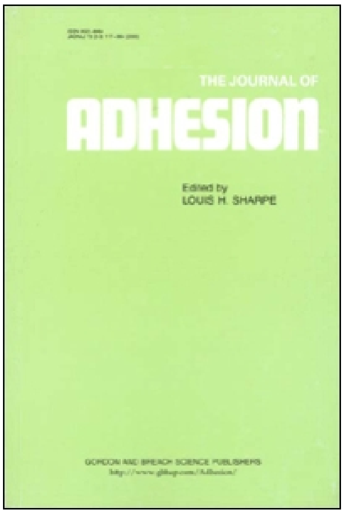

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Relaxation Properties and Chemical Nature of Polymer Surface Layers as Related to the Strength of Adhesive Joints with Metals

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Relaxation Properties and Chemical Nature of Polymer Surface Layers as Related to the Strength of Adhesive Joints with Metals

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A new approach based on the theory of elasticity is proposed to study relaxation properties of adhesive transition layers. It involves experimental evaluation of the rate dependence of the fracture energy of the bulk polymer and its adhesive joint.

The investigation of the interaction of a polymer surface layer with electroplated copper by XPS using the effect of differential charging (the latter produced by potential shift of the sample by 10V), makes it possible to identify the functional groups of adhesive brought into contact with substrate surface. For ABS copolymers a bond of $-O \ldots Cu$ type was formed.

The mechanism of adhesive contact formation and factors affecting the strength of adhesive joints could be understood better by determining the properties of surface and transition layers.

KEY WORDS relaxation properties; transition layer; boundary layer; copper plated ABS; surface analysis; XPS.

INTRODUCTION

The strength of adhesive joints is usually employed as a criterion of their service life. Dependences of the strength of adhesive joints on the Young's modulus, yield stress and relative strain of adhesive and adherend (substrate), *i.e.*, on the parameters characteristic of the bulk properties, are commonly used to describe the performance of adhesive joints. However, the strength of adhesive joints is, above all, dependent on the intensity of interfacial interaction even for cohesive type of failure. The existence of such a relationship between one of the basic parameters of fracture mechanics—the fracture energy—on the one hand, and the specific

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cohesive energy and surface free energy, on the other, was demonstrated in a number of papers.[1-4] The energy dissipation loss due to deformation of polymeric adhesives during breaking of adhesive joints was taken into account by introducing the dimensionless function $\varphi(\epsilon,v,T)$, where ϵ is strain, v-rate and T-temperature of testing. In its turn, the intensity of interfacial interaction should be governed by the chemical and deformation properties of the surfaces brought into contact. This fact is of special importance when formation of adhesive joints is preceded by prebonding treatment of the surface of the adherend, which, for instance, is the case with electroless plating of ABS plastics.

The most convenient method for investigating the chemical composition of the surface layer is XPS, as, on the one hand, the thickness of the layer subjected to analysis is rather small (20–25 Å), while, on the other hand, it provides the possibility to identify the functional groups (which, however, usually requires additional studies).

In the present work we have undertaken an attempt to assess the strength properties of adhesive joints between ABS copolymers and electroless plated copper relying on the chemical composition of polymer surface layers and their relaxation properties.

THEORY

It is an undisputable fact that in the course of adhesive joint formation a surface layer is formed at the surface of the adhesive and that its properties are essentially different from those of the bulk of the adhesive.[5-7] It was also demonstrated[8,9] that the structure of the surface layer is a gradient across the thickness of the layer; accordingly, within the surface layer it was suggested[10] to distinguish between the boundary and the transition layers. The properties of these should impose, in the final account, a decisive effect on the strength of adhesive joints. However, despite the acceptance of this fact, the bulk characteristics of adhesive are employed to assess the strength of adhesive joints, with the discrepancy between the obtained results and experimental data being attributed to the effect of internal stresses and/or manifestations of the weak (according to Bikerman[11]) surface layers. Certain attempts were undertaken to assess the properties of adhesives involved in adhesive joints of special test geometry; however, in practice these are actually confined to determination of the shear modulus for the "napkin-ring" specimen.[12]

The effect of chemical and relaxation properties of the polymer surface layers in polymer-metal adhesive joints on the strength of these joints can be most reasonably accounted for by means of the expression proposed by Andrews and Kinloch[2,4]

$$G_c = G_o + \varphi(\epsilon,v,T) \tag{1}$$

where G_c is the fracture energy, G_o is the parameter accounting for the intra- and interphase interactions, and $\varphi(\epsilon,v,T)$ is the loss function determined by the loading and deformation conditions of the adhesive joint. An analytical expression for the φ function can be derived on the basis of the theory of elasticity;[13] hence, such important service properties as the strength, durability, dynamic fatigue, etc., can be assessed.

According to the energy balance, adhesive joint fracture energy, G_c, may be expressed as:

$$G_c = G_o + \psi \tag{2}$$

where

$$G_o = \begin{cases} 2\gamma_a \\ W_{Ad} \\ 2a_1\gamma_a + a_2 W_{Ad} \end{cases} \tag{3a}$$

$$a_1 + a_2 = 1 \tag{3b}$$

γ_a is surface free energy of adhesive, W_{Ad} is thermodynamic work of adhesion per unit surface area, a_1 and a_2 are increments of cohesive and adhesive failure, respectively, ψ is energy per unit area, dissipated in fracture,

$$\psi = \frac{h_a}{V_a}\left(U_d - \frac{E_o \epsilon_o^2}{2}\right) \tag{4}$$

where U_d is energy of adhesive joint strain; E_o, ϵ_o are equilibrium Young's modulus and elastic strain of adhesive, respectively; V_a is the volume of adhesive and h_a its thickness.

