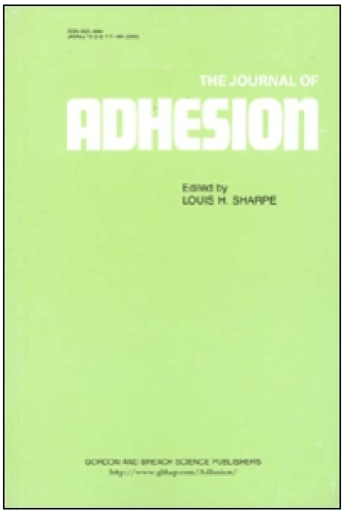

Heat Resistance Evaluation of Adhesive Joints in Terms of Stability Loss Temperature

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J. Adhesion, 1977, Vol. 9, pp. 51–61

Printed in Scotland

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(*Received April 7, 1977*)

The characteristics of evaluation of heat resistance of adhesive joints, i.e. the stability loss temperature (T_{T_s}) is suggested. Theoretical base of this characteristic is that heat resistance should be regarded as durability, in dependence with loading and temperature change law.

Stability loss temperature is determined according to the principle of thermomechanical testing. The investigations showed that there is a relationship between stability loss temperature, loading and the thickness of the adhesive layer. This relationship for adhesive joints of soft materials has a hyperbolic form.

If for adhesive joints the principle of superposition of destructions (Bailey criterion) exists, then, having durability equations, the stability loss temperature may be determined by calculation.

INTRODUCTION

The heat resistance of adhesive joints is assumed to be the property of preserving service ability, i.e. form and carrying ability at enhanced temperatures. The preservation of form, naturally, should be understood not in the absolute sense, but as the ability for a reversible deformation alone.

This definition is true for adhesive joints with the adhesives above glass transition temperature as well, including those of soft materials (i.e., rubbers, leather, textiles, etc.) though in these cases the reversible deformations of both adhesive layer and joint may increase considerably.

As a rule, the limit of heat resistance for rigid polymers is considered to be their glass transition temperature or, for crystalline polymers, the melting temperature of crystals. For soft polymers the limit of heat resistance in such a case is assumed to be their flow temperature within which non-reversible deformations occur at negligible loading supplied or even arbitrarily.

But under the effect of applied loading the occurring creep may result in a non-reversible loss of form at lower temperatures than glass-transition temperature (melting for solids) or flowing temperature (for soft bodies).

For this reason the temperature alone cannot determine the heat resistance of the material and it should be regarded as durability, i.e., depending on applied loading and temperature.

If heat resistance of adhesive joints is considered in this respect it should be evaluated in terms of time up to the moment of stability loss occurrence, e.g., up to the beginning of failure of adhesive joints or up to the beginning of the non-reversible displacement of adherent elements from their initial position due to applied loading and temperature.

Durability of adhesive joints as well as durability of materials may be determined in terms of the formula[1]:

$$\tau = \tau_0 \exp\left(\frac{U_0 - \gamma \tilde{P}}{RT}\right), \tag{1}$$

where τ is the time before the failure (durability); τ_0, U_0, γ are the equation parameters; R is the gas constant; $\tilde{P}$ and T are loading and temperature (K). This formula, known as a basic equation of durability, was theoretically grounded by S. N. Zhurkov.[2]†

For adhesive joints and, especially, adhesive joints of soft materials the Eq. (1) parameters γ and U_0 may be dependent on variables T and/or $\tilde{P}$. Then the formula (1) may become complicated. Sometimes for describing durability of adhesive joints of soft materials the following empirical formula might be convenient:

$$\tau = A_0 \tilde{P}^{-b} \exp\left(\frac{U}{RT}\right), \tag{2}$$

where A_0, b, U are the equation parameters. (The remaining values are the same as in Eq. 1.)

This formula, with tensions substituted for load $\tilde{P}$, was suggested by G. M. Bartenev[3] and it is justified for the description of durability of elastomers.

