Viscoelasticity and Morphology of Poly(ethylene-co-vinyl acetate)/Polyisobutylene Blends

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ABSTRACT: Blends of an ethylene/vinyl acetate copolymer (EVA) and polyisobutylene of various compositions were prepared by mechanical mixing at a temperature above the melting point of EVA (T_m^{EVA}) but below the upper critical solution temperature of 170°C for given blends. The rheological properties of the components and blends were studied in the region of small-amplitude oscillating deformation at temperatures above and below T_m^{EVA} in the frequency range of 0.01–100 rad/s. At temperatures lower than T_m^{EVA}, the rheological properties were determined by the existence of the yield stress. With diminishing frequency, the viscosity increased, and the plateau in the relaxation spectrum at low frequencies broadened. The morphology of the blends depended on the conditions of sample heating. The introduction of a finely dispersed filler into the blends led to an anomalous drop in the viscosity. The morphology of the systems that arose by mechanical blending of the molten components was the important factor in the rheological behavior. The observed effects were examined in the framework of the concept of structural networks formed in melts by nonmelted crystallites of EVA. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 2700–2707, 2006

Key words: blends; differential scanning calorimetry (DSC); relaxation; rheology

INTRODUCTION

The rheological properties of polymer blends are of great importance for processing polymeric materials. Many works have been dedicated to the rheology of two-phase (incompatible or immiscible) polymer blends (e.g., refs. 1 and 2). For such systems, some theories have been developed that allow us to calculate the viscoelastic properties of the blends from the rheological properties of the pure components[3,4] At the same time, there have been few investigations of the effects of the phase separation on the viscoelasticity. Until now, only blends of polystyrene and poly(vinyl methyl ether)[5] and poly(methyl methacrylate) with copolymers of styrene and acrylonitrile[6] have been studied. These blends possess lower critical solution temperatures and have been obtained from solutions of the components in a common solvent. There are data showing the effects of common solvents on the miscibility of two polymeric components.[1] Changing the common solvent allows us to obtain either homogeneous or heterogeneous blends.

The rheological properties of heterogeneous, two-phase blends are determined by the blend composition, ratio of the viscosities of each component, interfacial tension, and composition of the coexisting phases. An important role also belongs to the intensity of the mixing of polymer melts and the prehistory of mixing.

Earlier,[7] we found that for blends of chlorinated polyethylene and an ethylene/vinyl acetate copolymer (EVA; 45% vinyl acetate) prepared by the mechanical mixing of the melts of two polymers at the temperatures below and above the critical solution temperature, there is nonequilibrium. The viscoelastic characteristics measured with increasing temperature (the transition from the homogeneous state to the heterogeneous one) and with a subsequent lowering of the temperature (the transition from the heterogeneous region to the homogeneous one) do not coincide.

In this work, we investigated the effects of the prehistory of the blend preparation and morphology on the dynamic mechanical properties. Blends of EVA with polyisobutylene (PIB) were the object of the investigation. These blends are characterized by an upper critical solution temperature (UCST) of 170°C for a 1 : 1 composition.[8] In some cases, a small amount of a fine particulate filler was introduced into the melt.

It is known[1] that blends of these polymers obtained by mechanical mixing are turbid but become transparent when a filler (silica) is added. The introduction of a filler changes the temperature of phase separation.[9,10] Depending on the filler amount, this temperature may either increase or decrease. Various mechanisms for such effects have been discussed previously.[9,10]

EXPERIMENTAL

As the objects of investigation, two polymers were chosen: PIB (Trademark Vistanex, Ludwigshafen, Germany) and EVA (Trademark Evatan, Lyon, France). PIB (trademark Vistanex) had a molecular mass of 5.3×10^4 g/mol and a glass-transition temperature of $-72°C$ [according to data from differential scanning calorimetry (DSC)]. EVA (trademark Evatan) contained 27–29% vinyl acetate and had a melt index of 22–29 g/10 min, a melting point (T_m) of 72°C (EVA with more than 32% vinyl acetate is amorphous[11]), a softening temperature of 41°C, and a glass-transition temperature of $-22°C$ (DSC data and ref. 12). As a filler, the silica was taken with a specific area of 100 m^2/g. The ratios of components in the EVA/PIB blends were 9/1, 7/3, 5/5, 3/7, and $3/7 + SiO_2$. The unfilled and filled blends were prepared by twofold mixing at 100°C with a small-scale mixer of the rotation-plunger type. The shear rate in the narrow gap (0.1 mm) between the outer and inner cylinders was 500 s^{-1}. For dynamic measurements, the discs (diameter = 25, thickness = 0.8 mm) were prepared via hot pressing at 80°C.

