

Time–temperature correspondence prediction of stress relaxation of polymeric materials from a minimum of data

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Abstract

We have determined the stress relaxation of a longitudinal polymer liquid crystal (PLC), polypropylene and their blends containing 10 and 20% of the PLC at the constant strain of 0.5%. The results for nine temperature levels in the range between 20 and 100 °C were used to create master curves for $T_{\text{ref}} = 20$ °C. The temperature shift factors a_T were calculated using a general formula derived by one of us and based on free volume v^f and the chain relaxation capability model. The predicted values agree with the experimental ones for all materials studied within limits of the experimental accuracy. Moreover, the relation between the shift factor a_T and the reduced volume \bar{v} has been used to predict long-term behavior of the materials from a minimum (at least two sets) of data—providing also in this case reliable results. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Prediction of long-term performance from short-term tests continues to be the bottom line of polymer science and engineering (PSE) [1–5]. In this paper, we report results of determination of stress relaxation of polypropylene, a polymer liquid crystal (PLC) and two binary blends of these components. For each material we have performed experiments at several temperatures and combined the results to achieve long-term prediction for a single temperature.

We have used the theory of chain relaxation capability (CRC) [4–7] to calculate necessary shifts of isothermal

results to create a single curve. The results confirm also for our materials the validity of a general equation for the temperature shift factor [6–8]. Finally, using a procedure defined in 2001 [9] we have used two sets of results only to achieve long-term prediction comparable to that based on nine sets of isothermal results.

2. Chain relaxation capability

Relaxational processes in polymeric materials require free volume v^f . This fact forms the basis of the CRC model. CRC can be defined as the amount of external energy dissipated by relaxational processes in a unit of time per unit weight of polymer. Since the CRC theory has been described in some detail earlier [4–7], we now provide only its elements essential for understanding what follows.

When the mechanical force is applied, relaxational processes take place in a polymeric material: energy transmission across the chain and to the neighboring chains by segmental motions and entanglements; conformational rearrangements; bond stretching and angle changes leading to

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elastic energy storage; and phase transformations [4,5]. The larger v^f is, the larger the chain maneuvering ability and thus the higher is the CRC.

Free volume can be defined as

$$v^f = v - v^* \quad (1)$$

where v is the total specific volume (for instance in $\text{cm}^3 \text{g}^{-1}$) and v^* is the characteristic (also known as hard-core or incompressible) volume corresponding to an extremely high pressure and zero thermodynamic temperature conditions. The reduced volume \tilde{v} , the reduced temperature \tilde{T} and the reduced pressure \tilde{P} are defined as

$$\tilde{v} = v/v^*; \quad \tilde{T} = T/T^*; \quad \tilde{P} = P/P^* \quad (2)$$

where T and P are thermodynamic temperature and pressure; T^* and P^* are characteristic (incompressible) values for the same material. The former is related to the strength of interactions in the material; P^* is a complex function of the intermolecular interactions and the material structure represented by the binary radial distribution function $g(R)$ [10].

High values of v^f at elevated temperatures enable conformational processes to occur faster than at lower temperatures. This fact is the basis of long-term behavior prediction from short-term tests at several temperatures—explained in detail in Section 3. However, any method of varying v^f (such as varying stress and using the time–stress correspondence (TSC)) [3,8,9] provides a potential for long-term prediction. It just happens that the time–temperature correspondence (TTC) method is the most popular.

Calculations based on free volume require the value of v^* , which as well as T^* and P^* can be calculated using a specific equation of state. Very good results have been obtained repeatedly [9,11–16] by using the Hartmann equation [17,18] valid for both polymer melts and solids:

$$\tilde{P}\tilde{v}^5 = \tilde{T}^{3/2} - \ln \tilde{v} \quad (3)$$

Eq. (3) is based on the considerations of Litt [1] of the relationship between free volume and temperature. It was Litt who demonstrated first the direct proportionality between $\ln \tilde{v}$ and $\tilde{T}^{3/2}$.

3. Time–temperature correspondence principle

According to the TTC principle, events taking place at higher temperatures (higher v^f) are the same as those at lower temperatures but at longer times. Thus, shifting curves for several temperatures forming a single (master) curve as a function of time t provides information over many decades of time for that temperature for which no shift was made. The principle has been in use for at least half a century [19,20], not always with good results. In earlier papers we have shown [7,15,21] that erroneous predictions were caused not by the principle itself but by representing it by a limited use 1955 formula of Williams,

Landel and Ferry (WLF) [20]. As discussed by one of its creators [2], the WLF equation is limited in its use range and expected to give reliable results only between the glass transition temperature T_g and $T_g + 50 \text{ K}$.

