

# Viscoelastic Behavior of Chlorinated Polyethylene/Poly(ethylene-co-vinyl acetate) Blends in the Melt State

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**ABSTRACT:** Blends of chlorinated polyethylene and an ethylene vinyl acetate copolymer of various compositions were prepared by mixing in the melt state. Dynamic rheological properties of these blends were studied at different temperatures below, near, and above the  $T_s$ , the temperature of phase separation, and in a frequency range from 0.01 to 100 rad/s. It is shown that the time-temperature superposition principle is suitable in all investigated temperature ranges.  $G'$  versus  $G''$  representations for the blends were

found to be independent of temperature and varying weakly with the composition. Changes in the relaxation spectra  $H(\tau)$  were discovered which depend on the prehistory of the blend preparation and on thermal conditions in the working unit of a rheometer (increasing the temperature from 140 to 180°C or decreasing the temperature from 180 to 140°C). © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 1911–1918, 2003

**Key words:** blends; compatibility; relaxation; rheology

## INTRODUCTION

Rheological properties are of fundamental importance for the characterization and modeling of the flow behavior of polymers. Most investigations have dealt exclusively with two-phase polymer blends (see, e.g., refs. 1 and 2). Recently, theories have been developed that permit calculation of the viscoelastic behavior of such systems from the data on the viscoelastic properties of polymer components.<sup>3,4</sup>

It is known that the majority of miscible pairs of polymers has an LCST. The rheology of such blends has been thoroughly investigated.<sup>5–12</sup> Data on the dynamic mechanical properties of PS/PPO,<sup>5,6</sup> PS/PVME,<sup>7–11</sup> and PMMA/SAN<sup>12</sup> blends allow one to conclude that transition to a terminal behavior is more gradual for a blend than for the initial components if strong intermolecular interactions are operating between blend components. The phase-separation temperatures ( $T_s = 110^\circ\text{C}$ ) of the PS/PVME blends are higher than is the glass transition temperature ( $T_g = 100^\circ\text{C}$ ), especially at low PS contents. The time-temperature superposition (TTS) may be used to describe the viscoelastic response at temperatures below the LCST to  $10\text{ K} > T_g$ . These investigations have shown that phase separation does not influence the

