

Viscoelastic Behavior of Thermosetting Epoxy Mixtures Modified with Syndiotactic Polystyrene During Network Formation

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Received 11 October 2004; accepted 1 June 2005

DOI 10.1002/app.23061

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The rheological behavior of thermosetting epoxy mixtures modified with thermoplastic syndiotactic polystyrene (sPS) was monitored during the curing of the epoxy resin. The selected thermosetting system was diglycidyl ether of bisphenol A cured with 4,4'-methylene bis(3-chloro-2,6-diethylaniline) in the presence of various compositions of sPS (from 2.5 to 12.5 wt %). The storage and loss shear moduli of the systems were monitored during network formation. The validity of the Winter–Chambon criterion for the accurate determination at the gelation point from rheological data was demonstrated. The influence of the sPS concentration on the dynamic rheological properties of the samples was investigated. The experimental data showed that at sPS concentrations lower than 7.5 wt %,

phase separation induced a quick increase in the viscosity, which was related to a crystallization-induced phase separation of sPS. For sPS concentrations higher than 7.5 wt %, near the phase-inversion composition, the rheological behavior of the mixtures was characteristic of a cocontinuous structure. After the viscosity jumped at the onset of phase separation, a decrease in the viscosity was found, and later on, the viscosity increased again because of gelation. Additionally, the influence of the cure temperature on the rheological properties was studied. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 2348–2355, 2006

Key words: blends; gelation; syndiotactic polystyrene

INTRODUCTION

The mechanism of simultaneous curing and phase separation has been a topic of research for many years¹ because toughened thermosets have been widely used in many applications, but this mechanism is not fully understood.² Moreover, it is essential to gain a complete understanding of the dynamic mechanical properties of thermoset/thermoplastic blends during network formation to control the viscosity variation and gelation time (t_{gel}) during processing.^{3–6} Nevertheless, few studies have been focused on the events occurring during the reaction of thermoset/thermoplastic systems.

As a result, in the last decades, a better understanding of the cure process has become of foremost importance for thermoset/thermoplastic manufacturers to optimize the cure conditions. Bonnet et al.⁷ investi-

gated the effect of the poly(ether imide) (PEI) concentration on thermoset chemistry and on the rheological behavior of blends in the system PEI–(DGEBA/MCDEA) [where DGEBA is diglycidyl ether of bisphenol A and MCDEA is 4,4'-methylene bis(3-chloro-2,6-diethylaniline)].⁸ They found that when the PEI concentration was lower than 10–15 wt %, phase separation induced a rapid decrease in the viscosity. For concentrations close to the phase-inversion composition, a rheological behavior characteristic of a bicontinuous morphology appeared, with a strong dependence of the shape of the curves on the frequency. When the PEI concentration was higher than 30 wt %, phase separation led to a gradual increase in the viscosity. Kim and Char² monitored the rheological behavior of epoxy/poly(ether sulfone) (PES) mixtures during the curing of the epoxy resin. They detected some fluctuations in viscosity before an abrupt viscosity increase due to gelation. This behavior was attributed to the phase separation of PES from the epoxy matrix during isothermal curing. A similar study was conducted by Yu et al.⁹ They also monitored in situ the rheological behavior of PES/DGEBA mixtures during isothermal curing, but they used methyl tetrahydrophthalic anhydride instead of 4,4'-diaminodiphenylmethane as a curing agent. They found that both the viscosity and the storage modulus increased upon phase separation.

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Contract grant sponsor: European Commission (through the Research Training Network program under the name POLYNETSET); contract grant number: HPRN-CT-2000-00146.

Contract grant sponsor: Ministerio de Ciencia y Tecnología (Spain); contract grant number: MAT 2000-0293.

When bicontinuous phase structures were formed, the complex viscosity (η^*) showed a behavior similar to that observed by Bonnet et al.⁸

The viscosity is very sensitive to changes in the polymer chain length and branching and is therefore related to the molar mass and molar mass distribution.¹⁰ For non-network-forming systems that yield to linear and branched polymers, the viscosity determined via solution methods can be used for monitoring the structural development. However, for network-forming systems, the viscosity tends to infinity as the gelation point is approached, and incipient network formation occurs.^{11,12}

Various methods are available to determine the gelation point from rheological measurements. The simplest one is based on an extrapolation of η^* to infinity.¹⁰ In this case, it should be taken into account that the divergence of viscosity can also occur because of other phenomena, such as phase separation¹³ and vitrification,¹⁴ and care must be taken to not mistake these phenomena for chemical gelation.