The problem consists in calculating the amount of shifting of isothermal curves of a given property as a function of time. In order to create the master curve, the curves are shifted along the time axis by multiplication by the shift factor a_T defined as follows:

$$\sigma(t, T_{\text{ref}}, \varepsilon) = \sigma(ta_T, T, \varepsilon) \quad (4)$$

Thus we need the temperature shift factor a_T as a function of temperature T .

Based on the Doolittle equation relating viscosity η to free volume v^f [22] one of us has derived the following formula [6,7]:

$$\ln a_T = A + B/(\tilde{v} - 1) \quad (5)$$

Here A and B are material constants; B can be called the Doolittle constant since it appears in his formula. Eq. (2) is applicable below as well as above T_g ; with a simple (but unfounded) assumption it can be reduced to the WLF formula. Predrawn materials behavior can be described using Eq. (2) after a further generalization which includes the draw ratio [12]. Previous results for several kinds of polymers including polyethylenes [12], polyurethanes [11] and PLCs [15] containing four phases in the service temperature range [23] show that Eq. (5) provides good results when used in conjunction with the reliable Hartmann equation (3).

In 2000, a further generalization was achieved [8]: an equation for the combined shift factor $a_{T,\sigma}$, where σ is the stress level, was obtained. It reads:

$$\ln a_{T,\sigma} = A_{T,\sigma} + \ln T_{\text{ref}}/T + \ln[v(T, \sigma)/v_{\text{ref}}] + B/(\tilde{v} - 1) + C(\sigma - \sigma_{\text{ref}}) \quad (6)$$

The assumption $\sigma = \text{constant}$ reduces Eq. (6) to Eq. (5) as it should. In the following work we test the validity of Eq. (5) for polymer based blends as well as for the components. As outlined in Section 1, we use a procedure based on all available sets of experimental results as well as on two sets only.

4. Materials selection and experimental procedures

As noted in Section 2, the use of TTC principle did not always produce good results. There is still an opinion that TTC does not apply to polymers with polar groups and semi-crystalline polymers. This is why we have decided to investigate blends containing a PLC, which does not fulfill either of these conditions. Due to LC sequences, PLCs have excellent mechanical, thermal and electrical properties [24]. There have been investigations on PLC alignment under mechanical and magnetic fields [25–28], experimental and theoretical studies of unusual phase behaviors [29–31], blends [32–36] and their surface properties [37–39].

