

Viscoelastic Properties of Polystyrene–Polycarbonate Blends in Melt

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Synopsis

Viscoelastic properties of polymer blend melts of polystyrene–polycarbonate were investigated in a wide range of temperatures, frequencies, and compositions. It was established that the more essential changes in viscoelastic characteristics took place at small concentrations of one of the components and at low frequencies, probably because of a putting down of the slow relaxation processes. The marked decrease in the viscosity of the melts takes place in the region of phase separation due to thermodynamic incompatibility of the components and is in a good correlation with the appearance of excess free volume in the system.

INTRODUCTION

In the range of marked phase separation in melts of polymer blends, there may be observed a sharp decrease in the melt viscosity independent of the viscosity of the components.^{1–3} This decrease usually takes place in the region of small concentrations of one of the polymers. It can therefore be expected that a small addition of one polymer to the melt of another will influence the relaxation properties of the melt.⁴

The present work deals with investigation of viscoelastic properties of polystyrene (PS)–polycarbonate (PC) blends in melts at various ratios of components and in a wide range of frequencies and temperatures. Special attention was paid to small amounts of one of the components in melts because just in this range extremes of change in the viscosity of blends were earlier found.^{1–3} The given pair of polymers was chosen because both of them had comparatively close glass transition temperatures (100°C for PS and 140°C for PC). This enabled us to measure their viscoelastic properties near the transition region, i.e., under conditions where rheological characteristics are determined mainly by the free volume of the system and by its temperature dependence.⁵

We thus were able to compare the extreme changes in relaxation properties of the blends with changes in the free volume of the system, as has been done earlier.⁶

EXPERIMENTAL

The polymers were commercial polystyrene of density 1.05 g/cm³ and polycarbonate (Macrolon produced by Bayer AG) of density 1.20 g/cm³. The density of the blends was calculated according to the additivity rule. The viscosity-

average molecular masses were determined from the intrinsic viscosity and were for PS 4.8×10^4 and for PC 3.3×10^4 . The Mark-Houwink equation with constants taken from Rafikov et al.⁷ was applied. The binary blends were prepared by dissolution of both components in a common solvent (chloroform, concentration 5 g/100 ml) with subsequent evaporation of the solvent in 48 hr at 20°C and then to constant weight and pressure of 1–2 torr. From the films obtained, plates 200 μm thick were pressed at 200°C and 150 kg/cm². The PC concentrations in the blends were 0.5, 1, 2, 5, 10, 20, 50, 80, 90, 95, 98, 99, 99.5, and 100% by weight.

The real and imaginary parts of complex shear modulus G' and G'' were measured in the region of linear viscoelasticity using a specially developed⁸ elastoviscosimeter PIRSP-1M by changing the circular frequency ω in the range of 10^{-2} to 10 sec^{-1} and in the temperature interval of 180 to 260°C. All measurements were made in an inert gas.

RESULTS AND DISCUSSION

For the pure components PS and PC and their blends of various compositions, the dependences of elasticity modulus G' , loss modulus G'' , and dynamic viscosity η' on frequency were measured at different temperatures. Figure 1 shows such a dependence for PS. All curves obtained have the typical shape for polymeric systems. When circular frequency increases, there is a drop in dynamic viscosity, whereas moduli G' and G'' increase. Analysis of curves similar to those presented in Figure 1 shows that the dynamic viscosity of the studied polymer blends approaches asymptotically the constant value η_0 , which may be defined as the viscosity at zero shear stress:

$$\eta_0 = \lim_{\omega \rightarrow 0} \eta'$$

The η_0 values (the greatest Newtonian viscosity) were estimated for the blends

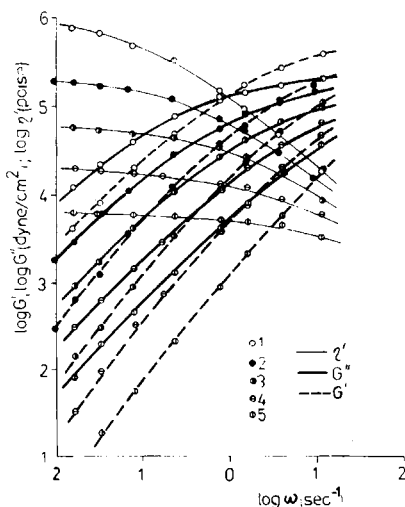


Fig. 1. Dependence of G' (dotted lines) and G'' and η' on circular frequency for PS at temperatures 180°C (1), 200°C (2), 220°C (3), 240°C (4), and 260°C (5).

