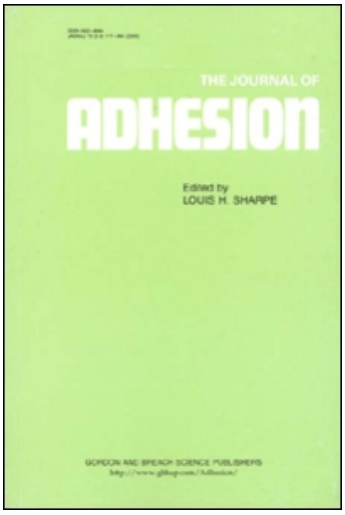

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Acoustic Emission at Fracture of Adhesion Contacts in Rigid Polymeric Composites

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The possibility of using the acoustic emission (AE) method for the characterization of the process of fracture of adhesion joints in strained rigid polymeric composites is discussed. Recorded as main informational parameters are the total count of AE signals, the count rate, the amplitude distribution of the signals and their frequency characteristics as well as the dependence of these quantities on the stress applied to the sample and on the straining time. Increase in the adhesion bond strength is shown to result in raising the total AE over the whole filler concentration range. The effect of the filler dispersity on the above-listed parameters has been ascertained. A technique for calculating the adhesion joint strength on the basis of the maximum of the AE signal count rate, fracturing stress, and amplitude characteristics of AE signals with allowance for the stress concentration in the formation of a polymeric sample is suggested.

KEY WORDS Acoustic emission; amplitude; count rate; signal; filler; matrix.

INTRODUCTION

Determining the strength of the adhesion bond between filler particles and a polymeric binder is a fairly complex and essential problem in the development of new composite materials. A thermodynamic approach to its solution might have been the most rigorous, but its applicability is very limited because of nonequilibrium methods used to determine the adhesion through breaking an adhesion joint. Calculated values of the adhesion interaction energy generally fail to agree with experimental results even for relatively simple systems. The adhesion value is, in most cases, estimated from the magnitude of the adhesion strength, thus characterizing the resistance of the adhesion joint to a fracture at the interface under the action of external forces. Here the separation can have the character of either an adhesion or a cohesion fracture, the latter occurring in a weak layer arising in the composite formation process.[1,2] The fundamental equation $W_a = W_c$, relating adhesion and cohesion, however, remains valid even when the fracture is of the cohesion character. This allows the adhesion strength to be evaluated from the break of continuity

of a composite material regardless of the place where the adhesion joint fracture process begins.

A combination of a rigorous thermodynamic approach to the problem of adhesion with its analysis within the scope of the fracture mechanics and physico-chemistry of the adhesion joint formation provides a means for solving one of the most essential problems in the development of dispersely-filled polymeric composites, the problem of estimating the adhesion interaction in such systems.

Known experimental methods for determining the strength of adhesion contacts for rigid polymeric composites are based on estimating the load corresponding to the moment of the break of continuity of the sample in its straining, which is judged from changes in its physico-mechanical properties, such as the mechanoemission of electrons, thermal effects, mechanoluminescence, light transmission,[3] gas permeability,[4] stress-strain diagram,[5] etc. The adhesion strength can be estimated from the formula:[5]

$$A = \frac{\sigma_{c.br.}}{2K_v^{2/3}} = \frac{\sigma_{c.br.}}{2\rho_m^{2/3}/\left[\rho_m + \rho_f\left(\frac{1-K_m}{K_m}\right)\right]^{2/3}}$$

where $\sigma_{c.br.}$ – stress at which a continuity break in the polymeric composite occurs;
K_v, K_m – volume and mass fraction of the filler;
ρ_m, ρ_f – density of the matrix and the filler.