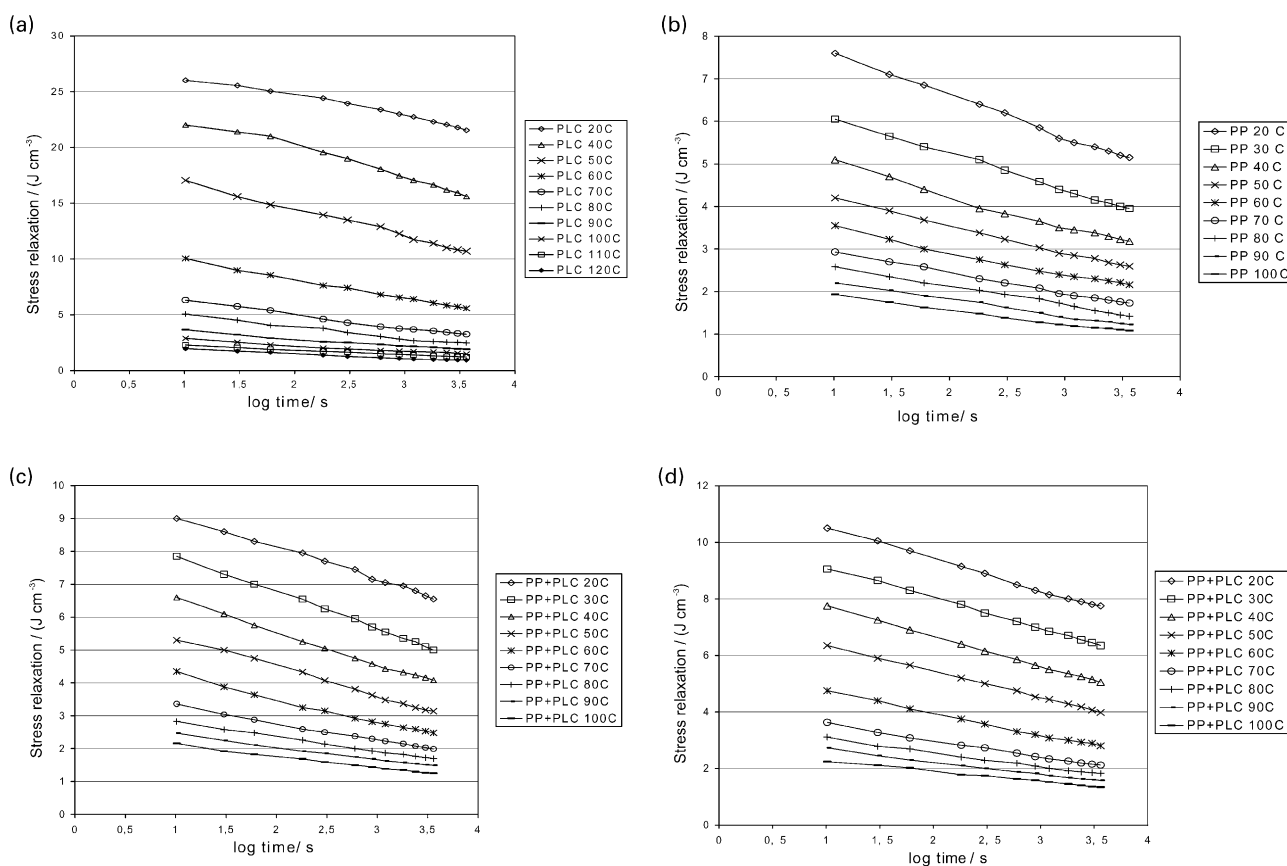


Fig. 1. (a) Stress relaxation data for the PLC; (b) stress relaxation data for PP; (c) stress relaxation data for PP blended with 10 wt% of the PLC; (d) stress relaxation data for PP blended with 20 wt% of the PLC.

PLCs are used in polymer blends as they can serve as reinforcing components or processing aids decreasing viscosity of the blend. This is why we have decided to study the behavior of polypropylene—a commercial polymer often modified by blending with other thermoplastics—and its two blends with the PLC.

In our experiments we have used isotactic polypropylene (PP) VB 65 11B, produced by Neste OY, Helsinki, Finland and the liquid crystalline copolyester LC-3000 by Unitika, Osaka, Japan containing 0.4 mol fraction of poly(ethylene terephthalate), the rest being *p*-hydroxybenzoic acid, PET/0.6PHB. Our liquid crystalline copolyester is a longitudinal PLC with LC sequences in the main chain and oriented along the chain backbone [24]. It forms four coexisting phases in its service temperature range [23] and was extensively characterized in earlier papers [15,23,32,33]. Two blends of PP and the PLC were prepared containing 10 and 20% of PLC by weight, using a single screw Goettfert extruder with 3 mm cylindrical die of the length/diameter (L/D) ratio = 20. The blends were granulated and injection molded with the temperature profile 170–225–230–245 °C in order to prepare plates which were used to cut the dog-bone specimens along the injection direction.

Stress relaxation measurements were conducted on an

MTS universal testing machine under the constant strain of 0.5% in the temperature range from 20 to 120 °C for the PLC and from 20 to 100 °C for PP and the blends. The first value of stress was measured 10 s after applying the load. At least three but usually five specimens were investigated.

The characteristic parameters (P^* , v^* , T^*) were obtained using experimental data from so-called Gnomix apparatus and fitting them to the Hartmann equation (3). The principle of the Gnomix apparatus has been already described in 1976 by Zoller et al. [40]. The sample to be studied can have any shape; its usual weight is between 1.5 and 2.5 g. It is first dried under vacuum for several hours and then placed in a rigid cell with flexible bellows at the bottom and degassed again. The volume which is not taken by the sample is filled by mercury all the time under vacuum. The cell is installed inside a pressure vessel in which pressures up to 240 J cm⁻³ (=240 MPa) and temperatures up to 400 °C can be maintained. The deflection of the bellows resulting from changes in temperature and/or pressure is measured with a linear variable differential transducer (LVDT). These deflections are converted into volume changes of the sample proper on the basis of well established P – V – T properties of mercury. We have used the same technique before for a series of liquid crystalline copolymers [41].

5. Stress relaxation results and master curves

Experimental isothermal stress relaxation curves for four investigated materials are shown in Fig. 1 as plots of stress versus time. Due to elastic deformation of investigated materials we have obtained similar relaxation curves of the Young modulus as well as the values of the stress. This is why we shall consider henceforth the stress relaxation results only.

