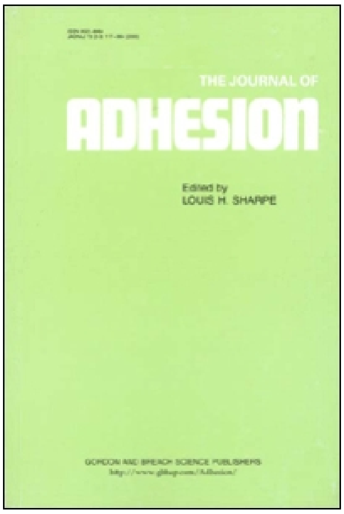

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Outline of an Algorithm for Computation of the Strength of Polymer Adhesive Joints

A. B. Silberman[a]; L. M. Pritykin[b]; V. L. Vakula[c]; I. I. Silberman[d]
[a] Institute of Physical Chemistry, USSR Academy of Sciences, Moscow, USSR [b] Institute of Civil Engineering, Dnepropetrovsk, USSR [c] Moscow Institute of Applied Biotechnology, The Chair of Physical and Colloid Chemistry, Moscow, USSR [d] Moscow Institute of Fine Chemical Technology, USSR

To cite this Article Silberman, A. B. , Pritykin, L. M. , Vakula, V. L. and Silberman, I. I.(1992) 'Outline of an Algorithm for Computation of the Strength of Polymer Adhesive Joints', The Journal of Adhesion, 38: 1, 1 — 18

To link to this Article: DOI: 10.1080/00218469208031264

URL: http://dx.doi.org/10.1080/00218469208031264

J. Adhesion, 1992, Vol. 38, pp. 1–18
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United Kingdom

Outline of an Algorithm for Computation of the Strength of Polymer Adhesive Joints

A. B. SILBERMAN

Institute of Physical Chemistry, USSR Academy of Sciences, Moscow, USSR

L. M. PRITYKIN

Institute of Civil Engineering, Dnepropetrovsk, USSR

V. L. VAKULA*

Moscow Institute of Applied Biotechnology, The Chair of Physical and Colloid Chemistry,
33 Talalikhina Street, Moscow 109818, USSR

I. I. SILBERMAN

Moscow Institute of Fine Chemical Technology, USSR

(Received October 30, 1989; in final form January 7, 1992)

An algorithm based on hierarchical polymer structure is proposed for calculation of the adhesive joint strength. This hierarchy enables one to describe the behavior of polymer adhesive joints taking into account specific characteristics of all the levels by combining together physico-chemical concepts of the formation of adhesive systems and their fracture mechanics.

In order to prove the validity of the described approach electroless copper plated ABS-copolymers were studied experimentally.

The developed approach makes it possible to take into consideration the effect of the parameters characterizing the formation of an adhesive joint on its strength properties.

KEY WORDS strength of adhesive joint; fracture energy; loss function; macromolecule adsorption; computational method; adhesion science and technology; theory; experiment.

1 INTRODUCTION

The problems concerning evaluation and prediction of the strength of adhesive joints are usually studied within the framework of mechanics of solids. Such an approach seems to be quite natural but it appears to be somewhat inadequate, since a number of factors (such as the effect of the nature and structure of adhesive and

---

*Corresponding author

substrate surfaces, the conditions and kinetics of adhesion interaction, the area of interfacial contact, etc.[1]) are left beyond consideration.

The physical chemistry of the formation of adhesive systems[1] and their fracture mechanics[2] still remain separate fields of adhesion science, each with its own formalism and area of application. On the one hand, scientists can not study the laws of adhesive joint formation without employing the strength properties of the systems investigated, as the strength of adhesive joint appears to be the only measure of the effectiveness of interfacial interaction. This effectiveness is presumed to be proportional to the parameters of mechanical origin. However, this assumption seems to be neither evident nor universal. On the other hand, the nature of adhesives and substrates, as well as the conditions of interfacial contact formation, are usually ignored by engineers designing the adhesive joints. Thus, in developing new adhesives and adhesive bonding techniques it is difficult to rely on the data that they obtain.

Contradiction between the two approaches is one of the most important problems in the science of adhesion and may be overcome by combining them. We consider that the main trend to achieve this task involves further development of the energy approach describing both the formation and the fracture of the polymer adhesive joints.

In this paper we have made an attempt to describe the fundamentals of the integrated energy concept and to elaborate the algorithm for calculation of the adhesive joint strength.

2 THEORETICAL

2.1 Basic Parameters

We attempt to develop a general approach on the basis of the hierarchy specific for polymer structure.[3] Each level of this hierarchy gives rise to its respective type of adhesion interaction. Thus, one has to define these levels, describe the adhesion interaction within each level in terms of corresponding fundamental characteristics, and determine its contribution to the values of the resulting parameters.

Taking into account the proposed hierarchy of polymer structure,[3,4] the original version was developed consisting of five levels shown in Figure 1.

The lowest molecular level corresponds to the monomer molecule, the characteristics of which are determined by its chemical nature and structure.

The next level appears to be the result of combining monomer molecules by covalent bonds into a macromolecule. Insofar as its end-to-end distance significantly exceeds its cross section, the macromolecule can assume different conformations; it is this fact that makes it necessary to introduce the third level—the macromolecular one.

On the other hand, macromolecule conformation is the result of the movement of segments; therefore, the segmental level arises between the molecular and macromolecular ones.

Supermolecular structure of polymers (and corresponding level, respectively)

