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Rheological behavior of thermoset/thermoplastic blends during isothermal curing: Experiments and modeling

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Abstract

The evolution of the viscoelastic properties of a molten thermoplastic/thermoset system during the course of the isothermal polymerization of the thermoset precursors has been investigated and modeled. Such systems are initially homogenous and phase separate upon polymerization of the monomers. In the present study, atactic polystyrene (85 and 60 wt%) is blended to a stoichiometric mixture diglycidyl ether of bisphenol A with 4,4′-methylenebis(2,6-diethylaniline). During the polymerization, polystyrene becomes the thermoplastic-rich matrix and an epoxy-rich dispersed phase appears. Both phases experience changes in their composition and viscoelastic properties. A rheokinetic model is proposed to take into account four contributions to the viscoelastic behavior: progressive deplastification of the polystyrene matrix involving a modification of the glass transition and thus of free volume, dilution of the network of entanglements of the matrix by the non yet converted low molar weight molecules, emulsion behavior after the separation of the epoxy-rich phase and finally interparticular interactions being assimilated to a mechanical percolation. Provided that the glass transition temperature of the matrix and the dynamic moduli of the neat components are known, the changes in the viscoelastic behavior of the system with time can be predicted with no ad hoc parameter and model calculations are in good agreement with the experimental data.

Keywords: Rheology; Modeling; Blends

1. Introduction

Thermoplastic/thermoset (TP/TS) blends result from the mixing of a thermoplastic polymer with the monomeric precursors of a thermoset. Before their polymerization, these low molar mass reactants show a miscibility window with the thermoplastic. Upon reaction, the molar mass of the species increases and the miscibility is progressively reduced until a liquid–liquid phase separation is initiated, at quite low conversion. Then, the homogenous mixture becomes biphasic and its morphology depends on composition, curing temperature and other specific processing parameters. Numerous studies have been devoted to the study of such complex systems as TP/TS blends from different points of view like morphology development and control [1,2], rates of reaction [3], mechanical properties [4,5] and review articles are available [6–8]. The evolution of the rheological properties of TP/TS have also been addressed but in a less extent. The authors have experimented on blends of poly(2,6-dimethyl-1,4-phenylene ether) (PPE) with different epoxy resins. Influences of the phase separation, gelation and vitrification on the dynamic viscoelastic properties during isothermal curing have been highlighted. A large range of compositions and temperatures have been considered [9,10]. However, very few studies deal with the modeling of the complex evolution of the rheological

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behavior of these systems. Indeed, the prediction of the linear viscoelasticity of emulsions may be considered as a first step toward that of TP/TS blends. In this field, the Palierne model [11] and other models [12] derived from the Kerner model [13] are excellent to calculate the modulus of non-concentrated immiscible TP blends and have been widely used in the literature. On the other hand, the linear and non-linear viscoelastic behaviors of concentrated emulsions for which interactions between particles must be considered have been addressed by Doi and Ohta [14] and Lee and Park [15]. The impact of the thermo-mechanical history has been included in emulsions models by Castro et al. [16]. Bonnet et al. have implemented an empirical modeling of the rheological evolution in a TP/TS blends. They decomposed the course of the reaction in three different stages and used the Einstein equation to take into account the influence of the dispersed phase [17]. The simulation was useful to quantify the effects of the different transitions and transformation which occur during the process.

The most fundamental aspect of TP/TS blends is their evolutive nature: miscibility, morphology, reactivity, volume fraction and composition of the phases and thus viscoelastic properties are continuously changing all along the isothermal polymerization process. Indeed, this complexity is the source of great difficulties that we intend to overcome by developing a global model for predicting the evolution of dynamic oscillatory moduli of TP/TS blends starting from basic data, and particularly the behavior of pure components. In that purpose we report the behavior of a blend for which the major component is atactic polystyrene (PS), mixed with a reactive epoxy system based on diglycidyl ether of bisphenol A (DGEBA) and 4,4′-methylenebis(2,6-diethylaniline) (MDEA). The proportion of polystyrene is 60 and 85 wt% so that the blends after polymerization consist of a polystyrene matrix with 40 and 15 wt% of crosslinked epoxy-amine particles. This particular system was preferred because a large set of experimental data is available as far as miscibility, reaction rate, composition and morphology evolution are concerned [18,19]. These data are required to implement the model.

2. Experimental

2.1. Materials

The thermoplastic used in this study is an atactic polystyrene (Lacqrene PS 1450 N; $M_n = 163{,}000\ \mathrm{g\ mol^{-1}}$, polydispersity index of 2) supplied by Arkema. The thermoset is composed of an epoxy monomer diglycidyl ether of bisphenol A supplied by Bakelite (LY556 polyaddition index = 0.15, $M_n = 382.6\ \mathrm{g\ mol^{-1}}$) cured with 4,4′-methylenebis(2,6-diethylaniline) (MDEA), supplied by Lonza with $M_n = 310.5\ \mathrm{g\ mol^{-1}}$ in stoichiometric proportions.

2.2. Blend preparation

Blends with 60 and 85 wt% of PS were prepared with a twin-screw extruder DSM Xplore 15 mL micro-compounder (DSM Xplore Netherlands). The liquid epoxy monomer was mixed with PS for 15 min at 150 °C and 20 rpm. This first step was necessary to dissolve the PS. Then, MDEA was introduced at the same temperature for 10 min at 50 rpm to limit the conversion of the thermoset. The homogenous mixture was pressed for 10 min at 130 °C under 200 bars of pressure to obtain specimens for viscoelastic measurements and samples for cloud point determination. In these conditions, the initial extent of epoxy-amine reaction during the preparation of sample was negligible. This was confirmed experimentally with differential scanning calorimetry (DSC).