Already in 1965, Kubat [42] suggested a representation of the stress relaxation curves in the coordinates $(\sigma - \sigma_i)/(\sigma_0 - \sigma_i)$ versus t ; here σ is the effective stress, σ_i the so-called internal stress which corresponds to the time $t = \infty$, while σ_0 pertains to $t = 0$. A comparison was made for a variety of materials, including metals and polymers. It turned out that the curves for so vastly different materials look similar, and all exhibit three regions: initial nearly horizontal, then a long central region, descending approximately linearly, and the final one (again approximately horizontal), which provides us with the value of σ_i . Curves for one material at several temperatures look similar in these coordinates.

To confirm the theory we have performed computer simulations of two kinds. We have simulated cluster relaxation recording cluster sizes [43] and, more importantly, stress relaxation as well as stress σ versus strain ε curves using the method of molecular dynamics (MD) for metal and polymers [44,45]. Both kinds of curves agreed with

experimental ones and confirmed the explanation of Kubat that stress relaxation occurs in clusters [46].

In the present work for convenience the curve for $T_{\text{ref}} = 20^\circ\text{C}$ (top curve in Fig. 1) is chosen as the reference curve for which by definition $a_T = 1$.

The shapes of the master curves we have obtained (Fig. 2) are similar for PP and the blends; the second derivative is positive ($\sigma''(t) > 0$), similarly as those investigated by Kubat and Rigdahl [46]. However, for the PLC master curve (Fig. 2(a)) the value of $\sigma''(t)$, initially negative, becomes positive for values of stresses measured at the temperature $T = 60^\circ\text{C}$.

Consulting the phase diagram of PET/*x*PHB copolymers we see that the glass transition temperature (T_g) of PET is equal to 62°C . Below T_g of PET we are in the region IV of the diagram containing PET crystals, PHB-rich islands, approximately isotropic PET-rich glass and PHB-rich glass. Above T_g of PET (region VII) PET-rich glass becomes the quasi-liquid; in spite of moving into a different region of the phase diagram the TTC is still applicable.

Consider now the PP master curve (Fig. 2(b)). T_g of PP is around 0°C , during our experiment PP does not undergo any phase changes. Furthermore PP as a semi-crystalline polymer does not show significant changes in master curve slope even in the T_g region. This may be explained by filler action of the crystallites that cause a reduction in segmental mobility. This is why the master curve is broad and flat compared to that of the PLC.