In numerous cases, however, the temperature for heat resistance evaluation might appear more conveniently as that at which the adhesive joint loses its stability under the effect of a certain loading (constant, varying, of any value, including approaching to zero as well).

Thus, if heat resistance is to be determined in the conditions of non-isothermal heating, enhancing the temperature in terms of the given law, the temperature at which the moment of stability loss will occur may be regarded

† For materials the load $\tilde{P}$ should be substituted by tensions in Eq. (1).

as some limit characteristic of heat resistance for the given law of load and temperature effect.

According to this principle the heat resistance of adhesive joints may be determined for any adhesive: thermoplastic, which at usual temperature exist in solid state, high elastic and elastoplastic as well. In any case, the temperatures at which plastic properties of the adhesive in the joint (at a given loading) practically do not make their appearance belong to the field of service life ability. But the temperature at which the appearance of plasticity (or creep) results in the loss of form of the adhesive joint is the limit temperature in terms of heat resistance characteristics and it determines the field of service ability at a given law of load effect. (Eventually, $\tilde{P}$ = const.) This temperature is referred to as stability loss temperature (T_{T_s}).[4] The dependence of stability loss temperature on the loading being determined, it is possible to obtain full information about the temperature range of service ability of adhesive joints and thus about their heat resistance dependence on loading.

THEORETICAL

Now we will consider the case when the adhesive joint is subjected to some constant loading $\tilde{P}_i$ at non-isothermal heating $T = T(t)$, where t is time.

The stability loss temperature of adhesive joints T_{T_s} is the function of time: for every $\tilde{P}_i$ = const. there is a dependence $T_{T_s} = f_1(t)$ and its reverse function $t = \varphi(T_{T_s})$. The latter expresses the time within which the temperature T_{T_s} is reached under the temperature change law $T(t)$, where $T \in [T_0; T_{T_s}]$. Naturally, $T_{T_s} = f_2(\tilde{P})$. Thus, $T_{T_s} = f(\tilde{P}; t)$.

Considering durability τ for adhesive joints at non-isothermal heating conditions it may be evaluated making use of a well known Bailey criterion if the superposition principle of destruction is fulfilled, supposing that $T = T(t)$:

$$\int_{t=0}^{t_{T_{T_s}}} \frac{dt}{\tau[\tilde{P}; T(t)]} = 1. \tag{3}$$

The calculation of τ is possible after the solution of (3) because $\tau = t_{T_{T_s}}$.

The method of solution of (3) is defined by the type of subintegral function This function, apparently, must correspond to the durability equation for the object being tested and the test conditions used.

Supposing that in the case being considered the Eq. (1) is used to describe durability as in the case of isothermal heating, we obtain:

$$\tau = \tau_0 \exp\left(\frac{U_0 - \gamma\tilde{P}}{RT}\right). \tag{4}$$

Furthermore, the type of Eq. (4) is defined by that of the function $T(t)$. In the general case of non-isothermal heating

$$\frac{dT}{dt} = f(t) \quad \text{and} \quad T = \int f(t)\,dt + c,$$

where $c = T_0$ correspond to the initial temperature of the test (at $t = 0$).

In the simplest case when the law of variation $T(t)$ is linear (dT/dt = const.)

$$T = at + T_0. \tag{5}$$

Substituting $T = T_{T_s}$ and $t = t_{T_{T_s}}$ into Eq. (5) and solving it in terms of T_{T_s} we obtain:

$$\frac{T_{T_s} - T_0}{a} = t_{T_{T_s}}, \tag{6}$$

where $t_{T_{T_s}} = \tau$. Substituting $t_{T_{T_s}} = \tau$ from (6) to (4) we obtain:

$$\frac{T_{T_s} - T_0}{a} = \tau_0 \exp\left(\frac{U_0 - \gamma \dot{P}}{RT(t)}\right). \tag{7}$$

Equation (7) is fulfilled at $T(t) = T_{T_s}$. Thus, (4) and (7) are durability equations in non-explicit form. The possibility of using index T_{T_s} for evaluation of heat resistance as durability is based by Eq. (7).