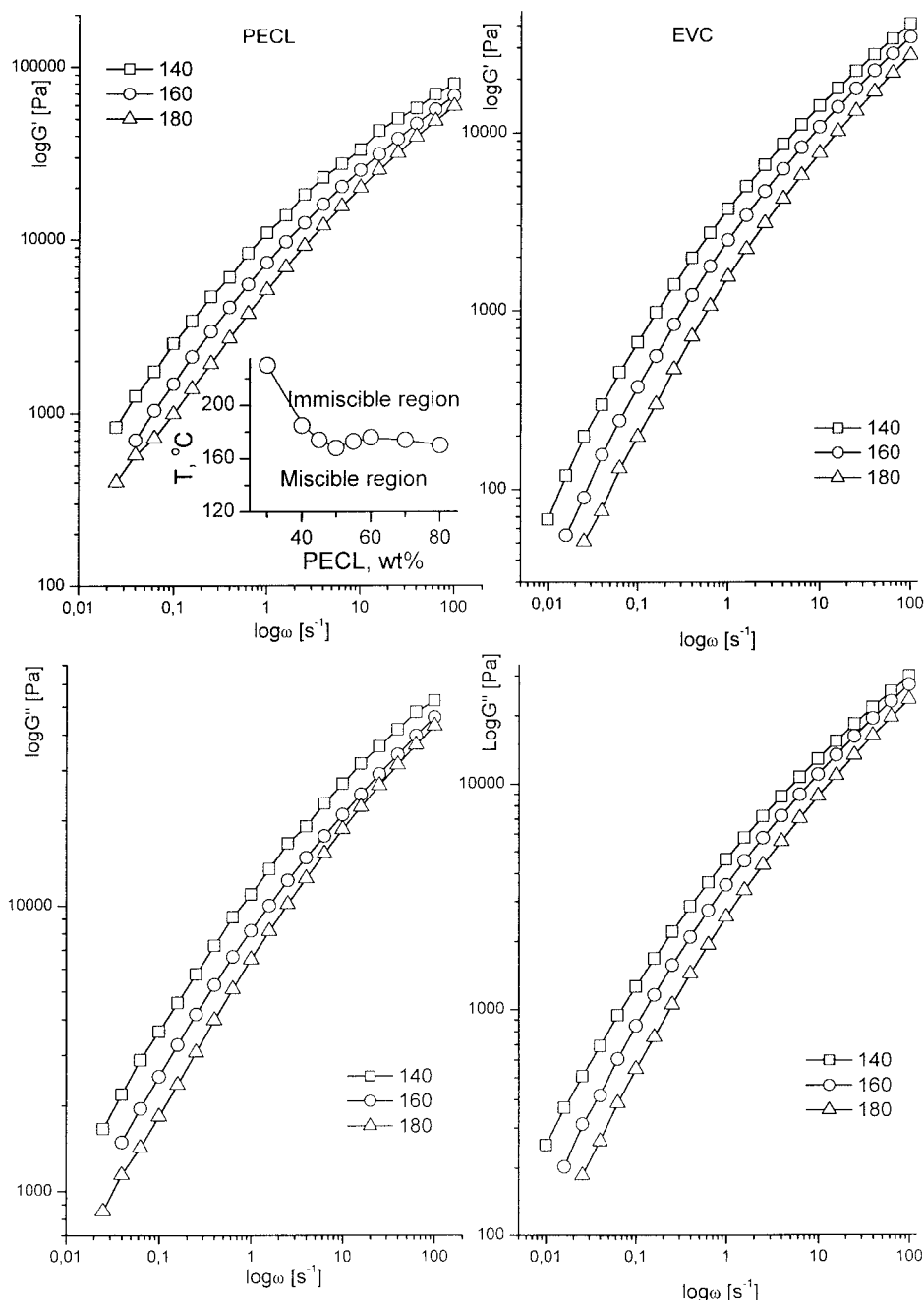
high-frequency behavior of blends; the low-frequency region is more sensitive to phase separation. It was also found<sup>9</sup> that phase separation exerts little effect on the relaxation behavior and the TTS may be applied to the dependencies of  $G'(\omega)$  and  $G''(\omega)$  measured at temperatures as high as 40 K above the LCST. Only at higher temperatures is the superposition not observed, due to a decrease in  $G'$ . On the contrary, Katsaros et al.<sup>10</sup> reported that phase separation resulted in an increase in  $G'$  but did not affect  $G''$ . It was shown that a plot of  $\eta'/\eta_0$  versus  $\eta''/\eta_0$  is more sensitive to phase separation than are the dependencies  $G'(\omega)$  and  $G''(\omega)$ . At the same time, for the PMMA/SAN blends,<sup>12</sup> a deviation from the TTS appeared at temperatures near the  $T_s$  ( $T > T_s + 15\text{ K}$ ). It is evident that there is a need for a more extensive study of such systems to understand the effects of phase separation on the low-frequency behavior of miscible polymer blends. The purpose of the present article was to estimate the viscoelastic properties of a miscible polymer blend—chlorinated polyethylene/poly(ethylene-co-vinyl acetate) (PECL/EVC),<sup>13,14</sup> which up to now has not been studied.

## EXPERIMENTAL

As the objects of investigation, commercial chlorinated low-density polyethylene (PECL; chlorine content 29.35% wt) having  $T_g = -16^\circ\text{C}$ , melting point  $T_m = 44^\circ\text{C}$ , and  $[\eta] = 0.865\text{ m}^3/\text{kg}$  (5% wt solution in tetrahydrofuran at  $20^\circ\text{C}$ ) and the ethylene vinyl acetate