Gent[15] suggested that energy dissipation in fracture is proportional to the intensity of interaction between adhesive and adherend:

$$\psi = G_o f(\epsilon, v, T) \tag{5}$$

hence, taking (3) into account,

$$G_c = G_o(1 + f(\epsilon, v, T)) = G_o \varphi(\epsilon, v, T) \tag{6}$$

To determine the mode of loss function for a joint of arbitrary geometry one can use the theory of elasticity. Then the relation determining U_d (work of fracture per unit interfacial area) is given as follows:[13]

$$U_d = \int_O^{\epsilon_m} P(\epsilon)\,d\epsilon \tag{7}$$

where $P(\epsilon)$ is the stress *versus* strain dependence and ϵ_m is the ultimate strain at break. Assume that the adhesive joint is loaded so that the time-dependence of strain is $\epsilon(\tau)$. In accordance with the Volterra[13] principle the response $P(t)$ to this action at time t is proportional to its level. The proportionality coefficient, *i.e.*, the function (nucleus) $K(t-\tau)$, is determined by the relaxation properties of the polymer adhesive. Then $P(t)$ can be expressed as follows:[13]

$$P(t) = \int_{-\infty}^{t} K(t-\tau)\epsilon(\tau)\,d\tau \tag{8}$$

According to Reference 13, the function may be written as:

$$K(t-\tau) = \sum_{n=1}^{N} A_n \frac{E_n}{\tau_n} \exp\left(-\frac{t-\tau}{\tau_n}\right) \tag{9}$$

where N is the number of polymeric phases; E_n, τ_n are the Young's modulus and relaxation time of the n-th phase, respectively, and A_n is the volume fraction of the n-th phase.

Hence, by comparing relaxation properties of the bulk adhesive and of its joints (assuming that in both cases $\epsilon(\tau)$ is the same), one can detect the variation in mechanical properties of the polymer transition layers and consequently evaluate the thermodynamic work of adhesion W_{Ad}. (Distinction is to be drawn[14] between boundary layers, located at the interface, and transition layers, that occur between the boundary layers and the bulk of the polymer).

The above equations make it possible to estimate the adhesive fracture energy for actually any pattern of the time-dependent strain. Let us discuss one of the most widely used deformation modes, *viz,* the constant strain-rate mode

$$\epsilon = v\tau \tag{10}$$

where the strain-rate v is constant. Combining eqs (8), (9) and (10) and taking into account the integration boundary conditions, we obtain

$$P(\epsilon) = \epsilon_o \sum_{n=1}^{N} A_n E_n^o \epsilon_n^o + (\epsilon - \epsilon_o) \sum_{n=1}^{N} A_n E_n^1 \left[1 - \frac{v\tau_n}{\epsilon - \epsilon_o}\left(1 - \exp\left(-\frac{\epsilon - \epsilon_o}{v\tau_n}\right)\right)\right] \tag{11}$$

where E_n^1 is the instantaneous Young's modulus and ϵ_o is the polymer elastic strain.

Since the ratio $\frac{\epsilon - \epsilon_o}{\tau}$ is approximately equal to the equilibrium rate of fracture v_e, the value of $\frac{\epsilon - \epsilon_o}{v\tau}$ is close to v_e/v and reflects the degree of equilibrium of the adhesive joint fracture. When v_e/v is higher than 1, the adhesive behavior is rubber-like; when $v_e/v \ll 1$, the adhesive becomes brittle and may be described in terms of continuum fracture mechanics. The first case is considered in References 1, 3 and 15, while the second is elaborated on in Reference 16.

When the polymer behavior is leathery, the relaxation time is expressed as:[17]

$$\tau_n = \tau_n^o \exp\left(-\frac{U - V_f P}{RT}\right) \tag{12}$$

where τ_n^o is the polymer constant, obtained experimentally; V_f is the volume within which the fracture takes place and U is the activation energy of fracture. Thus, the quantities P and τ_n appear to be mutually dependent (see eqs (11) and (12)). Consequently, to obtain an explicit function describing the adhesive joint strength as dependent on the strain rate one has to solve the system of non-linear equations ((11) and (12)). This solution is not simple, since the value of V_f depends on the degree of fracture equilibrium and, hence, on the rate of deformation.

Taking into account that in the case of polymer leathery behavior the derivative $dP/d\epsilon$ has a singular point, one can obtain the simple solution of the above system of equations. To simplify the problem let us consider a homogenous polymer, *i.e.* $N = 1$; then the derivative of (12) with respect to ϵ is:

$$\frac{d\tau_1}{d\epsilon} = -\frac{V_f \tau_1}{RT}\frac{dP}{d\epsilon} \tag{13}$$

The solution of the system of equations (11) and (12) by taking derivatives with respect to ϵ, is:

$$\frac{dP}{d\epsilon}=\begin{cases} E^{o},\ \epsilon\leq\epsilon_o \\ \dfrac{E^{1}\left(1-\exp\left(-\dfrac{\epsilon-\epsilon_o}{v\tau_1}\right)\right)}{1-\dfrac{V_fE^{1}(\epsilon-\epsilon_o)}{RT}\left[\dfrac{v\tau_1}{\epsilon-\epsilon_o}-\left(1+\dfrac{v\tau_1}{\epsilon-\epsilon_o}\exp\left(-\dfrac{\epsilon-\epsilon_o}{v\tau_1}\right)\right)\right]},\ \epsilon>\epsilon_o \end{cases} \tag{14}$$

This solution explains three major patterns of polymer behavior:

1. When $v_e/v>1$ and $V_f\ll\dfrac{RT}{E^1(\epsilon-\epsilon_o)}$, expression (14) may be written as:

$$\frac{dP}{d\epsilon}=E^{1}\left(1-\exp\left(-\frac{\epsilon-\epsilon_o}{v\tau}\right)\right) \tag{15}$$

Equation (15) is well-known for viscoelastic polymers.

2. For $v_e/v\ll1$ (high testing rates or low testing temperatures) the solution of equation (14) is

$$\frac{dP}{d\epsilon}=E^{1} \tag{16}$$

i.e. the polymer is a Hookean solid.

3. In the intermediate case the exact solution of (14) is required; however, for $\epsilon<\epsilon_o$ $\dfrac{dP}{d\epsilon}=E^{o}$, while for $\epsilon\simeq v$ $\dfrac{dP}{d\epsilon}=E_{ef}$ (E_{ef} is the modulus of rupture). These results are similar to expressions presented in Reference 18 for bulk polymers.