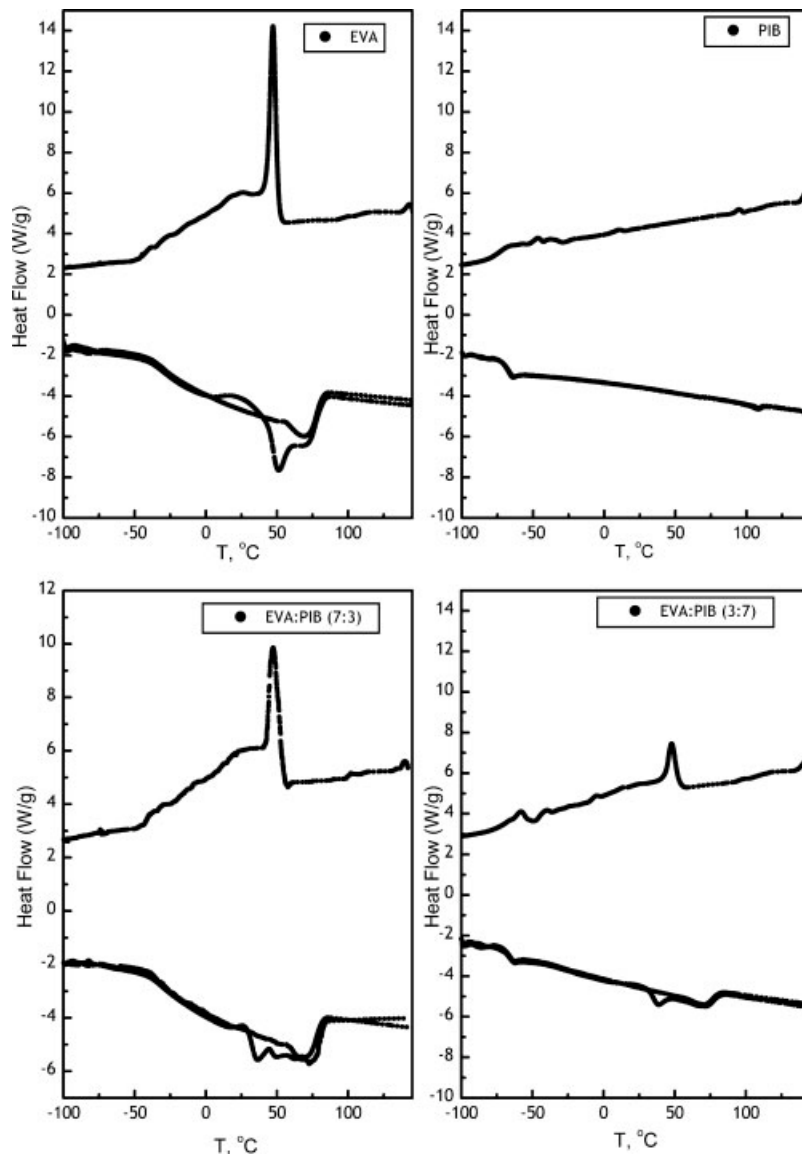The frequency characteristics of the storage modulus [$G'(\omega)$] and loss modulus [$G''(\omega)$] were measured

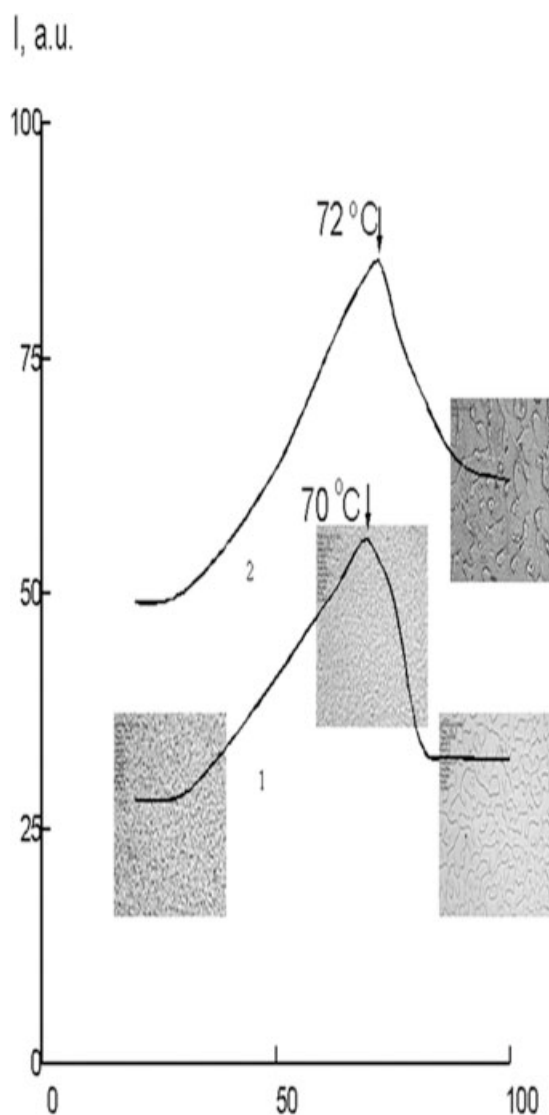**Figure 1** DSC curves of (a) EVA, (b) PIB, (c) 7/3 EVA/PIB, and (d) 3/7 EVA/PIB.