The blends and a thermoset without PS were also prepared in glass flasks heated in a thermoregulated oil bath at 177 °C. Samples were removed from the bath at selected time intervals and then quenched in iced water to stop the reaction. These samples have been used to measure the glass transition temperatures, to determine the gel point and to characterize the morphology.

2.3. Measurements

The polymerization experiments were carried out at a single temperature of 177 °C.

The phase separation time of the blends was determined in a light transmission device as the onset of the decrease of the light transmission during the isothermal polymerization, defined as the cloud point (the apparatus is home made). For the 85/15 blend, it was determined with the help of the micrographs.

The gelation time of the thermoset was defined as the time at which an insoluble fraction was observed in tetrahydrofuran (THF) solution. For this purpose, 80 mg of blend having experienced various curing times in a oven at 177 °C was dissolved in 20 mL of THF.

Glass transition temperature measurements were conducted with a Mettler (France) TA3000 differential scanning calorimeter under argon atmosphere. The experiments were carried out from −100 to 350 °C at a heating rate of 10 °C/min. The glass transition temperature (T_g) was taken at the onset of the inflection of the heat flow curve.

For transmission electron microscope observation (TEM), samples were ultra-microtomed at room temperature and, subsequently, vapor-stained using ruthenium tetroxide (RuO_4). TEM imaging was performed using a Philips CM 120 microscope operating at 80 kV accelerating voltage. The apparent particle diameter was determined by digitalizing TEM photomicrographs. Image analysis was used to determine the volume fraction of the dispersed phase in the way described by Meynie et al. [18].

The viscoelastic properties were measured at 177 °C in a Rheometrics dynamic analyzer (RDAII) operated with parallel plate geometry in oscillatory shear. The measurements were carried out within the linear viscoelastic domain. The variations of the moduli were recorded between 0.01 and $100\ \mathrm{rad\ s^{-1}}$ with 5 points per decade in order to get a reliable discrete relaxation spectrum.

For neat PS, 25 mm diameter parallel plates and a gap of 2 mm were used while the viscoelastic behavior of TS and blends has been measured using larger plates (40 mm, gap 1 mm) because of the low viscosity of the TS resin in the earliest stages of the polymerization.

The temperature was 177 °C and the apparatus was preheated to limit the conversion of the TS before the beginning of the experiment. Strain of 1% was found to be within the linear viscoelastic domain and it was sufficient to ensure a torque signal compatible with the range of the torque transducer. This value was used throughout the test.

3. Results and discussion

3.1. Behavior of the neat epoxy-amine during polymerization

The variation of the glass transition temperature of the neat DGEBA–MDEA themoset system and the evolution of the dynamic moduli during the polymerization at 177 °C are depicted in Fig. 1a and b. The glass transition temperature increases drastically from −25 to 150 °C during polymerization until completion of the network. The gel point can be detected on the rheological curve. It is characterized by a sharp increase of the elastic moduli at 22 min. Because the polymerization temperature is above the T_g of the totally converted epoxy-amine system, no vitrification occurs. Therefore, the plateau observed at the end of the experiment is due to the stabilization of the mechanical properties when the epoxy-amine reaction is complete.

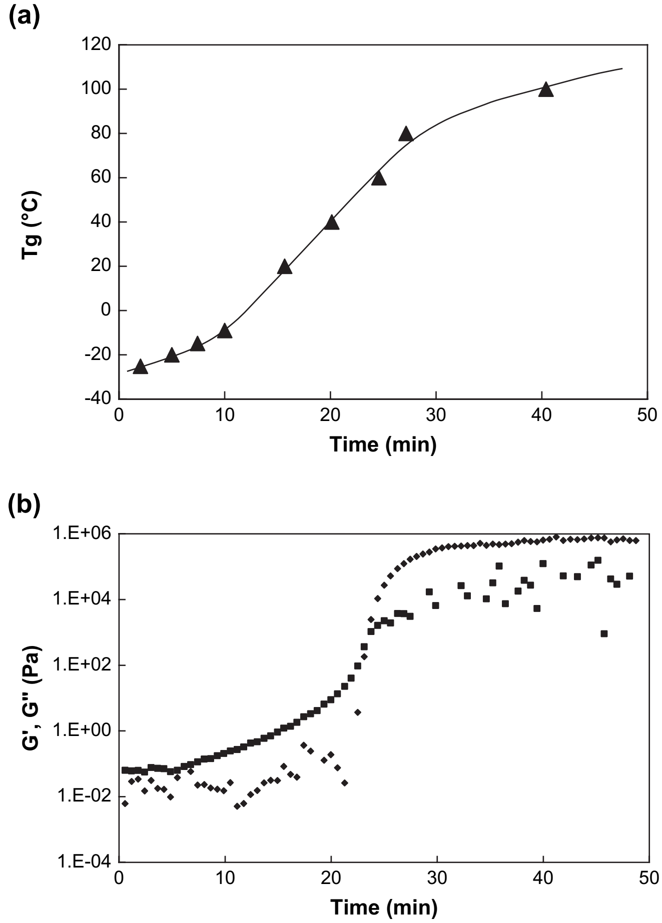

Fig. 1. DGEBA–MDEA polymerized at 177 °C. (a) Evolution of the glass transition temperature as a function of time and (b) storage modulus G' (◆) and loss modulus G'' (■) measured at $\omega = 10\ \mathrm{rad\ s^{-1}}$.

3.2. Behavior of the PS/DGEBA–MDEA blends

Obviously, the behavior of the thermoplastic/thermoset blend is much more complex than that of the corresponding neat epoxy-amine presented above.