Thus, under certain conditions eq (14) can be reduced to the relationships obtained by other authors.[1,16,18]

When

$$\frac{v\tau_1}{\epsilon-\epsilon_o}-\left(1+\frac{v\tau_1}{\epsilon-\epsilon_o}\exp\left(-\frac{\epsilon-\epsilon_o}{v\tau_1}\right)\right)<\frac{RT}{V_fE^{1}(\epsilon-\epsilon_o)} \tag{17}$$

$\dfrac{dP}{d\epsilon}>0$ (according to (13)); when the reverse is true, $\dfrac{dP}{d\epsilon}<0$. Hence, the derivative $\dfrac{dP}{d\epsilon}$ changes its sign at the point (ϵ_m, P_m), where ϵ_m and P_m satisfy the following equation:

$$\frac{v\tau_1}{\epsilon-\epsilon_o}-\left(1+\frac{v\tau_1}{\epsilon-\epsilon_o}\exp\left(-\frac{\epsilon-\epsilon_o}{v\tau_1}\right)\right)=\frac{RT}{V_fE^{1}(\epsilon-\epsilon_o)} \tag{18}$$

(such behavior complies with the leathery state of the polymer). At this point $\dfrac{dP}{d\epsilon}\to\infty$ (see eq (14)), however, the physical implications of this phenomenon lead one to infer that the $P(\epsilon)$ function passes through a maximum at the point (ϵ_m, P_m).

Indeed, it is common knowledge that the stress-strain curves for the bulk polymer and for adhesive joints display a maximum under such conditions.

Thus, solving the system of non-linear equations ((11), (18)) for $N=1$ one can evaluate τ and V_f at the point (ϵ_m, P_m) and then, from eq (12), the activation energy of fracture, U. Determination of these parameters is particularly significant for adhesive joints because of the presence of boundary and transition layers,[14] their properties being greatly different from these of the bulk.

The energy of adhesive joint deformation, U_d, can be calculated by means of double numerical integration of equation (14) (at first with respect to $d\epsilon$ from 0 to ϵ_m, then, in accordance with eq (7)) or by considering the area under the experimental stress-strain curve. Comparing G_c for the bulk adhesive and the adhesive joint at infinitely small strain rates, one can estimate the intrinsic fracture energy G and, consequently, the values of the loss function $\varphi(\epsilon,v,T)$.

Let us now consider the fracture modes observed in a polymer adhesive joint. Yamamoto and Hayashi demonstrated[19] that the type of failure changes from cohesive, at low test rates ($v \leq v_e$), to adhesive, at high rates ($v > v_e$). However, they did not take into account the relaxation character of polymer fracture, accounting for the formation of filaments of adhesive at deformation. If lifetime of those filaments is lower than the reciprocal rate of crack growth per unit length, the filaments are ruptured, hence, cohesive fracture occurs, although, according to Reference 19, it is to be of the adhesive type. (It should be noted that the type of failure depends on the degree of fracture equilibrium, *i.e.* on the ratio $\left.\frac{\epsilon-\epsilon_0}{v\tau}\right)$.

Thus, the description of relaxation properties of the transition layers of adhesive involves:

1. Experimental evaluation of the fracture energy of the bulk specimen[20] and the adhesive joint;[21] by comparing these values, one can assess the thermodynamic work of adhesion.
2. Experimental determination of the maximal stress P_m and corresponding strain ϵ_m for the bulk material and the adhesive joint at different test rates.
3. Calculation of V_f and τ by solving the system of non-linear equations ((11), (18)).

EXPERIMENTAL

1. Materials

The samples were prepared as follows: 88 × 53 mm plates 3.4 mm thick of ABS-copolymer (ABS-2020, Plastpolymer, USSR) were molded at the stock temperature 210°C, injection time 8 sec, injection pressure 10MPa, injection boost time 15 sec and mold temperature 80°C (in a mold without wax). These were etched for 10 min in an aqueous CrO_3 (400 g/l) + H_2SO_4 (400 g/l) solution at 62 ± 2°C. After flushing the samples with water they were neutralized in aqueous NaOH (40 g/l) solution for 10 min and treated for 5 sec with aqueous HCl (150 g/l) solution. The samples were then treated in 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

TABLE I
Relaxation properties of pure ABS-2020 and its adhesive joint with electroless copper

v, m/s	P, MPa	ϵ_m, $\times 10^{-6}$m	$\frac{\epsilon_m - \epsilon_o}{v\tau}$	τ_s,	V_f, $\times 10^{-7}$m^3	G_c^T, J/m^2	G_c^e, J/m^2
1.71×10^{-4}	7.60	2.62	3.12	38.60	3.67	12.46	12.49
	7.16	2.55	3.25	38.82	3.96	12.14	12.16
6.9×10^{-5}	7.10	2.94	3.97	140.2	4.00	21.25	21.28
	7.50	2.70	3.31	105.2	3.75	14.26	14.29
2.75×10^{-5}	6.40	2.22	3.09	192.8	4.52	8.11	8.14
	6.15	3.00	4.90	444.4	4.75	27.74	27.77
1.10×10^{-6}	6.30	2.46	3.65	648.1	4.60	12.52	12.55
	5.20	2.13	3.84	567.9	5.81	9.14	9.16
4.40×10^{-6}	4.37	1.35	2.37	454.9	7.25	1.49	1.51
	6.60	2.60	3.71	1763.2	4.36	14.61	14.64
1.76×10^{-6}	8.45	1.83	1.57	1183.0	3.27	2.43	2.45
	6.85	1.65	1.77	1149.6	4.17	2.04	2.06

The upper values in each column were obtained for the adhesive joint, the lower for bulk material

were electroless plated with copper by subjecting them to the effect of 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 (37%—15–20 ml/l), at room temperature for 25 min.

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

Styrene-acrylonitrile (SAN) and styrene-butadiene rubber (SBR), which are commonly used in the synthesis of ABS-copolymers, were employed to investigate the mechanism of etching. SAN samples were pretreated according to the above procedure. SBR samples were precipitated from aqueous latex by toluene; the films obtained were treated in the same way. The stress-strain curves were registered within a wide span of strain rates (3.22×10^{-9}–1.75×10^{-4} m/s) with a specially-designed loading test machine. The adhesive joints were tested by 90° peeling[22] and the bulk adhesive by compact tension.[23] The experimentally-obtained stress-strain dependences were employed for evaluation of τ and V_f according to eqs (11) and (18). These results and the values of fracture energy obtained by experiment (G_c^e) and calculated by double numerical integration of eq (14) (G_c^t) are presented in Table I.