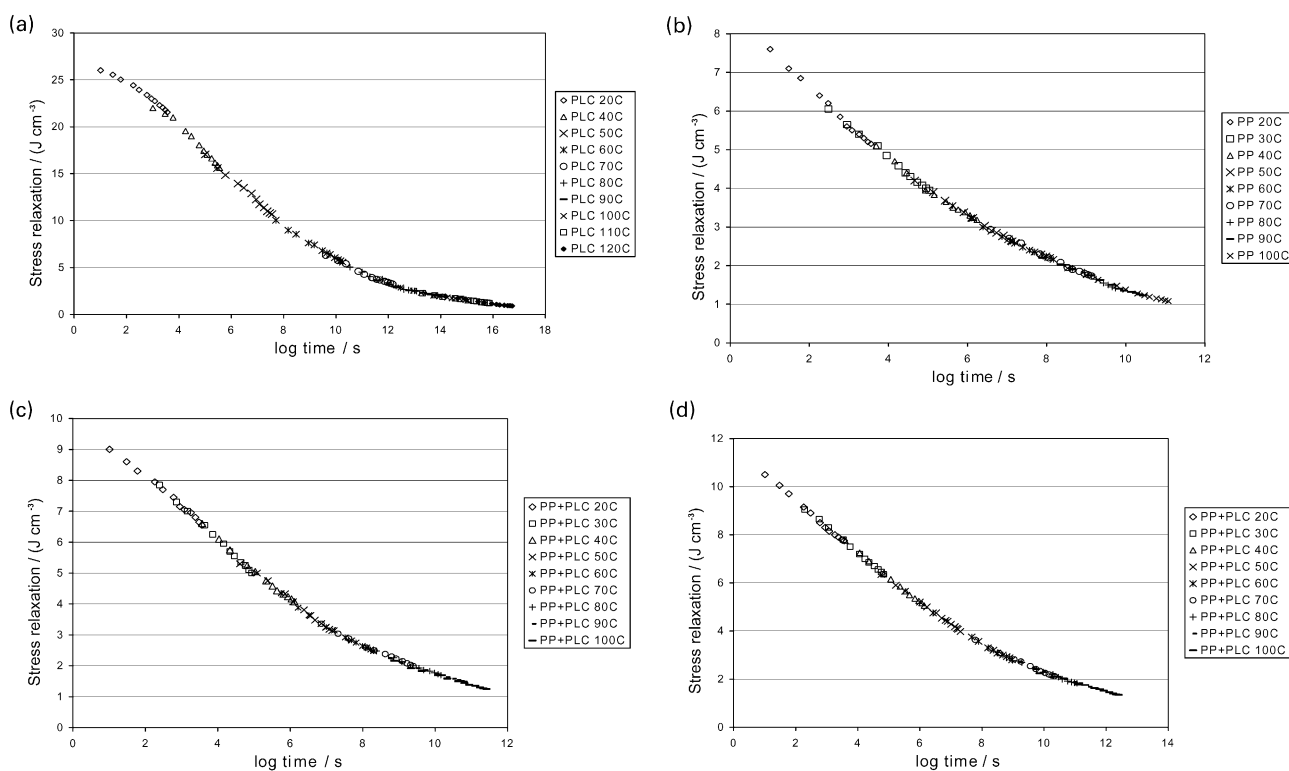


Fig. 2. (a) Master curve of stress relaxation for the PLC; (b) master curve of stress relaxation for polypropylene; (c) master curve of stress relaxation for the blend of polypropylene with 10% of PLC; (d) master curve of stress relaxation for the blend of polypropylene with 20% of PLC.

Table 1
Characteristic parameters for PP, PLC and two blends

Parameter	PP	PP + 10% PLC	PP + 20% PLC	PLC
P^* (J cm^{-3})	3901	4300	3750	2865
v^* ($\text{cm}^3 \text{g}^{-1}$)	0.910	0.885	0.900	0.667
T^* (K)	876	866	956	1396

The behavior of master curves of the blends (Fig. 2(c) and (d)) is close to the master curve for the PP. Apparently the PLC concentrations of 10 and 20% do not affect the curve shapes significantly.

6. Calculation of the shift factors from all data

In order to calculate the shift factors, we need the reduced volume \tilde{v} in Eq. (5). This value can be calculated using the Hartmann equation of state (3) from the characteristic (P^* , v^* , T^*) parameters of the materials. These parameters have been determined using the Gnomix apparatus described in Section 4. The results are listed in Table 1.

The characteristic parameters in Table 1 provide us also with information on morphology of the PP + PLC blends. In the PLC concentration range between 0 and 10% the reduced volume decreases as the quantity of oriented (high density) liquid crystal constituent increases. A further

increase in the PLC content leads to phase separation [23] and thus higher reduced volume.

As seen in Eq. (5), there should be a linear relation between $\ln a_T$ and $1/(\tilde{v} - 1)$. Fig. 3 shows this step of our work. The results for PP and the blend fit the linear relation with high accuracy; the PLC graph exhibits somewhat larger experimental errors but evidently Eq. (5) applies here as well.

The parameters A and B in Eq. (5) were calculated from experimental data; the results are listed in Table 2.

We recall the glass transition of the PET phase in the PLC at $T_{g \text{ PET}} = 62^\circ\text{C}$. In order to increase the accuracy of our model for PLC one can divide the results into two groups: those for temperatures higher than $T_{g \text{ PET}}$ and the results for the glassy state of PET, and calculate A and B parameters separately for both states. For example in the range between 70 and 120 °C (above $T_{g \text{ PET}}$) the parameters A and B are -6.9954 and 73.627 , respectively, obtained with good accuracy $R^2 = 0.9992$. The values are not identical to the full-range parameters but that is what could have been expected: The Doolittle constant changes with a change of region in the phase diagram of PLC. However, dividing the results into two regions is a complication, especially for multiphase materials, and it is not necessary. We obtain reliable results in spite of the glass transitions in our materials.

Fig. 4 shows the comparison of experimental and predicted values of shift factors versus temperature. As the