3.2.1. Phase behavior of the PS/DGEBA–MDEA blends

To capture the evolution of the PS/DGEBA–MDEA blends during the isothermal polymerization at 177 °C, it is interesting to examine three sets of experimental data in parallel: the variation of the experimental glass transition temperature (T_g) which reflects the variation of the composition of the phases, the morphology of the blend and finally the evolution of the rheological properties measured during the course of the polymerization.

These data are presented in Figs. 2 and 3 for the blends containing 15 and 40 wt% of epoxy-amine. The sequence of events occurring during the process is detailed hereafter.

1. Before phase separation, at 177 °C, the PS/DGEBA–MDEA blends are initially homogenous, therefore only one T_g is observed at the beginning of the process. The reaction of the monomers produces higher molar mass species that induce an increase of the T_g.
2. The phase separation is detected by the loss of transparency of the blends or with the help of microscopic observations because small epoxy-amine droplets are formed (diameter ~500 nm). It occurs approximately at 240 and 24 min, respectively, for 85/15 and 60/40 blends (arrows in Figs. 2a and 3a).
3. After phase separation, the blend is biphasic as can be seen from the TEM pictures in Figs. 2b and 3b. Thus, two T_gs are observed and they are attributed to the PS-rich and the epoxy-rich phases. The glass transition of the PS-rich phase was easily recorded for both systems. Results are shown in Fig. 6. Actually, it was not possible to record the glass transition of the dispersed phase in the 85/15 blend because of a weak signal. When two phases are created, they are not pure. Some epoxy monomers or *i*-mers remain in the polystyrene matrix while some short chains of polystyrene are trapped in the epoxy-rich droplets. The diffusion of monomers and oligomers out of the PS-rich phase explains the increase of the T_g versus time. In the same way, PS chains are progressively expelled from the epoxy drops as conversion proceeds. The feeding of the epoxy-amine drops by *i*-mers coming from the matrix and the diffusion of the short chains of PS out of the drops decrease the T_g, while the reaction of the epoxy-amine species increases it. The observed T_g of the epoxy-rich drops results

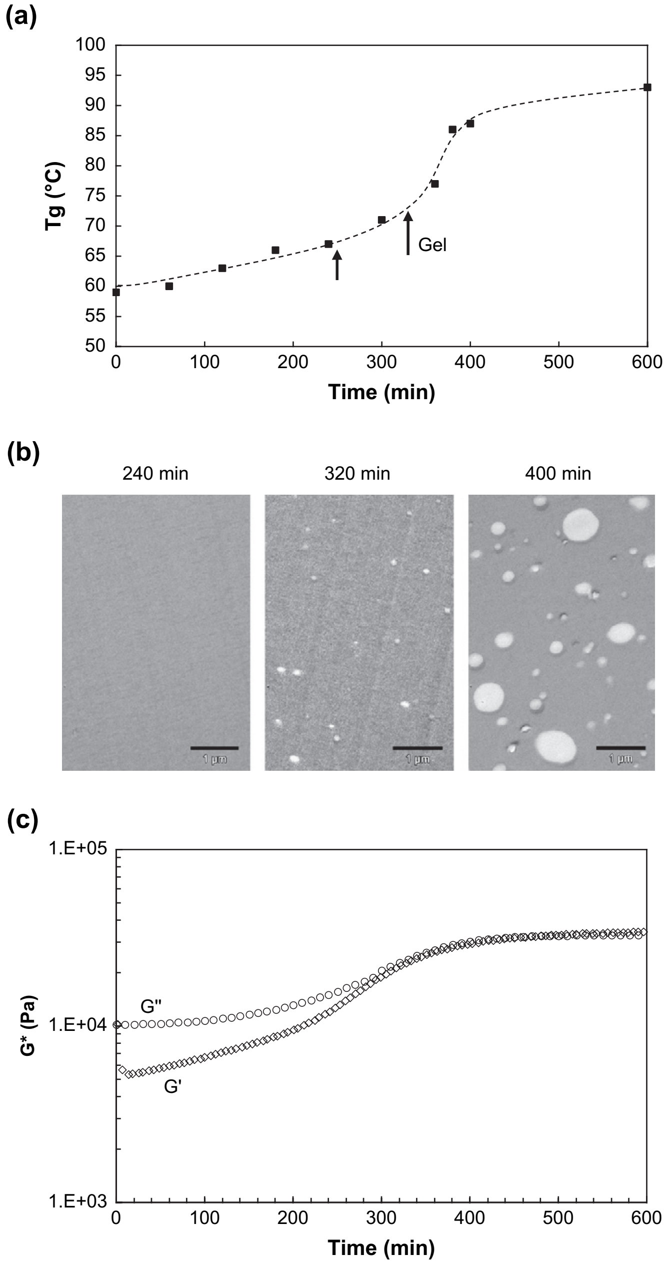

Fig. 2. PS/DGEBA–MDEA 85/15 polymerized at 177 °C. (a) Evolution of the glass transition of the polystyrene-rich phase (the T_g of the epoxy-amine-rich phase was not detectable), (b) morphology of the blend at different reaction times (the epoxy-amine drops appear in light grey), and (c) storage modulus G' (◇) and loss modulus G'' (○) measured at $\omega = 10\ \mathrm{rad\ s^{-1}}$. The arrows indicate the phase separation and the gel times.

from these antagonist influences. A slow purification of the phases takes place until the gel point and complete crosslinking of the thermoset. These evolutions are accompanied by the growth of the epoxy-amine domains that is clearly visible in the TEM pictures. The increase of the viscosity and elasticity of the droplets around the gel point slows down and finally stops their growth. At the end, the phases are almost purified since their T_gs are equal to those of the neat components (97 °C for the PS and 140 °C for the DGEBA–MDEA).