2. XPS Analysis of Interfacial Bonding

To analyze the chemical nature of the interface, mechanically debonded samples of copper-plated ABS-copolymer were examined both from the metal and the polymer sides. The differential charging phenomenon was employed to identify the func-

TABLE II

Chemical structure of ABS-copolymer at the different stages of its pretreatment (atomic %)

Element	Untreated	Etched	Activated	Electroless copper plated ABS polymer side	metal side
C_{1s}	87.9	70.3	56.6	85.7	64.4
O_{1s}	8.3	22.6	26.3	7.9	18.5
N_{1s}	3.8	4.7	1.22	3.7	3.7
Cr_{2p+}	—	1.0	—	—	—
S_{2p}	—	0.35	—	—	1.7
Sn_{3d+}	—	—	11.5	1.5	2.0
Pd_{3d}	—	—	2.9	0.2	0.5
Cl_{2p}	—	—	1.5	—	0.7
Cu_{2p+}	—	—	—	1.0	8.8

tional groups at the interface. When the metal strip is charged to -10 V, the charge of the remaining polymer particles is lower due to their high volume resistance (10^{16} Ohm). Then only the boundary polymer layer will be charged to a potential of -10 V. Shifting the obtained spectrum by 10 V to the right and comparing it with the spectrum of the uncharged sample, one can distinguish the functional groups at the interface.

XPS was performed on an XSAM-800 (Kratos, UK), equipped with MgK_α ($h\nu = 1253.6$ eV) and AlK_α ($h\nu = 1486.6$ eV) X-ray sources in an ultra-high vacuum system whose operating pressure was about 10^{-10} Torr. The instrument was calibrated against standard peaks: $Au_{4f} = 84.0$ eV; $Ag_{3d} = 368.3$ eV; CuLMM = 335.0 eV; $Cu_{2p} = 932.7$ eV. The obtained spectra were processed by means of the software package DS-800. Chemical structure of ABS-surface at the different stages of its pretreatment is shown in Table II.

DISCUSSION

1. The Nature of Interfacial Bonds

The curves in Fig. 1 show that surface concentration of hydroxyl, carboxyl and carbonyl groups increases after chromic acid etching of ABS-2020.* The component C—O of the C_{1s} line was presumed to be associated predominantly with the hydroxy functions since the spectra of ABS plastics were in good correlation with the spectra of PVA as a model system. Comparing the N_{1s}-lines (Fig. 2) before and after etching one can observe the oxidation of —C≡N to —N=O. Despite the widespread opinion to the contrary,[24] pretreatment in activating solution results in further polymer surface oxidation (while the initial C:O ratio is equal to 17.1, it decreases to 12.3 after etching and up to 5.0 after activation).

To understand the mechanism of the etching process of a composite polymer, the etched samples of its elastic (SBR) and plastic (SAN) phases were investigated. The

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*We believe that the initial occurrence of these groups is explained by the oxidation of the initial sample surface which takes place during moulding.

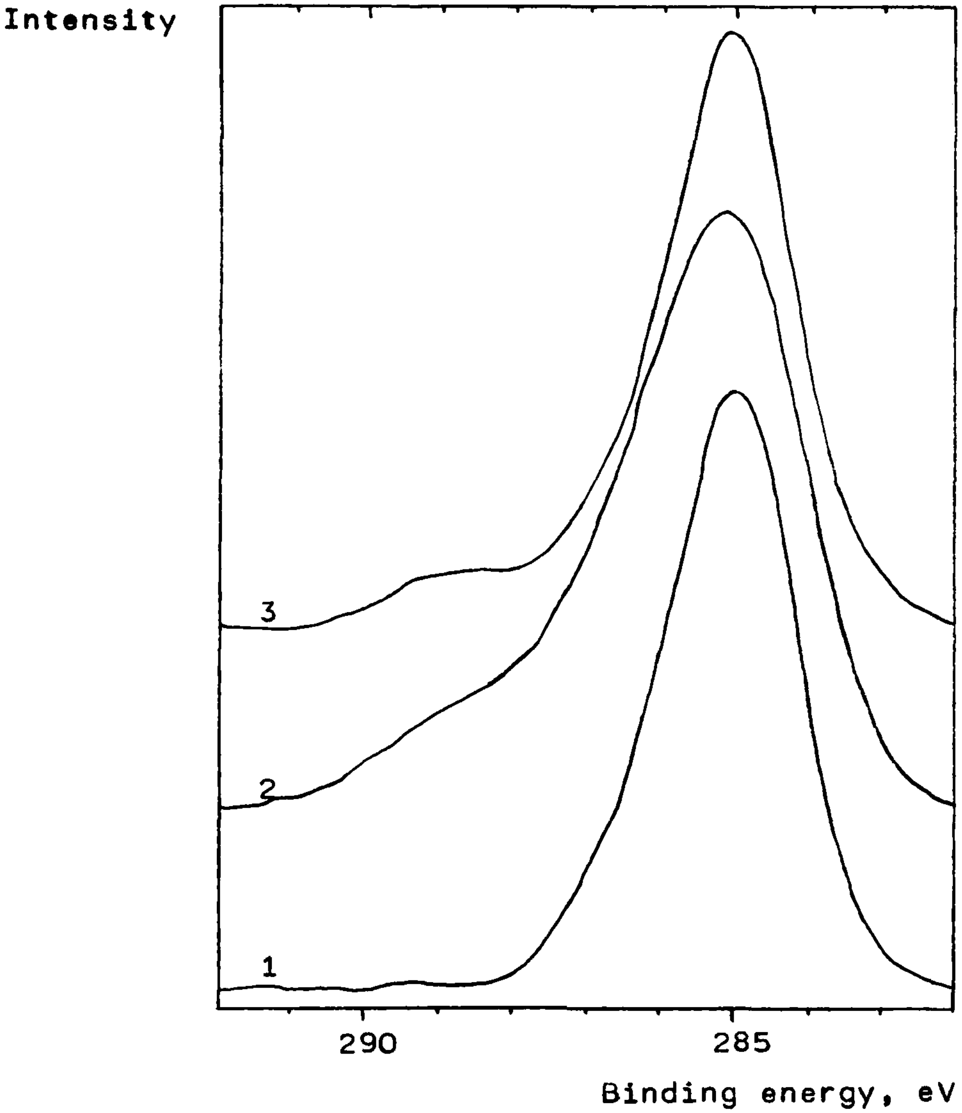

FIGURE 1 The C_{1s} XPS spectrum for ABS-2020: 1–untreated; 2–etched; 3–activated

spectra obtained for SAN (Fig. 3) and ABS-2020 (Fig. 1) are similar. However, the concentration of oxygen-containing functional groups in ABS is higher than that in SAN, and hence the full width at half height of the C_{1s} spectrum in Fig. 1 exceeds that in Fig. 3. As was shown in Reference 24, during ABS etching selective rubber oxidation is observed, and experimental results of SBR etching do indicate a slight oxidation (Fig. 4).