Another method used to determine the gelation point is to record it as the point of intersection of dynamic storage modulus (G') and dynamic loss modulus (G'') curves in small-amplitude oscillatory shear experiments. This definition was proposed by Tung and Dynes.¹⁵ However, Winter and coworkers^{16–20} showed that this definition is not universal and works only for the formation of certain types of networks of balanced stoichiometry. A more general method for detecting the gelation point from dynamic moduli data is based on the observation that at the gelation point, the loss tangent ($\tan \delta$) is independent of the frequency. In this case, the gelation point is defined as the reaction time at which $\tan \delta$ becomes independent of the frequency. Nevertheless, for thermoset/thermoplastic blends, often this criterion is not applicable because of the nonsimultaneity of the measurements for different frequencies.

In a previous article,²¹ the phase-separation and crystallization processes for a semicrystalline thermoplastic-(epoxy/amine) system were studied by dynamic oscillatory rheometry and by differential scanning calorimetry. Also, a transmission optical microscope equipped with a hot stage was used to observe the obtained morphologies at different times during the phase-separation and crystallization processes. Moreover, the morphology of the cured samples was studied by atomic force microscopy (AFM). This article is more deeply focused on the chemorheological study of mixtures of syndiotactic polystyrene (sPS) and a thermoset precursor, DGEBA, cured with MCDEA. Gelation was followed by dynamic mechanical measurements, and the gelation point was determined rheologically. Additionally, the effects of the sPS contents and the curing temperature on the rheological behavior of the mixtures were investigated.

EXPERIMENTAL

Materials and sample preparation

The epoxy resin used was DGEBA (DER-332), which was kindly supplied by Dow Chemical (Rheinmünster, Germany). It had an epoxy equivalent weight of 191.5 g/equiv. This epoxy resin was cured with a stoichiometric amount of an aromatic amine hardener, MCDEA, which was kindly supplied by Lonzacure (Lonza, Basel, Switzerland). The semicrystalline thermoplastic modifier used was sPS, which was provided by Dow Chemical (DCG Buna Sow Luena Olefinverbund GmbH, Basel, Switzerland) and is known under the trade name Questra QA 101. Its number-average molecular mass and weight-average molecular mass were 94,000 and 192,000 g/mol, respectively.

sPS-(DGEBA/MCDEA) mixtures were prepared with the procedure recommended by Schut et al.²² and described in our previous article.²¹ First, sPS pellets were powdered and dried overnight at 80°C in an air oven. Then, sPS-DGEBA mixtures containing different sPS weight percentages (2.5, 5, 7.5, 10, and 12.5%) were prepared by the dispersion of a weighed amount of sPS in DGEBA at 220°C in an oil bath under continuous stirring for 10 min. Afterwards, the mixture was transferred to a Wood's metal bath at 290°C and stirred for another 10 min until the complete dissolution of sPS. Simultaneously, MCDEA was melted in another test tube at the selected testing temperature, 210, 220, or 240°C, for 5 min. Finally, the molten MCDEA was added to the sPS-DGEBA mixtures, which were then cooled to the testing temperature and stirred for 30 s to start the curing reaction. A clear, homogeneous reaction mixture was obtained. Moreover, to obtain cured blends, the samples were kept for 2 h at 210, 220, or 240°C.

Techniques

Dynamic oscillatory shear experiments were performed at 210, 220, or 240°C on an Advanced Rheometric Expansion Systems (ARES, TA Instruments, Barcelona, Spain) with parallel plates 25 mm in diameter. The gap between the plates was about 1.2 mm. The transducer operating range was set to 0.2–200 or 0.2–2000 g cm, depending on the measured torque values.

The parallel plates were preheated to the operating temperature before a zero gap was set. The upper plate was then raised, and the liquid uncured sample was put on the lower plate. Measurements started as soon as the measured temperature reached the operating temperature. Experiments were performed at 0.5, 1, 2, and 5 Hz. Seven minutes after the start of the experiment, that is, roughly 1 min before phase separation, the applied strain was changed from 300 to 100%. Dynamic strain sweeps at a constant frequency

were used to find the linear viscoelastic region in which G' and G'' were independent of the strain amplitude. Data were collected and analyzed with Rhios Rheometrics software (Barcelona, Spain).

A Nikon Eclipse E600 optical microscope (Nagano, Japan) was used to study the morphology of the cured blends. Micrographs were captured with a Color View 12 camera with Analysis Auto 3.2 software (Soft Imaging System GmbH, Münster, Germany).

AFM topography images of the cryogenically fractured surfaces of cured mixtures were recorded in the tapping mode at room temperature with a Nanoscope IIIa Multimode scanning probe microscope (Digital Instruments, Santa Barbara, CA). Etched single-beam cantilever (225 μm long) silicon nitride probes with a tip nominal radius of curvature of 5–10 nm were used. The scanning rates ranged from 0.8 to 1.6 Hz/s. The sample line was 512, and the target amplitude was around 0.7 V. Height and phase images were recorded simultaneously during scanning. To obtain repeatable results of the blend morphology, different regions of the specimens were scanned. Similar images were obtained, thus demonstrating the reproducibility of the results.