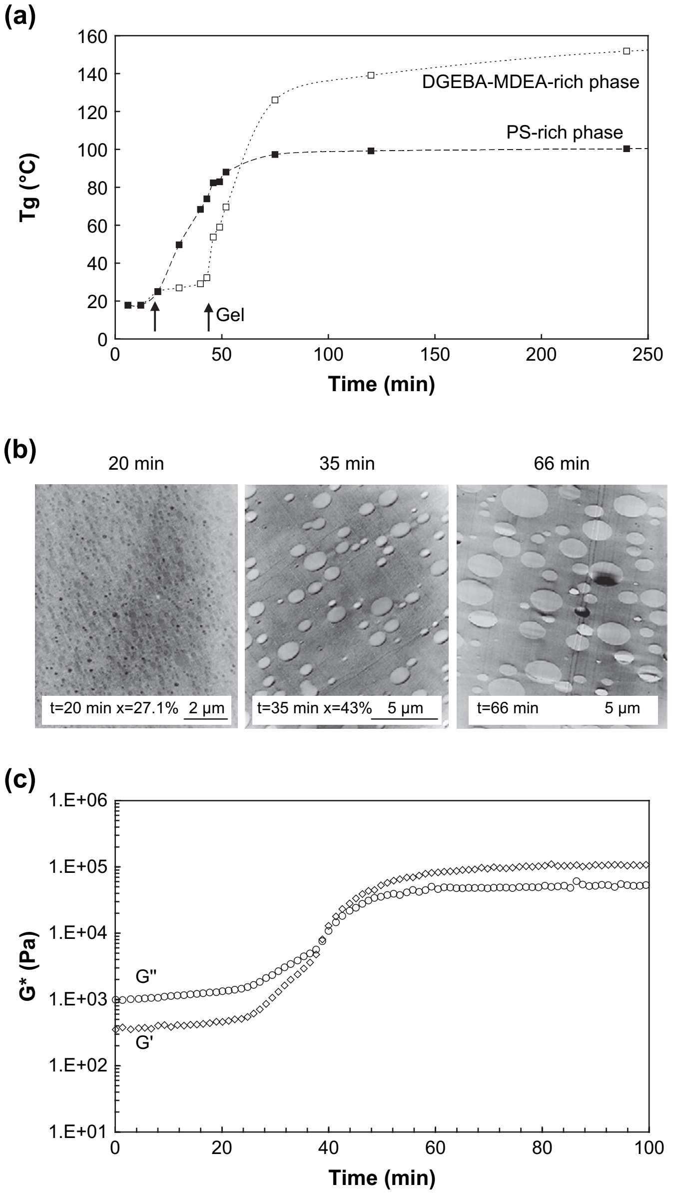

Fig. 3. PS/DGEBA–MDEA 60/40 polymerized at 177 °C. (a) Evolution of the experimental glass transition of the polystyrene-rich (■) and epoxy-amine-rich (□) phases, (b) morphology of the blend at different reaction times (the epoxy-amine drops appear in light grey), and (c) storage modulus G' (◇) and loss modulus G'' (○) measured at $\omega = 10\ \mathrm{rad\ s^{-1}}$. The arrows indicate the phase separation and the gel times.

The polymerization is faster for the more concentrated blend with 40 wt% of reactive species as can be seen from the phase separation times and gel times in Table 1.

Table 1
Characteristic times and epoxy conversions data for neat DGEBA–MDEA, PS/DGEBA–MDEA 60/40 and 85/15 blends

PS/DGEBA–MDEA	Phase separation time (min)	Conversion at phase separation	Gel time (min)	Conversion at gel
0/100	–	–	20	0.60
60/40	24	0.28	43	0.65
85/15	>240	0.28	320	0.67

3.2.2. Rheological evolution of the PS/DGEBA–MDEA blends

The evolution of the dynamic moduli during the polymerization of the epoxy-amine blended with polystyrene is significantly different from that of the neat thermoset. It is more complex because of the existence of a demixion and the subsequent continuous variation of the size and composition of the two phases formed during the polymerization.

Fig. 2c depicts the evolution of the moduli for a PS/DGEBA–MDEA 85/15 blend. An overall increase of the moduli is noted but three stages can be observed on these curves. They correspond to the phenomena described in the previous section.

1. Before phase separation, the molar mass of the thermoset species grows without inducing a phase separation. The slow increase of the moduli is linked to the increase of the glass transition of the homogenous mixture caused by the formation of these higher molar mass epoxy-amine species.
2. At phase separation, a change in the viscoelastic behavior is observed, which results in an inflection of the moduli. This transition corresponds to the evolution from the behavior of a solution (epoxy-amine dissolved in PS) to the behavior of an emulsion (epoxy-amine-rich droplets dispersed in molten PS-rich phase).
3. After phase separation, the moduli increase and finally, both G' and G'' stabilize when the reaction is complete. As the polymerization temperature is higher than the final T_g of the matrix and the dispersed phase, vitrification is not encountered in this blend.

The PS/DGEBA–MDEA 60/40 blend contains a higher fraction of epoxy-amine and this induces a difference in its rheological evolution after the phase separation: at nearly 38 min, a second inflection is detected (Fig. 3c). The authors agree to ascribe the first inflection to the initiation of demixion as proved experimentally by optical techniques (cloud point and microscopy) even though their accuracy can be questionable since the size of the demixing phase is very small at the early stages of nucleation and growth.