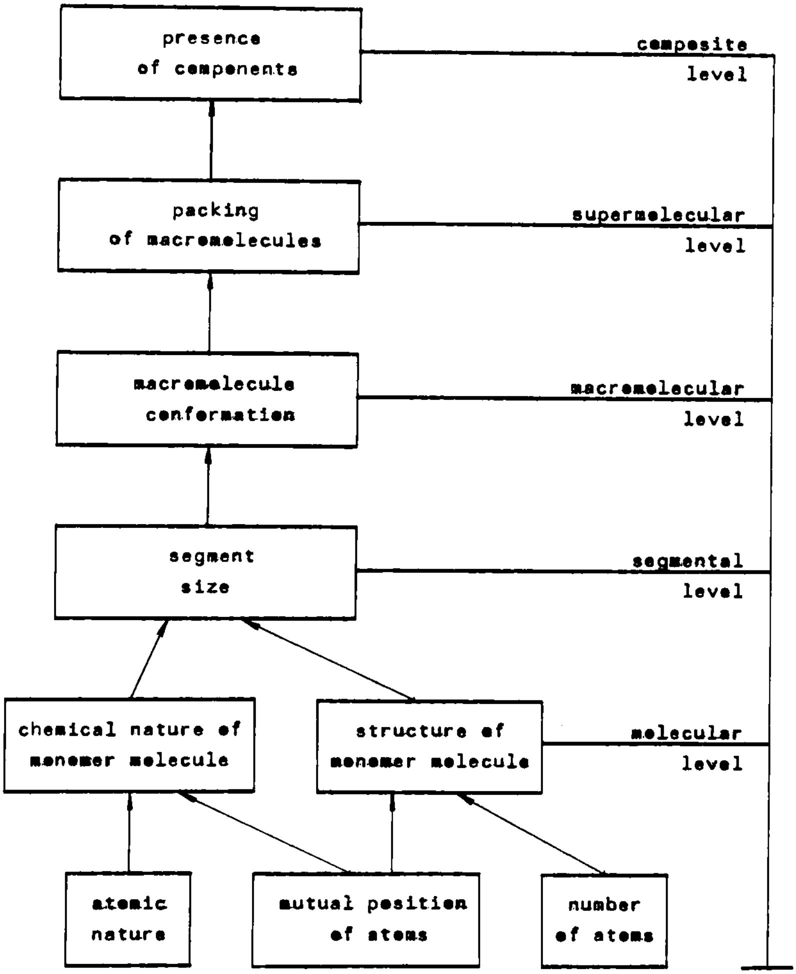

FIGURE 1 The hierarchy of polymer structure.

depends on mutual rearrangements and packing of macromolecules, which is determined by pre-history of the object.

Introduction of the various components (both low- and high-molecular) into the original polymer may result in the formation of a new microphase, thus giving rise to the highest of the considered levels—the composite level.

The hierarchy discussed enables us to describe the behavior of polymers taking into account specific characteristics of all of the levels mentioned above. This conclusion is valid for polymer adhesive joints as well. Neglecting the effect of the key parameters of polymers on the strength of polymer adhesive joints seems to give inadequate results.

Fundamental parameters at the molecular level are van der Waals radii, R_a, and volumes, V_a, of the corresponding atoms. These parameters govern the structure of the repeating unit of the macromolecule chain; their values have been tabulated.[5]

The parameters chosen to characterize the chemical nature of a monomer molecule are more complex. According to polarization theory, the refractive index, n, and refraction, r, can be used for this purpose.[1] In fact, these characteristics are closely connected with both cohesive[6] and surface[7] properties of polymers.

As to segmental level, it seems natural to evaluate the size of the segment by the number of links, s, in a freely moving unit. On the one hand, s is equal to the ratio of the cohesive energies of the segment (U^{s}_{coh}) and of the repeating unit ($U^{(1)}_{coh}$).[8] On the other hand, the movement of structural units under consideration may be more precisely described by the parameter of hindered rotation, f,[9] related to s. s can be experimentally evaluated within an assumed temperature range, the effect of internal stresses being ignored. Within the framework of the scaling concept[10] another independently moving kinetic unit, a so-called blob, is used in place of the thermodynamic segment. Therefore, s is substituted for the number of links in the blob, g, its size depending on the temperature, T, and the internal stress, γ^{b}_{a} (s is calculated by averaging g over T and γ^{b}_{a}).

The conformation of macromolecules, characterizing the behavior of a polymer on the macromolecular level, is governed by the chain end-to-end distance. When the values of V_a and R_a are known, it is sufficient to use the molecular mass, M, for the calculation of s. On the other hand, we have the molecular mass dependence of polymer surface energy.[11]

At the higher levels of the hierarchy (supermolecular and composite) the microscopic approximation is replaced by the macroscopic one, when the behavior of the system can be described in terms of continuum mechanics. Among them the viscosity, η, and the internal stress, γ^{b}_{a}, are of main importance for the description of the polymer's rheology, which is the most sensitive to the presence of other components.

Thus, the strength of adhesive joints may be expressed in terms of ten basic characteristics of a polymer: R_a,[5] V_a,[5], n,[7] $U^{(1)}_{coh}$,[5] U^{s}_{coh},[8,12] f,[13,14] g,[10] M,[15] η[16] and γ^{b}_{a}.[17]

To take into account the effect of the substrate, two parameters involving the molecular interaction between the adhesive and the substrate are added to this set: the interfacial energy, $U^{(1)}_{if}$, and the length of interfacial bond, l_{if}.[18] The last two parameters can be determined either by studying the formation of molecular contact area or by means of a method discussed below.

The whole set of 12 parameters is nothing but a data bank for the development of the algorithm to compute the strength, P_{Ad}, of a polymer adhesive joint.

2.2 Basic Concepts of the Algorithm

The adhesive joint strength, P_{Ad}, cannot be calculated using the listed 12 parameters on the basis of the present state of adhesion theory. We made an attempt to solve this problem by introduction of a hierarchical approach starting with the adhesion interaction at the highest levels.

To describe the adhesion interaction in terms of supermolecular and composite levels, the formalism of continuum mechanics can be used, taking into account, in addition, the effect of rate-temperature conditions of failure.

According to numerous experimental data, the rate-temperature dependence of the fracture energy, G^c_{Ad}, is written as follows[19]

$$G^c_{Ad} = G^o_{Ad}\, \phi_{Ad}\, (\epsilon, v, T) \tag{1}$$

The function $\phi_{Ad}\, (\epsilon, v, T)$ has not yet been analytically described within the framework of the present concepts.[19,20]

The work required for the fracture of a unit of interfacial area is

$$W = \int_0^{\epsilon_d} P(\epsilon)\, d\epsilon \tag{2}$$

The time-dependence of stress, $P(t)$, is given by an integral within the entire time period of deformation $\epsilon(z)$ weighted by the hereditary function $K(t-z)$:[21]

$$P(t) = \int_{-\infty}^{t} K(t-z)\, \epsilon(z)\, dz \tag{3}$$

For polymers, the best result can be obtained when the hereditary function is as follows:

$$K(t-z) = \sum_{n=1}^{N_p} K^n \frac{E^n}{\tau_i^n} \exp\left(-\frac{t-z}{\tau_i^n}\right) \tag{4}$$

At a constant rate of failure (in the case of the plane-strained state)

$$\epsilon(z) = vz \tag{5}$$

Substituting (4) into (3)

$$P(t) = \sum_{n=1}^{N_p} E^n v t \left[1 - \frac{\tau_i^n}{t}\left(1 - \exp\left(-\frac{t}{\tau_i^n}\right)\right)\right] \tag{6}$$