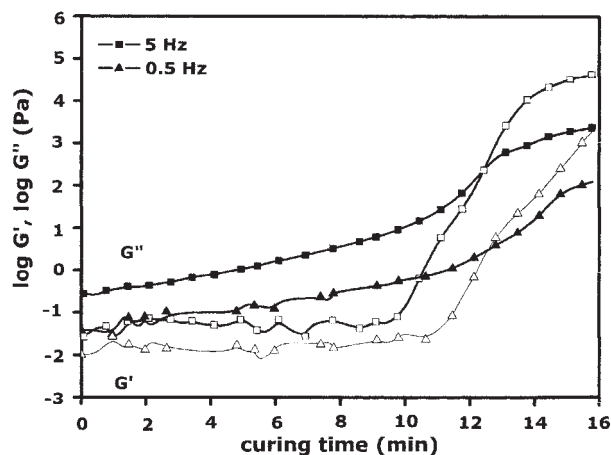
RESULTS AND DISCUSSION

The continuous monitoring of the viscoelastic behavior of a neat DGEBA/MCDEA mixture during network formation allows us to follow the events that take place during curing. At a critical extent of reaction, the epoxy/amine systems undergo a pseudophase transition from liquid to solid as network formation proceeds. The gelation point of a chemically crosslinked system is clearly defined as the time at which the weight-average molecular weight diverges.^{16,19,20} At this moment, covalent bonds connect across the whole volume of the curing material, and a macroscopic network is formed. On the basis of the Winter–Chambon criterion, the chemically crosslinking systems display the following behavior at the gelation point:^{16,18,23}

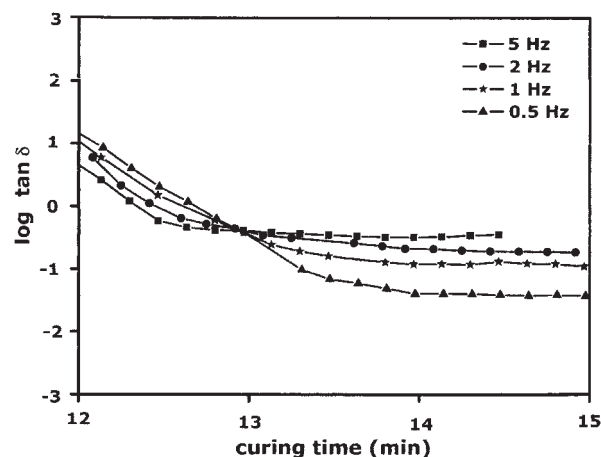
$$\tau(t) = S \int_{-\infty}^t (t - t')^{-n} \gamma(t) dt' \quad (1)$$

where $\tau(t)$ is the time-dependent shear stress and $\gamma(t)$ is the time-dependent shear strain. Equation (1) describes the shear stress in a critical gel that is being deformed at rate $\gamma(t)$ for a time t' ranging from $-\infty$ to t . As a result, at the gelation point

$$G'(\omega) \approx G''(\omega) \approx \omega^n \quad (2)$$



(a)



(b)

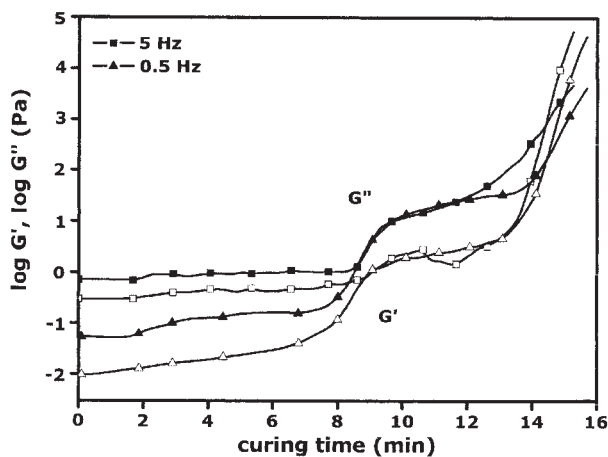
Figure 1 (a) G' (open symbols) and G'' (full symbols) versus the curing time for the neat DGEBA/MCDEA system during curing at 220°C at various frequencies and (b) $\tan \delta$ versus the curing time for the neat DGEBA/MCDEA system during curing at 220°C at various frequencies.