Figure 2 Intensity of the light scattering versus the temperature and morphology of (1) 3/7 EVA/PIB and (2) 3/7 EVA/PIB with 4% SiO$_2$.

in the region of linear viscoelasticity with a Rheometrix RMS-800 rheometer (Rheometrics Inc., Piscataway, NJ) (the working unit was plate–plate) in the frequency range of 0.01–100 s^{-1} at temperatures above and below $T_m = 72°C$ (70, 90, 110, and 130°C). The components of the complex shear modulus (G^*) did not depend on the deformation amplitude (linear viscoelasticity).

The morphology of the blends was studied with light microscopy. The temperature dependence of the light scattering was measured according to a method described in the literature.[13] The specimens for the light scattering measurements were prepared in the following way. Small amounts of the blends were placed between two glass covers and then were subjected to low pressure (pressure = 1 kg/cm^2) at 90°C to obtain a thin film (50 μm). The blends were main-

tained at this temperature and pressure for 15 min and then were slowly cooled to room temperature.

Calorimetric data were obtained with a V2.5 HTA differential scanning calorimeter.

RESULTS AND DISCUSSION

Data for DSC

The absence of any anomalies in DSC heating traces for pure PIB (Fig. 1) is the evidence of its noncrystalline state. In contrast, there are two pronounced endothermic peaks at 42 ± 5 and $70 \pm 3°C$ both for the pure EVA and for the EVA/PIB blends. The presence of two peaks can be explained either by the existence of two types of morphology or ordering in EVA or by the overlapping of local melting–recrystallization effects in the course of heating.[14] The occurrence of a single exothermic crystallization peak at a crystallization temperature of $47 \pm 3°C$ in the cooling DSC traces for both pure EVA and EVA/PIB blends and the correlation of their area with the EVA content testify to the probability of such an explanation.

With repeated temperature scanning of the cooled specimens, the endothermic peak in the region of $47 \pm 3°C$ is not observed. At the same time, a very diffuse exothermic process can be seen that precedes the melting of EVA. All these data show that under the condition of nonisothermal crystallization, various types of ordered structures can appear.

Light scattering and morphology

Figure 2 presents the temperature dependence of the light scattering intensity and morphology for unfilled
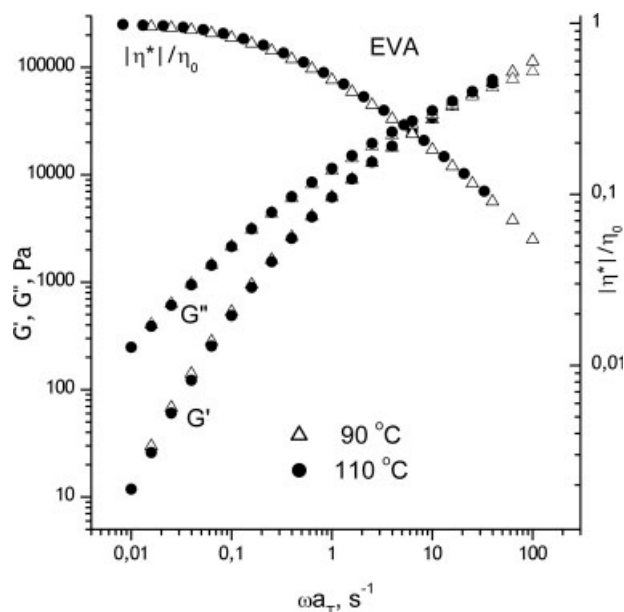

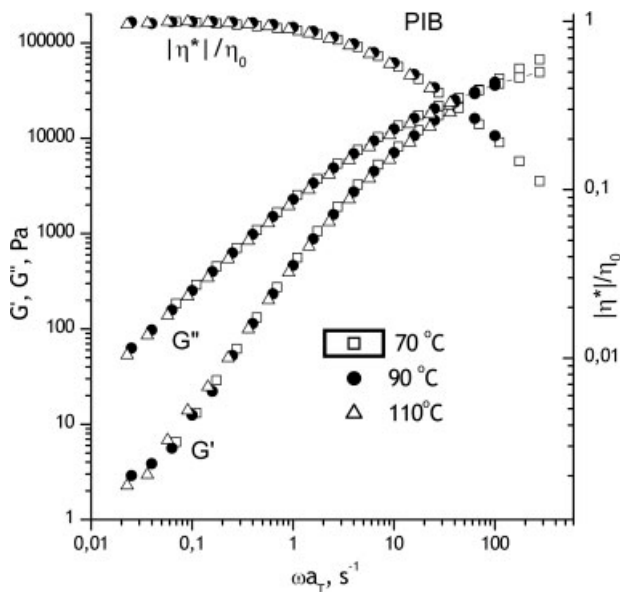**Figure 3** Master plots for G', G'', and $|\eta^*|$ of EVA.