However, considerable spreads in the $\sigma_{c.br.}$ value are here possible due to dissimilar sensitivities of mechanical properties of a polymeric material to the appearance of strain-induced discontinuities in it. In view of this, the search for suitably correct methods for determining the adhesion bond fracture stress represents a fairly complex and important problem, whose solution should allow for the phenomena accompanying the polymeric composite straining process. It should here be borne in mind that in the fracture of an adhesion joint the process itself is of a mixed character since a purely adhesion fracture never occurs.[6] The same is valid also in examining the continuity break conditions. It is, however, obvious that to evaluate an adhesion joint the location of the fracture region (interface or a weak boundary layer) is to a certain extent immaterial, the fact of the composite material fracture itself being essential. Experimenters are generally interested in the strength of an adhesion joint rather than in the (interfacial) adhesion strength itself. With an account of the above, a reliable estimation of the fracturing stress is absolutely essential. From this standpoint, one of the sensitive responses is the acoustic emission (AE),[7] showing up in emission of acoustic signals by a filled polymeric material when it is strained. The emergence of such signals is caused by a dynamic local rearrangement of the structure of the material under the action of the applied load. From the character of the signals it is possible to judge the nature of the crack formation processes in the system, in particular of a break of filler-matrix adhesion contacts.

EXPERIMENTAL

In the present report the AE phenomenon is employed to characterize the fracture of adhesion joints in rigid polymeric composites when the analysis is based on the following concepts.[8] In the process of straining a composite polymeric material consisting of a filler, a matrix, and an interfacial layer with differing elastic properties, the strain energy is mainly localized in filler particles, which have a higher modulus of elasticity.[8] This involves a stress concentration at the filler-matrix interface and in the adjacent region and formation there of microcracks whose position depends on the character of fracture (adhesion, cohesion, or mixed).

The origination of microcracks is accompanied by elastic vibrations whose energy and frequency depend on microcrack sizes;[9] the resulting AE signals can be detected only when their energy exceeds the discriminating threshold (background noises) of the acoustic emission equipment used. The number of detected AE signals is determined both by the number of sources (number of filler particles, *i.e.*, filler concentration) and by the energy of an individual signal, which depends on the amount of the strain energy stored in filler particles up to the point of microcrack formation. The signal energy is determined by the adhesion strength of filler-matrix contacts and by the stress concentration around filler particles.

In studying composite materials of an identical composition it is only the difference in the adhesion strength that exerts the governing effect on continuity break (crack formation) processes. With a strong adhesive interaction at the interface the amount of energy stored in filler particles is much greater than with a weak adhesion, with the result that the breaking of adhesion contacts involves in the former case the formation of large microcracks than in the latter one, which is accompanied by origination of AE signals differing in the energy and frequency from the background.

It follows from the above that the AE signal parameters, characterizing the microcracks originating at te break of adhesion contacts, can be utilized for evaluating the filler-matrix adhesion strength.

The present study has, for the first time, ascertained an interrelation between the character of the acoustic emission at a break of adhesion contacts in rigid polymeric composites under strain and the adhesion strength of such contacts for dispersely-filled systems, and has also involved an attempt to tackle the quantitative determination of the adhesion strength.

Studied samples were of a cured epoxy resin filled with dispersed quartz at a concentration of from 10 to 60 mass % of particles ranging in sizes from 50 to 180 μm. The strength of the adhesion interaction at the filler-matrix interface was varied by treating the filler with an agent preventing adhesion. The acoustic emission was studied for two types of strain, a uniaxial tension of the samples under study and their bending with a concentrated force.

Two versions of uniaxial tension tests were conducted. In the first version, the AE signals were detected by a piezoreceiver with a resonant frequency of 265 kHz and a bandwidth of 0.1–0.3 MHz; the loading was carried out on a tensile-testing machine at a constant rate of 0.2 MPa/min. In the second version, the AE signals

were detected by a wide-band piezoreceiver in a frequency range of 0.2–0.5 MHz; the loading was carried out on the tensile-testing machine at rates of 0.2; 0.4; 0.6; 2.0; 4.0; and 10.0 MPa/min. Standard AE parameters, the count rate ($\dot{N}$), the total count (N), and their amplitude distribution (with the use of an AI-1024 pulse analyzer), were recorded in both cases. With the aim of studying the kinetics of microfractures, the amplitude distribution of AE signals was recorded during the whole loading process at equal load change intervals of 4 MPa.

The frequency dependence of AE signals was studied in bending tests of samples by a concentrated force at a constant loading rate of 4 mm/min. The frequency spectrum of AE signals was analyzed with the use of a multichannel parallel-action spectrum analyzer that allowed a simultaneous analysis through 100 frequency channels (with a wide, $\Delta f = 20$ KHz, and a narrow, $\Delta f = 2$ kHz, band) over a frequency range of $f = 0.2$–2.0 MHz; the signals were received by a wide-band transducer with the so-called "resonance-free trail," offering an adequate uniformity of the amplitude-frequency response over the working frequency range of the instrument.