and $\tan \delta$ will be

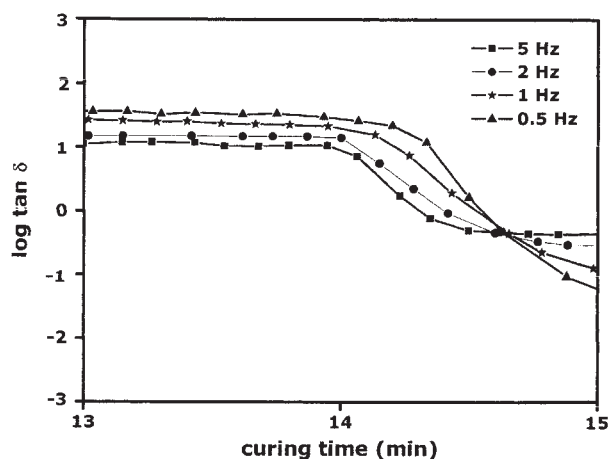
$$\tan \delta = G'(\omega)/G''(\omega) = \tan(n\pi/2) \quad (3)$$

Thus, at the gelation point, $\tan \delta$ is independent of the frequency, and G' and G'' have the same power-law frequency dependence. In this work, the Winter–Chambon criterion has been applied to determine the gelation point.

G' , G'' , and $\tan \delta$ for the neat epoxy/amine system during isothermal curing at 220°C are shown in Figure 1(a,b). As already shown by Chambon and coworkers,^{16,17} initially, when the curing sample was liquid, G'' was higher than G' . Subsequently, the G'' curve crossed the G' curve at 12.5 ± 0.25 min. Beyond the cross point, as is typical for neat epoxy/amine systems, G' was lower than G'' because a covalently



(a)



(b)

Figure 2 (a) G' (open symbols) and G'' (full symbols) versus the curing time for the 5 wt % sPS-(DGEBA/MCDEA) system during curing at 220°C at various frequencies and (b) $\tan \delta$ versus the curing time for the 5 wt % sPS-(DGEBA/MCDEA) system during curing at 220°C at various frequencies.

bonded network was formed during curing. On the other hand, all $\tan \delta$ curves [Fig. 1(b)] intersected at a single point, which was recorded as t_{gel} . The measured t_{gel} value was approximately 12.8 ± 0.25 min.

The chemorheological data obtained during the isothermal curing of the 5 wt % sPS-(DGEBA/MCDEA) system at 220°C are shown in Figure 2. The initial values of G' and G'' , shown in Figure 2(a), were similar to those for the neat DGEBA/MCDEA system described previously. The addition of sPS to the epoxy/amine system resulted in a sharp increase in both G' and G'' at times around 8 min, well before the increase in moduli due to gelation that took place around 15 min. As reported in a previous article,²¹ this increase in the viscosity can be related to the onset of phase separation, which is induced by the crystallization of

sPS. After the completion of the crystallization-induced phase separation (CIPS) process, both G' and G'' gradually increased with time because of the increase in the molecular weight of the epoxy matrix during curing. Approximately at 14.4 ± 0.25 min, the G' and G'' curves crossed each other, and afterwards, G' greatly exceeded G'' . These results are similar to those observed for the neat DGEBA/MCDEA system, thus indicating that the material undergoes a liquid-to-solid transition at this time. The changes in η^* , measured at various frequencies, during isothermal curing are illustrated in Figure 3 and clearly confirm the events that occurred in this system upon network formation. Also, the $\tan \delta$ curves recorded at different frequencies [Fig. 2(b)] intersect at a unique point at 14.6 ± 0.25 min, which marks the gelation point. The gelation point determined in this way is in quite good agreement with that recorded by the G' and G'' crossing criterion.

Therefore, the addition of 5 wt % sPS to the DGEBA/MCDEA system shifted the gelation point toward longer cure times, and this means that the addition of sPS resulted in a delay of the curing reactions.

To better understand the influence of the addition of sPS on the rheological behavior of sPS-(DGEBA/MCDEA) mixtures, dynamic oscillatory shear measurements were performed for DGEBA/MCDEA systems with various sPS contents. The time dependence of G' and G'' for sPS-(DGEBA/MCDEA) mixtures with different thermoplastic contents, less than 7.5 wt % sPS and more than 7.5 wt % sPS, is shown in Figures 4 and 5, respectively. The changes that occurred in η^* are shown in Figure 6. At the beginning of the curing reactions, the sPS-modified mixtures behaved as semidilute polymer solutions having viscosities lower than 1 Pa s. When phase separation occurred, both G' and

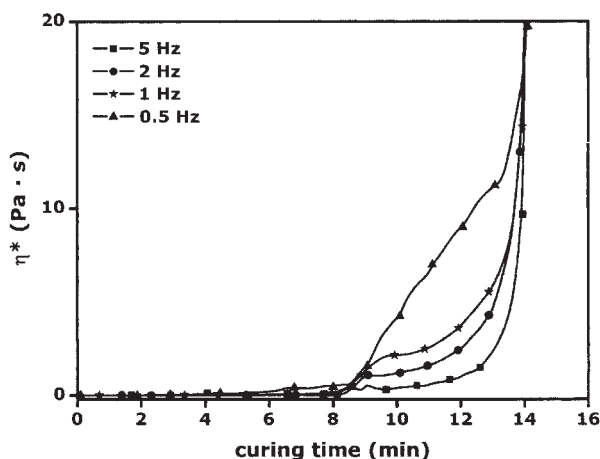


Figure 3 η^* versus the curing time for 5 wt % sPS-(DGEBA/MCDEA) at an isothermal curing temperature of 220°C at various frequencies.