Figure 4 Master plots for G', G'', and $|\eta^*|$ of PIB.

and filled EVA/PIB blends. With heating, changes in the morphology of the films take place, which can be seen in Figure 2. It may be supposed that the left lower picture (Fig. 2) corresponds to the structure formed by crystallites of ethylene sequences of the copolymer. With heating (rate = 2°C/min) up to 70°C, there is increasing light scattering because of the melting of the defective ethylene crystallites of EVA and the increasing total heterogeneity of the melts. This phenomenon is typical of critical opalescence. After reaching 70°C, at which the light scattering reached its maximum, the films were sharply cooled. The structure of the quenched films is shown in the middle of Figure 2. Under such conditions, the structural networks appear, which are probably formed by fine-grain ethylene crystallites. This effect leads to the specific viscoelastic behavior of the blends at 70°C (as discussed later).

A subsequent increasing temperature is accompanied by decreasing light scattering intensity because of the end of melting. After reaching 90°C, the blends were sharply cooled again. The morphology of such a film corresponds to the right lower photograph in Figure 2. One can suppose that this structure is an equilibrium one as the light scattering intensity with increasing temperature above 90° does not change any more. By the addition of 4% SiO_2, the value of the light scattering intensity becomes higher (which contradicts the literature data[1]). Above 90°C, the EVA/PIB blend with 4% SiO_2 has a structure of the inclusion-matrix type.

Viscoelastic properties

The inner self-consistency of the experimental data has been confirmed by the plotting of the general-

ized dependence of $G'(\omega)$, $G''(\omega)$, and the complex dynamic viscosity $[\eta^*(\omega)]$. Figure 3 and 4 show the dependence of EVA and PIB. The reduction temperature is $T_0 = 90$°C for both components. The reduction coefficient (a_T) is 2.51 for the copolymer and 2.77 for PIB. The absolute values of $\eta^*(\omega)$ ($|\eta^*| = |G^*(\omega)| = \{[G'(\omega)]^2 + [G''(\omega)]^2\}^{1/2}$) have been normalized by the values of the greatest Newtonian viscosity $[\eta_0 = \lim G''(\omega)$ at $G'' \to 0]$. In Figures 3 and 4, a brilliant temperature–frequency superposition of the initial $G'(\omega)$ and $G''(\omega)$ values is shown. For the copolymer, the superposition is realized only at temperatures greater than T_m.

Figures 5 and 6 present the typical frequency dependence of $G'(\omega)$ and $G''(\omega)$ at 70 and 90°C for unfilled and filled blends. The melting of EVA proceeds in the temperature range of 40–70°C (data of DSC). It may be supposed that at 70°C, a crystallite forms a continuous structure (infinite cluster). The latter may determine the specific viscoelastic behavior of the copolymer at 70°C: the dependence of the complex modulus on the frequency has a pronounced plateau at all frequencies with $G' > G''$. With increasing PIB content, the modulus in the plateau region diminishes. For the 3/7 EVA/PIB blend, the plateau can be observed only in the dependence of $G'(\omega)$ in the frequency diapason of $\omega > 01$–0.05 1/s), at which G' is greater than G'' In the range of middle frequencies
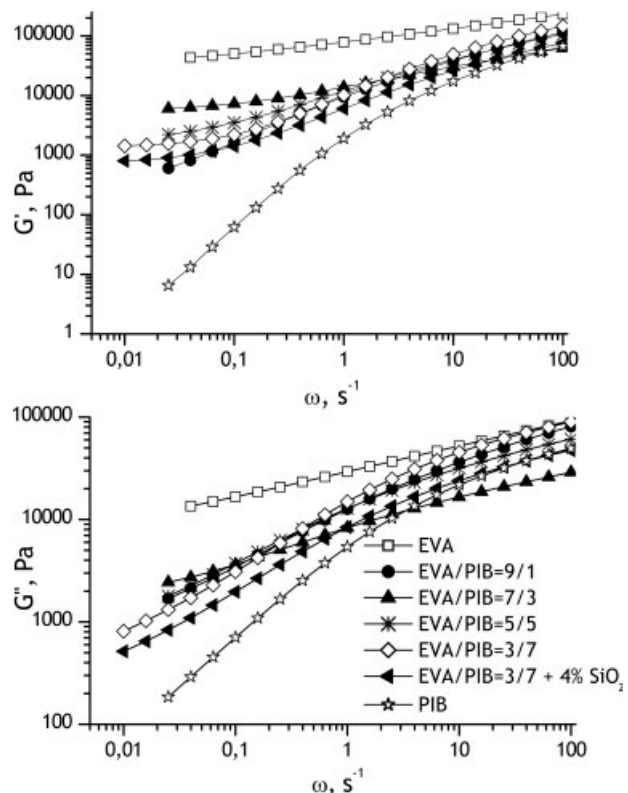