The discussion of this question is based on the example when durability is described by the formula of Eq. (1) type and $T(t)$ is a linear function. It is easy to show that in the cases when durability is described by some other formula, and dependence $T(t)$ is non-linear, the possibilities of using stability loss temperature for evaluation of heat resistance as durability are preserved, and the application of formula (3) is justified only by the existence of the superposition principle of destruction.

METHODS FOR DETERMINING STABILITY LOSS TEMPERATURE

The principle of thermomechanical testing[5] for determining stability loss temperature is used. Different types of objects, i.e., butt joints, lap joints, peeling strips might be subjected to testing. The diagram of defining T_{T_s} for adhesive lap joints for shear testing is shown in Figure 1. In the area of the lap edge two markers are put on the object, one on each adherent element. The object is enclosed in a thermal chamber. One end of it is rigidly fixed, the other is loaded by constant or variable loading. Then the object is heated at certain intensity of time-varying temperature and the change of the distance between the two markers is fixed Δl. After the test the graph Δl *vs.* T is built-up and T_{T_s} is found by analogy, the same as with flow temperature of materials (shown in the figure).

According to this method the temperature indicating the beginning of failure or non-reversible shear (displacement) of adherends with respect to one another may be accurately defined. Checking of non-reversibility of the shear may be accomplished by unloading the object—the temperature consequently is enhanced and if Δl is not decreased the deformation is, therefore, non-reversible.

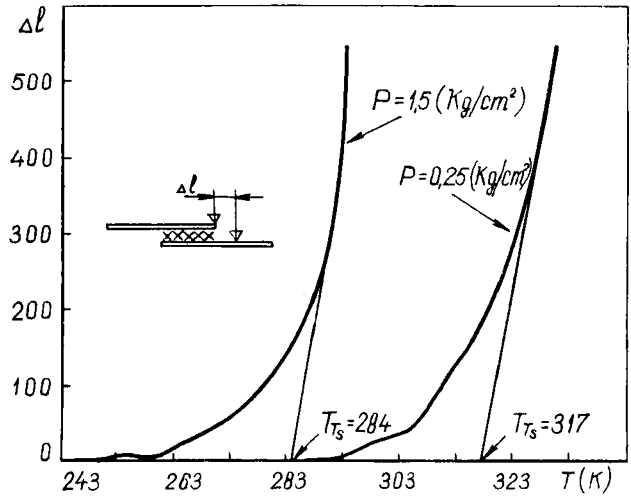

FIGURE 1 Curves Δl *vs.* T and methods of determining stability loss temperature.

It should be noted that the above method with the exception of T_{T_s} determination principally offers the possibility of obtaining thermomechanical curve of the adhesive in the adhesive joint† as well, which may be different from that for its free films. Therefore this method enables to define the whole set of properties of the adhesive in the joint (e.g., transition temperature, relaxation ability, structural changes).

The investigation of the methods for application of stability loss temperature for heat resistance (service ability) characteristics of adhesive joints of soft materials showed that after the occurrence of the moment of stability loss, even at small loadings, the decomposition of the object into two parts makes its appearance within some seconds or even less. During this time interval the temperature increases negligibly (within the error range of the test) with the exception of those rather rare cases when after the beginning

† For this it is necessary that the adherends during the experiment should be rigid to provide non-deformability. This may be achieved, for example, by increasing their thickness to the required value or applying loading of such value which practically does not cause any appreciable deformations. Note that the latter corresponds to the principle of thermomechanical testing.

of non-reversible shear the processes of structuring in the adhesive start with the increase of temperature.

Therefore, for practical purposes, when the test is made at constant loading and does not require especially high accuracy, the method for determining T_{T_s} may be simplified. In this case, the setting up of dependence $\Delta l(T)$ is not necessary and the temperature alone is fixed corresponding to the decomposition of adhesive joint into 2 parts (the moment when the constant load adjusted to one end of the object falls or the moment of the variable load drop).

In the experiments for peeling or double peeling, T_{T_s} may be determined as the temperature corresponding to the initial moment of failure of a loaded adhesive (constant or varying with time).

