

Possibilities of Strength Prediction of Adhesive Joints of Polymers by Master Curve Method

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Synopsis

In the present work it is shown that the strength, depending on temperature and strain, and durability, depending on temperature and static load, of adhesive joints of polymers with adhesive of elastomer type can be predicted from master curves, drawn according to the principle of temperature-time analogy. Shift factors, determined by the Williams-Landel-Ferry (WLF) equation with universal values of constants, have been used to draw the master curves. It allowed to find relations between reference temperature and glass transition temperature of the adhesive. Their existence can be explained on the basis of free volume theory. Referring to the analogous influence of temperature and the part of the plasticizer inserted into the adhesive, on the strength of adhesive joints the existence of temperature-concentration analogy has been determined on the phenomenological level. Nomograms have been suggested for the calculation of strength and durability values from the master curves. Their application is convenient for repeated usage of master curves.

INTRODUCTION

The master curve method is the result of the existence of definite analogies from which, up to the present, the temperature-time analogy has worked best.^{1,2} This analogy was supposed for the description of viscoelastic properties of polymers at the beginning and later was extended to their strength properties: the strength tested by constant strain rates³⁻⁸ and durability tested in static conditions.^{3,5,9}

Adhesive joints of polymers can be discussed as multicomponent (multi-layered) polymer systems. Thus, the principles determining their temperature-time strength dependence are the same as for individual polymers.¹⁰ It allows us to assume the existence of temperature-time analogy in terms of strength properties of adhesive joints and naturally suggests the possibility of using a master curve method to describe their temperature-time strength dependence which, for strength in the case of double-peeling, has been verified in the works of references.¹¹⁻¹⁵

The objective of the present paper is the investigation of the possibilities of application of a master curve method for working out the data of strength (in the cases of tests by double-peeling and shear) and durability, and also the definition of those differences which exist in selecting reference temperature depending on the type of a test. The positive solution of all these questions

enables us to predict strength and durability in cases where the dependence of these properties on the variables is difficult to describe mathematically.

As may be judged from available publications, two approaches for drawing of master curves are observed to be applied at present which can be defined respectively as physical^{1,2} and phenomenological.¹⁶ We shall shortly discuss their characteristic moments.

When the temperature–time analogy takes place, master curves are drawn using shift factor a_T , which is determined by the WLF equation¹⁷:

$$\log a_T = - \frac{C_1^s(T - T_s)}{C_2^s + T - T_s} \quad (1)$$

here T_s is reference temperature, T is some other temperature, and C_1^s and C_2^s are constants.

Typical for the physical approach is that the values of the coefficients C_1^s and C_2^s in the WLF equation are regarded constant equal to universal values $C_1^s = 8.86$ and $C_2^s = 101.6$. Hence, for most polymers, the reference temperature T_s satisfies the condition $T_s = T_g + 50^\circ$ (T_g is glass transition temperature), and there is no need to calculate T_s . Nevertheless, a number of authors have determined that not always $T_s = T_g + 50^\circ$, though $C_1^s = 8.86$ and $C_2^s = 101.6$ are customary. Namely, this was observed for adhesive joints¹³ and filled polymers.^{18,19} Because of such nonsimplicity in selecting T_s in relation to T_g , the definition of T_s becomes the first stage of drawing a master curve applying a physical approach.

The phenomenological approach is characteristic of the fact that T_s is selected on reasons of rationality. For example, giving creep data for polymers,¹⁶ the minimum test temperature is taken for T_s because such choice allows the prediction of a creep value at long times. The phenomenological approach may be effective for drawing durability master curves as well, because the reduction at minimum temperature extends the time interval. It allows prediction of a durability considerably longer in comparison with the durability found experimentally. After selection of T_s , it is necessary to determine the constants C_1^s and C_2^s according to empiric values of a_T . This problem can be solved by the method of numerical analysis.

We have made use of both approaches of drawing master curves.

TEMPERATURE–TIME ANALOGY APPLICATION FOR PREDICTION OF STRENGTH OF ADHESIVE JOINTS

The problem of drawing of master curves of the strength of adhesive bonds will be discussed here. The experimental data obtained by us will be used.

The strength of adhesive joints (Table I) tested by double peeling and shear was determined on the breaking machine in a thermal chamber. Before testing, the glued samples were kept until the solvent was practically completely eliminated.