The second inflection is generally ascribed to the gel point of the epoxy-amine domains [9,10,17,20]. This interpretation of the second inflexion is a matter of discussion because the gel point of TP/TS heterogenous blends cannot be easily measured with high accuracy especially when the thermoset is dispersed as very small particles. Also in such systems, the inflection of the modulus may be due to the existence of hydrodynamic interactions between the epoxy-rich particles. Indeed, above some critical volume fraction, the domains may interact with each others leading to a sudden increase of the overall modulus. Such phenomenon is generally attributed to a percolation mechanism that gives rise to a yield stress in particular in polymer filled system [21]. The behavior of the blend with 15 wt% of epoxy-amine confirms this hypothesis because in this case such interactions disappear. Only one inflection of the modulus is detected corresponding to the phase separation. This is observed in Fig. 2c where the modulus rises at 240 min and no other inflection is seen.

3.3. Rheokinetic model

The implementation of a rheokinetic model describing qualitatively and quantitatively the phase separation process has to integrate the various events presented in the above section. The purpose is to calculate the dynamic moduli all along the polymerization from the rheokinetic of the neat TS and the evolution of composition of the blend.

The model takes into account four features contributing to the observed rheological behavior:

- The progressive deplastification of the polystyrene matrix involving a modification of the glass transition and thus of free volume.
- The dilution of the network of entanglements of the PS molecules by the non-converted low molar mass molecules.
- The emulsion behavior after the demixion of the epoxy-rich phase.
- The appearance of interactions assimilated to a mechanical percolation between the dispersed domains above a certain critical volume fraction of minor phase.

3.3.1. Deplastification

The migration of the monomers and oligomers toward the dispersed epoxy-rich domains after phase separation produces a progressive deplastification of the polystyrene-rich phase. Its T_g consequently rises. This phenomenon leads to a modification of the free volume that can be taken into account by a modification of the relaxation times of pure polystyrene with the temperature T, by using a factor of translation, $a(t)$ in the form:

$$\log\{a(t)\} = -\frac{C_1^g\left(T-T_g(t)\right)}{C_2^g+T-T_g(t)}+\frac{C_1^g\left(T-T_{gPS}\right)}{C_2^g+T-T_{gPS}} \tag{1}$$

where $T_g(t)$ is measured value (Figs. 2 and 3), T_{gPS} is the glass transition of the PS, C_{1g} and C_{2g} are the WLF coefficients at T_g for the PS given in Table 2. These latter were fitted but the values found are very close to standard values for PS [22].

3.3.2. Dilution

During and after phase separation, the dilution of the entanglements between PS chains by the monomers present in the matrix is modifying their mobility. Pearson has proved that

Table 2
Data used for modeling the rheological behavior of PS/DGEBA–MDEA blends

C_{1g}	C_{2g} (°)	T (°C)	T_{gPS} (°C)	ω (rad s^{-1})	α (N m)	R (m)	Φ_∞	Φ_p
11.2	50	177	99	1, 10, 100	0.005	10^{-6}	0.4 or 0.15	0.18

this effect can be introduced by multiplying the relaxation times and the moduli by a factor involving the concentration of polymer in the solvent [23]. If Φ_∞ is the overall volume fraction of epoxy-amine in the blends, the volume fraction of polystyrene in the solvent is initially $1-\Phi_\infty$. During the polymerization, the concentration of the polystyrene in the matrix is $(1-\Phi_\infty+\Phi(t))$, $\Phi(t)$ being the volume fraction of the dispersed phase supposed to be composed exclusively of epoxy and amine. At the end of the process, the matrix is pure PS thus $\Phi_\infty=\Phi(t)$ and the dilution factor equals 1 meaning no dilution.

The corrected relaxation times, $\lambda_i'(t)$, and moduli, $g_i'(t)$, of the PS are obtained through:

$$\lambda_i'(t)=a(t)\{1-\Phi_\infty+\Phi(t)\}\lambda_i \tag{2}$$

$$g_i'(t)=\{1-\Phi_\infty+\Phi(t)\}^2 g_i \tag{3}$$

Where $\lambda_i(t)$ and $g_i(t)$ are the data for neat PS given in Appendix A.

Then, it is possible to calculate G' and G'' for PS matrix with the multimode Maxwell model:

$$G'_{PS}=\sum_i \frac{g_i'(\tau_i'\omega_i)^2}{\left(1+(\tau_i'\omega_i)^2\right)}$$

$$G''_{PS}=\sum_i \frac{g_i'(\tau_i'\omega_i)^2}{\left(1+(\tau_i'\omega_i)^2\right)} \tag{4}$$

$\Phi(t)$ is measured with the help of image analysis of the TEM pictures (see Appendix B).

3.3.3. Emulsion model

When the epoxy-rich droplets separate from the matrix, the biphasic mixture may be compared to an emulsion of two viscoelastic fluids. The complex moduli of the mixture are calculated with the Palierne model:

$$G^*_M(\omega,t)=G^*_{TP}(\omega,t)\frac{1+3\phi(t)H^*(\omega,t)}{1-2\phi(t)H^*(\omega,t)} \tag{5}$$

With:

$$H^*(\omega,t)=\frac{4\frac{\alpha}{R}\left[2G^*_{TP}(\omega,t)+5G^*_{TS}(\omega,t)\right]+\left(G^*_{TS}(\omega,t)-G^*_{TP}(\omega,t)\right)\left(16G^*_{TP}(\omega,t)+19G^*_{TS}(\omega,t)\right)}{40\frac{\alpha}{R}\left[G^*_{TP}(\omega,t)+G^*_{TS}(\omega,t)\right]+\left(2G^*_{TS}(\omega,t)+3G^*_{TP}(\omega,t)\right)\left(16G^*_{TP}(\omega,t)+19G^*_{TS}(\omega,t)\right)} \tag{6}$$

- G_{TP}* is the modulus of the PS-rich phase. It is calculated from the experimental relaxation spectrum of neat PS (see Appendix A), modified to take into account the two preceding contributions (deplastification and dilution).
- α/R is the ratio of the interfacial tension and the average radius of the epoxy-amine drops. This ratio is kept constant at 5000 N ($\alpha=0.005$ N m and $R=1$ μm).
- G_{TS}* is the modulus of the dispersed phase.