All the experiments involved frequency and amplitude filtering to eliminate foreign noises; the gain of the system was of 80–90 dB with a fixed counting threshold of 1 V for the amplified signal. The absence of foreign noises in the process of loading was checked by the existence of the Kaiser effect, nonreproducibility of the AE at repeated loadings to the level of the load attained in the initial loading.

Ten to fifteen experiments under identical conditions were conducted for every system of samples.

Origination of AE signals at a definite initial amount of straining, increase of the signal count rate in the course of straining and its sharp rise before the fracture were typical of all the samples under study; the AE of a pure epoxy resin was considerably less than that of its filled compositions.

The obtained dependences of the AE total count on the load for practically all the tested samples are close to linear in a logarithmic coordinate system and are in the general form described by the equation

$$\ln N = n_\sigma \ln \sigma + B.$$

The parameter n_σ of the equation is determined from the slope of the ln N vs ln σ curve and characterizes the temporal variation of the total count of AE signals at a mechanical loading of the sample; it is called the relative count rate. The parameter B was not considered, since its variation is mainly associated with a change in the acoustic contact of the AE transducer with samples, upon a re-installation of the transducer.

RESULTS AND DISCUSSION

Figures 1 and 2 present experimental dependences of the count rate, total count, amplitude and frequency distribution of AE signals and of the applied load on the straining time for samples of a cured epoxy resin with 20 mass % dispersed quartz (particle size, 125–160 μm), not treated and treated with an antiadhesive (in bending tests).[10]

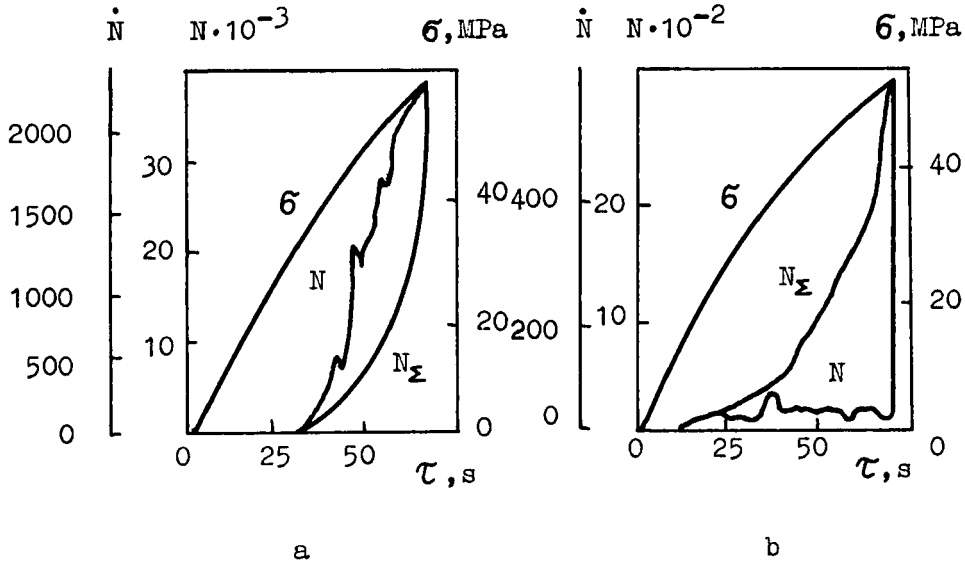

FIGURE 1 AE signal parameters and load as functions of straining time for samples of composite polymeric materials with filler untreated (a) and treated (b) with agent preventing adhesion; $\dot{N}$, events/s; $N \cdot 10^{-3}$ and $N \cdot 10^{-2}$, events.