For every experimental point, from 6 to 20 samples were tested according to the spread. The variation coefficient for different cases ranged from 5% to 15%. The results of the investigation of the strength of adhesive bonds are presented in Figure 1. Their further working out by the master curve method using the physical approach was done on the computer with the help of which the calculation of reduced variables and a simultaneous drawing of a

TABLE I
Investigation Objects for Strength: T_g , T_s , and f_g Values^a

Var. no.	System		Test type	T_g	T_s	$T_s - T_g$	f_g
	Adherend	Adhesive					
1.	PVC film (DOP 20 w.u.)	polyurethane composition Bostik-2531 + polyisocyanate	shear	273	323	50	0.025
2.	Diacetate cellulose film	nitrile rubber (SKN-40)	shear	255	305	50	0.025
3.	Leather	composition on the basis of polychloroprene and butylphenol-formaldehyde resin	shear	278	328	50	0.025
4.	Leather	same as above	double-peeling	278	323	45	0.027
5.	Diacetate cellulose film	polyurethane rubber UK-1 + polyisocyanate	double-peeling	276	308	32	0.034
6.	Diacetate cellulose film	polyurethane rubber Desmokol-400 + polyisocyanate	double-peeling	282	322	40	0.030

^a The failure of adhesive joints in all cases being through the adhesive, the glass transition temperature of its free films determined by a thermomechanical way according to appreciable deformations at small strains was taken for the glass transition temperature of the adhesive in an adhesive joint. The f_g parameter is a fractional free volume at the glass transition temperature.

master curve and the determination of optimal value of reference temperature were accomplished by special program.²⁰

Master curve dependences of reduced strength on the reduced rate on the coordinates $\log PT_s/T - \log Va_T$ for all investigated systems (Fig. 2) were drawn according to the equation^{11,12}

$$P(Va_T, T_s) = \frac{T_s}{T} P(V, T) \quad (2)$$

where P is strength, V is the rate of strain, a_T is the shift factor described by the WLF equation with the universal values of constants.

As can be seen from Table I (var. 1, 2, 3) in case of shear test, the difference $T_s - T_g = 50^\circ$ for all systems, as in most polymers. But in case of double-peeling, the value $T_s - T_g$ is not constant; besides, $T_s - T_g < 50^\circ$, which basically corresponds to the results of reference 13. This fact can be explained by referring to the theory of free volume.

If the WLF equation in form (1) with the coefficients $C_1^s \approx 8.86$ and $C_2^s = 101.6$ is used, the WLF coefficients C_1^g and C_2^g corresponding to the glass transition temperature T_g may be defined from the equations¹

$$C_1^g = \frac{8.86 \times 101.6}{101.6 + T_g - T_s}, \quad C_2^g = 101.6 + T_g - T_s. \quad (3)$$

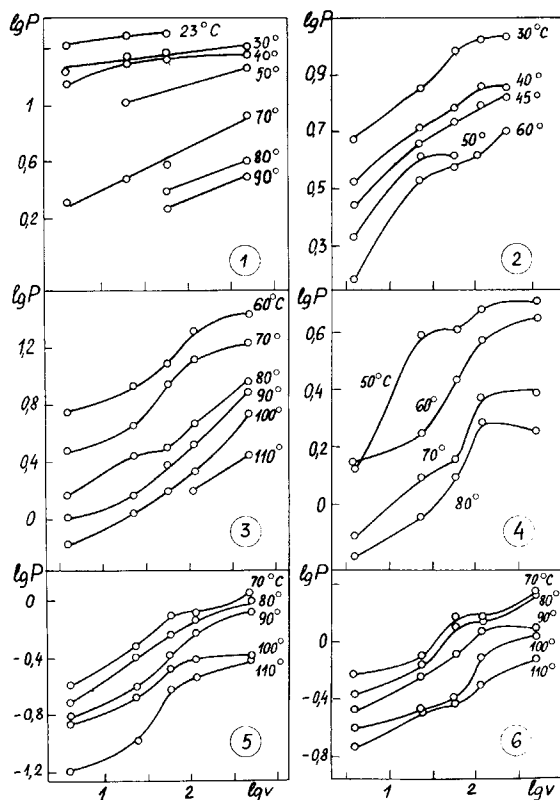


Fig. 1. Dependence of strength of adhesive joints on temperature and stress rate. Numbers correspond to numbers of variants in Table I.