At $t = \epsilon / v$

$$P(\epsilon) = \sum_{n=1}^{N_p} E^n \left[\epsilon - v\tau_i^n \left(1 - \exp\left(-\frac{\epsilon}{v\tau_i^n}\right)\right)\right] \tag{7}$$

Combining Eqs (7) and (2) yields

$$W = \sum_{n=1}^{N_p} \frac{E^n \epsilon_d^2}{2}\left[1 + \frac{v^2(\tau_i^n)^2}{\epsilon_d^2}\left(1 - \exp\left(-\frac{\epsilon_d}{v\tau_i^n}\right)\right) - \frac{\epsilon_d}{v\tau_i^n}\right] \tag{8}$$

At $v \gg 1/\tau_i^n$ the relaxation processes do not take place and the polymer breaks like a brittle body. In this case, at $N_p = 1$ according to (7):

$$P^c = E^1\, \epsilon_d \tag{9}$$

and (8) can be rewritten as follows:

$$W = \frac{E^1\, \epsilon_d^2}{2} \tag{10}$$

On the other hand, in accordance with the linear theory of brittle fracture, P^c and W are given by:

$$P^c = \frac{K_I}{(\pi a)^{1/2}} \tag{11}$$

$$W = 2\,G_{Ad} = \frac{K_I^2}{2E^1}\,a \tag{12}$$

Comparing (9) with (11) and (10) with (12) and taking into account that $K_I = P^c(\pi a)^{1/2}$ (for the plane-strained state)

$$\epsilon_d = \frac{K_I}{E^1\,(\pi a)^{1/2}} = \frac{P^c}{E^1} \tag{13}$$

Hence,

$$P(\epsilon) = \sum_{n=1}^{N_p} \frac{K_I^n}{(\pi a)^{1/2}} \left(1 - \frac{v\tau_i^n}{\epsilon}\left(1 - \exp\left(-\frac{\epsilon}{v\tau_i^n}\right)\right)\right) \tag{14}$$

$$W = 2 \sum_{n=1}^{N_p} G_{Ad}^{on}\, a\, \phi_{Ad}^n (\epsilon, v, T) \tag{15}$$

where

$$\phi_{Ad}^n (\epsilon, v, T) = 1 + \frac{v^2(\tau_i^n)^2}{\epsilon_a^2}\left(1 - \exp\left(-\frac{\epsilon_d}{v\tau_i^n}\right)\right) - \frac{\epsilon_d}{v\tau_i^n}$$

(the index, n, refers to the n-th polymer phase).

An adhesive joint is fractured when the work of external forces increases up to the critical value of G_{Ad}^c (energy criterion) or when the applied stress attains the critical value of P^c (stress criterion). The stress criterion is predominantly used when designing adhesive joints. However, it should be noted that the energy approach has a number of advantages including the independence of G_{Ad}^c on the geometry of adhesive joints.[22] Using Eqs (14) and (15) one can express both basic parameters (pertaining to these two approaches) in terms of relaxation properties of the polymer adhesive, thus combining them.

Substituting the function $\epsilon(z)$ (Eq (5)) into (3) makes it possible to calculate the values of adhesive joint strength at the different types of loading under arbitrary conditions.

Let us denote the strength of the adhesive-substrate interaction per unit interfacial area as F_{Ad}. Then for $N_p = 1$ at $v \gg 1/\tau_i^n$

$$P_{Ad}^c = \begin{cases} E^1\,\epsilon_d \text{ for cohesive failure: } F_{Ad} \geqslant E^1\,\epsilon_d \\ E^1\,\epsilon_a \text{ for adhesive failure: } F_{Ad} < E^1\,\epsilon_d \end{cases}, \tag{16}$$

where

$$\epsilon_a = \frac{F_{Ad}}{E^1} \tag{17}$$

When F_{Ad} is known, the rate-temperature dependences of the adhesive joint strength can be described in terms of Eqs (17), (16), (14) and (7).

The adhesive joint is a result of the formation of the interfacial area and, consequently, of the molecular contact. Therefore, F_{Ad} depends not only on the strength of interaction between the repeating unit of the adhesive and the substrate, F_{if}, but also on the ratio of the actual interfacial contact area to its maximum value. This dependence can be written as follows:[23]

$$F_{Ad}(t) = \int_{0}^{t} A(z) \int_{l_{if}}^{\infty} \frac{\partial N(t-z,x)}{\partial z} F_{if}(x)\, dx\, dz \tag{18}$$

The formation of the molecular contact can be thought of as adsorption of consecutive repeating units onto the substrate surface.[1] Thus, F_{Ad}, which is inherently a parameter pertinent to the highest levels of the hierarchy of polymer structure, appears to be governed by adsorption. The latter may be described at the lower hierarchical levels, *viz.* macromolecular and segmental. Thus, within the framework of the hierarchical approach, mechanical and physico-chemical theories of adhesion complement each other.

Let us consider the process of molecular contact formation. The time interval between the states with $(i-1)$ and i adsorbed links depends only on the states with $(i-2)$ and $(i+1)$ absorbed links. Hence, such a process can be described in terms of the Markovian chains method with continuous time. Then we can write Kolmogorov's equations:

$$\left\{\begin{aligned} \frac{dp_{ij}}{dt} &= \sum_{k} \lambda_{ik}\, p_{kj} \\ \frac{dp_{ji}}{dt} &= \sum_{k} \lambda_{ki}\, p_{jk} \end{aligned}\right. \tag{19}$$

where p_{ij} is the probability of macromolecule transfer from the state with i adsorbed links to the state with j adsorbed links $(j=\{i-1, i, i+1\})$; λ_{ij} is the first mode of this transfer. Solving the Eqs (19) with boundary conditions we obtain:

$$\begin{aligned} \frac{N(t)}{N_l} = s^{-1} \Bigg\{ & \sum_{i=1}^{N_l} \sum_{j=i-1}^{i+1} [1 - C^1_{ij} \exp(-\lambda^1_j t)] + \\ & \frac{N_l}{s} \sum_{i=1}^{s} [1 - (\sum_{j=1}^{s} C^2_{ij} \exp(-\lambda^2_j t)) (\sum_{j=1}^{N_l/s} C^1_{ij} \exp(-\lambda^1_j t))] \Bigg\} \end{aligned} \tag{20}$$

where N_l is the total number of macromolecule links; C^1_{ij} is the characteristic vector referring to adsorption of the different chain segments (*i.e.*, intersegmental adsorption); C^2_{ij} is the characteristic vector referring to adsorption of the different links of one and the same segment (intrasegmental adsorption); τ^1_j and τ^2_j are the times of inter- and intrasegmental adsorption, respectively; $\lambda^1_j = 1/\tau^1_j$ and $\lambda^2_j = 1/\tau^2_j$ are characteristic values of the matrices λ^1_{ij} and λ^2_{ij} corresponding to inter- and intrasegmental adsorption, respectively.

