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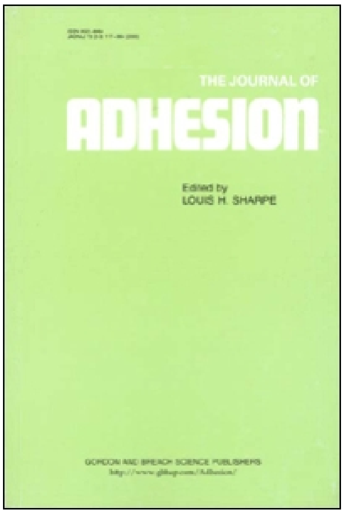

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Re: Contact Theory of Adhesion

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Note

Re: Contact Theory of Adhesion

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Recently we have developed a contact theory of adhesion published under the title "Interfacial Contact and Bonding in Autohesion".[1] The theory was formed for the case of polymers in a highly viscous state, where it is hard to bring them together for bonding. For low viscosity materials coalescence occurs very rapidly and contact is not a problem. However, most cases of adhesion that give us problems belong to the former case where establishment of contact between the two surfaces is the primary requirement. The rate of contact formation is controlled by the shape of the surfaces in contact, the viscous or viscoelastic properties of the material comprising them and the contact pressure. This is handled by extending Hertz' contact theory[2] by applying Alfrey's and Gurnee's elastic-viscous-viscoelastic analogy. Where-ever contact is established the interfacial bond strength may be obtained from molecular primary or secondary bond forces. This was obtained by using Good's[4] 6–12 Lennard-Jones potential treatment which is an extension of Hamaker's calculations.[5] Good has brought in the repulsive component in addition to the attractive forces. In case of polystyrene it is found that the intermolecular van der Waals' forces are sufficient to yield interfacial bond strength values equivalent in magnitude to the tensile strength of the polymer.

Recently, Voyutskii[6] takes contention with the above theory. According to him diffusion of molecules across the interface controls the bond strength. Their theory is based on a series of experiments under varying conditions of time, temperature, and pressure.[7] However, not all the results of their experiments can be explained by their theory.

Voyutskii says that the variation of autohesion with time is an important factor indicating that the diffusion phenomenon is the basis of self-adhesion. However, this may be explained from the contact point of view too. In the case of viscous or viscoelastic bodies, deformation is a time dependent process in which the contact area is a function of time, stress field or pressure and viscous and viscoelastic properties of the material.

In passing, we may mention that the autohesive strength at zero time is not zero, as measured by Voyutskii, due to initial contace being established at flat portions which are almost always present.

According to Voyutskii, the temperature dependence of diffusion may be written as:

$$D = D_0 \exp(-E_d/RT)$$

where D is the diffusion constant at absolute temperature T, E_d is the activation energy and D_0 is a constant.

Activation energy of autohesion E_p has been found to be 2800 calories per mole, a value which is characteristic of the activation energy of diffusion processes. Voyutskii, therefore concludes that self-adhesion must be a self-diffusion process. In his recent note, he gives plenty of evidence of diffusion taking place at the interface. We have no contention with this evidence. Diffusion is a natural phenomenon that occurs when two bodies are in contact. However, the bodies have to be brought in contact first.

We have already pointed out how time dependence of autohesion or contact is controlled by the viscosity. Now, the dependence of viscosity on temperature is very analogous to that of the temperature dependence of diffusion and we may write mathematically:

$$\eta = \eta_0 \exp(-E_{vis}/RT)$$

where η is the viscosity at temperature T, E_{vis} is the activation energy and η_0 is a constant.

Although actual elementary molecular processes involved in diffusion and viscosity are different, the overall activation energies of the two are very much the same.[8] For example, E_{vis} of tetrachlorethane is 2995 cal/mole, that of tetrabromoethane is 3745 with a mean value of 3370. The activation energy for mutual diffusion of these liquids is of the order of 3490.

According to Voyutskii's experiments, autohesion increases to a limiting maximum value with increasing pressure. Since pressure does not affect the diffusion rate process, he makes a passing remark that pressure influences autohesion by ensuring complete contact which is achieved at the expense of either elastic or plastic deformation of irregularities on the surface.

In fact, Voyutskii discounts the contact portion mostly by saying that this stage of bonding is trivial, Contact is taken for granted.

Diffusion of one species in another or in itself is a function of their solubilities in each other. Considering the case of adhesion of polymers to metals, it is usually found that the bond strength is somewhere between that of the polymer and the metal. Now at the bonding temperatures, the molecules of metal usually are immobile and the mutual solubilities may be estimated to be negligible. If diffusion were operating in such a case one would expect zero bond strength.

It would be wrong for us to assume that diffusion does not take place during autohesion. Its contribution to the bond strength seems insignificant. For diffusion to take place, the surfaces have to be brought together first, which is usually the major portion of the task of making two surfaces stick together. Once two surfaces are brought together, say within the range that molecular forces can take over, the interfacial bond strength is the same as that of a solid polymer. Any other process, such as diffusion, that will take place at the interface cannot improve upon this. It merely results in rearrangement of molecules which is always going on, in any case, in molten polymers.

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