Graft polymerization of acrylonitrile and styrene on to rubber globules leads to the formation of the so-called "transition phase." It consists not of SAN-matrix

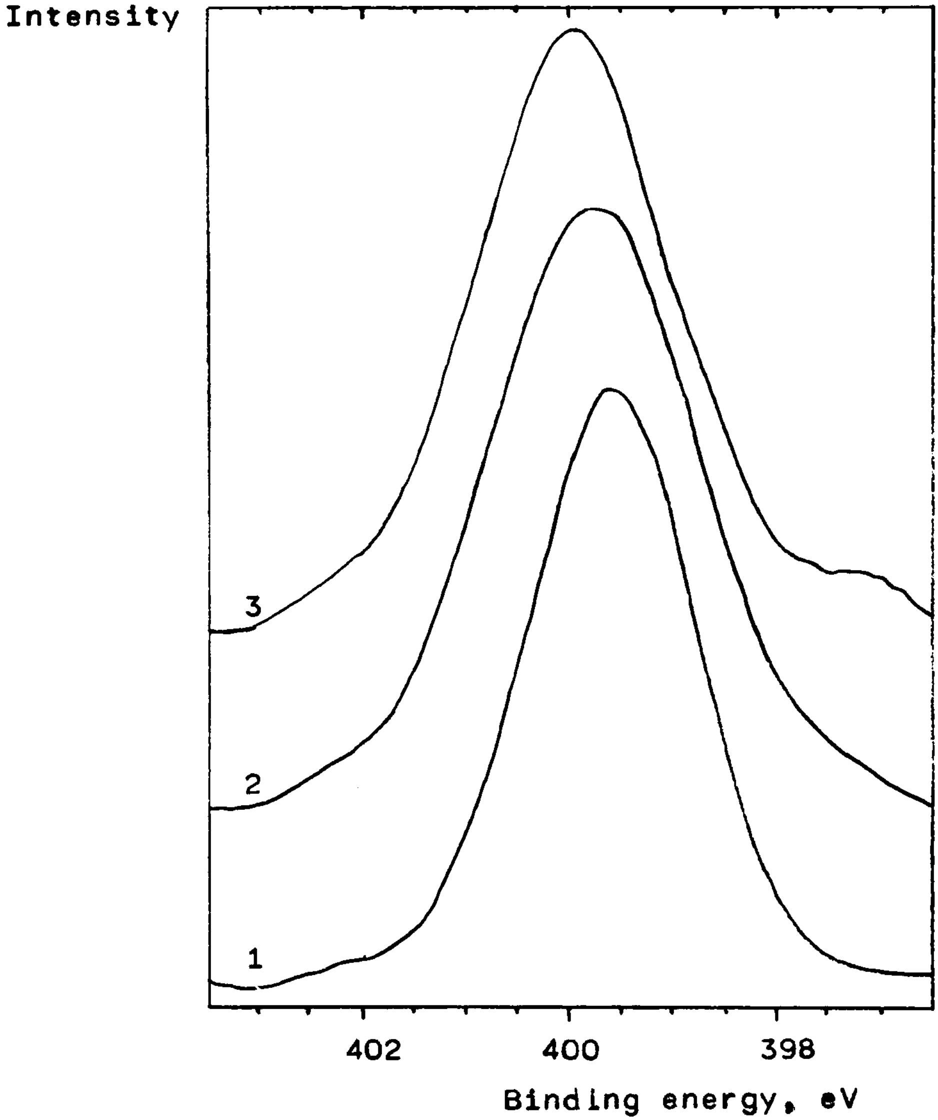

FIGURE 2 The N_{1s} XPS spectrum for ABS-2020: 1–untreated; 2–etched; 3–activated

alone, but of polybutadienestyrene as well, the amount of which increases with the rate of chromic acid diffusion. Hence, the degree of oxidation of SAN-matrix in ABS-copolymer is higher than that in pure SAN. The volume fraction of the transition phase depends on the parameters of the co-polymerization process. When thickness of the transition layer is high (*i.e.* for Lustran PG-299[25]) etching leads predominantly to crazing, thus increasing the strength of the corresponding adhesive joint; when this thickness is small, the transition layer is dissolved and rubber globules are "washed out" (as in ABS-2020).[23]