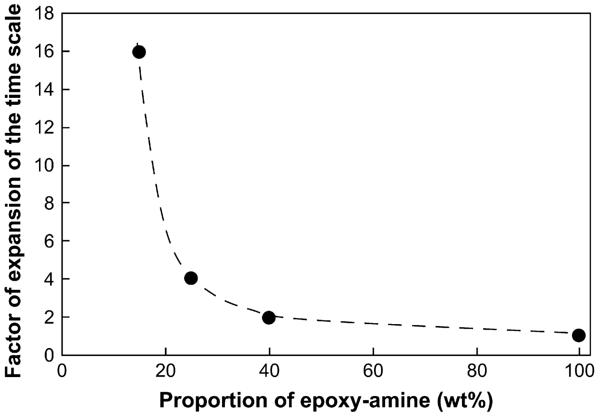

Fig. 4. Time expansion coefficient applied to the moduli of DGEBA–MDEA before the gel point for PS/DGEBA–MDEA blends with different compositions. The line is a guide for the eye.

The modulus of the dispersed phase $G_{TS}*(\omega,t)$ cannot be obtained directly because the exact composition of the epoxy domains is not known. We have considered that the dispersed phase is composed of epoxy-amine with the same reactivity than the neat epoxy-amine. However, before phase separation, an expansion of the time scale has been applied to account for the slower reactivity of the epoxy-amine homogenously diluted into the PS. Also, we supposed that all the epoxy-amine drops have the same conversion although Riccardi found that a distribution of conversion may exist among the drops [19].

The expansion factor could probably be related to the concentration of the reactive species but no simple relation was found thus an experimental adjustment has been done based on the gel time values of several blends (Fig. 4). Finally, the values of $G_{TS}*(\omega,t)$ used are presented in Appendix C.

3.3.4. Emulsion model with threshold

The Palierne model is not able to describe the concentrated blends because it does not include the possible mechanical interactions between the dispersed droplets. At this point, it is important to remind that for TP/TS blends, the volume fraction of the drops is continuously increasing so that above a certain critical concentration or percolation threshold, physical interactions may appear. This part of the model is the most original since it allows to generalize the model beyond the volume fraction where mechanical interaction exists between the epoxy-amine domains. It is assumed that when the fraction of dispersed phase exceeds the fraction ϕ_p at which the percolation starts (0.36 and 0.18, respectively, for monodisperse and polydisperse spheres), a continuous percolation path is created

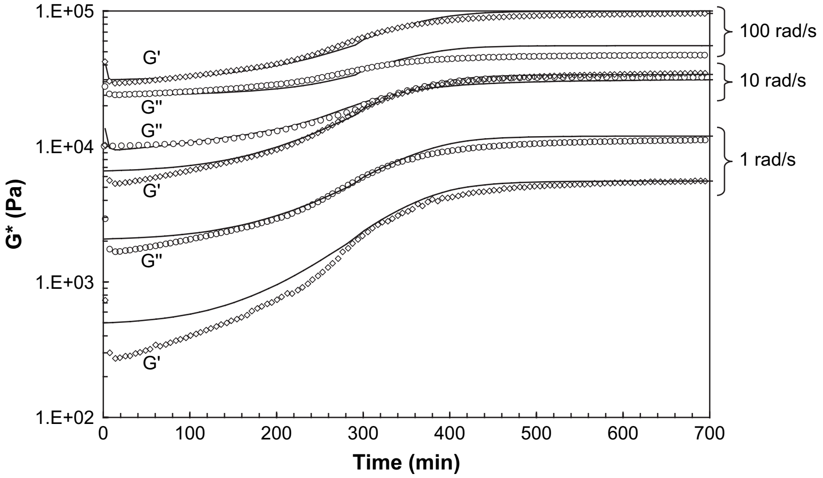

Fig. 5. PS/DGEBA–MDEA 85/15 polymerized at 177 °C. Evolution of the storage modulus G' (◇) and loss modulus G'' (○) measured at $\omega = 1$, 10 and 100 rad s^{-1}. The symbols are the experimental data and the continuous lines are the calculated.

whose contribution to the final modulus is related to the percolated volume fraction, $\phi(t) - \phi_p$. The global modulus is therefore expressed as:

$$G^*(\omega,t) = G^*_M(\omega,t) + \left(\phi(t) - \phi_p\right) G^*_{TS}(\omega,t) \tag{7}$$

$G^*(\omega,t)$ being the complex modulus of the TP/TS mixture, $G_M{}^*(\omega,t)$ is the modulus calculated with the Palierne model, and $G_{TS}{}^*(\omega,t)$ is the experimental modulus of the neat thermoset.

The term linked to the percolation is taken into account starting from the time where $\phi(t) - \phi_p$ becomes positive. This original aspect is detailed elsewhere [24].