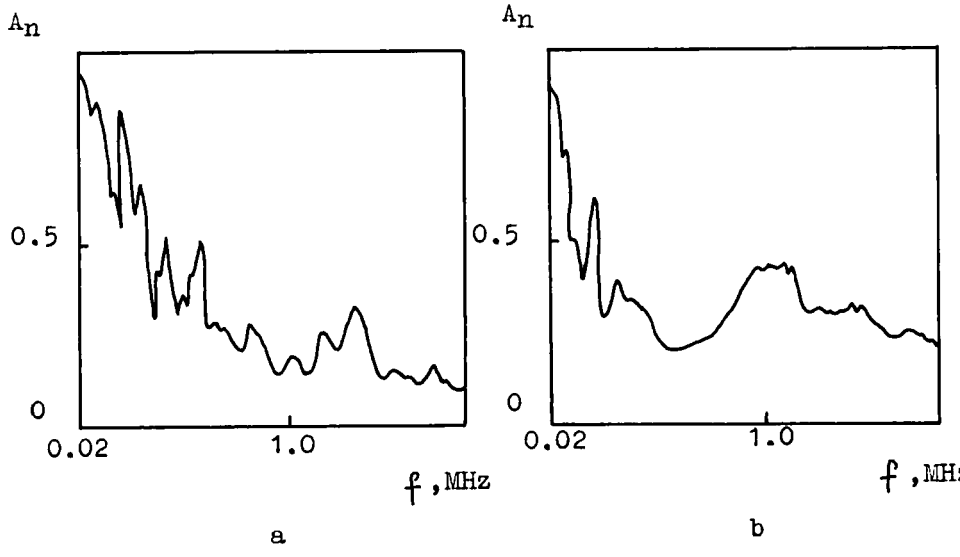

FIGURE 2 Spectral distribution of AE signals for samples of composite polymeric materials with filler untreated (a) and treated (b) with agent preventing adhesion at pre-rupture straining stage A_n, arbitrary units.

From the figures it can be seen that for samples of the epoxy resin with an antiadhesive-treated filler, as compared with those with an untreated filler, the number of AE signals declines (the total count and count rate decrease by an order of magnitude), the AE signal spectrum shifts towards higher frequencies, the relative count rate n_σ decreases from 7.82 to 3.55, and the sample strength drops from 58 to 48 MPa. AE signals arise here at lower loads and the count rate varies insignificantly in the course of loading. For samples with an untreated filler the AE signal count rate rises with increasing load during the whole straining process. The obtained dependences are accounted for by the fact that the filler treatment with an antiadhesive reduces the filler-matrix adhesion interaction and, thereby, leads to break of contacts at the interface at lower stresses in the sample and, as a consequence, to origination of AE signals of a lower energy and a higher frequency.

A similar effect of the filler treatment with an antiadhesive was also noted in the uniaxial tension tests of the samples: the AE signal number decreases by an order of magnitude, the relative count rate n_σ declines from 7.1 to 4.0, and sample strength decreases from 40 to 35 MPa, these characteristics varying insignificantly over the whole loading rate range studied.

The AE character is substantially affected by the concentration and dispersion of the filler. As can be seen from Fig. 3a, the total AE at initial straining stages rises with increasing filler concentration and declines at filler concentrations of over 20 mass %. The AE rise is associated with an increase in the number of emitting particles, and its further drop with a decline in the energy of acoustic signals at

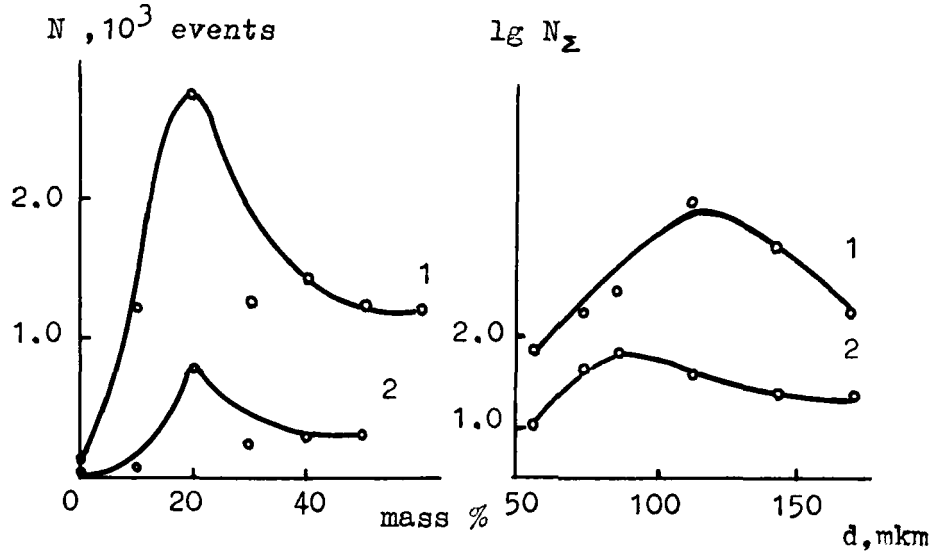

FIGURE 3 AE total count at fracture as a function of concentration (a) and dispersion (b) of filler (concentration, 20 mass %) untreated (1) and treated (2) with agent preventing adhesion.