The chemical nature of the polymer side of debonded samples is similar to that

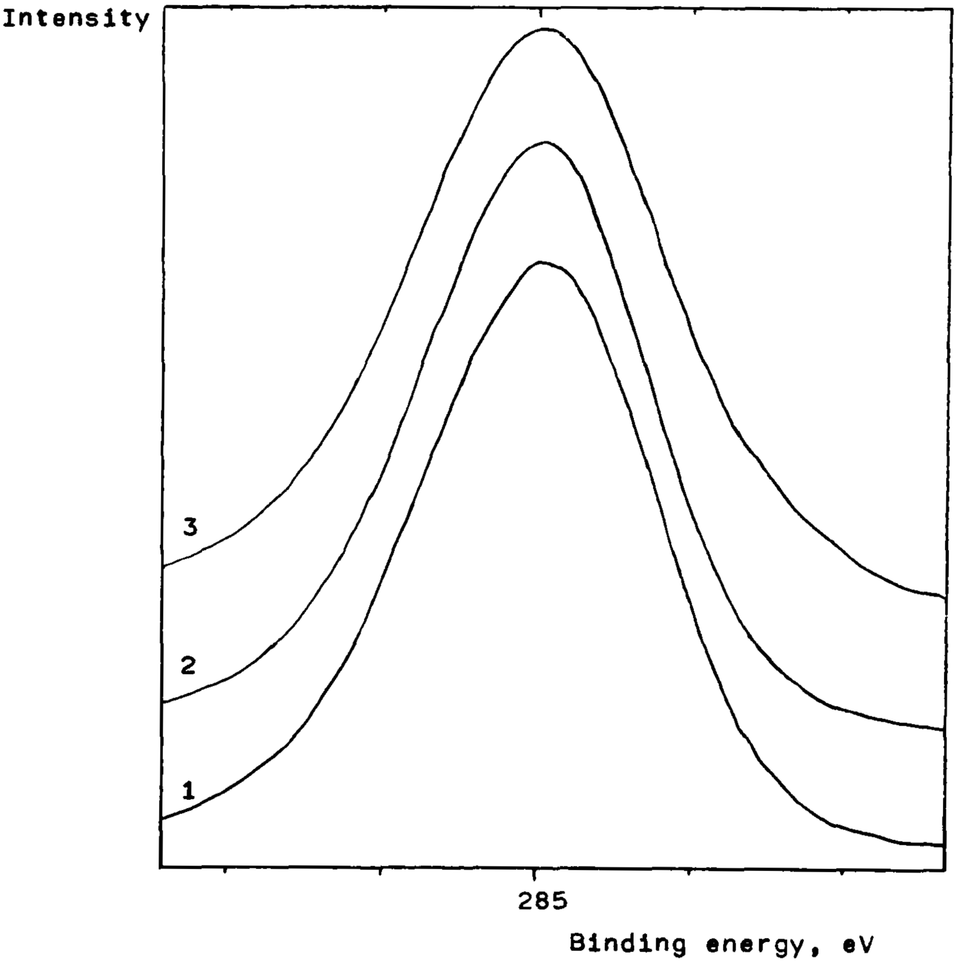

FIGURE 3 The C_{1s} XPS spectrum for SAN: 1–untreated; 2–etched; 3–activated

of the untreated ABS (the C:O ratio is close to 17.1). A significant amount of residual polymer at the metal side of debonded specimens indicates a cohesive type of failure.

Auger-transition CuLMM (curve 1 in Fig. 5) shows that at the metal side copper is presented in the form of Cu^0 and Cu^+. Curve 1 in Fig. 6 shows a shake-up satellite attributed to a small amount of Cu^{2+}. This satellite is shifted by charging the sample (curve 2 in Fig. 6), which is the evidence that Cu^{2+} is distributed within the polymer layer. The same conclusions can be made concerning Cu^0 (see curve 2 in Fig. 5). Thus, copper is present at the interface in the form of Cu^+ ions.

It should be noted that the O_{1s} line of the metal-side spectrum (Fig. 7) has a new component with a peak at 531.7 eV as compared with the spectrum of the activated polymer sample; its second peak at 533.2 eV is attributed to oxygen in Cu_2O. The 1.4 eV shift of the latter peak may be explained by the transformation of Cu_2O to copper hydroxide or alkoxide.[26] This cannot be ascribed to the formation of CuOH,

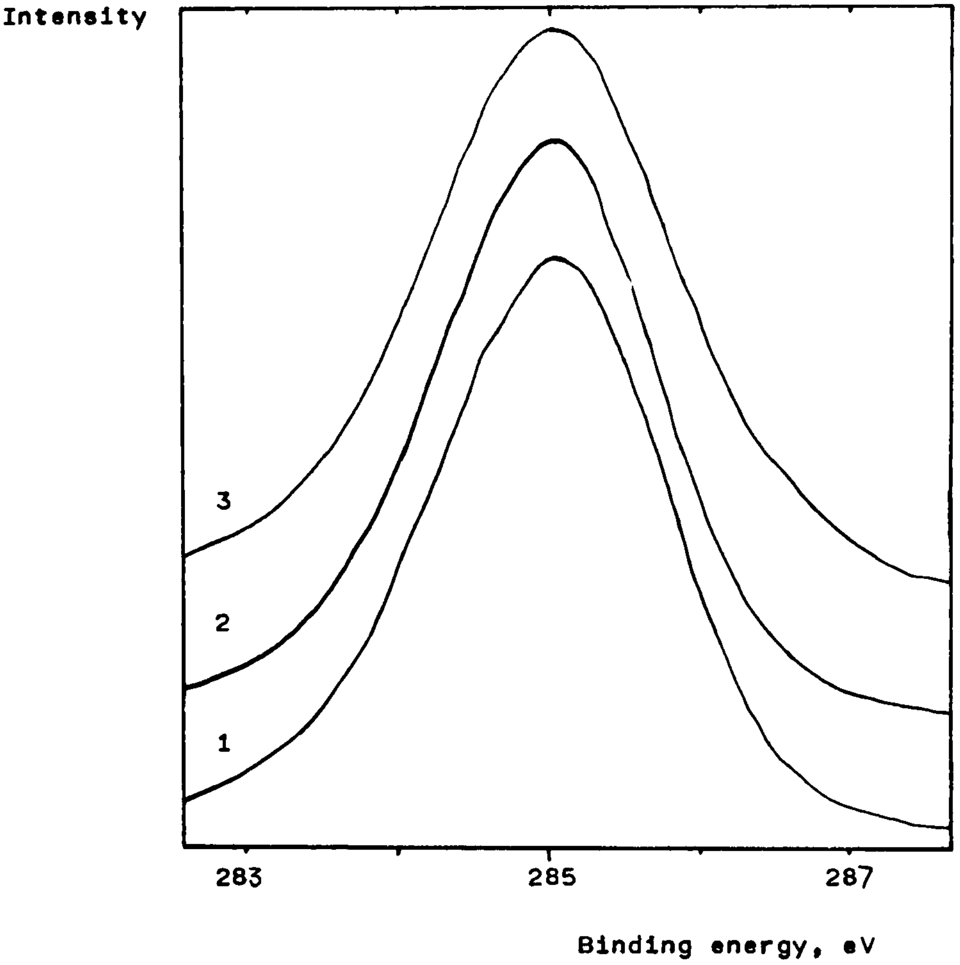

FIGURE 4 The C_{1s} XPS spectrum for SBR: 1–untreated; 2–etched; 3–activated

since the pH of the copper plating solution is equal to 12.8. Thus the component with a peak at 531.7 eV is to be attributed to copper alkoxide: $>$C—O—Cu. As charging of the sample does not shift this component (curve 2 in Fig. 7) copper alkoxide is present at the surface and is involved in the generation of interfacial bonds.* High intensity of this peak (531.7) enables us to confirm that the number of chemical bonds is rather high, resulting in cohesive failure of adhesive joints. Thus it may be concluded that the value of G_o is governed by the cohesive energy

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*We failed to explain the high energy side of curve 2 in Fig. 7 since this curve is strongly distorted due to the effect of differential charging.