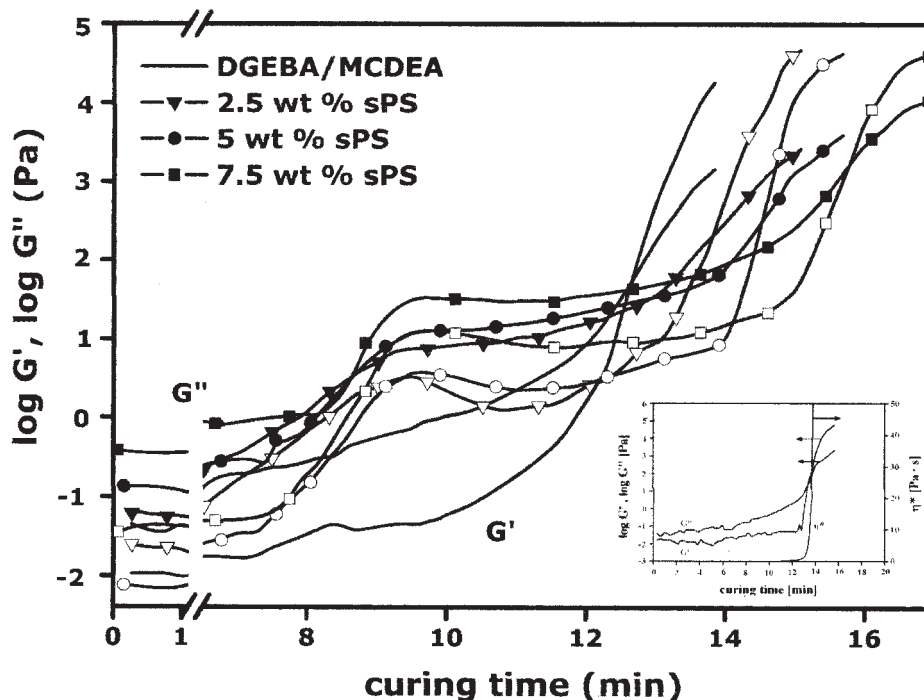


Figure 4 Evolution of G' (open symbols) and G'' (full symbols) versus the curing time for the sPS-(DGEBA/MCDEA) systems containing 2.5, 5, and 7.5 wt % sPS. The insert is an evaluation of G' , G'' , and η^* versus the curing time for the aPS-(DGEBA/MCDEA) system containing 5 wt %.

G'' increased quickly, in 7–9 min, almost at the same time and independently of the sPS content, except for the blend containing 12.5 wt % sPS, which presented a sharp change 2 min earlier. On the other side, η^* increased abruptly, at times depending on the sPS concentration.

On the one hand, for sPS concentrations lower than 7.5 wt % (Fig. 4), the preliminary phase-separation process was followed by a swift increase in the vis-

cosity. By a comparison with the corresponding profiles for the aPS-(DGEBA/MCDEA) system (where aPS is atactic polystyrene),²¹ shown in the inset of Figure 4, this behavior can be attributed to the crystallization of sPS from the epoxy-amine matrix because reaction-induced phase separation (RIPS) in aPS-(DGEBA/MCDEA) blends does not change significantly either the G' and G'' profiles or the η^* profiles.

At this point, it should be recalled that, for thermo-plastic/thermoset mixtures, phase separation can be

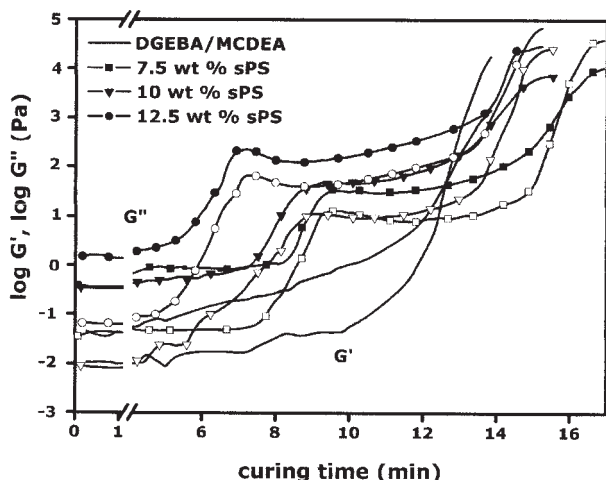


Figure 5 Evolution of G' (open symbols) and G'' (full symbols) versus the curing time for the sPS-(DGEBA/MCDEA) systems containing 7.5, 10, and 12.5 wt % sPS.