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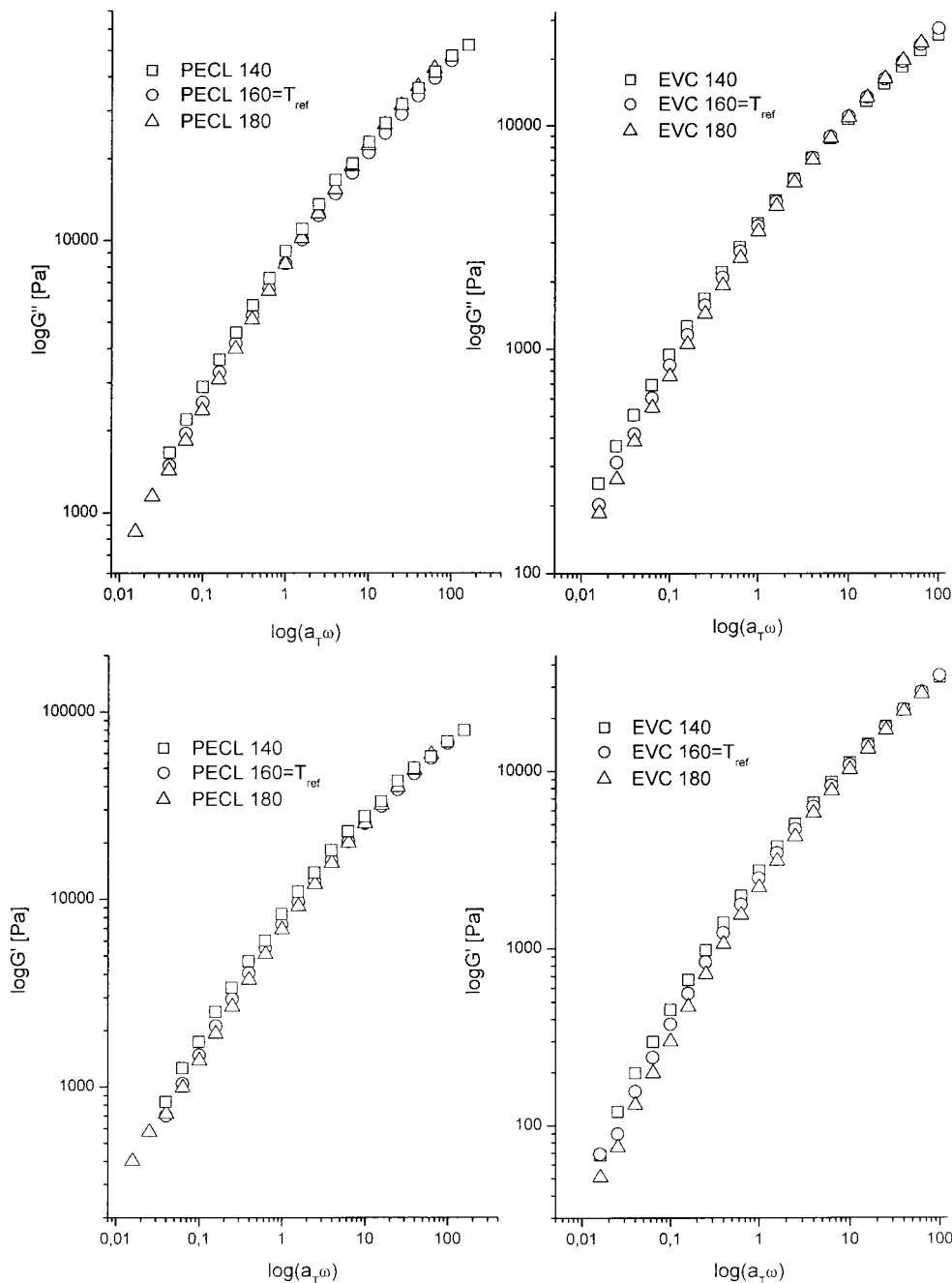
**Figure 1** Frequency dependencies of the storage ( $G'$ ) and loss ( $G''$ ) moduli for the initial components at different temperatures. The binodal curve of the PECL–EVC blends was obtained from cloud-point measurements.

copolymer (EVC) Levapren 45 (Bayer, Leverkusen, Germany, with a rated 45% content of vinyl acetate) having  $M_n = 3.77 \times 10^4$ ,  $M_w = 2.56 \times 10^5$ ,  $M_w/M_n = 5.16$ ,<sup>13</sup> and  $T_g = -24^\circ\text{C}$  were selected.

The PECL/EVC blends of compositions (by weight) of 9/1, 8/2, 7/3, and 3/7 were prepared by mixing the components in a micromixer of a rotator–plunger type (a gap between rotor and inner cylinder of 0.25 mm, minimal charging of 3.5 g, shear rate in the gap of  $500 \text{ s}^{-1}$ ) at 140 and  $175^\circ\text{C}$ , corresponding to homogeneous

and heterogeneous regions on the phase diagram. It should be noted that the specimens for measurements of  $G^*(\omega)$ , as contrasted to other studies,<sup>5–12</sup> were prepared by the mixing of the components in the melt state.