The values of C^1_{ij} and C^2_{ij} were calculated as follows.[18] To find the elements of the matrix of transfer probabilities the spline-function of the distribution of the polymer chain end-to-end root-mean-square distance (see Figure 2) was employed. Area 1 in this figure corresponds to the movement of links within the blob with a non-Gaussian distribution function:

$$P^1_N(\bar{R}) = \left(\frac{\bar{R}}{\xi}\right)^g P^1(\xi) \tag{21}$$

area 2 corresponds to the movement of blobs with a Gaussian distribution function:

$$P^2_N(\bar{R}) = \exp\left(-\frac{3\bar{R}^2}{2R^2}\right) P^2(\xi) \tag{22}$$

where $P^i(\xi)$ is the corresponding normalizing function.

The problem of numerical evaluation of the matrix elements is solved within the framework of the scaling concept[10] according to which the term "blob" is used instead of "thermodynamic segment" (accordingly, s is replaced by g—number of links in the blob).

When a macromolecule is deformed by the force, F, at temperature, T, the average distance between the chain ends is expressed as follows:

$$< | \bar{R} | > = N_l l \left(\frac{Fl}{K_B T}\right)^{2/3}, \frac{Fl}{K_B T} \gg 1 \tag{23}$$

where l is the length of the repeating link.

The number of links in the blob in the deformed macromolecule, g_f, is given by:

$$g_f = \left(\frac{K_B T}{Fl}\right)^{5/3} \tag{24}$$

and the length of each blob $\xi = l\, g_f^{3/5}$.

According to Taylor's equation[10]

$$R^2 = l^2 N_l f \tag{25}$$

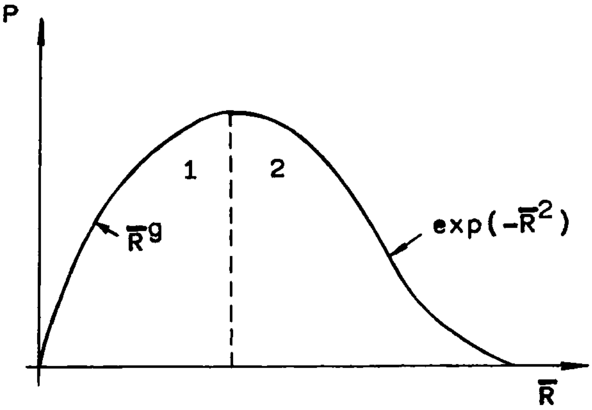

FIGURE 2 Distribution function for the polymer chain end-to-end distance.[10]

According to the scaling concept

$$R^2 = l^2 n_l^{\nu} \tag{26}$$

where ν is a scaling parameter characterizing the change of dimension of the macromolecule space.

Combining Eqs (25) and (26) yields

$$\nu = \frac{\lg f + \lg N_l}{\lg N_l} \tag{27}$$

For a three-dimensional case the size of a blob in a non-deformed macromolecule g_l is expressed as:

$$g_l = \nu/6 \tag{28}$$

Combining this relationship with Eqs (24) and (27)

$$g = \begin{cases} g_l = \dfrac{\lg N_l}{6\,(\lg f + \lg N_l)}, & g_l < g_f \\ g_f = \left(\dfrac{K_B T}{Fl}\right)^{2/3}, & g_l > g_f \end{cases} \tag{29}$$

$$R^2 = \xi^2 N_l/g \tag{30}$$

2.3 The Algorithm and the Procedure for its Application

The above approach makes it possible to derive the relationships between the selected parameters (Section 2.1) which can be used as a basis for calculating the kinetic parameters of the adhesive joints and the values of its strength. Thermodynamic, mechanic and geometric parameters, both calculated and experimental, used for this purpose, are listed in Table I. The scheme of the algorithm presented in

TABLE I
Parameters of the algorithm*

Objects Parameters	Adhesive	Adhesion interaction	Adhesive joint
Molecular	$\frac{M, n, r}{g, s, f, \eta}$	$\frac{l_{if}, U_{if}^{(1)}}{\tau_{Ad}, N(\tau)}$	
Thermodynamic	$\frac{}{U_{coh}^{(1)}, U_{coh}^{s}, \sigma, T_g, T_m, T\ \ , T_f}$	$\frac{T}{U_{Ad}}$	$\frac{}{G_{Ad}, G_{Ad}^{o}}$
Mechanical	$\frac{\gamma_a^b, P_a^c}{E_a, \nu_a, \epsilon_a, \tau_\alpha, \tau_\beta}$	$\frac{P_{Ad}^c}{}$	$\frac{}{E_{Ad}^{\cdot}(\epsilon, v, T), P_{Ad}(v, T), \phi_{Ad}(\epsilon, v, T), P_{Ad}}$
Geometrics		$\frac{}{A(\tau)}$	$\frac{b_{Ad}, h_a, h_s, l_{Ad}, d_{Ad}}{}$

*Numerator—given parameters; denominator—calculated parameters

Figure 3 comprises all parameters, logistic and experimental, needed to calculate the discussed characteristics of the adhesive joint strength. Corresponding equations are either listed in this paper (they are numerated with the figures in parentheses) or are extracted from the references (these are given in brackets). Three blocks may be distinguished within the algorithm, each corresponding to one of the basic theoretical concepts of adhesion conventionally applied to interpret the behavior of adhesive joints.

Block I describes the formation of an adhesive joint in terms of physical chemistry of adhesion involving appropriate parameters. Block II is based on the formalism of continuum mechanics, particularly the hereditary theory of elasticity. Block III describes the fracture of adhesive joints of different geometry in terms of fracture mechanics. The interrelation of the three blocks reveals that, although these concepts are different, by their essence they complement each other within the framework of the methodology developed.