origination of microcracks because of an overlap of fields of individual emitting particles and also due to increasing interface area between polymer and filler. The decrease in AE signal energy leads to the diminishing number of signals recorded. Figure 3b presents the total AE as a function of dispersity of the filler, treated and not treated with an antiadhesive, at its concentration of 20 mass %. As seen, the particle size and nature of the filler substantially affect the spectrum of the total AE. The filler treatment with an antiadhesive reduces the number of AE signals, while the character of the dependence of the total AE on the filler concentration and particle size remains unchanged.

Energetic parameters of microcrack formation are characterized by the amplitude distribution of AE signals which, for the whole test time, is shown in Fig. 4. A decrease in the filler-matrix adhesion interaction results in a shift of the maximum of the amplitude distribution of AE signals towards lower amplitude values for all the studied filler concentrations, which is evidence that the AE signal energy declines with decreasing strength of the adhesion contact.[11] The possibility of regis-

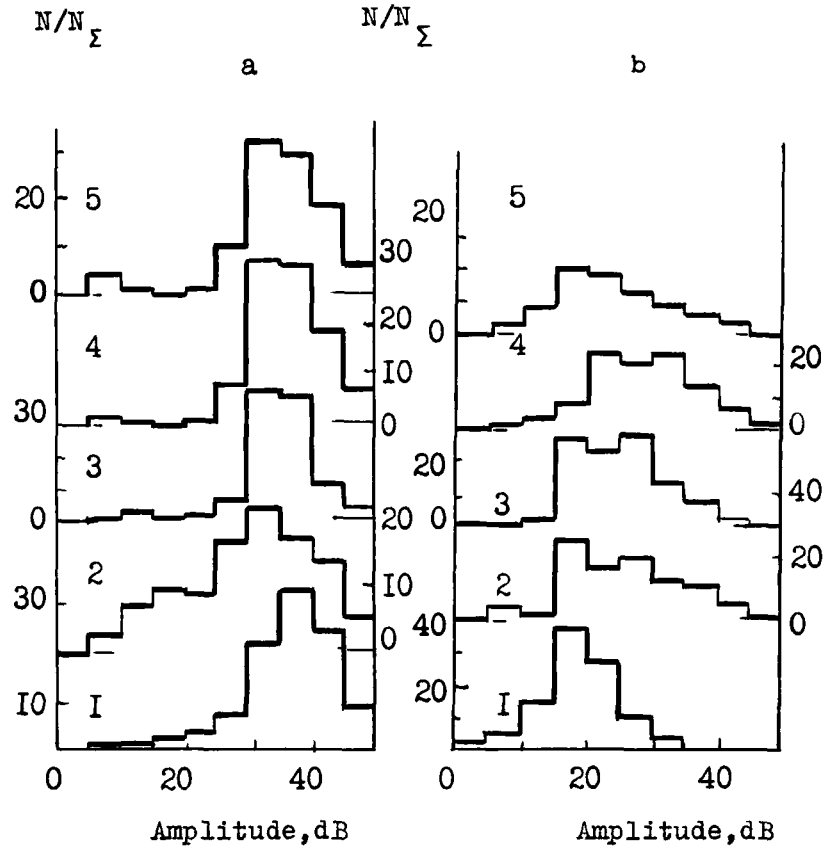

FIGURE 4 Amplitude distribution of AE signals for samples filled with untreated (a) and treated (b) disperse quartz. Filler concentration: 10 (1); 20 (2); 30 (3); 40 (4); and 50 mass % (5).

tration of AE signals with amplitude less 20 dB is determined by using the threshold for the amplified signal.