Then the physical meaning of the constants C_1^g and C_2^g may be presented on the basis of the following relations:

$$C_1^g = \frac{1}{2.303 f_g}, \quad C_2^g = \frac{f_g}{\alpha_f} \quad (4)$$

where f_g is a fractional free volume for T_g , and α_f is the difference of thermal expansion of coefficients above and below T_g .

Equations (3) and (4) taken together make it possible to find a fractional free volume f_g from T_s and T_g values, the minimum value of which in case of double-peeling equal to 0.027 exceeds the universal value equal to 0.025. In our case, evidently, this could be explained referring to the dependence of Poisson's ratio μ on strain.

Poisson's ratio may be defined by the formula

$$\mu = \frac{1}{2} \left(1 - \frac{\partial}{\partial \epsilon} \ln v \right) \quad (5)$$

where v is the volume of the sample and ϵ is the relative lengthening.

It is determined^{21,22} that for the stretch of elastomers at great deformations $\mu < 0.5$, and it decreases when the deformation is increased.

During double-peeling, the adhesive operates chiefly under the stretch conditions; therefore, in our case $\mu < 0.5$ for deformations which are close to fail-

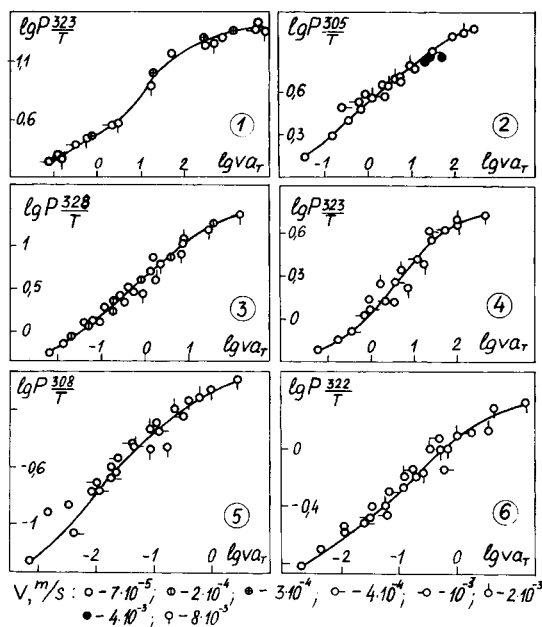


Fig. 2. Master curves of strength of adhesive joints. Numbers of curves correspond to numbers of variants in Table I.

ure. From formula (5) we get that $\partial v/\partial \epsilon > 0$ if $\mu < 0.5$. In this way, when the stretch occurs, an increase in volume of the adhesive takes place and fractional free volume of the layer of the adhesive in the stretched state will be greater than in the nonstretched state.

While testing adhesive joints by shear, the thin layer of the adhesive limited by two adherent planes operates under the conditions close to simple shear, for which, as is known,¹ full and consequently free volume as well does not change. Referring to these assumptions, the fact that while testing an adhesive joint by shear fractional free volume f_g practically is constant can be explained. Therefore, the value of the reference temperature satisfies the equality $T_s = T_g + 50^\circ$.

APPLICATION OF TEMPERATURE-CONCENTRATION ANALOGY FOR STRENGTH PREDICTION OF ADHESIVE BONDS

The analogy method is based on the usage of different factors accelerating the processes of relaxation. The role of such factors may be played by temperature (temperature-time analogy), humidity of the material (humidity-time analogy¹⁶), etc. For joints with the adhesives differing in degree of plasticization, the role of accelerating factor may be played by the quantity of plasticizer inserted into the adhesive.

On the other hand, it is known²³ that the influence of temperature on the strength of adhesive joints in general may be analogous to that of the plasticizer, which allows to predict the existence of temperature-concentration analogy different from common analogies.

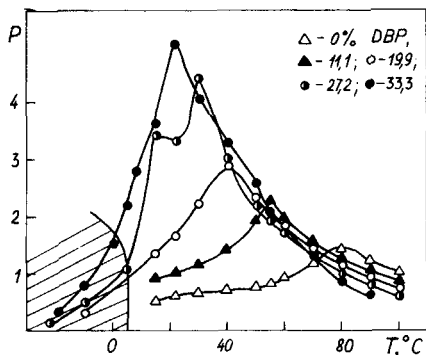


Fig. 3. Strength dependence of adhesive joints on temperature and degree of adhesive plasticization.

