones, was then added to the vials. Hydroquinone (Aldrich) was also added as an inhibitor in order to prevent premature polymerization. The final compositions of photoinitiator and hydroquinone in each of the vials were 1 and 2 wt % of monomers, respectively.

Two different hydrophobic fumed silicas, Aerosil R805 and R974, were used to prepare the composite thiol–ene system. Both fumed silicas were obtained from Degussa Corp. and had an average primary particle size of 12 nm in diameter. The surface chemistries of these fumed silicas are shown in Figure 1b. The R805 fumed silica contains n-octyl (C8H17) surface groups while the R974 fumed silica contains methyl surface groups. In each case, the functional groups are present at 50% coverage, with 50% of the original silanoid groups remaining on the surface. The concentrations of each of the fumed silicas used in the experiments ranged from 2 to 6 wt % of monomers. The fumed silica was added to the monomer in each of the vials. A high shear Silverson mixer was utilized to mix the contents in the vials at a rate of 9500 rpm for several minutes to ensure effective dispersion of the silica. The samples were degassed by placing the vials in a vacuum oven for several hours. The final thiol–ene formulation was then prepared in a separate vial by adding stoichiometric amounts of the silica-filled monomers, and the resulting formulation was mixed with a stir bar.

**Characterization before UV Curing.** A Rheometrics dynamic stress rheometer (DSR I1) was used to characterize the pre-cure rheological properties of the samples. Experiments were performed at 25 °C on a cone-and-plate fixture having a diameter of 40 mm and a cone angle of 0.04 rad. The linear viscoelastic range of each sample was first determined by a stress sweep. A fresh sample was then loaded and subjected to a steady preshear, following which a dynamic frequency sweep was conducted within the linear viscoelastic regime of the sample.

**In Situ Rheology during UV Curing.** A Rheometrics mechanical spectrometer (RMS-800) in conjunction with specially designed fixtures was used to monitor the dynamic rheological properties of the thiol–ene formulations during UV curing. A detailed description of these fixtures can be found elsewhere. A 200 W Oriel mercury lamp was used to generate the UV radiation. A narrow band interference filter maintained the radiation at a 365 nm wavelength, and neutral density filters attenuated the radiation intensity to 0.10 mW/cm². The intensity was measured prior to each experiment by using an International Light 1400A radiometer. The sample thickness was fixed at 800 μm for each experiment, and the experiments were all done at 25 °C.

Fourier transform mechanical spectroscopy (FTMS) was used for monitoring the elastic (G′) and viscous (G″) moduli during UV cross-linking. The FTMS technique allowed the simultaneous measurement of moduli at several different frequencies. This is an improvement over conventional dynamic time sweeps, since all the data are acquired in one experiment that would otherwise have required several time sweep experiments. The frequencies selected for FTMS were 1, 5, and 50 rad/s. The total applied strain of 1.875% was within the linear viscoelastic range for all samples.

**Real-Time FTIR Spectroscopy.** The FTIR experiments were performed using a Nicolet Magna-IR System 750 spectrometer with a DTGS-KBr detector. The thiol–ene sample was sandwiched between two 25 mm × 4 mm BaF2 crystals using a 50 μm Teflon O-ring spacer. This was then inserted in a Spectra Tech presslock holder and placed inside the
spectrometer sample chamber. Details of this real-time FTIR technique can be found elsewhere.1,5 UV radiation was generated using a 200 W Oriel mercury lamp, and the samples were subjected to the same radiation wavelength and intensity as in the rheological experiments. All the experiments were performed at a temperature of 25 °C.