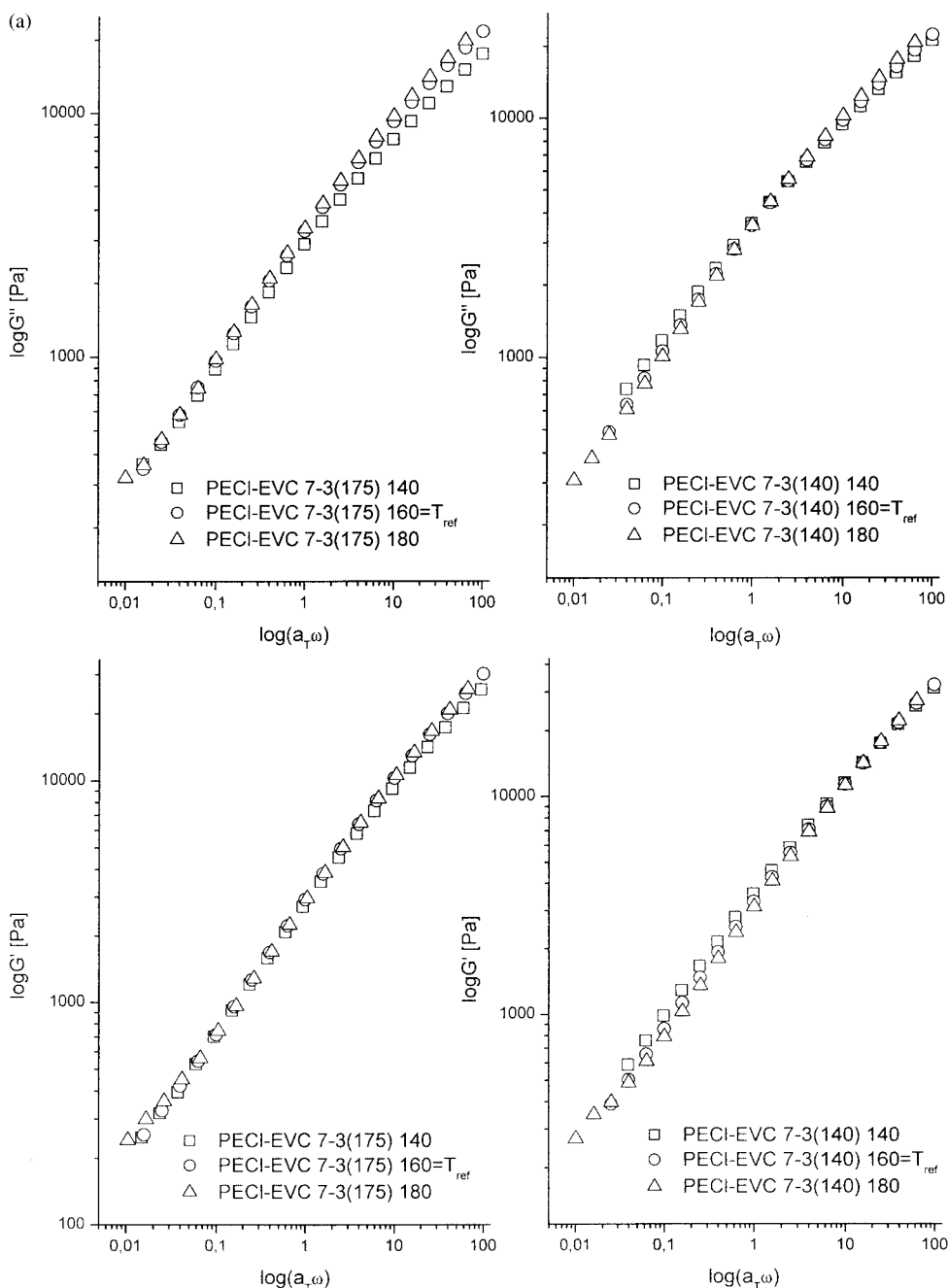
The cloud-point temperatures were determined using light scattering as abrupt temperatures increase its intensity. Films for determination of the cloud point were obtained from solutions of the blends in tetrahydrofuran. A phase diagram of the PECL/EVC blends is shown in Figure 1.