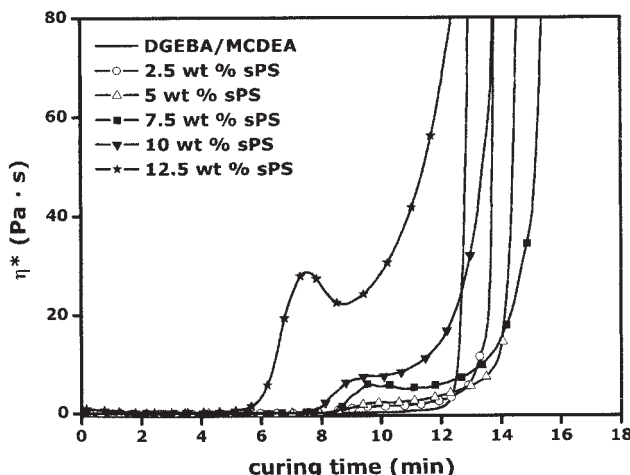


Figure 6 η^* versus the curing time for the sPS-(DGEBA/MCDEA) systems containing different amounts of sPS.

induced by the curing reaction, that is, RIPS, and also by crystallization of the thermoplastic (CIPS). As demonstrated in a previous article,²¹ for sPS-(DGEBA/MCDEA) mixtures, CIPS is responsible for the rise in η^* , around 7–8 min, before the sharp increase in the viscosity that is observed at gelation. RIPS can lead to an increase or decrease in the viscosity, depending on the generated morphology.^{2,8,9} However, as reported by Bonnet et al.⁸ for a DGEBA/MCDEA system with a low PEI concentration showing a particulate structure, RIPS from an epoxy matrix was followed by a rapid decrease of η^* instead of the increase that takes place for sPS-(DGEBA/MCDEA) mixtures. Additionally, it is well known that during the isothermal crystallization of semicrystalline thermoplastics, η^* increases when crystallization starts,^{24–27} and this confirms CIPS in the sPS-(DGEBA/MCDEA) system.

On the other hand, as can be seen in Figure 6, for sPS concentrations higher than 7.5 wt %, the behavior appears to be more complex. At the beginning of phase separation, a rapid increase in η^* took place; thereafter, a decrease in viscosity was found, and finally the viscosity increased again as a result of gelation. The initial increase in η^* can be explained by the fact that the molecular mobility of the epoxy chains might be reduced by CIPS. After that, a cocontinuous structure is formed, and the molecular mobility of epoxy chains is again higher; this results in a decrease in the viscosity. The behavior of the sample after phase separation is always complicated because parameters such as the composition and the epoxy conversion of both phases and the extent of reaction in each phase are changing continuously.

Taking into account that, for neat DGEBA/MCDEA and for 5 wt % sPS-(DGEBA/MCDEA) mixtures, the gelation point determined as the G' and G'' crossing is similar to that defined on the basis of the Winter-Chambon criterion, in that following, we have taken the point at which G' equals G'' as the gelation point. For sPS concentrations lower than 7.5 wt %, the gelation point shifted toward a longer curing time with increasing sPS contents, and this means that the addition of sPS resulted in a delay of the curing reactions, possibly because of a dilution effect. On the contrary, at sPS contents higher than 7.5 wt %, t_{gel} decreased with increasing sPS contents. Additionally, the values of η^* for the 12.5 wt % sPS-(DGEBA/MCDEA) system were four times higher than the values for mixtures containing less than 7.5 wt % sPS. As demonstrated in a previous article,²¹ the final morphology for cured samples of low sPS contents consists of small sPS spheres dispersed in a continuous epoxy/amine matrix, but for sPS concentrations around 7.5 wt %, the final morphology of sPS-(DGEBA/MCDEA) changes from particulate to cocontinuous. Therefore, both the decrease in the t_{gel} values and the increase in the values of η^* during phase separation with increasing