The IR spectra were obtained one after the other in order to ensure that the UV-curing process was analyzed in real time. Each of the spectra has a resolution of 4 cm$^{-1}$. The S-H stretching vibration of the thiol functional groups at 2570 cm$^{-1}$ was monitored to determine the progress of the reaction. Also, the aromatic out-of-phase C-H deformation vibration from the methyl benzophenone photoinitiators at 830 cm$^{-1}$ was used as the internal standard since this peak remained unchanged during the course of the experiment. The thiol and internal standard absorbance peaks were integrated by using the FTIR software. The conversion of the thiol functional group at any time t was then calculated as follows:

$$x(t) = [A(0) - A(t)]/A(0)$$ (1)

where x(t) is the conversion at time t, A(0) is the normalized area (with respect to 830 cm$^{-1}$) of the initial unreacted thiol peak, and A(t) is the normalized area of the thiol peak at time t.

Results and Discussion

Neat Thiol–Ene System: Rheology during UV Cross-Linking. We first describe the gelation behavior of a neat thiol–ene system containing no added fumed silica. This system has been studied in detail earlier,1 and we only present the essential features of the rheology here. At t = 0, we expose the sample to UV radiation. As the sample undergoes cross-linking, we monitor the elastic modulus (G') and the viscous modulus (G'') at various frequencies using the FTMS method. To verify whether the Winter–Chambon criterion holds, we plot tan δ for various frequencies as a function of UV exposure time. Such a plot is shown for the neat thiol–ene system in Figure 2. We find that all the tan δ curves intersect at a single point, which corresponds to the gel point in accordance with the Winter–Chambon criterion. The gel time $t_{gel}$ for the neat polymer from this plot is approximately 1000 s. Such rheology data on gel times corroborate well with that obtained using FTIR measurements in conjunction with the Flory–Stockmayer theory of gelation.1

Filled Thiol–Ene Systems: Rheology before Cross-Linking. We now turn our attention to thiol–ene polymers with fumed silica fillers and examine their precure behavior under dynamic rheology (Figure 3). In the case of R805 fumed silica, at 2% silica concentration (Figure 3a), the sample moduli show strong frequency dependence, with G'' dominating G' at low frequencies. The 4% and 6% R805 samples (Figure 3b,c) show higher levels of the moduli, but the moduli continue to be frequency dependent. These features in the rheological response are characteristic of weakly structured systems and indicate that the R805 silica flocculates only weakly in thiol–ene samples.

In contrast, formulations containing the R974 fumed silica show rheological characteristics of strongly flocculated systems. For a sample with 2% R974 silica (Figure 3a), the moduli are much less frequency dependent than that of the corresponding R805 sample and exhibit higher values at low frequencies, suggesting a relatively more flocculated structure. The 4% and 6% R974 samples (Figure 3b,c) exhibit moduli with a very weak frequency dependence, with G' greater than G''. This means that these samples are effectively physical gels. These results indicate that the R974 silica strongly
flocculates in thiol‐ene samples, forming physical gels at high silica concentrations. We have thus produced a range of filled systems containing varying microstructures. The next step is to determine how these colloidal microstructures affect chemical cross-linking of the polymeric matrix under UV irradiation.

Filled Thiol‐Ene Systems: Rheology during UV Cross-Linking. We now consider the evolving rheology of thiol‐ene formulations containing R974 during UV cross-linking. Figure 4 shows tan δ as a function of UV exposure time for 2%, 4%, and 6% R974 samples. In each case, the tan δ curves at the various frequencies converge and intersect at a single instant in time. This suggests that the Winter‐Chambon criterion is indeed valid even for these filled systems and that the intersection point corresponds to the gel time of the system. To the best of our knowledge, this is the first example of a well-characterized filled polymer system for which the Winter‐Chambon criterion has been applied. Interestingly, a previous study on the thermal cross-linking of a filled polymeric material (a commercial chlorobutyl elastomer formulation containing fillers and other additives) also demonstrated the convergence of tan δ values at the gel time.