The temperature strength dependence of the adhesive joints of diacetate cellulose films with the adhesive which is PCV resin plasticized to different degrees by DBP was investigated with the aim of verifying this supposition. The strength of adhesive joints was determined in the temperature range of 251–373°K for which the adherend was in a glass state and the adhesive was in various physical states, from glass state to viscous-flowing. Concentration of DBP in the adhesive varied in the range of 6–33.2 vol-%.

The strength of all adhesive joints for shear was defined by strain (3.3×10^{-3} m/sec) rate.

The dependence of strength P on the temperature T for different plasticizer concentrations in the adhesive C is shown in Figure 3. As may be seen from the wide temperature interval, the dependences $P(T)$ have extreme characteristics. The nature of such dependences is explained in reference 23. In our case, in the temperature range to the left of extreme curves $P(T)$, i.e., for $T < T_{P_{max}}$, the failure of adhesive joints occurred along the boundary layer. Besides, for temperatures corresponding to the shaded area in Figure 3, the failure occurred at a great rate, the surface of the failure being mirror-like (analogy with brittle failure). For temperatures $T > T_{P_{max}}$, the character of failure gradually changed to mixed and finally to cohesive through adhesive.

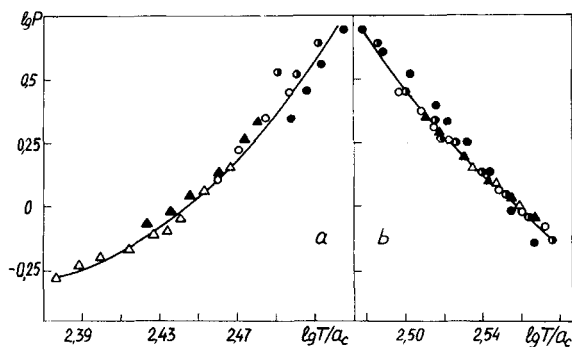


Fig. 4. Master curves of strength of adhesive joints in the temperature area below (a) and above (b) $T_{P_{max}}$.

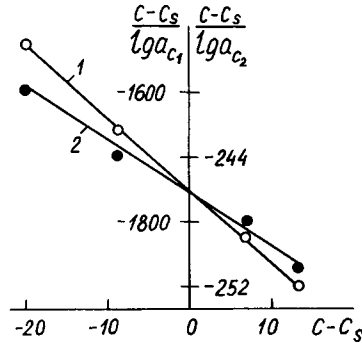


Fig. 5. Concentration dependence of $\log a_c$ in the temperature area above (1) and below (2) $T_{P_{\max}}$.

The drawing of one master curve for the whole temperature interval in case of extreme dependences $P(T)$, evidently, has no sense, since above and below $T_{P_{\max}}$ the character of the failure of adhesive joints and the factors determining the change of strength with change in temperature are different²⁴: in case of failure along the boundary layer below $T_{P_{\max}}$, the relaxation properties of the adhesive are determining. Above $T_{P_{\max}}$ in case of a cohesive failure through adhesive (or mixed), the determining properties are those of cohesion strength of the adhesive layer.

Therefore, the master curves of strength were built separately for temperature areas $T < T_{P_{\max}}$ and $T > T_{P_{\max}}$ having chosen $C_s = 19.9$ for reduction concentration (Fig. 4). Note that the points belonging to the shaded area (Fig. 3) are not put on the master curve because relaxation properties of the adhesive practically do not appear at temperatures of 251–278°K for the systems being discussed.

The shift factor $\log a_c$ used for the drawing of master curves was determined as an arithmetical mean distance along the horizontal lines between the base curve (the curve corresponding to reduction concentration) and the rest curves. Because the experimentally found values $\log a_c$ corresponding to both temperature intervals ($T < T_{P_{\max}}$, $T > T_{P_{\max}}$) on the coordinates $C - C_s / \log a_c - (C - C_s)$ being put on the straight lines (Fig. 5), the concentration dependence $\log a_c$ is described by the equation which is analogous to the equation for the description of a_T :

$$\log a_c = - \frac{b_1(C - C_s)}{b_2 + C - C_s} \quad (6)$$

where b_1 and b_2 are constants. Their values are found by the least-squares method (for $T < T_{P_{\max}}$, $b_1 = 8.67$, $b_2 = 2131$; for $T > T_{P_{\max}}$, $b_1 = 0.11$, $b_2 = 190$).