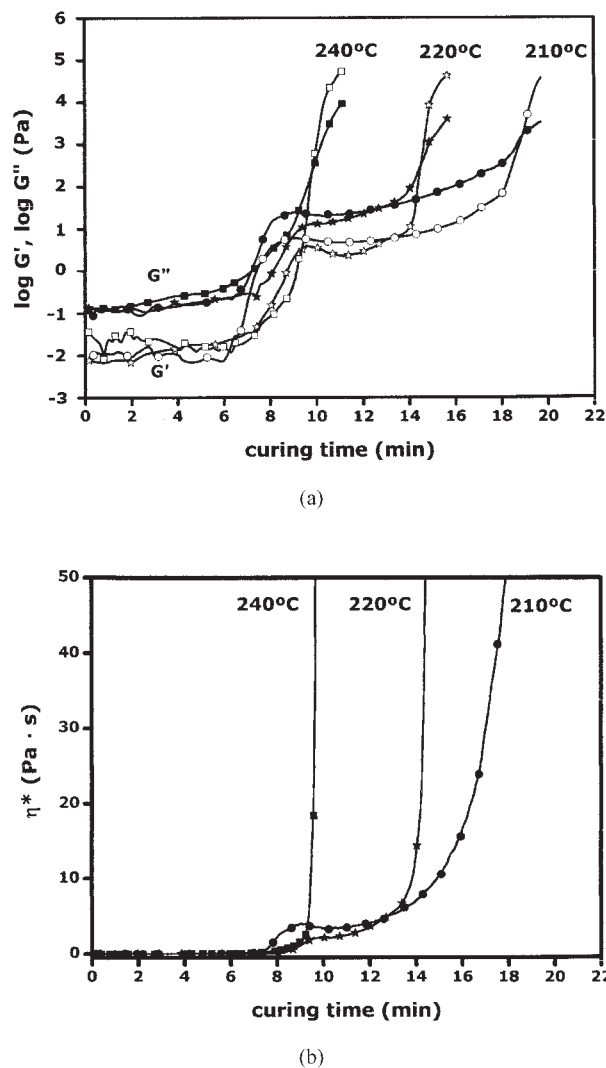


Figure 7 (a) Evolution of G' (open symbols) and G'' (full symbols) versus the curing time for the 5 wt % sPS-(DGEBA/MCDEA) system cured at different temperatures at 1 Hz and (b) evolution of η^* versus the curing time for the 5 wt % sPS-(DGEBA/MCDEA) system cured at different temperatures at 1 Hz.

sPS contents are probably due to the crystallization of sPS in a cocontinuous structure.

To clarify the influence of sPS crystallization on the rheological behavior of these mixtures, the effect of the curing temperature on the viscoelastic properties of 5 wt % sPS-(DGEBA/MCDEA) was also investigated. The rheological curves for this mixture curing at 210, 220, and 240°C are shown in Figure 7. The times at which η^* [Fig. 7(b)] and both shear moduli [Fig. 7(a)] started rising were similar at 210 and 220°C. The only difference was that for the blend cured at 220°C, the viscosity increased in a period between 6 and 9 min, whereas for that cured at 210°C, this increase was faster, and it was produced at curing times ranging from 6 to 7 min. The slower increase at 220°C was the result of a slower crystallization rate of sPS at this