**Figure 2** Master plots for  $G'$  and  $G''$  of the initial components.

The storage  $G'(\omega)$  and loss  $G''(\omega)$  shear moduli were measured with a Rheometrics RMS-800/RDS-II rheometer (parallel-plate geometry) at small amplitudes of harmonic vibrations and three temperatures (140, 160, and 180°C) in a frequency window spanning about four decades ( $\omega = 10^{-2}$  to  $10^2$  rad/s). Experiments were performed both with an increase of the temperature from 140 to 180°C and a decrease of the temperature from 180 to 140°C [only for the PECL/EVC 7/3 prepared at  $T_{\text{mix}} = 175^\circ\text{C}$ ;

denoted in the figures as (inv)]. The upper temperature (180°C) of the experiments was limited by the thermostability of PECL. The holding of PECL into the working unit of a rheometer at the temperature of 140°C for 3.5 h did not lead to pronounced changing of its complex dynamic viscosity. The storage time of the initial components and their blends at measurements of  $G^*(\omega)$  in the temperature range from 140 to 180°C and, vice versa, from 180 to 140°C did not exceed 2.5 h.



**Figure 3** (a,b) Master plots for  $G'$  and  $G''$  of PECL-EVC blends.

## RESULTS AND DISCUSSION

As an example, Figure 1 presents the dependencies of  $G'(\omega)$  and  $G''(\omega)$  for PECL (Fig. 1) and EVC (Fig. 1) at various temperatures. The same dependencies were obtained for PECL-EVC blends of compositions 9-1, 8-2, 7-3, and 3-7. The analysis of these dependencies shows that, for the initial components and for their blends at all temperatures in the region of low frequencies, the exponents in the relations  $G' \approx \omega^\alpha$  and  $G'' \approx \omega^\beta$  are lower as compared with those of the

flexible polymers ( $\alpha = 2$  and  $\beta = 1$ ).<sup>15</sup> In our case, we have  $\alpha = 1.0$  and  $\beta = 0.7$ . This may have resulted from the fact that we could not reach the terminal zone for the used polymers, where  $G' \propto \omega^2$  and  $G'' \propto \omega$ .

The inner self-consistency of the experimental data for the initial components and blends was proved by constructing the master curves (Figs. 2 and 3) using the TTS. It is seen from Figures 2 and 3 that there exists excellent superposition of the experimental dependencies of  $G'(\omega)$  and  $G''(\omega)$  for the initial components and