The tan δ curves in Figure 4 first increase, reach a maximum, and then subsequently decrease. This nonmonotonic behavior of tan δ becomes more pronounced at higher filler concentrations. This is in contrast to the behavior of the neat system (Figure 2), where all the tan δ curves decrease monotonically with time. In both the neat and filled systems, however, the convergence point of the tan δ curves occurs only during the decreasing portion of the curves. In other words, beyond the gel point, tan δ decreases monotonically in all cases as the samples become increasingly more elastic. Likewise, the initial increase in tan δ with time for the filled systems implies an initial period during which the viscous modulus increases more rapidly than the elastic modulus. Indeed, Figure 5 illustrates these features in a plot of G' and G'' as a function of UV exposure time for the 4% R974 formulation.

On the basis of Figure 5, we can qualitatively follow the changes in the filled system during cross-linking. Initially, G' is larger than G'' since the 4% R974 sample is a physical gel made up of silica particles interconnected through weak, physical bonds. As chemical cross-linking proceeds via step-growth polymerization, small covalently linked polymer clusters are initially formed. Their main contribution is to increase the viscosity of the polymeric liquid and, by extension, the viscous modulus G''. Consequently, G'' grows more rapidly than G' and tan δ exceeds unity. As the viscosity of the fluid phase surrounding the silica particles increases, the viscous stress exerted on the particles becomes so great that it disrupts the particulate network. Metzner in his review gives a viscosity cutoff of 100 Pa·s, beyond which long-range particulate structures cannot survive in a liquid medium. Beyond this point, chemical cross-linking dominates, and the growing polymer clusters connect into a sample-spanning cluster at the gel point. Thus, the gel point corresponds to network formation via chemical cross-links. The fact that the Winter‐Chambon criterion is obeyed also suggests that there is a self-similar structure at the gel point called the critical gel. Beyond the gel point, elastic effects dominate, since the network is capable of storing energy. This is why G' increases at a more rapid rate than G'' (i.e.,
\text{The gel times for the filled and the neat systems indicate that the presence of fillers slows down the chemical cross-linking of the polymer. For a 2\% R974 sample, the gel time is 1200 s, while for the 6\% R974 sample, the gel time increases to 1400 s.}

We now examine the gelation behavior in the presence of R805 fumed silica. Figure 6 shows \( \tan \delta \) curves for both the R805 and R974 formulations show the same nonmonotonic behavior. The only difference is that the Winter–Chambon criterion holds for the R974 but not the R805 formulations. As mentioned already, the above criterion holds only if the sample-spanning cluster at the gel point is a “critical gel”, i.e., a self-similar, fractal structure. Thus, the failure of the Winter–Chambon criterion for the R805 systems suggests that no self-similar structure exists at the gel point.

As a first approach, one might try to explain the differences between the R805 and R974 systems based on their precure rheology. Rather surprisingly, however, there does not appear to be any correlation between the precure rheology and the behavior at the gel point. For example, the rheology of the 2\% R974 sample appears similar to that of the 4\% R805 sample since both are weakly flocculated dispersions. Yet, the former obeys the Winter–Chambon criterion while the latter does not. It is also worth emphasizing that both the 4\% and 6\% R974 samples are physical gels before UV cross-linking. All the same, the Winter–Chambon criterion is valid for these systems as they undergo chemical cross-linking. Thus, the presence of a physical network in the precure sample, per se, does not rule out the applicability of the Winter–Chambon criterion. On the contrary, a sample can be a physical gel before UV irradiation and a chemical gel after UV irradiation.

\text{Filled Thiol–Ene Systems: Cross-Linking Kinetics Using Real-Time FTIR Spectroscopy. We now examine the kinetics and mechanisms of cross-linking in the presence of fillers using real-time FTIR spectroscopy. The question is whether there are major differences between the filled systems and the neat polymer and, moreover, between the R805 and the R974 systems. The FTIR technique yields plots of the thiol conversion, } x(t), \text{ as a function of UV exposure time. Such plots are shown in Figure 7 for formulations containing R974 silica. We note that as the fumed silica concentration increases, the conversion at a specific time becomes lower. This suggests that fumed silica has a retarding effect on the kinetics, in line with our findings from rheology of longer gel times with increasing filler concentrations. This result is valid for both the R805 and R974 silicas.}

\text{The conversion data can be further analyzed to ascertain the reaction mechanism. From our previous studies, we know that the thiol–ene reaction follows second-order kinetics.}
Comparison of the reaction kinetics of the neat thiol–ene system and that containing R974 (methyl-terminated) silica.