under investigation using dependences $\log \eta' = f(G'')$. At $G'' \rightarrow 0$, $\log \eta' \rightarrow \log \eta_0$. From the frequency dependences of G' , G'' , and η' at various temperatures, the generalized frequency dependences of $G'_r = G' T_0 \rho_0 / T \rho = f_1(\omega a_T)$ and $G''_r = G'' T_0 \rho_0 / T \rho = f_2(\omega a_T)$ were constructed on the basis of the temperature-time superposition principle,⁹ where ρ and ρ_0 are material densities at temperatures T and T_0 and $a_T(T)$ is the temperature reduction factor. As reduction temperature, $T_0 = 200^\circ\text{C}$ for all the blends was taken. To construct the generalized curve of the dynamic viscosity as a function of frequency, the experimental data were plotted in coordinates $\eta'/\eta_0 = f_3(\omega a_T)$.

Some examples for PS, PC, and their blends with a components ratio 1:1 are presented in Figures 2-4. Dependence a_T on temperature for all blends is given in Figure 5. It turned out to be impossible to obtain a single generalized characteristic of viscosity for a given polymer blend. This is well apparent from Figure 6, where the dependences of $\log(\eta'/\eta_0)$ on $\log(\omega a_T)$ for all concentrations are given. In this figure, the upper border of the shaded region of the experimental data scattering is related to the system PS + 1% PC, the lower border is related to PS, whereas the plotted line corresponds to data for PC and the PS:PC (1:1) blend. The discrepancy between the given functions $\eta'/\eta_0 = f(\omega a_T)$ for each blend begins at logarithm of the reduced frequency equal to -2.5 and increases with increase in ωa_T . At $\log(\omega a_T) = 2$, the difference between $\log \eta'/\eta_0$ reaches 1.2 for limit cases.

It is known that reduction of viscosity data for polymeric systems using temperature-time superposition is possible only when the relaxation spectra and their changes are similar.⁴ Therefore, one can conclude that by mixing of two chemically different polymers an essential change of spectral function takes place; this change should be more pronounced in the range of small concentrations of one of the components. Indirect evidence for this statement is supplied by the distinctions in temperature dependence of the reduction factor a_T for various blends (Fig. 5).

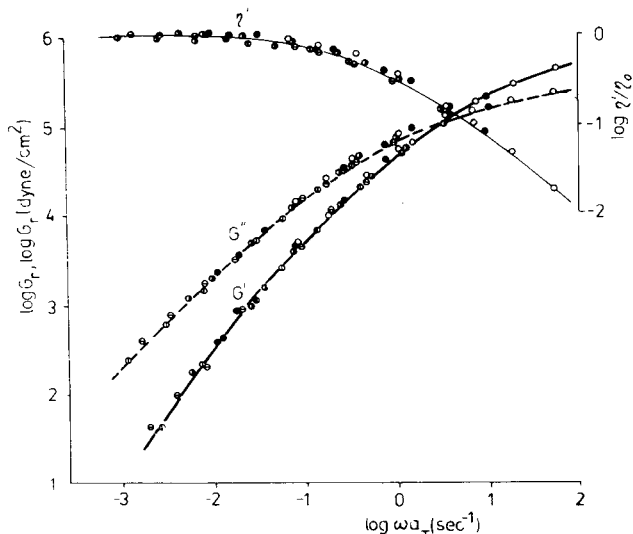


Fig. 2. Dependences of reduced moduli G' and G'' and η' on reduced frequency for PS. For key to symbols see Fig. 1.

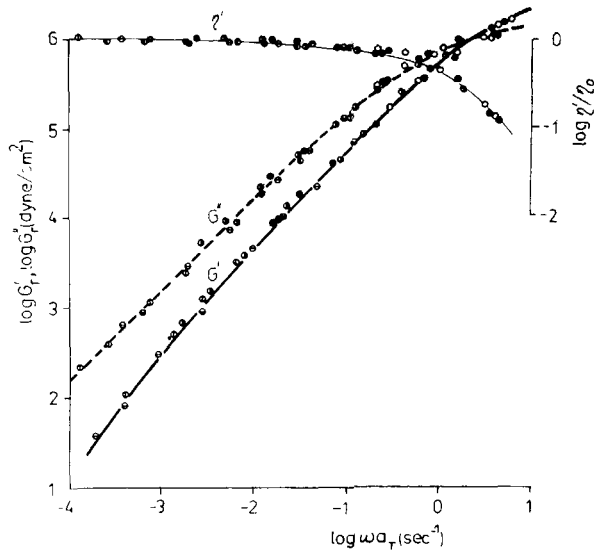


Fig. 3. Dependences of reduced moduli G' and G'' and η' on reduced frequency for PC. For key to symbols see Fig. 1.