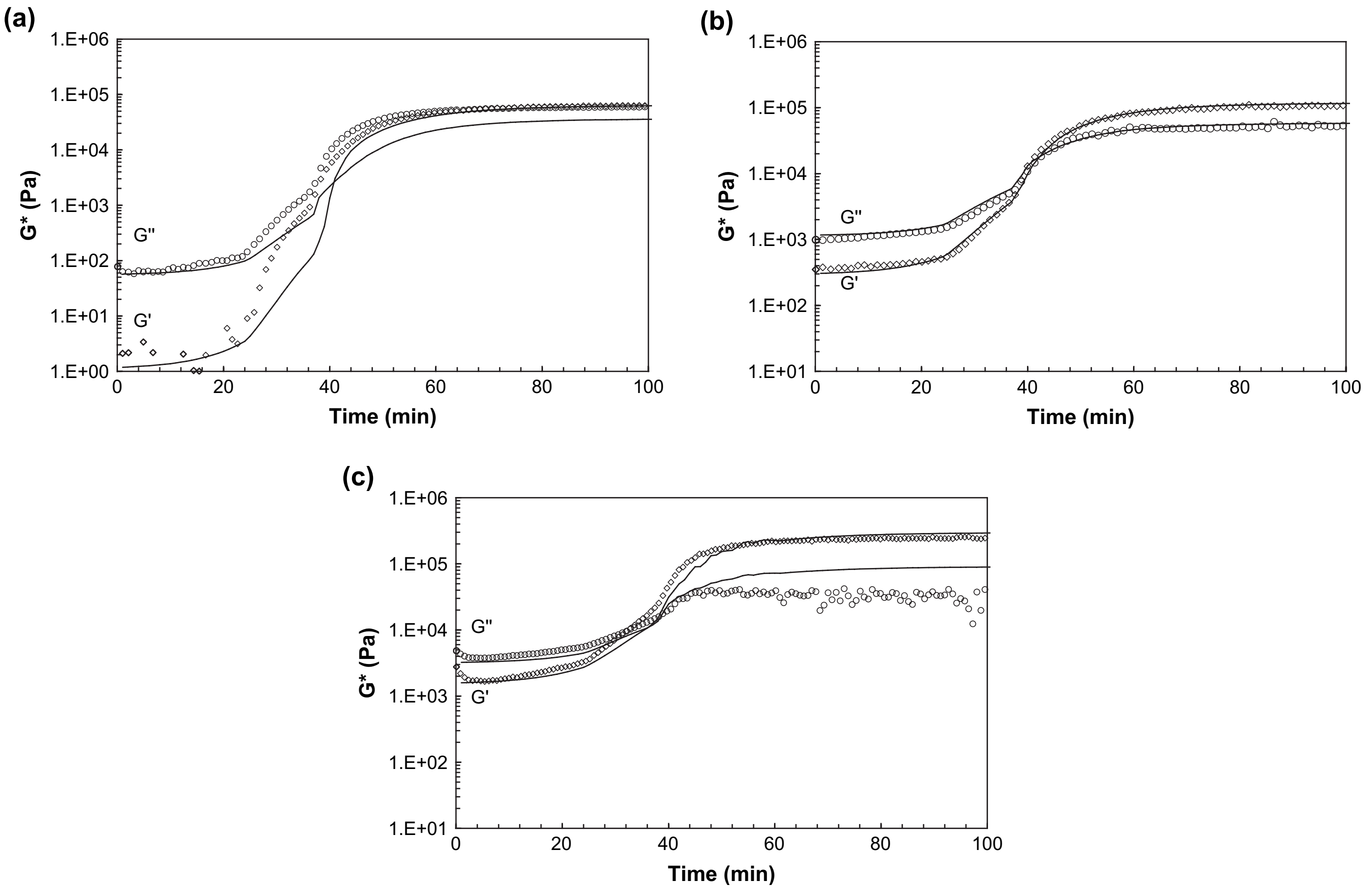

Fig. 6. PS/DGEBA–MDEA 60/40 polymerized at 177 °C. Evolution of the storage modulus G' (◇) and loss modulus G'' (○) measured at $\omega =$ (a) 1, (b) 10, and (c) 100 rad s^{-1}. The symbols are the experimental data and the continuous lines are the calculated.

3.3.5. Global calculation and comparison with the experiments

The parameters of the model are the WLF coefficients, the α/R ratio, the time expansion coefficient, and the percolation threshold ϕ_p. Their values are either known or ''universal'', or easily measurable. The only adjustable parameter is the percolation threshold.

The results of the calculation including the four effects described previously are plotted in comparison with experimental data in Figs. 5 and 6.

The behavior of the blend containing 15 wt% of epoxy-amine is well captured by the model at the three frequencies under investigation except that G' and G'' are overestimated at the beginning of the polymerization. This feature is somewhat surprising because the first stage of the process where the blend is homogenous should be easier to model than the rest of the process. Note that for this blend, the proportion of dispersed phase is always below the percolation threshold ($\phi_p = 0.18$) so that the contribution of the mechanical interactions is not included in the modulus.

The blend containing 40 wt% of epoxy-amine is particularly well described by the calculation at 10 rad s^{-1} because the model has been optimized for this frequency. A satisfactory agreement is also obtained at 1 rad s^{-1} while it is not as good at high frequency. Now, the modulus of the monophasic blend is very well captured as well as its final value. Only the intermediate stages show some discrepancies. The high concentration of the blend implies that the percolation threshold is exceeded at a given time of the process so that the additional term in Eq. (7) becomes effective. The value of the percolation threshold was actually fitted with the help of these data and one can note that it corresponds fairly well with the theoretical value expected from the percolation theory (0.18).

4. Conclusion

The present work addresses the modeling of the linear viscoelastic behavior of a thermoplastic/thermoset blend in the course of its polymerization above the glass transition of the final blend. The observed behavior, related to the simultaneous phenomena of polymerization and demixing, is fairly described by a rheokinetic model taking into account four contributions: progressive deplastification of polystyrene, dilution of the network of entanglements, behavior of emulsion, and interactions between particles. The last phenomenon is modeled by a threshold added to the emulsion model. Calculation of the dynamic oscillatory viscoelastic moduli of the reactive mixture can be achieved starting from the knowledge of the properties of neat polystyrene, of the variation of the glass transition temperature of the thermoplastic-rich matrix and of the behavior of the neat thermoset during the course of polymerization. To be completely predictive, the model should integrate a modeling of the variation of the glass transition temperature of the epoxy derived from the kinetics of polymerization.

