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## The Journal of Adhesion

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### What is the Reason for Adhesion and Adhesive Joint Strength?

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## Note

### What is the Reason for Adhesion and Adhesive Joint Strength?

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Recently some papers were published, where criticism of current theories of adhesion had been given.<sup>1,2,3</sup> As a most general theory the rheological theory of adhesion has been proposed, or the theory of mechanical deformation of adhesive joints. This conception should be very useful if only it could give any reasonable clue to understanding of the cause of interfacial adhesion.

Unfortunately, the rheological theory does not account for why there is adhesion at all between two solids or solid and liquid and therefore this theory cannot be named as the theory of adhesion, but only adhesive joint strength.

Really, according to Sharpe,<sup>3</sup> the strength of adhesive joints is not determined by interfacial forces because "clean failure in adhesion is a highly uncommon occurrence." Such affirmation we think hardly can be accepted. To clear the matter up we must distinguish between two definitions—adhesion and adhesive joint strength.

There is a thermodynamic definition of the work of adhesion—and this is an equilibrium value, and there is a definition of adhesive joint strength, which is kinetic in character, depending on the rate of peeling. It is very well known that the theoretical strength of solids does not correspond to their real mechanical strength. Theoretical strength is determined by molecular forces whereas real strength is dependent on the structure defects and other causes, which can be compared for example with those described by

Bikerman as weak boundary layers. In the course of deformation of a solid there is also a great heat dissipation due to nonequilibrium conditions of deformation.

Therefore we believe that the following relation between the definition of "adhesion" and "adhesive joint strength" must exist: adhesion is equal to the adhesive joint strength only for ideal structure of boundary layers and for equilibrium conditions of failure, i.e., for deformation at infinitely small rate. It means that depending on deformation conditions the adhesive joint strength may be different (as it is very well known) and at the same time the equilibrium adhesion is invariant (compare with the new method of determination of the quasiequilibrium work of adhesion proposed by us recently).<sup>4</sup> The value of thermodynamic work of adhesion, if it could be correctly found, is the only quantity characterizing the value of adhesion and which has physical meaning independent of test conditions or conditions of joint formation.

Thus we can expect correlation between thermodynamical work of adhesion and real adhesive joint strength and there is nothing strange in it. It is only extraordinary that such a simple thing may lead to discussions and misunderstandings.

Now it is essential to discuss the relation between adhesion and cohesion strength taking into account that failure is preferentially cohesive, in the adhesive or the adherends. For this purpose let us consider the phase boundary for two one-component phases without mutual solubility. Polymers at the interface with metals and minerals can be considered as such a system. Most polymer-polymer couples also belong to these systems.

The cohesion energy of two phases are  $W_{k1}$  and  $W_{k2}$  and  $W_{k1} > W_{k2}$ . The adhesion work at the interface between these phases is  $W_a$ . As  $W_{k1}$ ,  $W_{k2}$  and  $W_a$  are constituents of the free energy of the system phase 1-phase 2, let us try to find the value  $W_a$ , at which the total free energy is minimal. As minimization of values  $W_{k1}$  and  $W_{k2}$  is predetermined by initial conditions, changes are possible for  $W_a$  only. As the border between two phases is impermeable, the single way of minimization of  $W_a$  is reaching the value of  $W_{k2}$ ,

$$W_a = W_{k2} \quad (1)$$

This equality can be proved in the following way. As

$$W_{k2} = 2\gamma_2 \quad (2)$$

and

$$W_a = \gamma_1 + \gamma_2 - \gamma_{12} \quad (3)$$

where  $\gamma_i$  — the surface tension of phase  $i$  and  $\gamma_{12}$  is the interfacial tension,

combining with Eq. (1) we obtain

$$2\gamma_2 = \gamma_1 + \gamma_2 - \gamma_{12} \quad \text{or} \quad \gamma_{12} = \gamma_1 - \gamma_2 \quad (4)$$

The latter equation is known as the rule of Antonow, which can be applied to a majority of investigated systems. Therefore we can conclude that Eq. (1), derived on the base of minimization of free energy of the system, is correct.

It follows that in the absence of specific forces of interaction at the interface and changing of molecular polarizability, the thermodynamical work of adhesion is determined by cohesion energy of the weak component. Therefore to improve the adhesive joint strength we have to use adhesives of high cohesion strength. This conclusion thus follows from an elementary treatment without regard to complex and multilayered structure of boundary layers of adhesives on solid surfaces.

In conclusion we can say that the phenomena of adhesion are based on a clearly determined molecular mechanism and that adsorption mechanism is the only such mechanism. All the phenomena connected with failure of adhesive joints are complicated by mechanical, electrical and structure effects which are decisive for failure in agreement with references 1 and 2. Recognizing the correctness of the rheological theory of adhesive joint strength, it is impossible at the same time to ignore the chemical nature of adhesives, their polymeric character (for the most part) and all the specifics which determine the behaviour of polymers in surface layers<sup>5,6</sup> and their adhering to solids (the existence of functional groups, steric regularity of chains, molecular conformation and aggregation and others).

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