Let us describe the procedure of the application of the algorithm. Making use of the equations involved in Block I one can calculate the area of interfacial contact and the number of the adsorbed repeating links. The values of these parameters are determined from the characteristics of the adhesive and conditions of its interaction with the substrate. The surface energy of the adhesive is determined by the experimental values of the refractive indexes and the calculated values of refraction

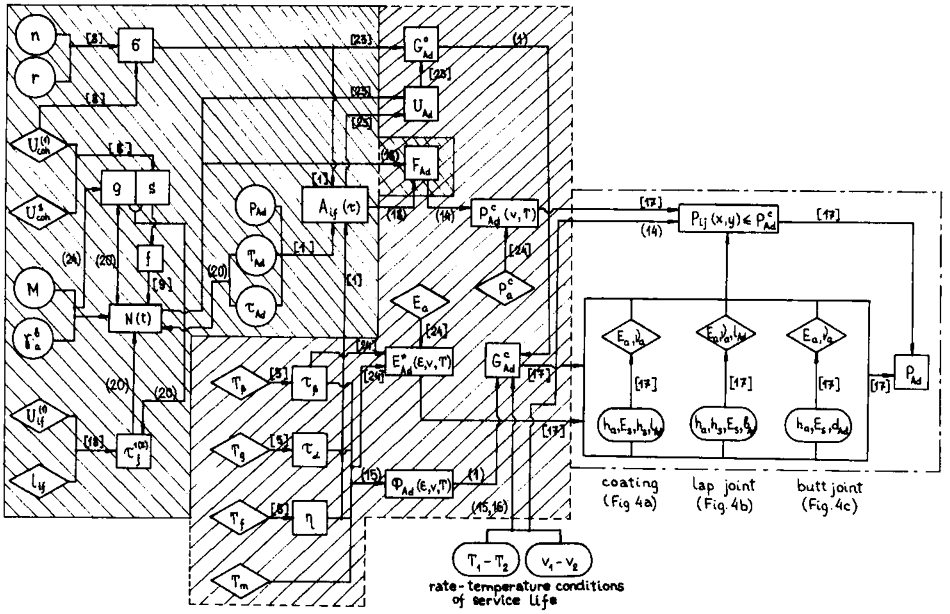

FIGURE 3 Algorithm layout

▧ —Block I, ▨ —Block II, ▭ —Block III.

Given parameters: ○—experimental, ◇ —calculated; parameters to be computed— ☐
Equations listed in this paper are numbered in parentheses, corresponding references are given in brackets.

and the cohesive energy of the repeating units. Insofar as the formation of interfacial contact depends on the parameter of hindered rotation, the cohesive energy of the segment and the number of links in the blob (according to Eq (29)) have to be employed. Using the results obtained, we can evaluate the number of adsorbed repeating links of the adhesive (*i.e.*, the number of interfacial bonds) as well as the value of interfacial area A_{if} and its dependence on the temperature, applied pressure and time of the adhesive joint formation. Thus, the strength of adhesion interaction F_{Ad} can be found.

In Block II, polymer internal fracture energy G^o is computed using the parameters calculated in the previous block: surface energy of the adhesive and the energy of adhesion interaction. The dissipative properties of the adhesive (the loss function ϕ_{Ad} (ϵ,v,T)), which are dependent on its relaxation characteristics, may thus be evaluated and the fracture energy of the adhesive joint G^c_{Ad} be found. Using the rate-temperature dependence for G^c_{Ad} we can choose the proper adhesive for the required service conditions.

Applying the logistic of Block III, one may calculate the strength of the adhesive joint P_{Ad} of definite geometry (Figure 4), either in terms of the method of finite elements or by means of fracture mechanics. The preliminary results of its verification were already discussed.[25]

In the next section we describe the operation of the Blocks I and II and the experimental verification of the results obtained.

3 BLOCKS I AND II: EXPERIMENTAL VERIFICATION

3.1 Materials and Methods

In order to prove the validity of the described approach acrylonitrile-butadiene-styrene (ABS) copolymers-electroless copper systems were studied experimentally. Two grades of ABS-plastics were used: Lustran® PG-299 (Monsanto, USA) and ABS-2020 (Plastpolymer, USSR).

The test samples were prepared as follows: 10 × 10 cm polymer plates were etched for 10 min in an aqueous solution of CrO_3 (400 g/l) + H_2SO_4 (400 g/l) at 62 ± 2°C.

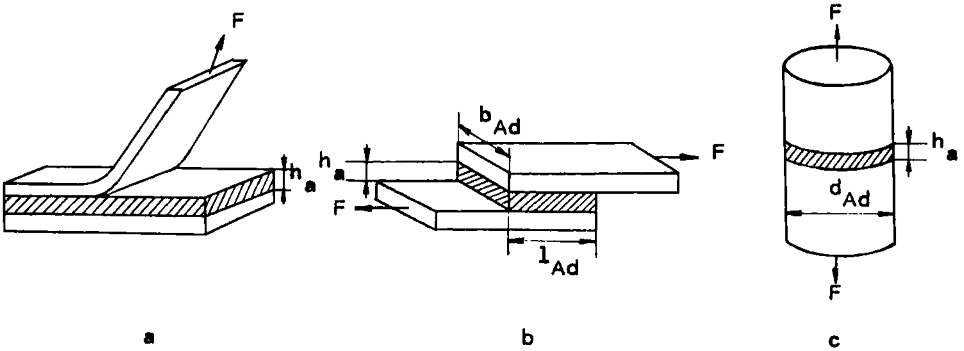

FIGURE 4 Main geometry of adhesive joints: a—coating, b—lap joint, c—butt joint.

After flushing, the samples were neutralized for 10 min in aqueous NaOH (400 g/l) solution and accelerated for 5 sec in aqueous HCl (150 g/l) solution. Then the samples were treated in an activating solution ($PdCl_2$—1 g/l, $SnCl_2 \cdot 2H_2O$—20 g/l, HCl—120 g/l, NaCl—95 g/l) at room temperature for 5 min. After washing, the samples were electroless plated with copper in the following solution: $CuSO_4 \cdot 5H_2O$ (30 g/l), K,Na = tartrate (190 g/l), NaOH (30 g/l, to pH = 12.8), $NiCl_2 \cdot 6H_2O$ (5 g/l), $Na_2CO_3 \cdot 12H_2O$ (30 g/l), $Na_2S_2O_3$ (1 mg/l), CH_2O (formaldehyde) (37%—15–20 ml/l) at room temperature for 25 min.

After final washing and pickling, the samples were electroplated to obtain 30 μm thick copper films and annealed at different temperatures for 6 hours.

The adhesive joints were tested by peeling, with a precision 0.48 N, within the wide range of rate-temperature conditions. Spectra of internal friction were registered in the wide range of temperatures using the universal torsion pendulum method. The control samples (without electroplating) were also examined by means of this method.