Let us now discuss the dependence of the greatest Newtonian viscosity of the blends on their composition at various temperatures (Fig. 7). Introduction of 1% PC into PS leads to a sharp decrease in blend viscosity, the intensity of the viscosity decrease being slightly dependent on temperature and rather more on frequency. For example, η_0 decreases 13-fold, whereas dynamic viscosity η' decreased only threefold (at $\log \omega = 0.6$). An increase in PC content in the blend up to 5% leads to considerable increase in viscosity which after this concentration

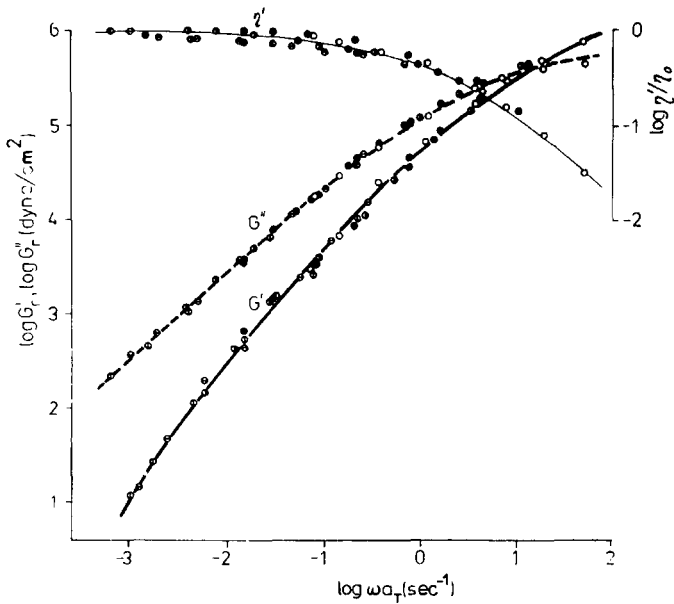


Fig. 4. Dependences of reduced moduli G' and G'' and η' for PS-PC blend (ratio 1:1) Key as in Fig. 1.

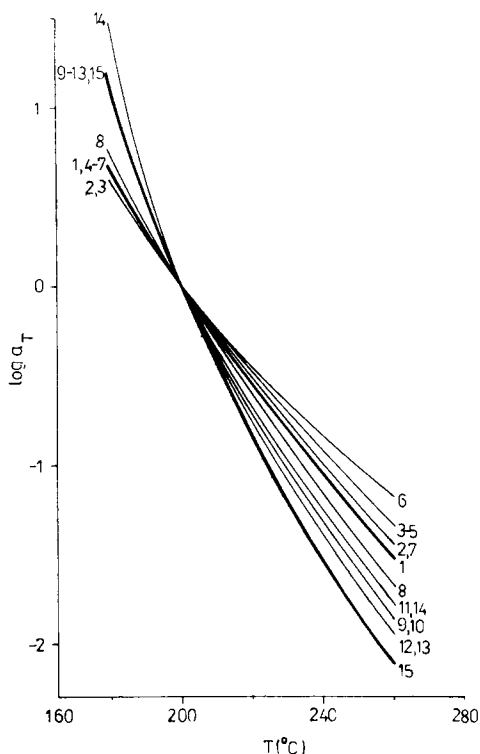


Fig. 5. Temperature dependence of reduction factor a_T for PS, PC, and their blends. PC content in the blend (wt %): 0 (1); 0.5 (2); 1 (3); 2 (4); 5 (5); 10 (6); 20 (7); 50 (8); 80 (9); 90 (10); 95 (11); 98 (12); 99 (13); 99.5 (14); 100 (15).