Figure 7. Thiol conversion as a function of UV exposure time for the neat thiol–ene system and that containing R974 (methyl-terminated) silica.

Figure 8. Comparison of the reaction kinetics of the neat thiol–ene system with that containing R974 (methyl-terminated) silica shown in terms of $1/(1 - x)$ as a function of UV exposure time. Here, $x$ corresponds to the extent of thiol conversion.

of the form

$$\frac{dx}{dt} = k(1 - x)^2$$

(2)

where $x$ is the thiol conversion, $t$ is the time, and $k$ is the rate constant. Integrating this expression yields

$$\frac{1}{1 - x} = kt + 1$$

(3)

A plot of $1/(1 - x)$ as a function of $t$ should therefore be a straight line with slope $k$. Such a plot is shown in Figure 8 for the neat polymer and a representative formulation containing filler. The two systems show identical behavior: the plots are linear over the range of conversions, but with a kink at intermediate conversion. The kink has been explained before as indicating a slowing down of the reaction once a specific conversion has been reached.\(^1\) The main point from these data is that the fillers do not affect the reaction mechanism since the reaction remains second-order. However, the presence of filler does significantly lower the rate constant $k$ (at high conversion). Finally, no differences exist between R805 and R974 samples in terms of their kinetics.

Breakdown of the Winter–Chambon Criterion: Possible Reasons. The previous analysis provided no insight as to why the Winter–Chambon criterion breaks down for the R805 silica-based samples. The Winter–Chambon criterion is violated if the sample-spanning cluster at the gel point is a noncritical gel (i.e., not self-similar). This is apparently the case for the R805 samples, possibly because the silica interferes with the gel formation. As yet, it is not clear how this occurs, but the nature of the silica–polymer interface may hold the key.

Violations of the Winter–Chambon criterion (i.e., nonintersection of the loss tangents) have been documented in a few previous instances.\(^26\) Richtering et al.\(^26\) examined the crystallization kinetics of a polyester system at different temperatures. The loss tangents did not intersect for a specific temperature and this was attributed to abnormal growth kinetics that precluded the formation of a self-similar structure in this case. Ilvasky et al. studied nonstoichiometric polyurethane\(^27,28\) and epoxide\(^28,29\) systems where the gel point is reached when all the limiting reactants have reacted. The loss tangents for both systems had a slight dependence on frequency at the gel point. The authors suggested that a highly polydisperse, nonfractal structure was formed at the gel point at these nonstoichiometric compositions. Finally, Izuka et al.\(^30\) showed that, for certain compositions of a semiinterpenetrating polymer system, the loss tangents did not intersect during polymerization. They attributed this to possible phase separation before the gel point, which interfered with the formation of self-similar structures.

Alternate Criterion for Gel Point in Filled Systems. Filled polymer melts, such as the thiol–ene/ fumed silica systems studied here, present a unique situation in cross-linking studies. It is possible for a sample to be a physical gel prior to cross-linking, with infinite viscosity and elastic character (nonzero equilibrium modulus). Chemical cross-linking turns the material into a covalently cross-linked network with a much higher modulus. In such systems, and especially in cases where the Winter–Chambon criterion does not hold, an alternate method is needed for determining the gel point. Before the advent of the Winter–Chambon criterion, the gel point used to be identified by the divergence of the viscosity or the first appearance of a nonzero equilibrium modulus. However, both these methods are clearly inappropriate for our present systems. A viable alternative based on the evolution of the critical strain\(^31\) is discussed below.