EXPERIMENTAL DATA AND DISCUSSION

Experimental data for determining stability loss temperature dependence on the load values ($\tilde{P}_i$ = const.) are shown in Figure 2 and dependence on the adhesive layer thickness (h) are shown in Figure 3. The adhesive joints shown in Table I were subjected to testing. It is evident that the dependences $T_{T_s}(\tilde{P})$ and $T_{T_s}(h)$ are straightline in logarithmic coordinates and of decreasing character. Consequently they are hyperbolic:

$$T_{T_s} = a_1 \tilde{P}^{-k_1}, \tag{8}$$

$$T_{T_s} = a_2 h^{-k_2}. \tag{9}$$

a_1, k_1, and a_2, k_2 are the parameters of the equation (8) and (9) respectively. Their values for the systems tested are given in Table I.

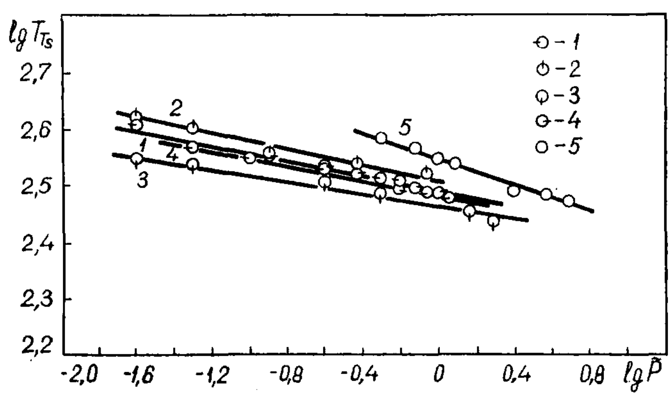

FIGURE 2 Stability loss temperature T_{T_s} dependence on loading $\tilde{P}$. The numbers of the curves correspond to the number of variants in Table I.

TABLE I

	Elements of adhesive joints			Dependences $T_{T_s}(\tilde{P})$ Equation (8)				Dependences $T_{T_s}(h)$ Equation (9)		
	Adherend	Adhesive	Thickness of the adhesive h (mm)	parameters a_1	k_1	Value range of $\tilde{P}$(kg/cm^2) and T_{T_s} (K)	Loading $\tilde{P}$ (kg/cm^2)	parameters a_2	k_2	Value range of h (mm)
1	Diacetate cellulose film	SKN–40	0.15	304	0.07	0.025–1.125 403–299	0.100	335	0.028	0.01–0.58
2	The same	Adhesive on the polychloroprene basis	0.05	322	0.07	0.025–0.875 417–331	0.125	317	0.020	0.03–0.58
3	PVC film (33.3% Dioctylphtalate)	SKN–40	0.12	289	0.06	0.025–2.00 353–272	—	—	—	—
4	Chrome Leather	The same	0.15	307	0.06	0.05–1.00 365–307	0.250	316	0.027	0.02–1.10
5	The same	Polyurethane adhesive Bostik 2531	0.11	351	0.19	0.50–5.00 383–295	1.250	317	0.030	0.08–1.04

Notes: 1. The mean relative error of the approximation of dependences $T_{T_s}(\tilde{P})$ and $T_{T_s}(h)$ according to Eqs. (8) and (9) in all cases did not exceed 1–1.5%.

2. The experiments were carried out at linear law of temperature change with time with the intensity of 2 K/min (accordingly, 2 deg/min, C).

The physical value of these parameters may be explained in terms of their mathematical values. Thus, a_1 corresponds to the T_{T_s} value for $\tilde{P} = 1$; therefore, this parameter may be applied as a comparative characteristic of relative values T_{T_s} for various adhesive joints. The parameter k_1 is the intensity index of varying values of T_{T_s} with varying load $\tilde{P}$ and, thus, characterises the creep resistance of adhesive joints.