The selection of the count rate ($\dot{N}$) and total count (N) as the information parameters make it possible to record the kinetics of break of adhesion contacts and to determine the load at which the break occurs. The count rate *vs* straining time curve, shown in Fig. 5, exhibits a pronounced maximum, whose positions for samples with a treated and an untreated filler are substantially different. Its position for samples with a treated filler, for a constant loading rate of 0.2 MPa/min, corresponds to a load of 16 MPa, and for samples with an untreated filler, to 38 MPa. The obtained dependences of the AE total count on mechanical stresses acting in the sample are close to linear in a logarithmic coordinate system, as can be seen in Fig. 6, and are approximated by two straight-line segments. The load corresponding to the point of their intersection (*i.e.*, to an abrupt change in the relative count rate) is the

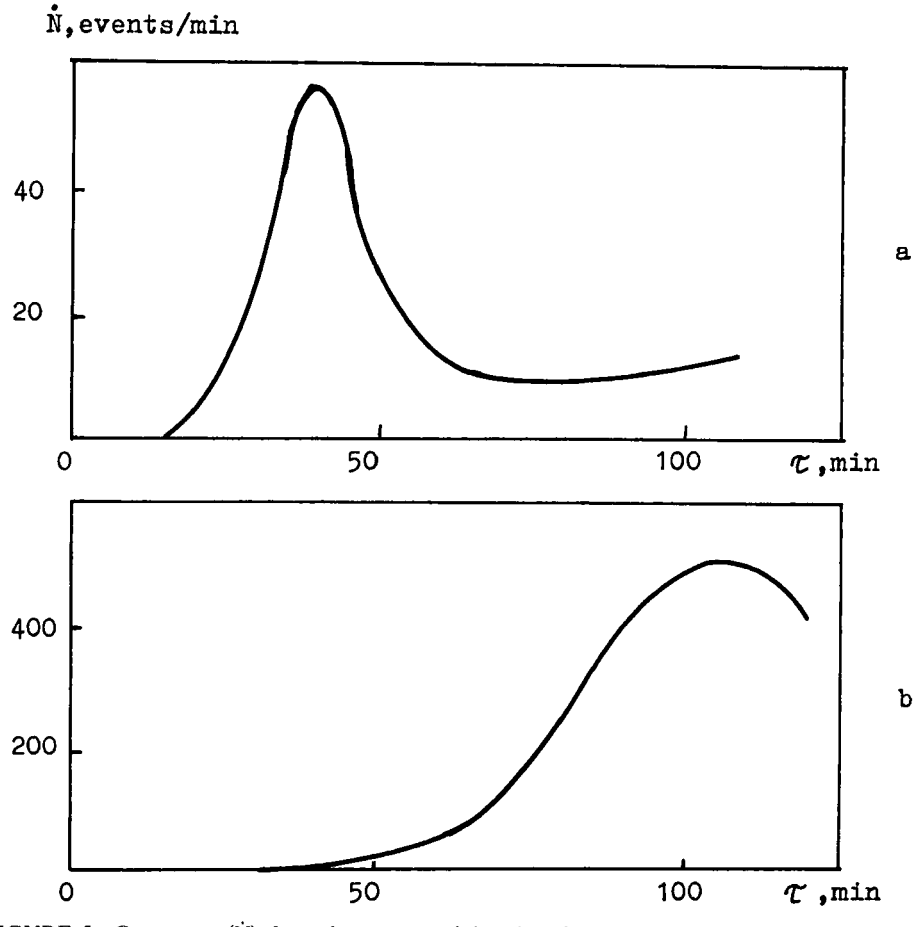

FIGURE 5 Count rate ($\dot{N}$) dependence on straining time for samples containing 20 mass % filler treated (a) and untreated (b) with agent preventing adhesion. Loading rate 0.4 MPa/min.