drops again and reaches a second minimum at 10% PC. In the concentration range of 10–50% PC, the viscosity of the blends increases essentially; the subsequent increase in viscosity is not so remarkable. At 0.5% PS in PC, there is a third minimum of viscosity as a function of composition. It is remarkable that in the whole range of composition the blend viscosity is lower as compared to additive values. This apparently is a result of thermodynamic incompatibility of the two polymers. It is worth noting that in the regions of marked phase separation of the two-component system, a sharp decrease in viscosity takes place, as was observed by Lipatov¹ and Lipatov and Lebedev.² The only slight changes in viscosity in the concentration range of 5–50% are due to that fact that PC is a discontinuous phase in this range. At comparable concentrations of the

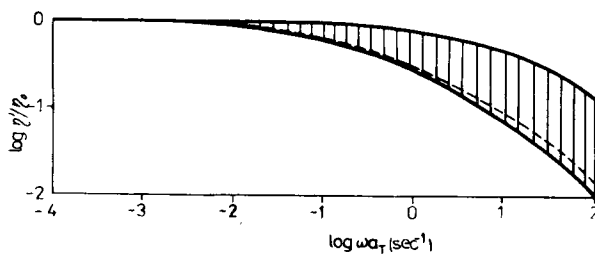


Fig. 6. Generalized characteristic of dynamic viscosity for PS-PC blends.

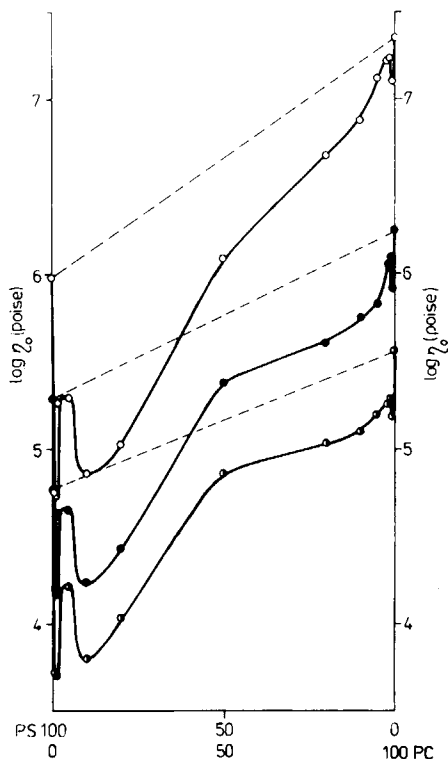


Fig. 7. Dependence of greatest Newtonian viscosity on composition for PS-PC blends at various temperatures. Key as in Fig. 1.

components, the observed phase inversion leads to a rather remarkable drop in viscosity (PC concentration 50–90%). It was of interest to compare the viscosity changes with other viscoelastic characteristics at various ratios of the components. Figure 8 presents the concentration dependence of reduced elasticity moduli and loss moduli at a logarithm of reduced frequency equal to -1 . Full analogy in changes of dynamic modulus and viscosity with composition is observed. However, the intensity of changes of viscoelastic properties as a function of circular frequency is different for small amounts of one of the components in the blend. Most sensitive to frequency is the elasticity modulus G' . This is seen from Figure 9, where the scale of moduli changes with frequency is shown for the blend with 1% PC. In the range of small additions of PC to PS the reduced loss modul decreases 12.5-fold at $\log \omega_r = -2$ and 1.7-fold at $\log \omega_r = 1.6$, whereas the elasticity modulus changes 35- and 2.9-fold at corresponding frequencies. The data presented in Figures 8 and 9 allow the conclusion to be drawn that the scale of changes in G' and G'' for small concentrations of one of the components does not depend on temperature. The most dramatic changes in viscoelastic properties at small ratio of the components take place in the region of low frequencies. That means that for the changes observed, those structure elements in the melt that have high relaxation times are responsible.

That is why we consider the relaxation spectra of the blends as their most fundamental characteristics. The calculation of relaxation spectra $H(\theta)$ was performed using the well-known method of Ninomiya-Ferry¹⁰ from the de-