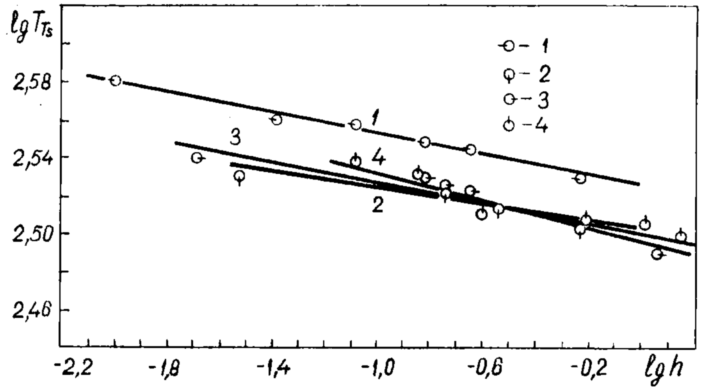

FIGURE 3 Stability loss temperature T_{T_s} dependence on the thickness of the adhesive layer h. The numbers of the curves correspond to the number of variants in Table I.

Parameters a_2, k_2 make the same sense in relation to the thickness of the adhesive layer.

The existence of the dependence $T_{T_s}(h)$ of (9) type proves that heat resistance of adhesive joints with the elastomer type adhesive depends on the thickness of the adhesive layer. It may be of practical value for products while designing optimum geometric parameters of adhesive joints.

It is interesting to note that the relationship $T_{T_s}(\tilde{P})$ for double peeling test also has the form corresponding to the formula (8). The values of T_{T_s} for any kind of test slightly depend on the nature of the law of temperature changes with time (linear, hyperbolic, logarithmic, etc.). If, for example, for linear law of temperature change with time it reached the values of $T_1 \sim T_{T_s}$ with the time Δt the condition $T_1 \sim T_{T_s}$ approximately (with the accuracy of some degrees) will be fulfilled at any other selected law of permanent temperature gain, if the temperature reaches T_1 value within the same time range Δt. On the other hand, as will be shown below, the values of T_{T_s} essentially depend on the intensity of temperature change with time.

This, apparently, is the evidence that index T_{T_s} is a representative of heat resistance characteristic or temperature range of service ability of the adhesive joint.

The possibilities of applying formula (3) for determining T_{T_s} by calculation with durability equations of adhesive joint present are illustrated by the results given in Tables II and III.

TABLE II

$\tilde{P}$ (kg/cm²)	Experimental data $\bar{t}_{T_{T_s}}$ (sec)	$\bar{T}_{T_s}$ (K)	Calculated data $t_{T_{T_s}}$ (sec)	T_{T_s} (K)
1.0	3060	405	3180	409
2.0	2490	386	2420	383.7
3.0	2040	371	2020	370.3
4.0	1650	358	1750	361.3
5.0	1500	353	1550	354.7

In this table the mean arithmetical experimental values of time up to the moment of stability loss $\bar{t}_{T_{T_s}}$ and temperature $\bar{T}_{T_s}$ calculated after six tests are given. The interval of variations of experimental values did not exceed 3 K.

TABLE III

$\tilde{P}$ (kg/cm²)	T_0 (K)	Experimental data a (K/sec)	$\bar{t}_{T_{T_s}}$ (sec)	$\bar{T}_{T_s}$ (K)	Calculated data $t_{T_{T_s}}$ (sec)	T_{T_s} (K)	$\Delta = \bar{T}_{T_s} - T_{T_s}$
		0.03465	632	344.9	540	341.7	3.4
3.0	323	0.0970	312	353.3	268	349.0	4.3
		0.03465	1124	342.0	1104	341.3	1.6
3.0	303	0.10548	517	357.6	440	349.4	6.4
		0.03465	874	333.3	836	332.0	1.2
4.0	303	0.1155	415	351.0	324	340.0	11.0

Consult Table II.