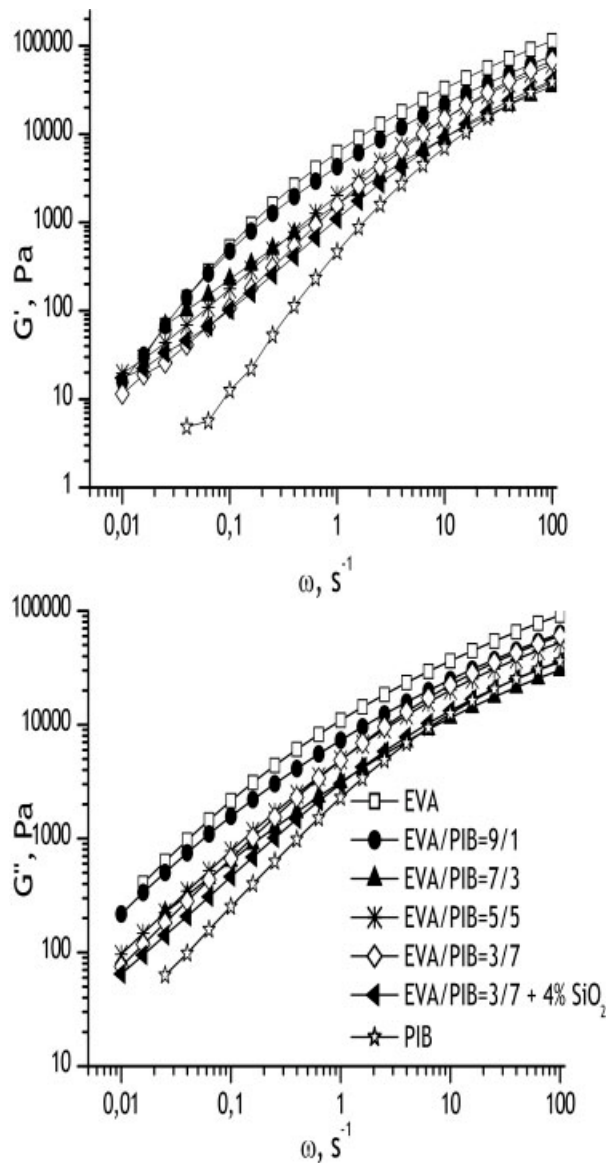**Figure 5** G' and G'' versus the frequency for EVA, PIB, and their blends at 70°C.

Figure 6 G' and G'' versus the frequency for EVA, PIB, and their blends at 90°C.

($\omega > 0.05$ 1/s), G'' is greater than G'. Such behavior is typical for amorphous, flexible-chain polymers and their blends in the viscous flow range.[15] Therefore, the yield behavior of $G^*(\omega)$ (the existence of the yield point) in the region of the low frequencies, which is typical of EVA and its blends with PIB, is determined by the peculiarity of the structure formed at 70°C. At temperatures above the EVA T_m for the copolymer and its blends with PIB, there is a dependence of $G'(\omega)$ and $G''(\omega)$, which is typical for polymers with flexible chains.[15]

The frequency dependence of $|\eta^*(\omega)|$ for EVA, PIB, 3/7 EVA/PIB, and 3/7 EVA/PIB with 4% SiO$_2$ is shown in Figure 7(a) for 70°C and in Figure 7(b) for 90°C. At temperatures lower than T_m for EVA

and its blends with PIB, the viscoplastic behavior and the existence of the yield point can be observed (increasing viscosity with decreasing frequency). Such a picture is typical for filled polymers. At temperatures greater than T_m, both the polymers and their blends behave as usual unfilled melts. However, the presence of a filler affects the dependence of $|\eta^*(\omega)|$ at $\omega < 0.1$ s^{-1}.