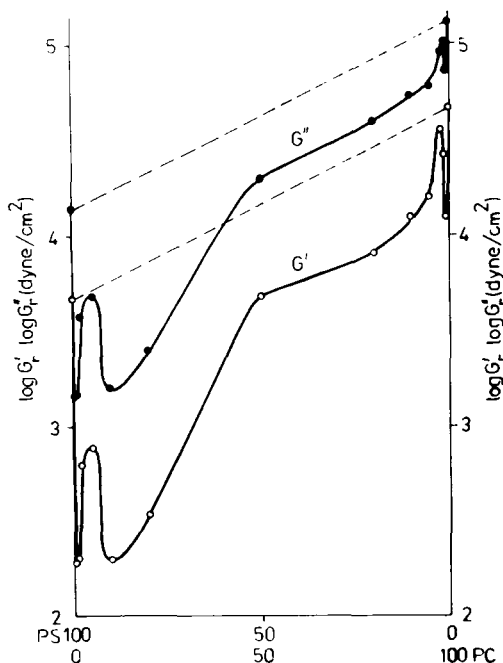


Fig. 8. Dependence of reduced moduli G' and G'' on composition for PS-PC blends at $\log \omega_r = -1$.

pendence of reduced frequencies. All calculations were performed by computer. Figure 10 represents the spectral characteristics of PS melts,¹ PC melts,² and their blends.²⁻¹⁰ The essential difference in relaxation times spectra for the systems under investigation is evident. By introducing small amounts of PC (0.5, 1, and 10%) into PS or 0.5% PS into PC, a sharp decline in the slow relaxation process takes place. This great difference in the relaxation spectra manifests itself in viscoelastic properties. This difference is more pronounced at low frequencies than at high ones.

To understand the reasons for the changes observed, it is important to compare the relaxation characteristics with changes in free volume of the system. For this purpose we have presented the data on the temperature dependence of the greatest Newtonian viscosity for PS, PC, and their blends in Vogel equation coordinates¹¹ (see Fig. 11):

$$\ln \eta_0 = \frac{A + B}{T - T_0}$$

where A , B , and T_0 are empirical constants. In the framework of the free-volume concept, the parameter T_0 represents some critical temperature at which the free volume vanishes. From Figure 11 it is seen that the dependence $\log \eta_0$ on $1/T$ is nonlinear in the temperature range of 180–260°C and may be adequately described by the Vogel equation. The calculated values of the parameters of the Vogel equation are given in Table I.

In accordance with the Tamman criterion,¹² the liquids change into the glassy state at a temperature where their viscosity reaches 10^{13} poises. From the Vogel equation, the values of the glass transition temperatures T_g were calculated using

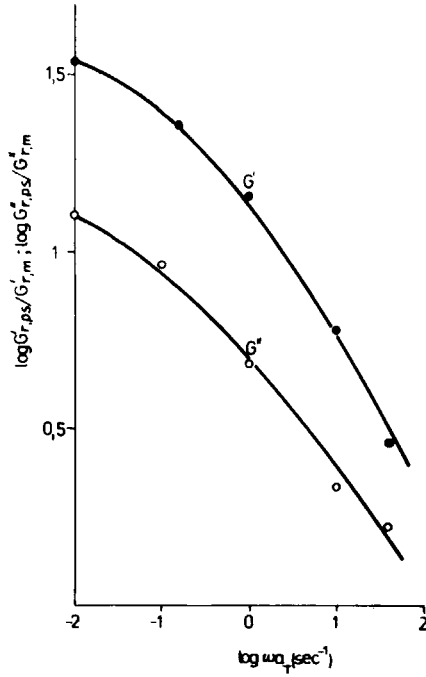


Fig. 9. Dependence of ratio of reduced moduli G' and G'' in PS and PS-PC blend (99:1) on reduced frequency.

the parameter values given in the table. From the equation¹³

$$f = \frac{T - T_0}{B}$$

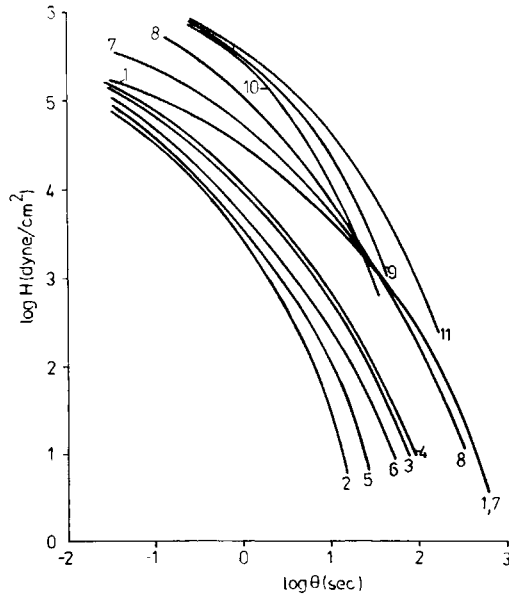


Fig. 10. Relaxation times spectra for PS-PC blends at various compositions (PS wt %): 0 (1); 0.5 and 1 (2); 2 (3); 5 (4); 10 (5); 20 (6); 50 (7); 80 (8); 98 (9); 99.5 (10); 100 (11).