3.2 Results and Discussion

Dependence of $P_{Ad}/E^1\epsilon_d$ *vs* $v\tau_i^n/\epsilon$ obtained according to Eq (7) for $N_p = 1$ is shown in Figure 5. Using the above mentioned coordinate axes makes it possible to apply this dependence to polymers with different relaxation times. The curve is similar to that reported by Yamamoto *et al.*[26] for cohesive failure of polymer adhesive joints. They used the method of finite elements but did not succeed in determining an analytical expression for the P(v) function. The rate dependences of the strength of adhesive joints, obtained experimentally for elastomers[19,20] and plastomers[27] are similar to those shown in Figure 5. Figure 6 shows the experimental results describing the rate-temperature dependences of the strength of adhesive joints. At $\lg va_T = 0$ (a_T is the WLF factor) the strength decreases abruptly. Using the values of the strength within the interval $-7 < \lg va_T < -3$, values for F_{Ad} and ϵ_a were calculated (Table II).

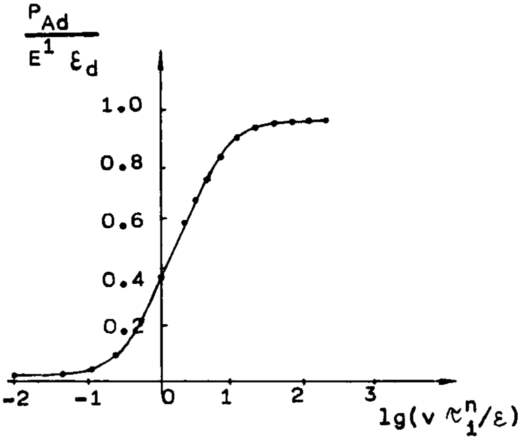

FIGURE 5 The influence of test conditions on the strength of ABS-copolymer adhesive joints.

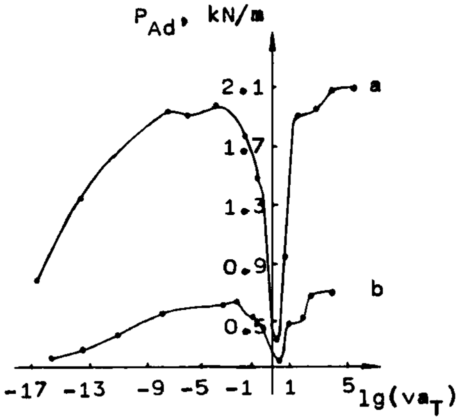

FIGURE 6 Rate-temperature dependences of the peel strength of the electroless copper plated ABS-copolymers: a—Lustran® PG-299, b—ABS-2020.

TABLE II
Adhesion and mechanical properties of ABS-copolymers

Type of polymer	F_{Ad}, kN/m	E_a, $\times 10^3$ MPa	ϵ_d, %	W, $\times 10^{-5}$ J/cm
ABS-2020	0.7	2.0	0.35	1.225
Lustran® PG-299	2.1	2.7	0.77	8.16

Thus, the developed approach is valid for experimental data which may be interpreted within the framework of the higher levels (supermolecular and composite) of structural hierarchy; moreover, it enables one to evaluate F_{Ad}, which is the parameter characterizing interaction at the lower hierarchical level (see Figure 1).

Computation of the kinetics of adhesive joint formation was carried out for the model system styrene-butadiene rubber (SBR)-electroless copper. This system was chosen because the glass-transition temperature of SBR varies within a wide temperature range depending on the styrene-butadiene ratio in the copolymer.

The results of computation are presented in Figure 7, where temperature dependences of the time of intersegmental adsorption, τ_1, ($\tau_1 = 1/\lambda_1$) for different glass-transition temperatures of SBR adhesive are shown as lg λ_1 *vs* 1/T (°K) plots. For $T = T_g$, λ_1 increases step-wise reaching its maximum value at $T = T_g + 60°$ and then drops sharply; such behavior is in accordance with numerous experimental data.[1]

The value of g, averaged over the wide temperature range, is equal to the number of links in the thermodynamic segment experimentally found for SBR.[12]

As was mentioned above, for the experimental study samples of electroless-copper-plated ABS were used. The most peculiar feature of the formation of adhesive joints under such specific conditions is that complete interfacial contact is achieved immediately. Then Eq (18) can be written as

$$F_{Ad}(t) = \int_0^t N(t-z,x)\, F_{if}(x)\, dx \qquad (31)$$

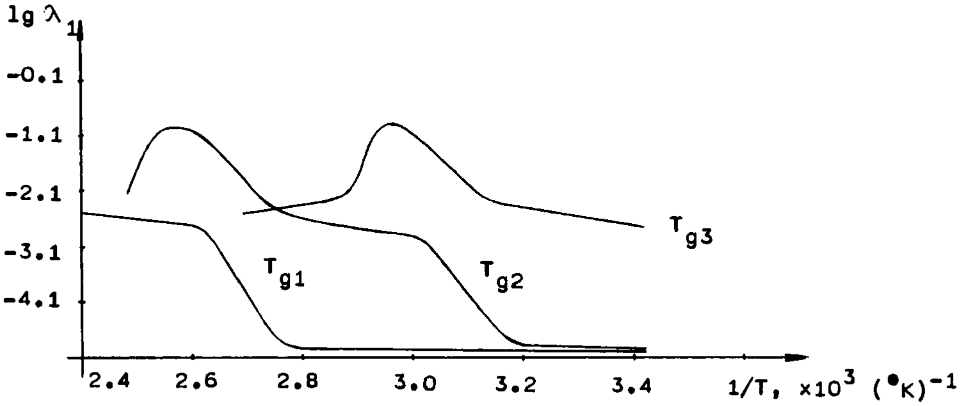

FIGURE 7 Calculated time of interblob adsorption *vs* reciprocal temperature for different SBR samples ($T_{g1} = 0°C$, $T_{g2} = 60°C$, $T_{g3} = 110°C$).

With chemisorption taking place during the formation of the adhesive joint, *i.e.* when chemical bonds of known energy and length are formed, Eq (31) is replaced by the following:

$$F_{Ad}(t) = F_{if} N(t) \qquad (32)$$

Taking into account Eq (17), the reduced adhesive joint strength P_{Ad}/P_{Ad}^{max} is equal to $N(t)/N_l$.