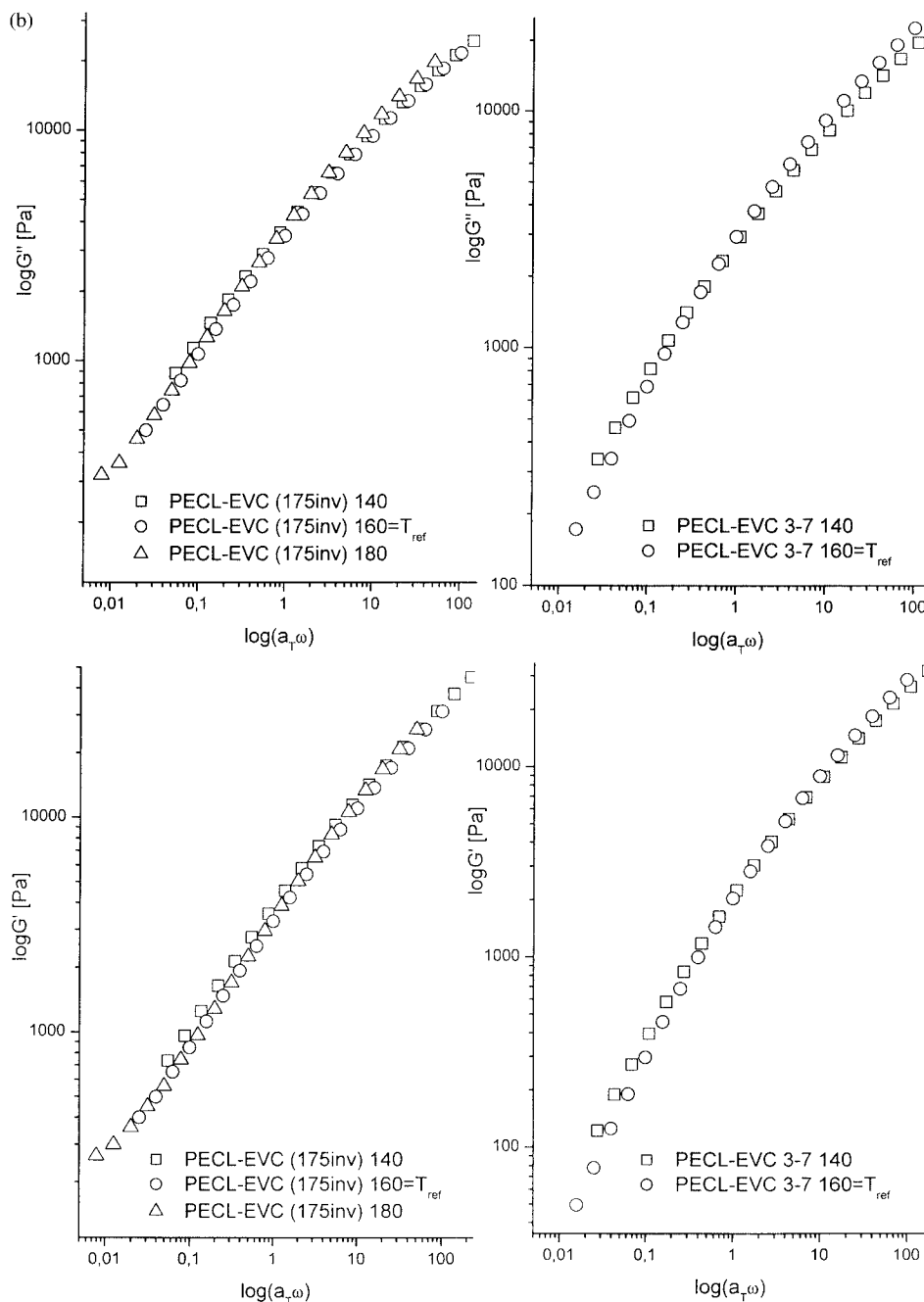
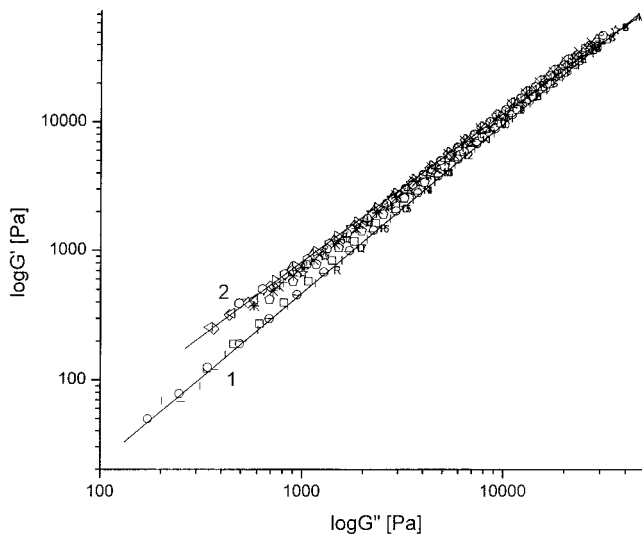


Figure 3 (Continued from the previous page)

blends prepared by mechanical mixing at 140 and 175°C. However, for the blend of 7–3 composition, mixed at 175°C, some distortion of the TTS is observed in the region of high values of  $a_T \omega$  [Fig. 3(a)]. In the temperature interval of 180 to 140°C [see Fig. 3(b)], this blend shows the superposition of  $G'(\omega)$  by using  $a_T = 1.75$  and the superposition of  $G''(\omega)$  at  $a_T = 2.2$ .

To establish the difference between homogeneous and heterogeneous blends, Han et al.<sup>16,17</sup> proposed a criterion which is based on the presentation of  $G'$  as a function of  $G''$ . Such a dependence is given by the

generalized curve for miscible polymers at different temperatures. For immiscible pairs, the dependence of  $G'(G'')$  may be presented by a series of curves, each one being shifted in relation to the other for various compositions and temperatures. This concept was applied in this work for PECL, EVC, and their blends at 140 and 160°C (Fig. 4). As seen, two master curves exist, which are expressed more at low values of  $G'$  and  $G''$ . The dependencies  $G'(G'')$  for PECL, EVC, and a 7–3 blend (obtained by mixing at 175°C) are described by one curve (curve 1, Fig. 4). This composi-



**Figure 4**  $G'$  versus  $G''$  of the PECL, EVC, and PECL-EVC blends at different temperatures.

tion corresponds to the homogeneous region on the phase diagram in the temperature interval of 140–180°C. The second master curve represents the data for all other blends, obtained by mixing at 140 and 175°C (curve 2, Fig. 4). In such a way, the obtained results meet the Han concept for the miscibility region (140 and 160°C). This concept<sup>16,17</sup> is correct also for the heterogeneous region (temperature of 180°C in Fig. 4; the data are not given).