Thus, the possibility of drawing a master curve of strength making use of a shift factor which is determined by eq. (6) shows that, in the case being discussed, the temperature–concentration analogy takes place.

Evidently, the use of this analogy may seem to be valuable for strength prediction depending on temperature for joints on adhesives containing plasticizer and for strength prediction of plasticized polymers as well.

DURABILITY PREDICTION OF ADHESIVE JOINTS UNDER LOAD BY MASTER CURVE METHOD CONDITIONS

Durability master curves, i.e., master curves with long-life strength under a static load depending on temperature, are interesting for the prediction of strength properties of adhesive joints, too.

The objects of investigation for durability were lap adhesive bonds (Table II). The durability was determined in a thermostat at constant temperature ($\pm 1^\circ$ accuracy) in air. Adhesive bonds were tested under constant static load.

To get every experimental point, from 6 to 20 samples were tested depending on the spread. The variation coefficient was 20–25%.

The failure of adhesive joints with the adhesives in a high elasticity state strongly depends on time and, as shown in reference 10, on the time corresponding to the beginning of the failure at the points of stress concentration may essentially differ from the time of complete failure. Thus, the two indexes of durability were determined experimentally: τ_1 for the beginning of the failure on the edge of the lap and τ_2 for the moment of the dividing sample into two parts.

The results of the experimental investigation of durability of adhesive joints are shown in Figure 6.

Master curves (Fig. 7) for the systems shown in Table II were drawn on the coordinates $\log \bar{P}T_s/T - \log \tau/a_T$ making use of the shift factor $\log a_T$ determined by WLF equation with the universal coefficient values (\bar{P} is a static load).

It may be seen from Table II that, in all the cases discussed, the difference $T_s - T_g$ is not constant, but for both indexes of durability $T_s - T_g < 50^\circ$. Besides, the differences $(T_s - T_g)_1$ and $(T_s - T_g)_2$ corresponding to τ_1 and τ_2 are different, and always

$$(T_s - T_g)_2 < (T_s - T_g)_1. \quad (7)$$

The principles determined for T_s values have a definite physical meaning and may be explained (analogically with the case of strength) referring to the theory of free volume.

The value of free volume should be dependent on the time in which the sample is in a stress state and the accelerating development of a structure defect occurs.²⁵ Under these conditions, the fractional free volume should increase. Consequently, the longer the sample remains in a stress state, the greater the fractional free volume should be. Together with the increase in fractional free volume, the difference $T_s - T_g$ decreases (supposing that in

TABLE II
Investigation Objects for Durability: T_g, T_s Values

Var. no.	System		T_g	$(T_s - T_g)_1, (T_s - T_g)_2$	
	Adherend	Adhesive			
1.	PVC film (DOP 20 w.u.)	SKN-40	255	20	15
2.	PVC film (DOP 70 w.u.)	SKN-40	255	14	10
3.	Diacetate cellulose film	SKN-40	255	25	19

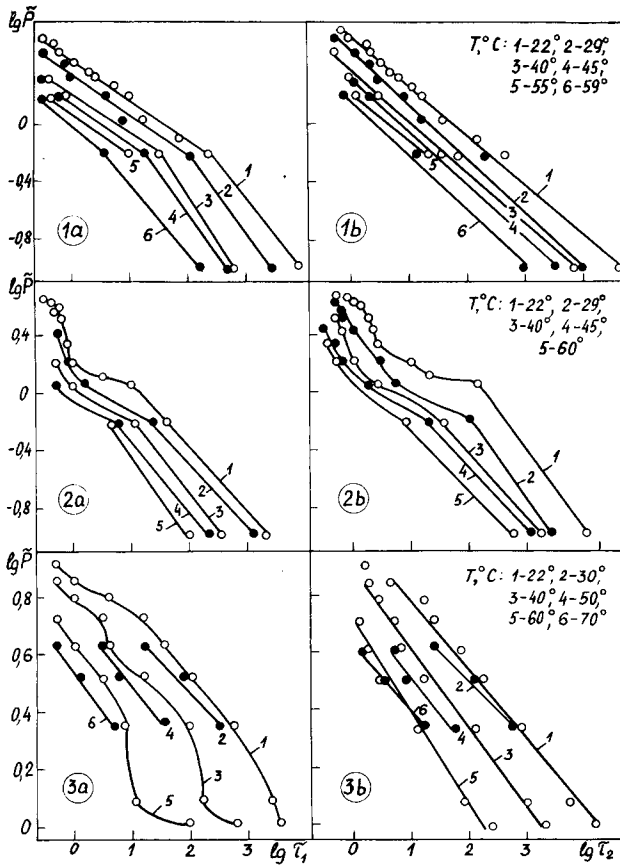


Fig. 6. Dependence of durability τ_1 (a) and τ_2 (b) of adhesive joints on temperature and static load. Numbers correspond to number of variants in Table II.