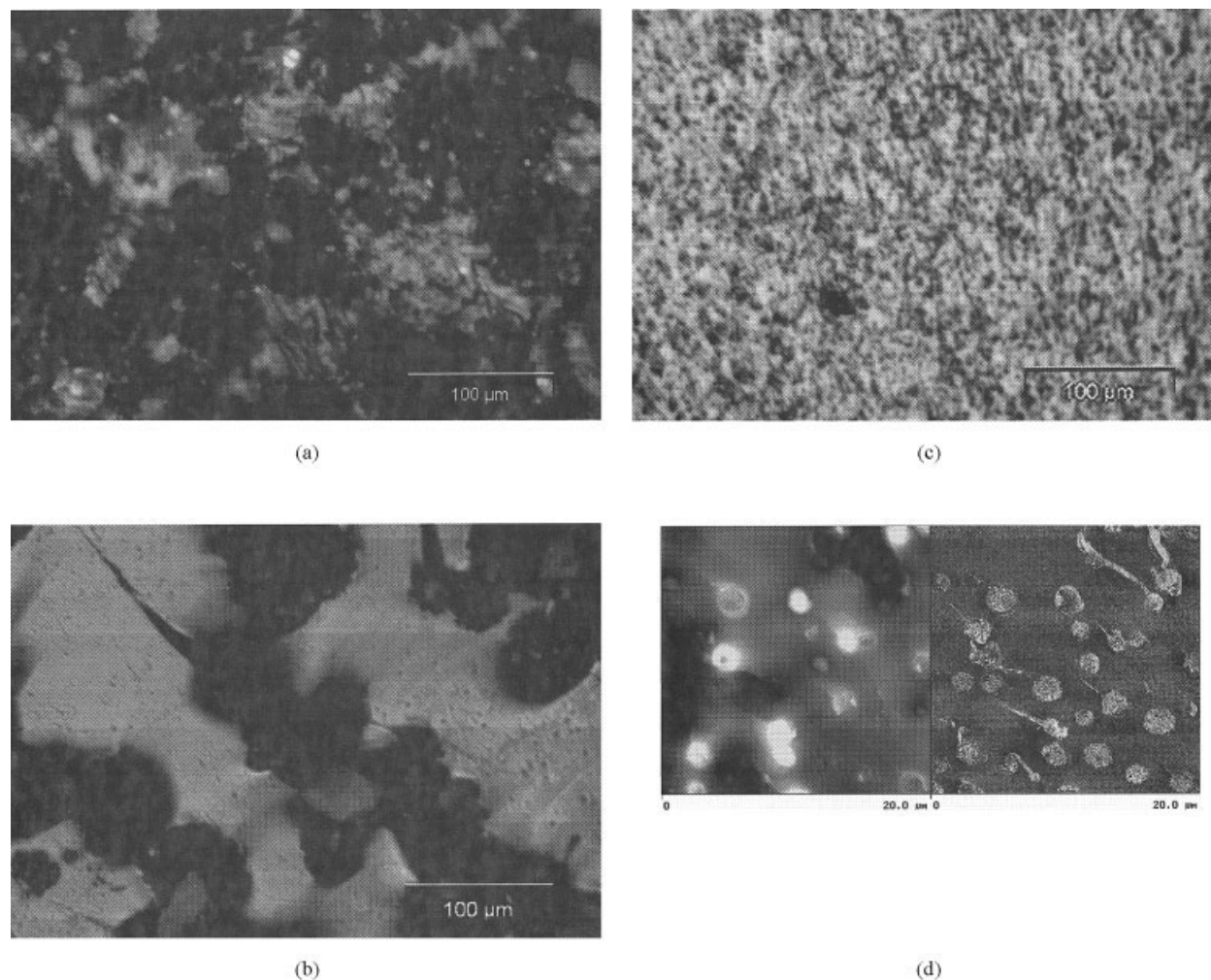


Figure 8 Cryogenically fractured surfaces of 5 wt % sPS containing sPS-(DGEBA/MCDEA) samples cured at (a) 210, (b) 220, and (c) 240°C for 2 h, as observed by optical microscopy. A detail of the sample cured at 240°C, as observed by AFM, is presented in part d.

higher temperature. For the sample cured at 240°C, however, no fluctuations before η^* tended to infinity were detected. Thus, a clear influence of the crystallization of sPS has been observed for the samples cured at lower temperatures, leading to CIPS, whereas RIPS seemed to occur at 240°C.

The influence of the curing temperature on the final morphology for the 5 wt % sPS-(DGEBA/MCDEA) mixture is shown in Figure 8. For mixtures cured at 210 or 220°C [Fig. 8(a,b)], the final morphology was similar. Big spherulites, formed by the effect of CIPS, embedded in a continuous matrix were observed. The spherulites formed at 220°C were smaller than those crystallized at 210°C. This was due to the fact that the initial increase of η^* at 220°C was slower at this temperature than that at 210°C. In addition, the decrease in t_{gel} with the curing temperature seemed to lead to a lesser amount of spherulites in the epoxy matrix.

Nevertheless, the final morphology was significantly different for the highest curing temperature

(240°C). No sPS spherulites were detected; only particles around 2 μm in diameter dispersed in the epoxy matrix were found [Fig. 8(c,d)]. No fluctuations in η^* before an abrupt viscosity increase due to gelation were observed at this temperature by rheological measurements. Because spherulites were not detected, it seems that an increase in the curing temperature hindered the sPS crystallization, and so phase separation proceeded by RIPS.

CONCLUSIONS

A chemorheological analysis of various sPS-(DGEBA/MCDEA) mixtures during curing was performed on an ARES rheometer. The different phenomena that took place upon curing—gelation, RIPS, and CIPS—were followed by dynamic mechanical measurements. The Winter-Chambon criterion was applied to determine the gelation point. Moreover, the gelation point obtained from the Winter-Chambon

criterion was in good agreement with that recorded with the G' and G'' crossing criterion. The addition of less than 7.5 wt % sPS to the DGEBA/MCDEA system shifted the gelation point toward longer cure times, and this means that the addition of sPS resulted in a delay of the curing reactions, probably because of a dilution effect. For sPS concentrations higher than 7.5 wt %, when the morphology was changing from particulate to cocontinuous, t_{gel} decreased with increasing sPS concentrations. A strong influence of CIPS on a liquid–solid transition of sPS–(DGEBA/MCDEA) systems could be noted.

Additionally, the effect of the curing temperature on the viscoelastic behavior and on the morphology for the 5% sPS–(DGEBA/MCDEA) mixtures was studied. A high curing temperature accelerated the gelation process. Moreover, a strong RIPS and CIPS influence on the shape of the rheology curves was observed. For lower curing temperatures, an increase in G' , G'' , and η^* with time was found, as a result of CIPS. On the contrary, for the highest curing temperature, no fluctuation in G' , G'' , and η^* before gelation was found. The viscoelastic behavior of 5% sPS–(DGEBA/MCDEA) corresponded well to a morphology variation. Both sPS spherulites and sPS particles, formed by CIPS and RIPS, respectively, and dispersed in an epoxy matrix, were found for mixtures cured at 210 and 220°C, but only sPS particles dispersed in the epoxy matrix (RIPS) were found for a mixture cured at 240°C.

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