The marked decrease in $\eta^*(\omega)$ of the blends containing 4% filler (Fig. 7) and the blends with 2% filler at 110 and 130°C is interesting. We suppose this effect is due to the preferential adsorption of the fraction of higher molecular mass of the copolymer at the filler surface, which should lead to a decrease in the total viscosity of the blend. Similar effects of reducing the viscosity of filled polymers by the introduction of small amounts of particulate fillers have already been described.[16–19] The lowering of the viscosity of blends
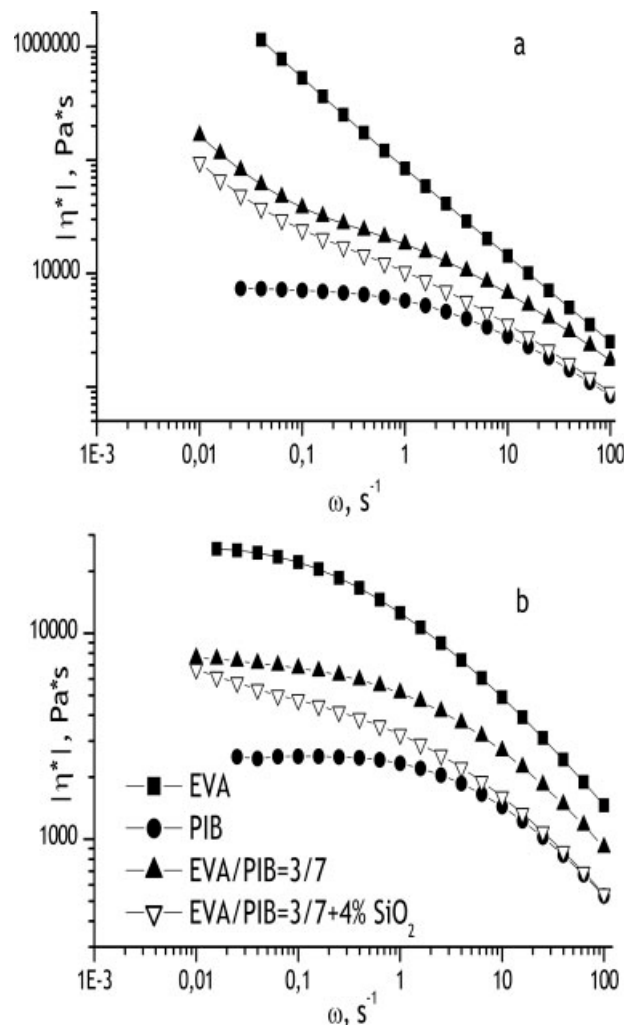

Figure 7 Frequency dependence of η^* for EVA, PIB, 3/7 EVA/PIB and 3/7 EVA/PIB with 4% SiO$_2$ at (a) 70 and (b) 90°C.

under the action of small filler amounts is shown in this work for the first time.

The diagrams of lg $|\eta^*|$ versus the blend composition (Fig. 8) at various frequencies and temperatures are typical S-shape curves for the two-phase polymer blends. At the same time, the experimental data for the 9/1 and 7/3 blends are situated below the additive values at all temperatures except 130°C, and at low frequencies, either additive dependence or positive deviations from the additivity at PIB concentrations above 50% occur. The latter fact may support increasing interaction between the two polymers as the critical point is approached (the blends under investigation are characterized by a UCST of ca. 170°C at 1 : 1 a ratio[8]).

To establish the difference between homogeneous and heterogeneous blends, Chuang and Han[20] proposed a criterion 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 $G'(G'')$ dependence may be presented by a series of curves shifted in relation to one another for various compositions and temperatures. This concept has been used in this work for EVA, PIB, and their blends at various temperatures (Fig. 9; the data for 110 and 130°

are not given to not encumber the graph). The $G'(G'')$ dependence is linear and, for individual components, does not depend on the temperature (for EVA only at temperatures greater than T_m). At temperatures lower than T_m for EVA, the function $G'(G'')$ is linear only at high values of the moduli, whereas at low values of G' and G'', nonlinearity takes place. It may be supposed that this nonlinearity is connected to the formation of a continuous network whose junction points are formed by ethylene crystallites of EVA. This effect can be seen at low frequencies. At the same time, for the EVA/PIB blends, the function is linear and depends on the composition only at high values of the shear moduli.