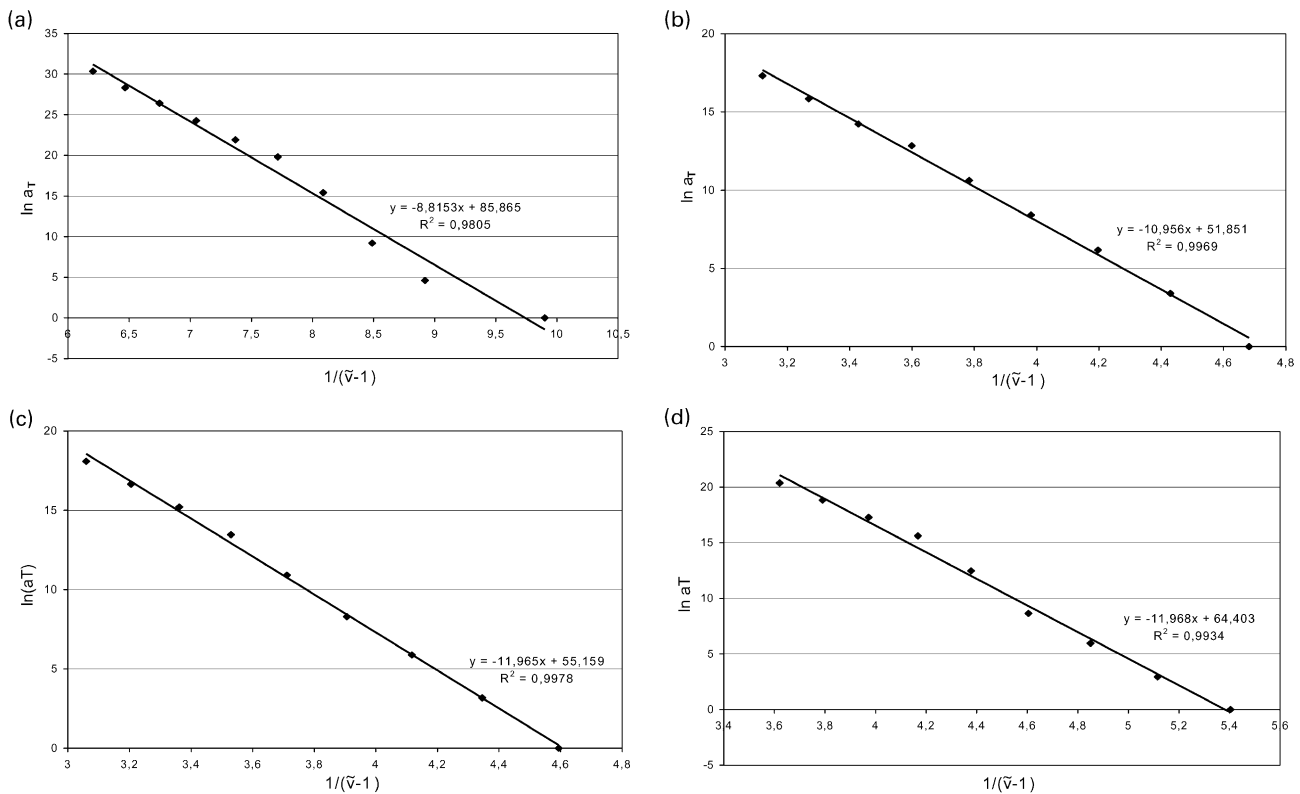


Fig. 3. (a) Plot of $\ln a_T$ versus $1/(\tilde{v} - 1)$ for the PLC; (b) Plot of $\ln a_T$ versus $1/(\tilde{v} - 1)$ for PP; (c) Plot of $\ln a_T$ versus $1/(\tilde{v} - 1)$ for PP blended with 10 wt% of the PLC; (d) Plot of $\ln a_T$ versus $1/(\tilde{v} - 1)$ for PP blended with 20 wt% of the PLC.

Table 2
The set of linear parameters (*A* and *B*) from Eq. (4)

Parameter	PP	PP + 10% PLC	PP + 20% PLC	PLC
<i>A</i>	51.851	55.159	64.403	85.865
<i>B</i>	−10.956	−11.965	−11.968	−8.8153
Accuracy (R^2)	0.9969	0.9978	0.9934	0.9805

Table 3
Complete set of experimental and predicted $y = ax^2 + bx + c$ equation parameters

		<i>a</i>	<i>b</i>	<i>c</i>	R^2 (accuracy)
PP	Full set	−0.0025	−0.0543	0.9364	0.9992
	Minimum of data	−0.0022	−0.0585	0.9455	0.9999
PP + 10% PLC	Full set	−0.0019	−0.0632	1.0572	0.9983
	Minimum of data	−0.0025	−0.0538	1.0318	0.9990
PP + 20% PLC	Full set	−0.0023	−0.0502	1.0926	0.9992
	Minimum of data	−0.0021	−0.0510	1.0874	0.9995
PLC	Full set	−0.0027	−0.0501	1.5381	0.9976
	Minimum of data	−0.0039	−0.0252	1.4645	0.9997

values predicted by the model (continuous line) fit the experimental data we can conclude that the proposed model serves well not only for the components but also for the blends.