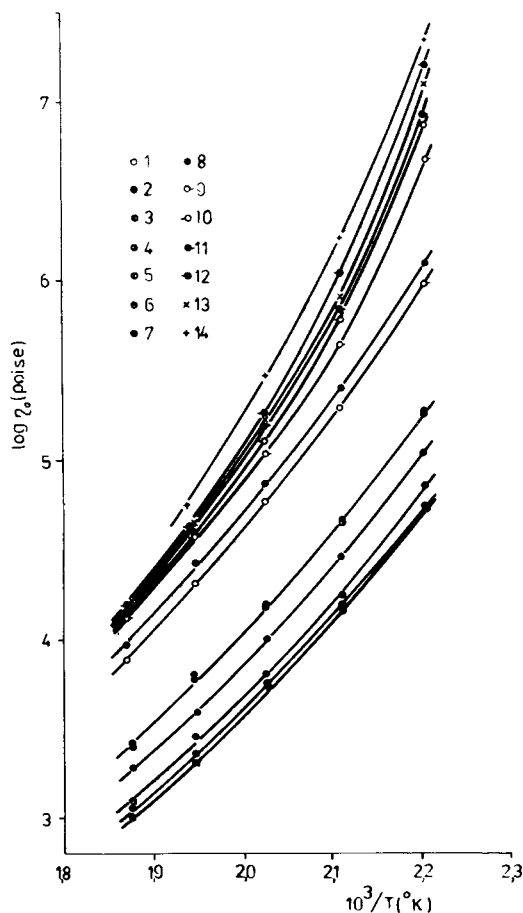


Fig. 11. Temperature dependence of greatest Newtonian viscosity for PS, PC, and their blends. PC content in the blend: 0 (1); 0.5 (2); 1 (3); 2 (4); 5 (5); 10 (6); 20 (7); 50 (8); 80 (9); 90 (10); 95 (11); 98 (12); 99.5 (13); 100 (14).

the fractional free volume f was calculated both at T_g and $T = 200^\circ\text{C}$. The last column of the table represents the values of apparent flow activation energy E_{200} (which is dependent on temperature) at 200° , this value being connected with B and T_0 by the relation^{11,13}

$$E = RB \left(\frac{T}{T - T_0} \right)^2$$

TABLE I
Parameters of Vogel Equation (T_g , f_g , f_{200} , and E_{200}) for PS, PC, and their Blends

System	A	B	T_0 , K	T_g , K	f_g	f_{200}	E_{200} , kcal/mole
PS	0.737	1877	309	373	0.034	0.087	31
PC	2.011	1464	355	407	0.035	0.081	47
PS + 0.5% PC	2.278	970	341	376	0.036	0.136	25
PS + 5% PC	2.266	1163	336	378	0.036	0.118	27
PS + 10% PC	3.704	616	371	394	0.037	0.166	26
PC + 0.5% PS	5.598	625	395	421	0.042	0.125	45

From the data given in the table, it is seen that introducing a small amount of one component into another leads to essential changes in Vogel equation parameters, fractional free volume, and activation energy. The results show that the experimentally observed drop in the viscosity of the blends at small concentrations of the addition may be connected with increase in fractional free volume. The increase in f takes place for the whole range of compositions. This fact is in a good agreement with results in Lipatov and Vilenskii.¹⁴ The increase in glass temperatures for the blends as compared with T_g of the individual components, which is seen from the data of Table I, has no proper explanation at present.

CONCLUSIONS

The results of the investigation of the changes in viscosity and viscoelastic properties of PS and PC blends in melt have shown that more essential changes take place by introducing small amounts of one component into another and proceed in the range of low frequencies. The mechanism of action of small additions consists probably in a sharp decline in the slow relaxation processes. That means that the component added in small amounts modifies the structure elements of the main component in the melt and is responsible for high relaxation times. The increase in the free volume by blending leads to a drop of viscosity in the system and meets the conditions for a more speedy relaxation process.

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