The relaxation spectrum [$H(\tau)$] was calculated from the data for $G'(\omega)$ and $G''(\omega)$ with the computer program NLREG based on the method of nonlinear regularization by Tikhonov.[21] These spectra are presented in Figure 10 at 70 and 90°C for individual components and some blends. One can see that the dependence of $H(\tau)$ on the relaxation time (τ) for both components (for EVA at temperatures greater than T_m) can be presented by smooth curves showing relatively fast decay (a region of high τ values). That decay begins at a characteristic relaxation time (τ_c) for PIB of approximately 0.75 (70°C) or 0.47
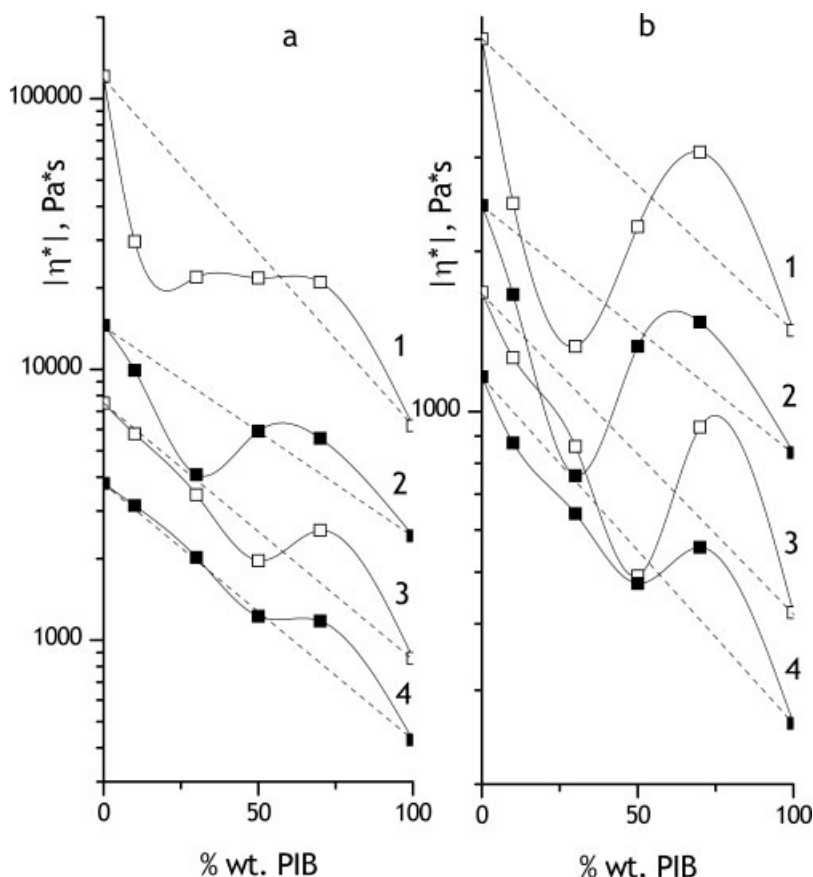

Figure 8 Dependence of η^* for the EVA/PIB blends at (1) 70, (2) 90, (3) 110, and 130°C (4): (a) $\omega = 0.631\ \text{s}^{-1}$ and (b) $\omega = 39.81\ \text{s}^{-1}$.

(90°C) and for EVA of approximately 12.1 s (90°C). The values of τ_c for pure unfilled and filled blends average between 0.47 and 12.1 s. At 70°C, the dependence of $H(\tau)$ on τ is a linearly and weakly decreasing function, without any τ_c value in the investigated range of $\tau = 1/\omega$. For the blends at 70°C and $\tau > 12$ s, there can be observed a distinct plateau of $H(\tau)$. These effects are connected with the appearance of the yield behavior of the system at low frequencies because of the formation of a structural network.