7. Master curve creation from a minimum of data

The next aim of our work is the attempt to create master

curve from a minimal amount of data thus avoiding extensive experimentation. Based on logarithmic axis of shifted time ($\log(ta_T)$) versus logarithmic values of stress we have used the least squares method to represent the experimental data by a simple second-degree polynomial. A similar method is described in some detail in the previous paper [9]; it was applied there to the TSC. We now apply an

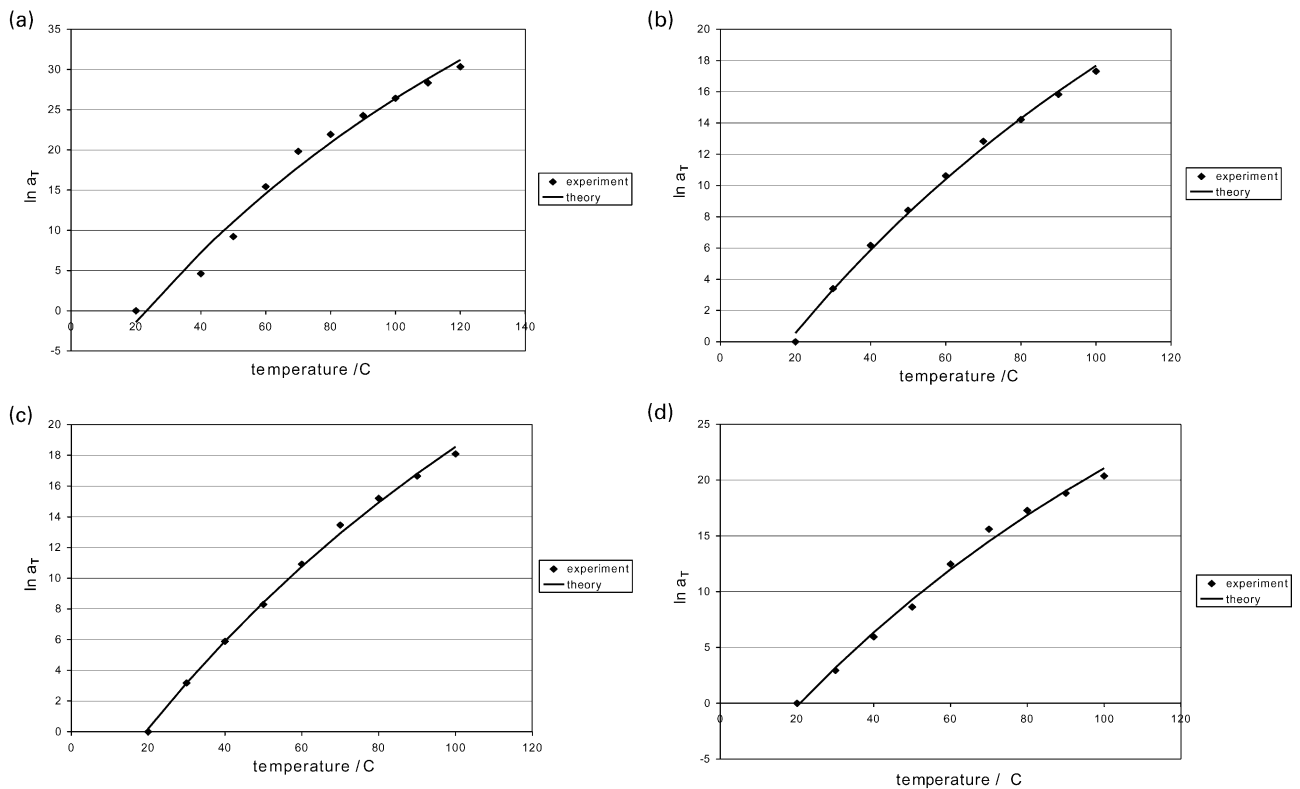


Fig. 4. (a) Theoretical and experimental values of shift factor for the PLC; (b) theoretical and experimental values of shift factor for PP; (c) theoretical and experimental values of shift factor for PP blended with 10 wt% of the PLC; (d) theoretical and experimental values of shift factor for PP blended with 20 wt% of the PLC.