Making use of the data on phase structure of ABS-copolymers,[28] the dependences of $C_{ij}^{1,2}$, $\lambda_j^{1,2}$ and s *vs* annealing temperatures were calculated. Substituting temperature dependences of these parameters into Eq (20) we obtain the dependence of $N(t)/N_l$ *vs* annealing temperatures shown in Figure 8 (curve 2). The experimentally-obtained dependence of P_{Ad}/P_{Ad}^{max} *vs* annealing temperatures is also presented in Figure 8 (curve 1). As the deviation between the calculated and experimental values of the reduced strength of the adhesive joints is not more than 10%, it can be concluded that the approach developed gives a quite adequate description of the kinetics of adhesive joint formation of complete interfacial contact.

The calculations carried out for macromolecular and segmental hierarchical levels include the parameters which are determined at the molecular level—l_{if} and $U_{if}^{(1)}$.

Using x-ray photoelectron spectroscopy it was shown for a great variety of polymer-metal joints,[29] and in particular for electroless metal plated ABS-copolymers,[30] that the polymer-metal interaction is realized in the form of polymer-$O^- - Cu^+$ type of bond. The magnitude of the energy of such a bond is close to that of the hydrogen bond.

We believe that reliable values of the strength of interphase (adhesion) interaction cannot be calculated by any of the conventional destructive methods. The developed approach makes it possible to take into consideration the effect of each of the parameters listed in Section 2.1 and their combined effect on the value of the adhesive joint strength.

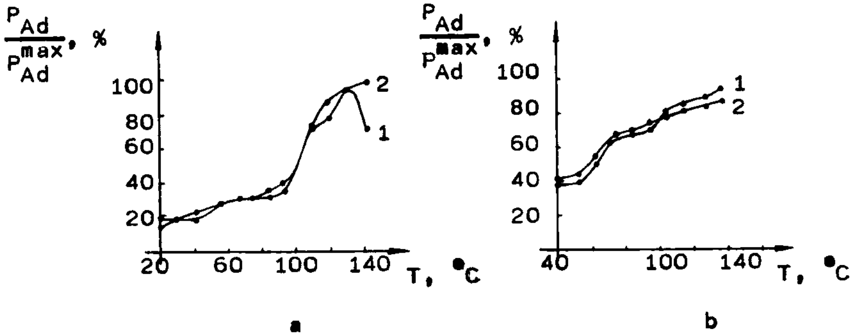

FIGURE 8 Reduced strength of the electroless copper plated ABS-copolymers (a—Lustran® PG-299, b—ABS-2020) *vs* annealing temperature: experiment—curve 1, theory—curve 2.

4 CONCLUSION

A procedure for evaluation of the strength of adhesive joints can be developed on the basis of the presented approach, relying on a minimal set of initial data describing the adhesive joints. Moreover, the procedure can give an opportunity for the proper choice of adhesives and manufacturing parameters of the adhesive joints (such as annealing temperature, applied pressure and contact time).

A number of the most important problems in adhesion science and technology can be quantitatively solved within the framework of the algorithm relying on contemporary theoretical and experimental knowledge. One of these problems involves the analysis of the effects of the chemical nature of an adhesive and a substrate,[31] and interaction conditions between components of the adhesive joint, on energetics and kinetics of adhesion. It should be particularly noted that the effects of the parameters used in this paper can now be elucidated in their complexity and in simultaneous and mutual action. Moreover, it becomes possible to take into account not only the geometry and the service life of adhesive joints but also their influence on the joint performance parameters. On the other hand, the developed approach gives an opportunity to solve the reverse problem, involving molecular design of the adhesive[31] (including its transition layers[18,23]) and the substrate, and to choose the parameters of adhesive joint formation. We believe that these results can provide an adequate basis for developing reliable methods for the prediction of adhesive joint performance.

References

1. V. L. Vakula and L. M. Pritykin, *Polymer Adhesion. Physico-Chemical Principles* (Ellis Horwood, Chichester, 1991).
2. A. J. Kinloch, *Adhesion and Adhesives* (Chapman and Hall, London, 1987).
3. L. M. Pritykin, G. A. Zaichenko and I. Y. Fokin, *Probl. Chem. and Chem. Technol. (USSR)*, **60**, 30 (1980).
4. L. M. Pritykin, A. B. Zilberman, I. I. Zilberman and V. L. Vakula, *Plaste und Kautschuk*, **38**, (3), 91 (1991).
5. A. A. Askadskii, *Pure Appl. Chem.*, **46**, (1), 19 (1976).

6. A. A. Askadskii, S. N. Prozorova and G. L. Slonimskii, *Vysokomol. Soed. (USSR)*, **18A,** (3), 636 (1976).
7. L. M. Pritykin, *Vysokomol. Soed. (USSR)*, **21A,** (4), 757 (1981).
8. L. M. Pritykin, A. A. Askadskii, E. G. Gal'pern and V. K. Korshak, *Doclady Acad. Nauk (USSR)*, **273,** (6), 1424 (1983).
9. M. V. Volkenshtein, *Configuration Statistics of Polymer Chains* (USSR Acad. Sci. Publ., Moscow-Leningrad, 1959).
10. P. de Gennes, *Scaling Ideas in Polymer Physics* (Cornell Univ. Press, Ithaca-London, 1979).
11. L. M. Pritykin, Y. V. Emel'anov, N. I. Steshenko and I. Geszy, *Vysokomol. Soed. (USSR)*, **26B,** (6), 438 (1984).
12. L. M. Pritykin, A. A. Askadskii and V. V. Korshak, *Vysokomol. Soed. (USSR)*, **27A,** (8), 1633 (1985).
13. *Polymer Handbook*, J. Brandrup and E. H. Immergut, Eds. (Wiley, N. Y., 1966).
14. Y. S. Lipatov, A. E. Nesterov, T. M. Gritsenko and R. A. Veselovskii, *Handbook of Polymer Chemistry* (Naukova Dumka Publ., Kiev, 1971), p. 412.
15. *Polymer Molecular Weight*, P. Slade, Ed. (N. Y., 1975).
16. *Viscosity and Flow Measurements. Laboratory Handbook of Rheology* (N. Y., 1963).
17. G. R. Anderson, S. J. Bennett and K. L. DeVries, *Analysis and Testing of Adhesive Bonds* (Academic Press, N. Y., 1977).
18. A. B. Silberman, Cand. Sci. Thesis. Kazan Chem. Technol. Inst. (1987).
19. E. H. Andrews and A. J. Kinloch, *Proc. Roy. Soc. Lond.*, **332A,** 385 (1973).
20. A. Ahagon and A. N. Gent, *J. Polymer Sci.: Polymer Phys. Ed.*, **13,** 1285 (1975).
21. I. Narisava, *Strength of Polymer Materials* (Chimiya, Moscow, 1987) Russian translation of Japanese Edition.
22. A. B. Silberman and L. M. Pritykin, Suppl. Chap 9 in Russian Edition of Reference 2 (Mir, Moscow, 1991).
23. A. B. Silberman, V. E. Archireev and V. L. Vakula, *J. Adhesion*, **34,** 241 (1991).
24. Y. N. Rabotnov, *Collected Papers. Problems of Deformable Solid Mechanics* (Nauka, Moscow, 1991).
25. I. I. Silberman, I. A. Tutorskii and V. L. Vakula, in *Adhesion and Adhesive Joints* (DNTP Publ., Moscow, 1991), p. 5.
26. S. Yamamoto, H. Hasahiko and I. Inoue, *J. Appl. Polymer Sci.*, **19,** 2107 (1975).
27. K. Kanamaru, *Koll. Z. und Z. Polymere*, **192,** (1–2), 51 (1963).
28. A. B. Silberman, B. S. Fridman, V. E. Archireev, M. S. Guseva and A. G. Liakumovich, *Plasticheskie Massy (USSR)*, **2,** 52 (1989).
29. J. M. Burkstrand, *J. Appl. Phys.*, **52,** (7), 4795 (1981).
30. P. A. Kirpytchnikov, B. S. Fridman, A. B. Silberman, Y. M. Pashunin, M. S. Guseva and V. E. Archireev, *Doclady Acad. Nauk USSR*, **305,** (4), 900 (1989).
31. L. M. Pritykin, V. L. Vakula and M. G. Dranovskii, *Kautschuk i Resina (USSR)*, **3,** 18 (1985).