The durability equation of (2) type in this case was obtained using common methods[1] from experimental data of determining durability at some constant temperatures and constant loadings. Accordingly, the dependences $\tau(T)_{\tilde{P}_i}$ and $\tau(\tilde{P})_{T_j}$ were set up and after their mathematical description the durability equations $\tau(\tilde{P}; T)$ were obtained. Afterwards, these equations were substituted in (3) and for the given law of $T(t)$ T_{T_s} was determined by calculation. Similarly, for the same law of $T(t)$, the values of T_{T_s} were determined experimentally and compared with calculated ones.

In Table II the results for adhesive joints of PVC artificial leather, of Japanese production (VL–3), and footwear rubber "Kozhvolon" with the adhesive which is the composition on the basis of butadienacrilonitrile rubber SKN–40 and melamineformaldehyde resin are presented. The durability equation for these adhesive joints had the following form:

$$\tau = 10^{-13}\bar{P}^{-5,4} \exp\left(\frac{44.8-4.4 \cdot 10^{-2}T}{RT}\right).$$

The experimental definition of T_{T_s} was carried on at constant loadings of various values and at linear law of temperature variation with time $T = 303+2t$.†

In Table III the results for adhesive joints of cotton fabric (Kirza) and footwear rubber "Kozhvolon" with polychloroprene adhesive are presented. Durability equation is

$$\tau = 10^{-13}\bar{P}^{-4,6} \exp\left(\frac{31.0-1.7 \cdot 10^{-2}T}{RT}\right).$$

For experimental determination of T_{T_s}, as well as for the above case, constant loadings were applied and temperature was varied according to linearity law $T = at+T_0$ with different intensity (a, K/sec).

We can see from Tables II and III that at negligible intensity of temperature increase (in our case of the order of 2 deg/min for $a = 0.03465$) the calculated values of T_{T_s} coincide sufficiently well with experimental ones. At greater intensity (of the order of 6 deg/min for $a = 0.09$–0.11) the experimental values are higher than the calculated ones. It is in accordance with the thermo-fluctuational conception of strength[2] for which the destruction of the body occurs in time as a result of thermal fluctuations, and the gain of destroyed interatomic bonds as well as the intensity of fatigue crack development in the body depend on the quantity of thermal energy applied and accumulated by it.

Stability loss temperature is the limit temperature referring to the service ability of the adhesive joint. It depends, as was shown above, on the time and, apparently, for greater intensities of temperature increase during heating its values are greater. At this point it should be remembered that polymer bodies at short time thermal effect are capable of withstanding temperatures considerably higher than at long-time effect and this difference sometimes is tens of degrees and more.

The above mentioned experimental evidence of the dependence of T_{T_s} on the heating time also suggests the relationship between heat resistance and

† Since in the formulas (1), (2), (8), (9) the temperature is substituted according to K scale, here it is also given in the same scale. For this case it corresponds to the intensity change value of 2 deg/min, C.

durability and confirms the index T_{T_s} as a boundary characteristic of heat resistance and, consequently, service ability of adhesive joints.

CONCLUSIONS

For determining service ability range of adhesive joints the supplied characteristics of stability loss temperature T_{T_s} might be used.

For obtaining complete characteristics of heat resistance of adhesive joints the evidence of the dependence of stability loss temperature T_{T_s} on applied loading is of primary importance. On designing geometric parameters of adhesive joints it is useful to know the dependence of T_{T_s} of adhesive joints on the layer thickness of the adhesive, and on designing technological parameters of thermal effect on the objects having adhesive joints the dependence of T_{T_s} on the law of temperature variation (mostly on the intensity) with time.

If, however, the law of temperature variation with time $T(t)$ and geometric parameters of the joint are set *a priori*, for example, as a result of technological and operational regulations, then the dependence $T_{T_s}(\tilde{P})$ fully determines the range of service ability of adhesive joints.

Evidently, in such cases for determining the dependence $T_{T_s}(\tilde{P})$ it is necessary to apply temperature rate corresponding to the conditions for which heat resistance is to be evaluated (in other words, to select appropriate parameters of $T(t)$ function). This enables the evaluation of heat resistance under the conditions optimally approaching real ones instead of common laboratory methods which, as a rule, are able to give rather indirect and approximate information.

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