From the initial data [ $G'(\omega)$  and  $G''(\omega)$ ], the relaxation time spectrum  $H(\tau)$  was calculated using the computer program NLREG, based on the method of nonlinear regularization by Tikhonov.<sup>18</sup> The results are given in Figure 5. Paying no attention to the peculiarities of the relaxation behavior in the region of low relaxation time, one can note the relatively fast decay of  $H(\tau)$  (region of high  $\tau$ ) which begins at characteristic relaxation times. For example, for PECL, EVC, the 7–3 blend (mixing at 175°C), the 7–3 inv blend (mixing at 175°C), and the 7–3 (mixing at 140°C), the values of  $\tau$  are, correspondingly, 4.8, 1.9, 8.9, 4.6, and 4.5 s. Therefore, EVC has the lowest relaxation time,  $\tau_1$ , whereas the 7–3 PECL-EVC blend (mixed at 175°C and subjected to testing by changing the temperature from 180 to 140°C) possesses the greatest relaxation time. Other systems have comparable values of  $\tau_1$ . PECL's apparent activation energy  $\Delta E_1$  for this relaxation process found, from the plot  $\log(\tau_1) = f(1/T)$ , is approximately 24 kJ/mol. This value is close to the activation energy of the PECL viscous flow, found from the dependence of the complex viscosity on the reverse temperature.

From the point of reptation model of polymer flow,<sup>19</sup> "fast" decay may be connected with the disen-

tanglement process, that is, with full exit of a polymer chain from the virtual tube of entanglements. This effect may be characterized by the corresponding maximum of relaxation time  $\tau_{\max} = \langle h^2 \rangle / D$  (here,  $\langle h^2 \rangle$  is the mean-averaged distance between the end of the unperturbed chain in the state of a melt and  $D$  is the self-diffusion coefficient). By using for EVC and PECL in the melt at 160°C the tabulated value<sup>20</sup> of  $\langle h^2 \rangle / M = 0.66 \times 10^{-20} \text{ m}^2$  and  $D \approx 5.0 \times 10^{-17} \text{ m}^2/\text{s}$  (found from the data available<sup>21</sup> for branched polyethylene), we found the most probable molecular masses of the fraction responsible for the fast ( $\tau_{\max,1} = \tau_1^{\text{EVC}} = 1.9 \text{ s}$  and  $\tau_{\max,1}^{\text{PECL}} = 4.8$ ) component of the spectrum of the relaxation time. This crude estimation seems to be rather acceptable for the EVC specimen used in our work (the discrepancy between  $M_1^{\text{EVC}}$  and  $M_n$  does not exceed 20 %).

The data given in Figure 5 show a marked change of the extension of the relaxation spectra in the plateau region depending on the specimen prehistory [compare Fig. 5(c), (d), and (e)]. It may be supposed that at such conditions the structure of the blend 7–3 is realized, at which the destruction of the dynamic networks of entanglements under the action of oscillation proceed at essentially various relaxation times. The splitting of  $H(\tau)$  for the specimen PECL-EVC 7–3 inv [compare Fig. 5(c) and (d)], is observed which probably shows various structural transformations in blends of the same composition. These effects depend on the temperature of the initial heat treatment of the blend and on the process direction (storage of the specimen at isothermal conditions in the working unit of the rheometer), which corresponds either to the region of a homogeneous [Fig. 5(c)] or a heterogeneous [Fig. 5(d)] state.

## CONCLUSIONS

The experimental results show some peculiarities of the viscoelastic behavior of the blends of PECL and the EVC. The principle of TTS is valid practically for all compositions of the blends at temperatures below and above the temperature of phase separation. It was found that the dependence of  $G'$  on  $G''$  (Han concept) does not depend on the temperature and changes weakly with the composition. The nonequilibrium state of the blends, which is determined by the chosen method of mixing, leads to the realization of various structural transformations. These transformations depend on the prehistory of the specimens and on the direction of the heat-treatment process at isothermic conditions in the working unit of a rheometer. This, in turn, determines the broadening of the pseudoplateau in the relaxation spectrum  $H(\tau)$  and its splitting.