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Appendix

The data presented in the appendix have been used to implement the rheokinetic model.

Appendix A. Determination of relaxation times of the polystyrene matrix

The linear viscoelastic behavior of the matrix is expressed through the use of a discrete spectrum of relaxation times (τ_i, g_i) at 177 °C. This relaxation spectrum of Table A was calculated from the linear viscoelastic data of PS in oscillatory experiments at 177 °C. Both the experimental values and the calculation from the relaxations spectrum are plotted on Fig. A.

Table A
Calculated relaxation times (λ_i), moduli (g_i) and viscosity (η_i) of virgin PS at $T = 177$ °C

λ_i (s)	g_i (Pa)	$\eta_i = g_i\lambda_i$ (Pa s)
0.00250	128,000	319
0.0236	46,600	1100
0.110	33,100	3650
0.468	18,900	8830
1.91	6800	13,000
7.73	1320	10,200
32.1	104	3350

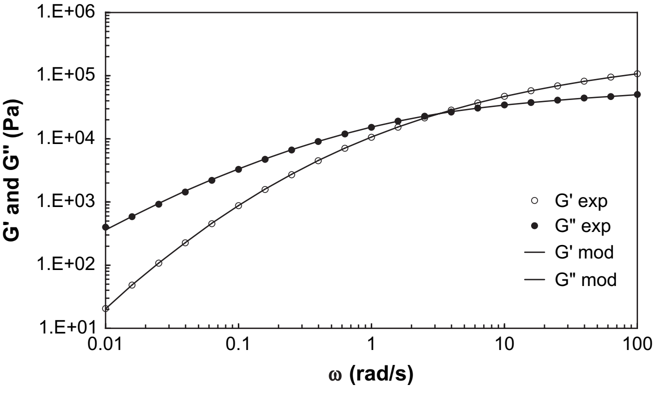

Fig. A. Dynamic moduli of molten PS at $T = 177$ °C. Measured are shown in symbols and calculated are the continuous lines.

Appendix B. Values of the modulus used for the epoxy-amine rich dispersed droplets

The modulus of the epoxy-amine rich droplets was assimilated to that of the neat epoxy-amine after having applied a time shift to the period of time preceding the gel point (Fig. B).

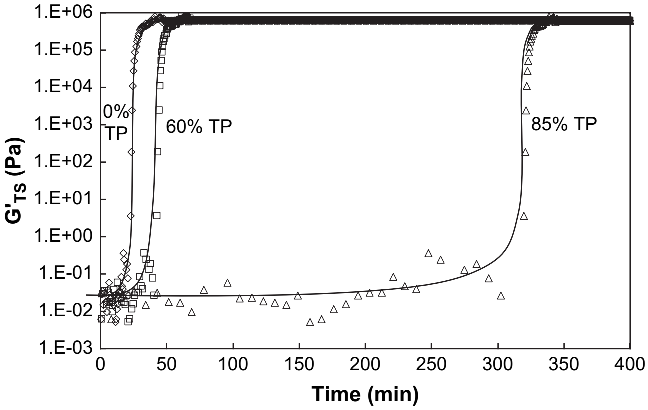

Fig. B. Visualization of the time scale modification used to account for the variations of the storage modulus of the epoxy-amine droplets. The time expansion coefficient depends on the dilution of the reactive species in the blend. The same modification was applied to the loss modulus.

Appendix C. Volume fraction of the epoxy-amine dispersed domains

A determination of the volume fraction of the dispersed phase versus the reaction time has been performed on the TEM pictures. The results are shown in Fig. C. When phase separation is achieved, the glass transition of the PS-rich phase can be calculated by a biunequivocal approximate relation between the volume fraction of dispersed phase and the glass transition of the components. Let $\phi(t)$ and ϕ_∞ be the volume fraction of the dispersed phase at time t and at the end of the polymerization, respectively. Assuming that PS is plastified by the unreacted monomers fraction $(\phi_\infty - \phi(t))$, and that the epoxy drops do not contain polystyrene chains, it is possible to calculate the volume fraction of the dispersed phase with the help of the Fox–Flory equation:

$$\frac{1-\phi(t)}{T_{\mathrm{g}}(t)} = \frac{\phi_\infty - \phi(t)}{T_{\mathrm{gepoxy}}} + \frac{1-\phi_\infty}{T_{\mathrm{gPS}}} \tag{1A}$$

T_{gepoxy} and T_{gPS} are the T_{g}s of the neat PS and of unreacted DGEBA–MDEA.

The mass fraction is assimilated to the volume fraction since the densities of PS and epoxy-amine are not different.

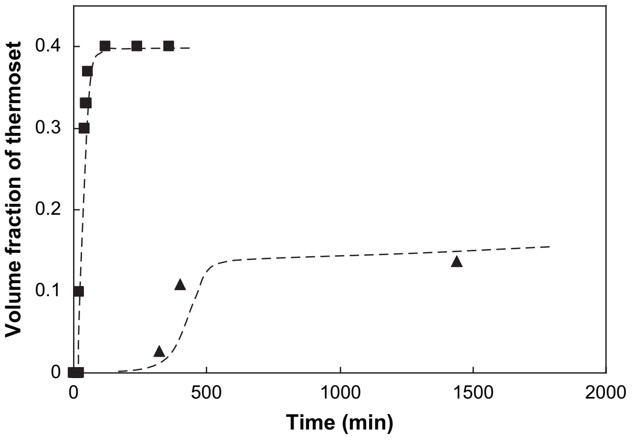

Fig. C. Evolution of volume fraction of the dispersed phase obtained during the polymerization of PS/DGEBA–MDEA 60/40 and 85/15 at 177 °C.

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