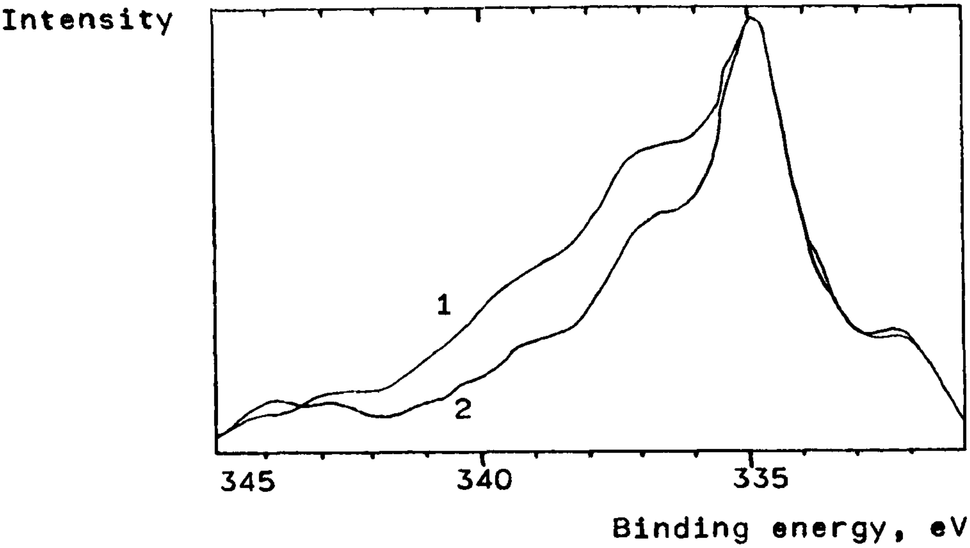

FIGURE 5 The CuLMM Auger-spectrum for metal side of debonded electroless copper plated ABS-2020: 1–uncharged; 2–charged to −10V

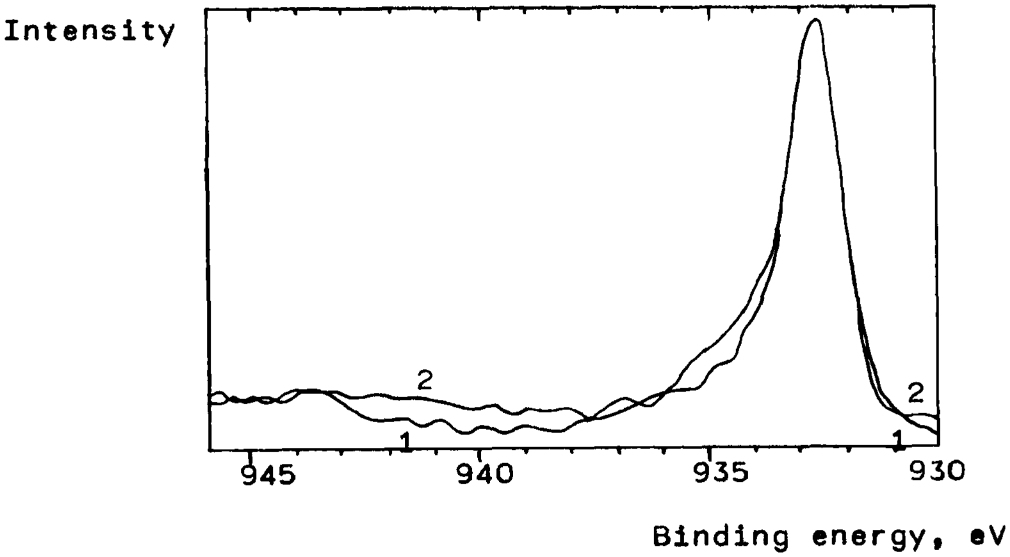

FIGURE 6 The Cu_{2p} XPS spectrum for metal side of debonded electroless copper plated ABS-2020: 1–uncharged; 2–charged