eq. (1) $C_1^s = 8.86, C_2^s = 101.6$). The existence of inequality $T_s - T_g < 50^\circ$ and inequality (7) may thus be explained.

As has been mentioned in the introduction, the use of the WLF equation with universal coefficient values is not necessary and, concerning prediction, it is not always rational. We have tested another way of drawing durability master curves when T_s is selected arbitrarily (according to the purpose of rationality), using the durability of adhesive joints of diacetate cellulose films glued together by a polyurethane adhesive Desmokol-400. The results of the experiment are presented in Figure 8.

Having assumed $T_s = 363^\circ\text{K}$, we determined $\log a_T$ values (by analogy as was the case with $\log a_c$) and calculated constants C_1^s and C_2^s in eq. (1) by the least-squares method: $C_1^s = 5.66$ and $C_2^s = 56.15$. The basis according to which the dependence of type (1) for $\log a_T$ was selected is illustrated in Figure 9a.

A durability master curve (dotted line) is given in Figure 9b drawn according to the data of short-time tests (up to 7 hr). From this figure, we can see that on the basis of a master curve the durability up to 65 days of adhesive joints being tested at reference temperature can be predicted. Therefore, the

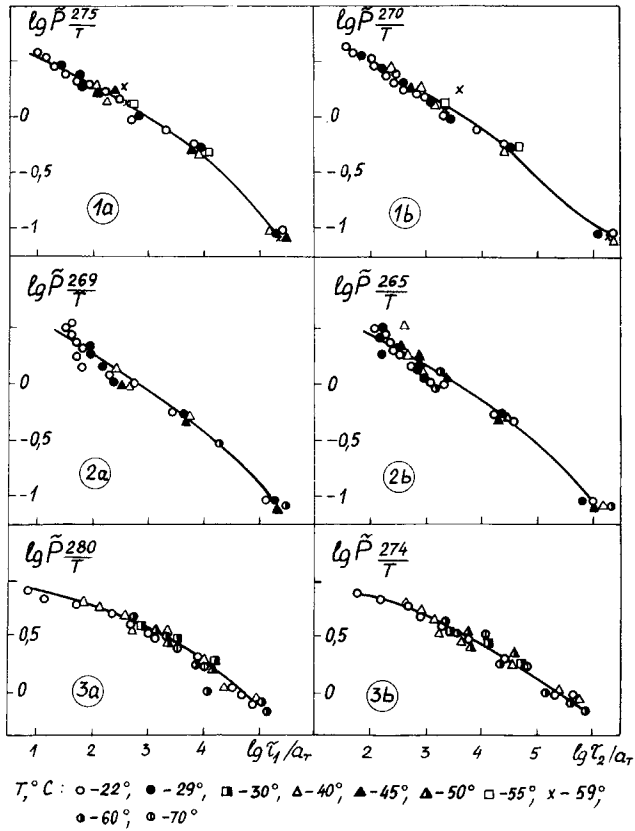


Fig. 7. Durability master curves τ_1 (a) and τ_2 (b) of adhesive joints. Numbers of curves correspond to numbers of variants in Table II.

time interval during which the prediction may be carried out is considerably extended in comparison with the interval in which the durability is determined experimentally at the expense of a rational choice of T_s .

Consequently, the use of the above-mentioned phenomenological approach of drawing master curves according to the results of short-time tests may give information about the prolonged behavior of adhesive joints. This also suits the case of individual polymers.

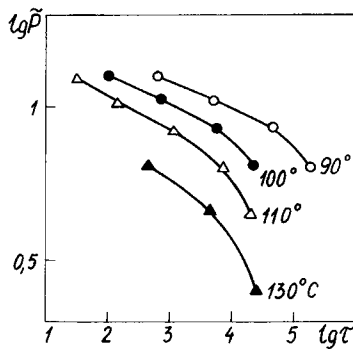


Fig. 8. Dependence of durability curves of adhesive joints on temperature and static load.