List of Symbols

a	half of cracklength
a_T	WLF factor
A(z)	time dependence of the interfacial area
A_{if}	interfacial area
b_{Ad}	width of adhesive joint
C^1_{ij}	characteristic vector referring to intersegmental adsorption
C^2_{ij}	characteristic vector referring to intrasegmental adsorption
d_{Ad}	diameter of butt joint
E^n	Young's modulus of the n-th phase of polymer
E_a	Young's modulus of the bulk adhesive
E_s	Young's modulus of the substrate
E^*_{Ad} (ϵ, v, T)	complex Young's modulus of the adhesive in the adhesive joint
f	parameter of hindered rotation

F	applied force
F_{Ad}	strength of the adhesive-substrate interaction per unit interfacial area
F_{if}	strength of interaction between the repeating unit of the adhesive and the substrate
g	number of links in the blob
g_f	number of links in the deformed macromolecule
g_l	number of links in the non-deformed macromolecule
G_{Ad}	energy release rate
G^{o}_{Ad}	intrinsic fracture energy of the adhesive joint
G^{on}_{Ad}	intrinsic fracture energy of the n-th phase of the adhesive in the adhesive joint
G^{c}_{Ad}	fracture energy of the adhesive joint
h_a	thickness of the adhesive layer
h_s	thickness of the substrate layer
$K(t-z)$	hereditary function
K_B	Boltzmann constant
K_I	stress-intensity factor
K^n	volume fraction of the n-th phase of the polymer
l	length of the repeating link
l_{Ad}	length of the lap joint
l_{if}	length of interfacial bond
M	molecular mass
n	refractive index
$N(t)$	time dependence of the number of macromolecule links
$N(t-z,x)$	number of repeating units of the adhesive at the distance, x, from the substrate surface at the moment, $t-z$
N_l	total number of macromolecule links
N_p	number of polymer phases
$P(\epsilon)$	stress-strain function
$P(t)$	time dependence of stress
P_{Ad}	strength of adhesive joint
P^{max}_{Ad}	maximum value of the strength of adhesive joint
P^{c}_{Ad}	critical stress of adhesive joint
P^{c}	critical stress
P^{c}_{a}	critical stress of bulk adhesive
$P^{1,2}(\xi)$	normalizing functions
$P^{1,2}_{N}(\bar{R})$	distribution functions of the chain end-to-end distance
$P_{ij}(x,y)$	stress distribution in adhesive joint
p_{Ad}	applied pressure at the adhesive joint formation
p_{ij}	probability of macromolecule transfer from the state with i adsorbed links to the state with j adsorbed links
r	refraction
$\bar{R}$	polymer chain end-to-end root-mean-square distance
R_a	van der Waals radius of the atom
s	number of links in the segment
T	temperature

T_β	β-transition temperature of the adhesive
T_g	glass transition temperature of the adhesive
T_f	flowing temperature of the adhesive
T_m	melting temperature of the adhesive
T_{Ad}	temperature of adhesive joint formation
t	time
U_{Ad}	energy of interfacial interaction
$U_{coh}^{(1)}$	cohesive energy of the repeating unit
U_{coh}^{s}	cohesive energy of the segment
$U_{if}^{(1)}$	energy of interfacial bond
v	rate of fracture
V_a	van der Waals volume of the atom
W	work required for the fracture of the interfacial area unit
γ_a^b	internal stress
ϵ	current strain
ϵ_a	fracture strain at adhesive failure
ϵ_d	fracture strain at cohesive failure
$\epsilon(z)$	time dependence of strain
ν	scaling parameter characterizing the change of dimension of the macromolecule space
ν_a	Poisson's ratio of the adhesive
η	viscosity
$\phi_{Ad}\ (\epsilon,v,T)$	mechanical loss formation of the adhesive joint
$\phi_{Ad}^{n}\ (\epsilon,v,T)$	mechanical loss function of the n-th phase of the adhesive in the adhesive joint
λ_{ij}	mode of macromolecule transfer from the state with i adsorbed links to the state with j adsorbed links
λ_j^1	characteristic value of the matrix λ_{ij}^1
λ_j^2	characteristic value of the matrix λ_{ij}^2
λ_{ij}^1	matrix of transfer probabilities referring to intersegmental adsorption
λ_{ij}^2	matrix of transfer probabilities referring to intrasegmental adsorption
ξ	blob length
σ	surface energy of the adhesive
τ_α	time of α-relaxation of the adhesive
τ_β	time of β-relaxation of the adhesive
τ_{Ad}	time of adhesive joint formation
τ_i^n	relaxation time of the n-th phase of polymer ($i=\alpha$ or $i=\beta$ corresponding to α- or β-relaxation, respectively)
τ_j^1	time of intersegmental adsorption
τ_j^2	time of intrasegmental adsorption