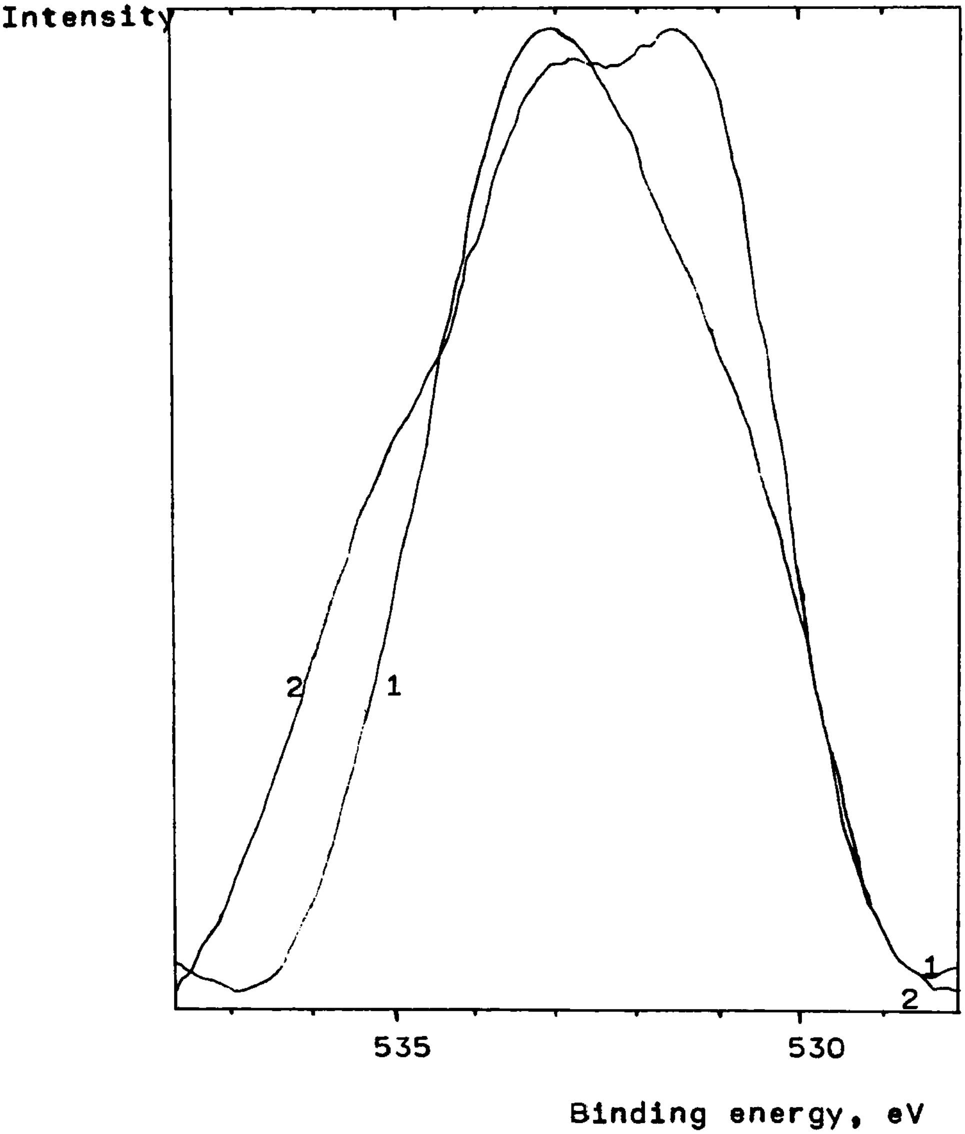

FIGURE 7 The O_{1s} XPS spectrum for metal side of debonded electroless copper plated ABS-2020: 1–uncharged; 2–charged

of the transition layer. If the polymer etching is accompanied by destruction of matrix chains, the cohesive energy of the transition layer is lower than that of the bulk polymer.

2. Relaxation Properties of the Transition Layer

Experimental rate-dependences of fracture energy for bulk adhesives (curve 2) and their joints (curve 1) are plotted in Fig. 8. The curves are similar, with curve 1 shifted

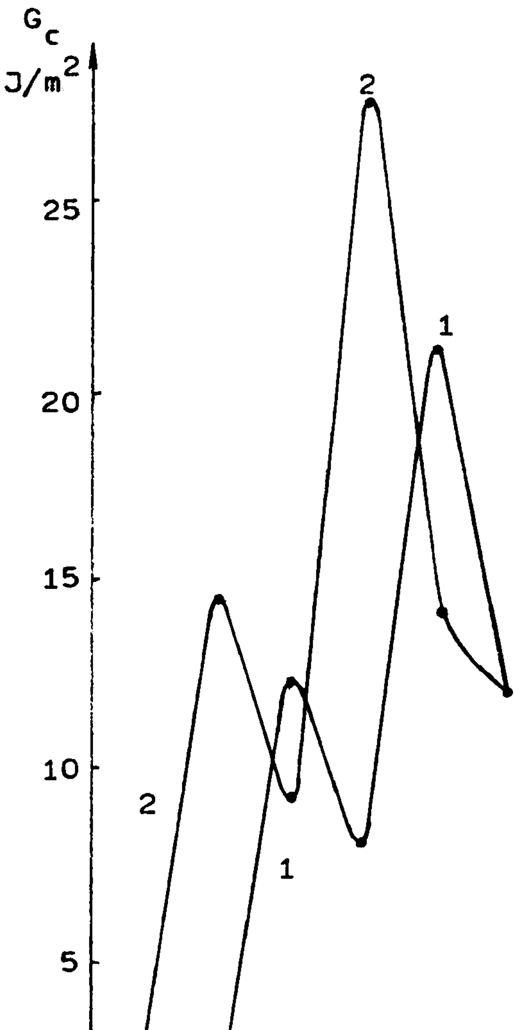

FIGURE 8 The fracture energy, G_c, *vs* the rate of testing, v: 1–for adhesive joints; 2–for bulk adhesive

with respect to curve 2 by a constant value. Thus, rate-temperature equivalence can be applied in this case,[1] the shift of the curve corresponding to the respective decrease of glass-transition temperature of the transition layer. This fact, and smaller values of G_c for adhesive joints, validate the assumption concerning the destruction of the matrix chains in the transition layer.

Two maxima on the curves in Fig. 8 are in good accord with experimental data.[27,28] The peaks on the left correspond to the glass transition.[27] When the rate of testing is approximately equal to the equilibrium rate, the ratio $\frac{\epsilon-\epsilon_0}{v\tau}$ is close to 1 (see Table I). When the testing rate is high, the lifetime of unbroken filaments (which can be computed according to eq (12) using the data presented in Table I) of adhesive is less than the reciprocal rate of crack growth and, consequently, failure is cohesive in character; this result is also confirmed by XPS data.

The appearance of the second peak can be associated with the leathery state of the polymer under corresponding rate-temperature conditions; this process proceeds only ahead of the crack tip. The experimental data (Table I) show that the values of G_c for bulk polymer and its adhesive joint at the same $\frac{\epsilon-\epsilon_0}{v\tau}$ are similar.

Finally, it should be noted that theoretical values of fracture energy (G_c^t), in a wide range of testing rates, are in good agreement with experimental data (G_c^e), thus confirming the consistency of the proposed approach (Table I).

According to the data presented in Table II, the initial ABS-copolymer has the same chemical nature as the polymer side of the debonded adhesive joint, and it greatly differs from the polymer remaining on the metal side of the debonded sample. It leads to the conclusion that failure occurs in the transition layer. The values of the surface free energies of the bulk polymer and its transition layer in the adhesive joint are obtained using eq 3a and are equal to 1.028 and 0.99 J/m^2, respectively. Thus the structure and, hence, the relaxation properties, of the transition layer are modified due to the changes in the stacking order of macromolecules. (It is worthwhile to note that the glass-transition temperature of the transition layer differs from its value for the bulk polymer).

Based on the data presented, we may conclude that the strength of electroless copper plated ABS-copolymers is determined by mechanical properties of the transition layer.

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