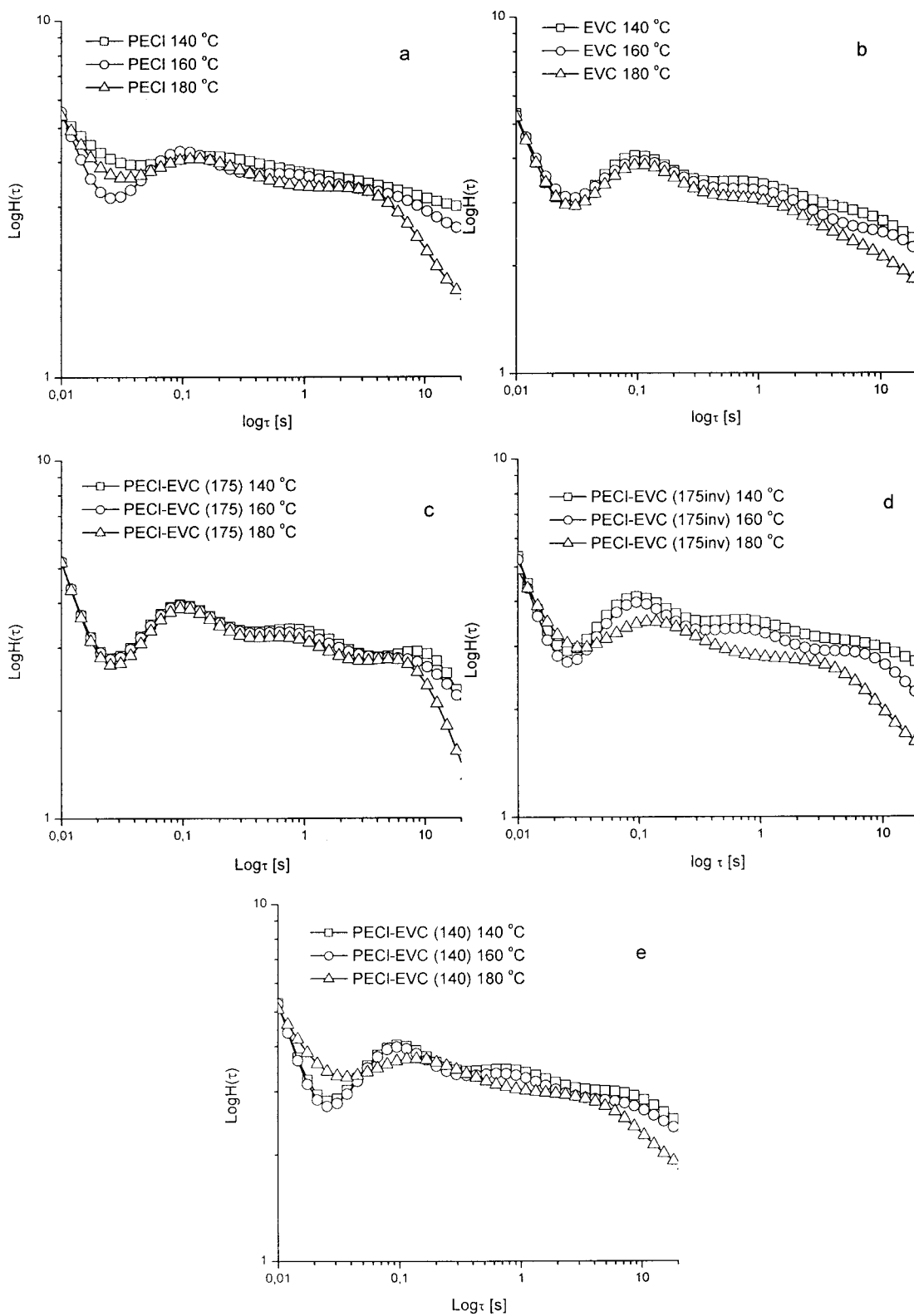


Figure 5 Relaxation time spectra for PECL, EVC, and PECL-EVC blends at different temperatures.

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