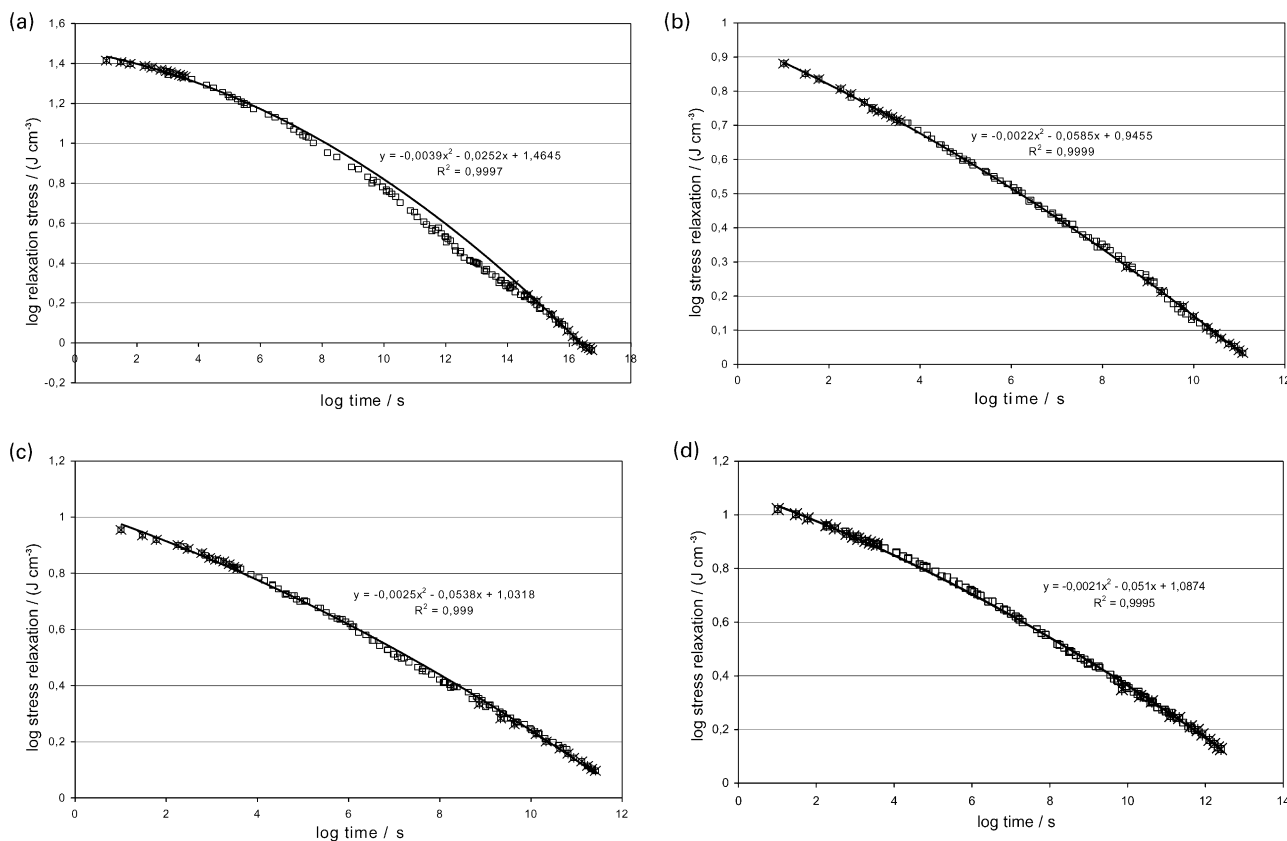


Fig. 5. (a) Comparison of stress relaxation values: experimental (\square) and predicted (+) by the second-degree equation for the PLC; (b) comparison of stress relaxation values: experimental (\square) and predicted (+) by the second-degree equation for the PP; (c) comparison of stress relaxation values: experimental (\square) and predicted (+) by the second-degree equation for PP blended with 10 wt% of the PLC; (d) comparison of stress relaxation values: experimental (\square) and predicted (+) by the second-degree equation for PP blended with 20 wt% of the PLC.

analogous treatment with the TTC principle as the basis. We shall use the more accurate second-degree equation: $ax^2 + bx + c$ instead of $ax^2 + c$. The approximation made from the whole sets of data and the prediction based only on the first and the last runs can be compared in Fig. 5. Fig. 5 (logarithmic stress scale) shows the same data as Fig. 2 (linear stress scale) because we needed linear stress scale to show clearly the differences between the master curves and logarithmic stress scale provided us with the possibility of high accuracy prediction of stress by the second-degree $ax^2 + bx + c$ equation.

All the pertinent parameters are summarized in Table 3. Although deviations between predicted and approximated curves occur for the PLC due to the glass transition mentioned previously, the predicted relaxation stresses are accurate for all materials.

Our calculations prove that the minimum-data prediction method can be applied not only to simple polymeric materials, but also to polymer blends and multiphase systems we have investigated.

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