During chemical cross-linking, strong, covalent bonds are formed, which cannot be disrupted by shear. In contrast, fumed silica agglomerates by physical bonds that result from weak colloidal interaction forces. Consequently, these bonds are shear-sensitive, and they can be reversibly disrupted by even small deformations. We can study the shear sensitivity of a sample under oscillatory shear by progressively increasing the strain amplitude in a strain sweep experiment. The strain at which the elastic modulus begins to decrease is called the critical strain $\gamma_c$, and it signifies the linear viscoelastic limit of the sample. Thus, the critical strain indicates the strength of bonds in the system, and it can reveal the transition from a physical to a chemical gel.

We performed such strain sweeps after different UV exposure times for several filled thiol–ene samples. At each point, the UV light was shut off while conducting the strain sweep. We have ascertained that no dark curing (i.e., cross-linking in the absence of UV radiation)
occurs in our system. Figure 9 shows the critical strain of various filled samples as a function of UV exposure time. The critical strain of each sample is normalized with respect to its precure critical strain. The precure critical strain is typically very small, indicating the weak nature of the physical cross-links. On the other hand, the critical strain of the neat polymer during UV cross-linking exceeds 100% because the strong chemical bonds can withstand large strains.

The critical strain behavior of all the samples in Figure 9 shows similar trends. At the outset (t = 0), each sample is a flocculated dispersion with a very low critical strain. As the sample is irradiated, chemical cross-links are formed. The material response now encompasses both the physical links between fumed silica aggregates and the chemical links in growing polymeric clusters. Nevertheless, since the weaker physical bonds will be the first to break, the samples continue to show a low critical strain. In fact, for an extended period of time, the critical strain remains identical to that of the precure samples. After a certain cross-linking time, however, there is a dramatic increase in the critical strain, indicating that the rheological response is now dominated by the chemical cross-links. The higher value of critical strain persists thereafter, as the cross-linking proceeds to completion.

An important issue to determine is whether the jump in the critical strain $\gamma_c$ coincides with the formation of the chemically cross-linked network. The 6% R974 sample allows us to test this hypothesis. Since the $\delta$ s intersected for this system (Figure 4), we already have an estimate of its gel time $t_{gel}$ (~1400 s). Figure 9 indicates that, within experimental error, the critical strain also diverges at approximately 1400 s. Thus, the divergence of the critical strain indeed marks the chemical gel point. Data for the 2% and 4% R974 (not shown) further confirm the equivalence between the two independent estimates of gel time. Turning now to the 6% R805 sample, the rapid increase in critical strain occurs around 1900 s, which is then an estimate of gel time for this sample. Likewise, the gel times for 2% and 4% R805 are 1150 and 1350 s, respectively. In all cases, the gel time from critical strain measurements slightly exceeds the time at which there is a weak convergence in the $\tan \delta$ curves (Figure 6). We have thus identified an alternate criterion for gel point that applies to filled polymeric systems: it is the point at which the critical strain changes dramatically from a low value, characteristic of physical bonds, to a high value, characteristic of chemical bonds.

**Conclusions**

In this study, we examined polymer systems with colloidal fillers undergoing UV cross-linking, with specific emphasis on the rheology at the gel point. Prior to cross-linking, the filled materials exhibited viscoelastic or gel-like behavior due to formation of different micro-structures from the fumed silica particles. Exposure to UV radiation introduced chemical cross-links, which eventually transformed the samples into dense polymer networks. Samples containing R974 (methyl-terminated) fumed silica obeyed the Winter–Chambon criterion at their gel point since their loss tangents intersected at a single point. In contrast, the loss tangents for samples containing R805 (octyl-modified) fumed silica did not converge. This indicates that no critical gels were formed at the gel point for these samples. The microstructure in the samples prior to cross-linking had no influence on the gel point rheology. Kinetic studies showed that the silica fillers only affected the reaction rate constant, not the mechanism of the cross-linking reaction. With the breakdown of the Winter–Chambon criterion for the R805 samples, we suggest an alternate method for identifying the chemical gel point in filled systems. This method utilizes the dramatic increase of the critical strain at the gel point, since the dominant linkage in the system shifts from weak, physical bonds to strong, covalent bonds at this point.

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**References and Notes**

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