From the point of view of reptation theory of polymer flow,[22] the fast decay of $H(\tau)$ can be explained by the full withdrawal of a polymer chain from the virtual tube formed by the neighboring macromolecules. This effect is characterized by the characteristic maximum relaxation time ($\tau_{max} = \langle h^2 \rangle / D$, where $\langle h^2 \rangle$ is the mean-average distance between the ends of unperturbed chains in the melt and D is the self-diffusion coefficient). Using the tabulated values of $\langle h^2 \rangle / M = 0.66 \times 10^{-20}$ m² [23] and $D = 5 \times 10^{-17}$ m²/s (found from the data available for branched polyethylene),[24] we can find values of molecular mass (M) for the fraction of PIB responsible for the fast region of the relaxation time spectrum ($\tau_{max} = \tau_c = 0.47$ s). The estimated value of $M \approx 4 \times 10^3$.
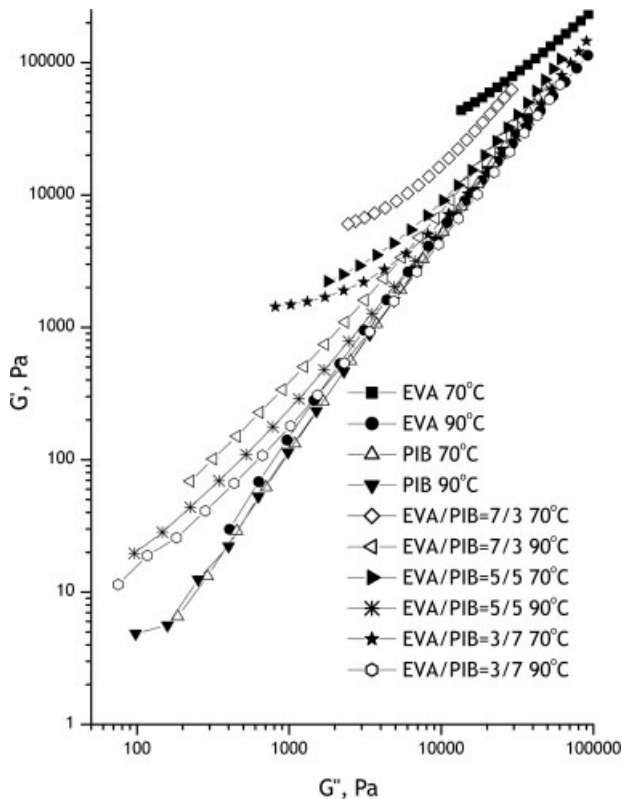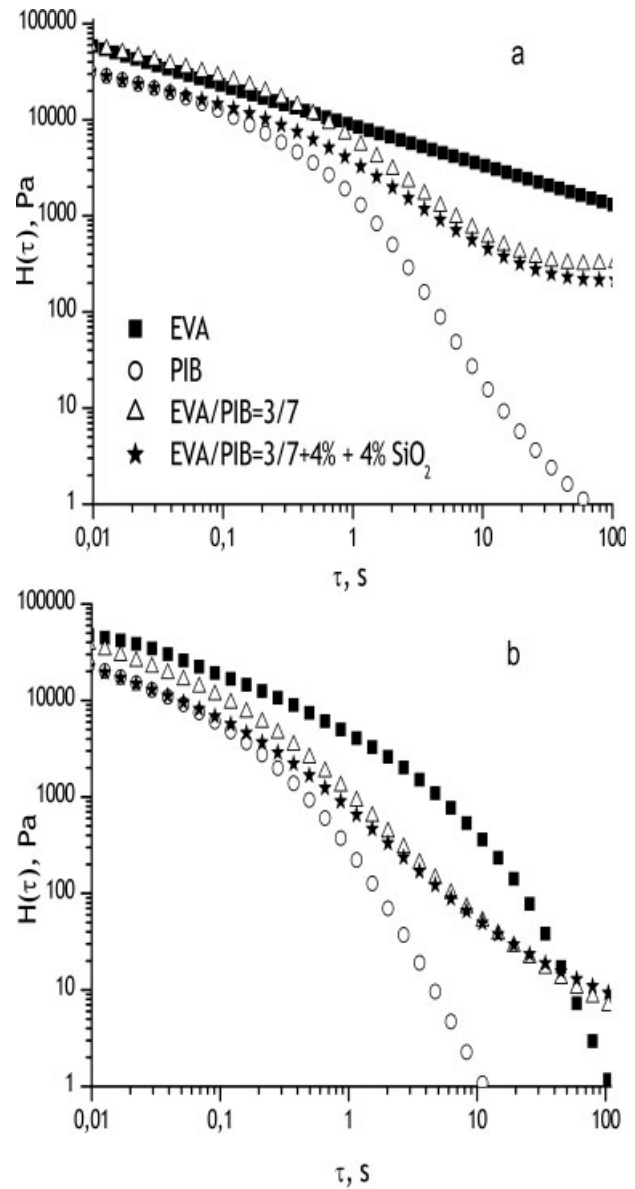

Figure 10 Relaxation time spectra for EVA, PIB, 3/7 EVA/PIB, and 3/7 EVA/PIB with SiO_2 at (a) 70 and (b) 90°C.

CONCLUSIONS

The results of this study show the effects of the prehistory of the blend preparation on the viscoelastic properties. This effect may be connected to the morphology of the system, which arises with the mechanical blending of the molten components. As shown earlier,[7] the rheological behavior of amorphous binary blends of chlorinated polyethylene and EVA (systems with a lower critical solution temperature), prepared by mechanical mixing in a range of temperatures corresponding to either homogeneous or heterogeneous structures, depends on the direction of stepwise temperature changes (i.e., heating or cooling). Within the limits of the experimental uncertainties, the viscoelastic properties in the cooling cycle

Figure 9 G' versus G'' for EVA, PIB, and their blends at different temperatures.

are not reproducible in the heating cycle. An even more complicated situation arises when one of the components retains its crystallinity in the course of cooling after blending. The morphology of such systems changes during repeated heating directly in the working block of a rheometer. More significant morphological changes in the temperature interval of the measurements have been observed for binary blends containing particulate fillers. In this case, spinodal structures typical of pure binary blends are transformed into a droplet-matrix-type morphology. In the latter case, we can observe an anomalous decrease in the viscosity.

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