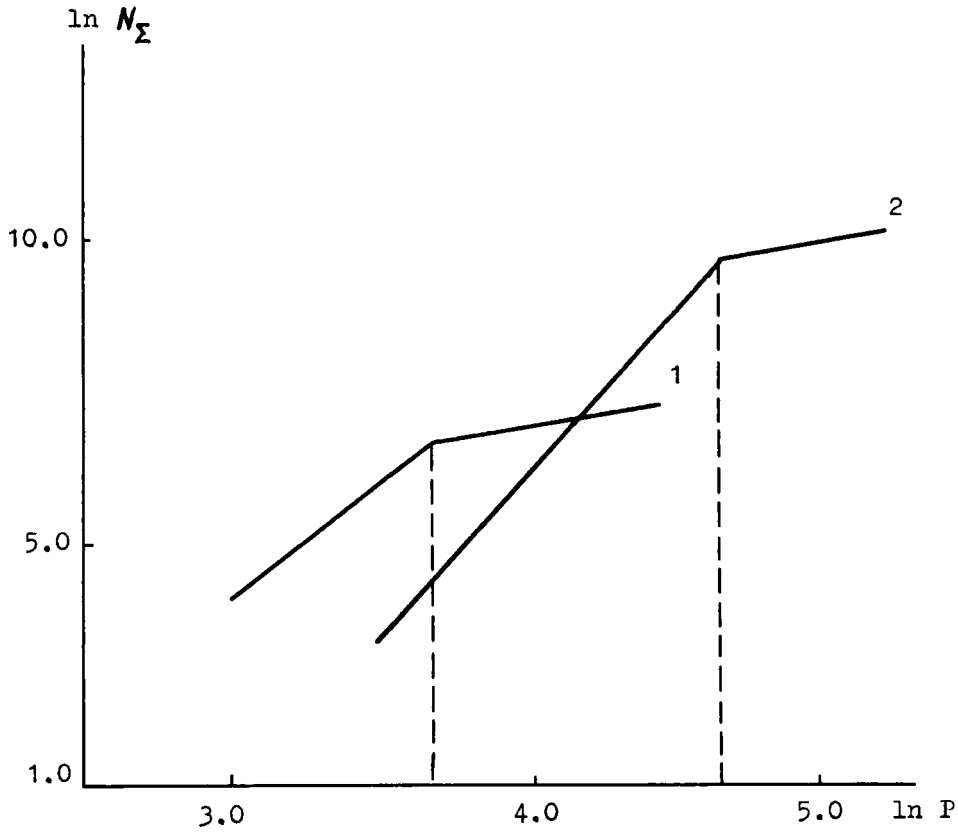

FIGURE 6 Logarithmic dependence of total acoustic emission on load for filled epoxy resin samples with filler treated (1) and untreated (2) with agent preventing adhesion.

load corresponding to the maximum AE signal count rate, which characterizes the maximum of the break of adhesion contacts of the filler with the most probable particle size (*i.e.*, that corresponding to the maximum of the filler particle size distribution curve). This makes possible a quantitative determination of the adhesion bond strength for the filler with the most probable particle size for polymeric composites with a disperse filler with a known particle size distribution. For a polydisperse filler the sizes of its particles affect the magnitude of the stress concentration near the particles (the stress at a pole of a rigid spherical particle is 1.8–2.0 times that in the matrix[13] and, therefore, when determining the critical stress $\sigma_{c.br.}$ for polymeric composites containing a disperse filler, one should take into account the stress concentration in the sample as well as its change with the filler concentration and size and shape of particles: that is, an increase in the filler concentration reduces, and an increase in the particle size increases, the stress intensity coefficient for the sample.[13]

Having accepted the above points and determined the load at which the maximum of the AE signal count rate for the most probable filler size is observed, we can

calculate the adhesion joint fracture stress. For this purpose the amplitude distribution of AE signals, the AE count rate, and their dependence on the load are recorded. When the load corresponding to the maximum count rate has been reached, then the stress is equal to $\sigma_{c.br.}$ and corresponds to an average stress in the sample, which includes the stress of a truly adhesion fracture and the stress counterbalancing internal stresses at the interface.

On the other hand, analyzing the kinetics of variation of the amplitude characteristics of AE signals (Fig. 7) allows an evaluation of the adhesion bond fracture