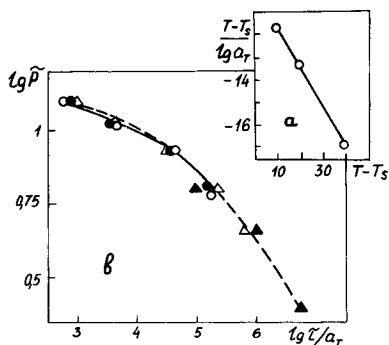


Fig. 9. Temperature dependence of shift factor (a) and durability master curve (b). Continuous line represents curve of control test.

METHODS FACILITATING THE APPLICATION OF MASTER CURVES

Master curves are practically valuable because according to them, the predicted index for such values of variables for which experimental investigation was not carried out can be calculated. For this, the proper analytic-graphic calculation of the index being predicted should be done from a master curve.

Such a way is not rational. Nomograms worked out for this purpose are considerably more effective for repeated use. These nomograms may be used for the prediction of strength of polymers as well, because master curves for polymers are drawn on the same coordinates.

Such a nomogram is illustrated in Figure 10. The principle of nomograms from aligned points is taken as a basis for the drawing of this one. The determination of an unknown value of strength is given by keys A-B-C, C-D-E, D-F-G, and H-G-K.

A nomogram for durability calculation is drawn by analogy.²⁶

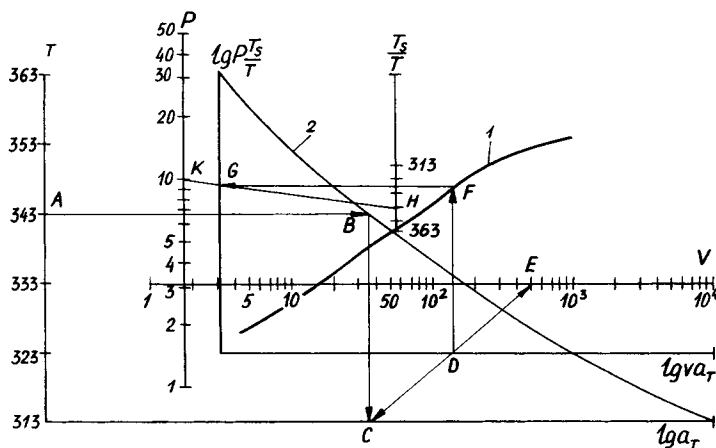


Fig. 10. Nomogram for strength calculation from a master curve for adhesive joints of films PVC (DOP 40 weight units) with polyurethane glue Bostik-2531: (1) master curve; (2) $\lg a_T$ plot.

CONCLUSIONS

The investigations showed that strength and durability of adhesive joints of polymers depending on the parameters of external influence (such as temperature, rate, load) may be predicted from master curves drawn according to the temperature-time analogy principle. Shift factor determined by the WLF equation with universal values of constants may be used for drawing of master curves. It has also been found that $T_s - T_g < 50^\circ$ in the double-peeling test of the adhesive joints and $T_s - T_g = 50^\circ$ in the lap test. Inequality $T_s - T_g < 50^\circ$ takes place in the case of durability, too.

Besides, the difference $(T_s - T_g)_1$ corresponding to the time of the beginning of the failure of the adhesive joints is always greater than the difference $(T_s - T_g)_2$ corresponding to the time of complete failure in the range of one adhesive system. The relations found between reference temperature and glass transition temperature may be explained in reference to the theory of free volume. The relations revealed between T_s and T_g give *a priori* possibility to select the reference temperature values or even that temperature interval in the range of which its optimal value exists, taking into account the test type.

In this article, the way of drawing a durability master curve is discussed, too, when the temperature is selected arbitrarily. Then the agreement of empiric values of shift factor with the WLF equation is realized by a proper correction of the coefficients of the equation.

On the phenomenologic level, the existence of temperature-concentration analogy for the strength of joints of polymers with the adhesives differing by the degree of plasticization was determined. It has been found that concentration dependence of the shift factor is described by an equation analogous to the WLF equation.

Nomograms for practical purposes of strength and durability prediction for adhesive bonds according to master curves are suggested.

The master curve method which is used for working out experimental data of strength properties of adhesive joints plays the same part as approximation methods in the aspect of their prediction allowing to determine the functional dependence of the properties investigated on the variables according to experimental results.

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