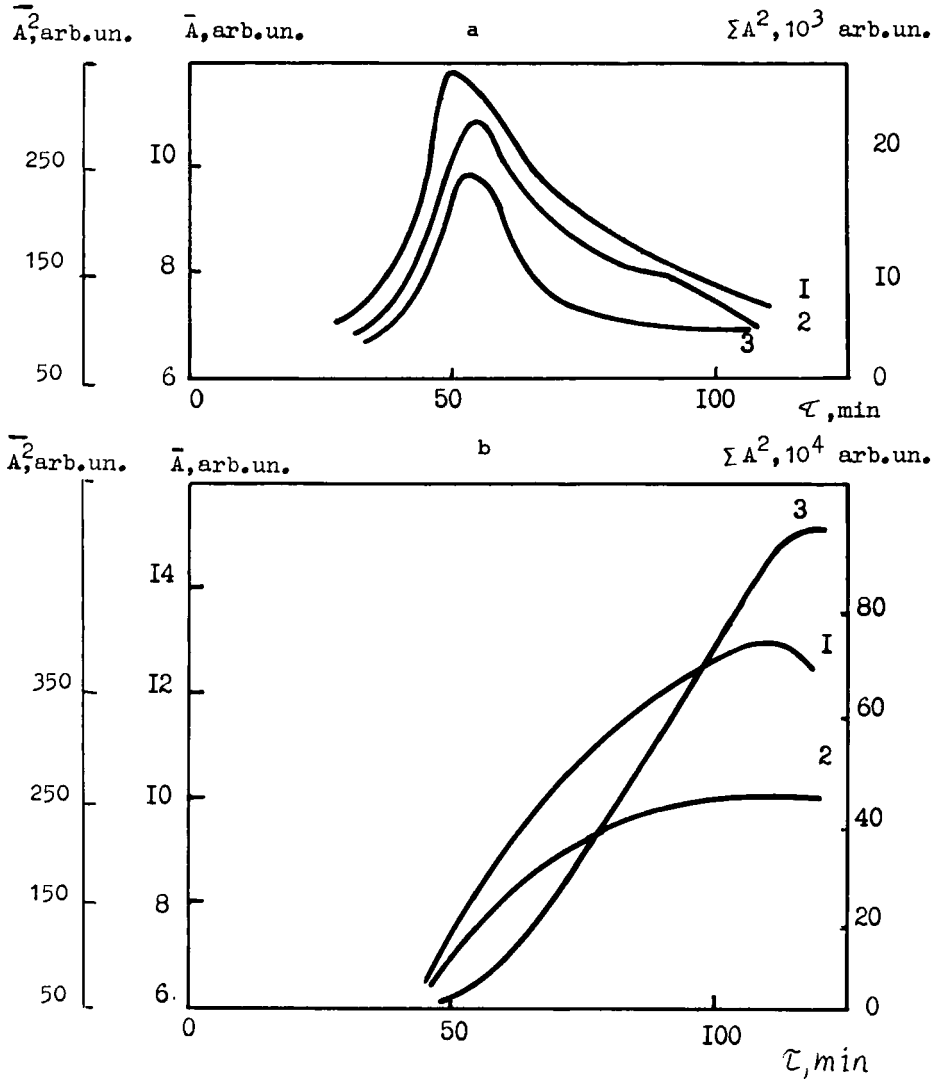

FIGURE 7 Variation of average amplitude (1), average (2) and total (3) energy of AE signals with straining time for samples containing 20 mass % filler treated (a) and untreated (b) with agent preventing adhesion. Loading rate 0.4 MPa/min.

energy, since a mean-square amplitude of the signal is proportional to the energy of the AE signal forming at a break of adhesion bonds. This is well illustrated by Fig. 7, where it can be seen that a decrease in the filler-matrix adhesion interaction results in a shift of the maximum of amplitude characteristics (average and total energies of signals) towards lower loads. Expressing the bond energy in absolute units calls for introduction of a parameter allowing for the distortion of the signal at its detection, which is extremely complex. Due to this, the signal energy can be expressed as a relative value with respect to the mean energy of the AE signal of a standard sample, which is similar to that of the sample under study in all the parameters, but which has the maximum filler-matrix bond strength.

CONCLUSION

The obtained results made it possible to ascertain a relation between the variation of AE parameters and the magnitude of the adhesion interaction at the filler-matrix interface in rigid polymeric composites, as well as to suggest a technique for calculating the adhesion joint strength on the basis of the maximum AE signal count rate, fracturing stress, and amplitude-frequency responses of the signals, with allowance for a complex-stressed state of the polymeric matrix at the filler particle surface, arising in the formation of the material.

Thus, it follows from the above that the acoustic emission method can be recognized as one of the better methods for detecting the adhesion contact break processes occurring in a polymeric composite as it is strained, as well as for a quantitative determination of the strength of such contacts.

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