

## Modern State of Models for Fundamental Adhesion - A Review Extended Abstract

Wulff Possart<sup>†</sup>

### ABSTRACT

Advanced adhesive technologies and demanding applications of adhesive joints can no longer be developed successfully by the traditional "trial and error" approach. Appropriate technical solutions require reference to a reliable basis of well-established scientific knowledge about the elementary mechanisms of adhesion (i.e. the 'fundamental adhesion') as they are responsible for the capability of the compound to transmit mechanical force between the adhesive and the substrate surface (i.e. the 'practical adhesion'). Adhesion mechanisms also influence the formation of polymer structure in the adhesive and the resulting macromolecular dynamics in the interphase that is formed in the adhesive near to the substrate. These manifold molecular factors rule the macroscopic behaviour of an adhesive bond line in terms of mechanical and other physical properties as well as in terms of durability. This paper reviews the level of refinement that understanding of fundamental adhesion has achieved up to now.

### THE DYNAMICS OF MACROMOLECULES AT THE BOUNDARY TO A SECOND PHASE

According to the results of theoretical polymer physics (see e.g.<sup>(1,2)</sup>), the surface of a linear amorphous polymer exists in one of two states before it comes into contact with a second material. Either the macromolecular coils are flattened and their segments arrange preferentially parallel to the surface or the segment concentration drops at the surface as compared to the bulk.

The kinetics of interphase formation are

still poorly understood. Most scientific work refers to the equilibrium state.

### Polymer-Polymer Interphases

The equilibrium structure of the interphase is ruled by the polymer-polymer compatibility which is described by the Flory-Huggins interaction parameter  $\chi_{AB}$ . For  $\chi_{AB}$  smaller than the critical value  $\chi_{AB}^{crit}$ , the polymers are compatible (with  $\chi_{AB}^{crit} = 0.5 \cdot (N_A^{-0.5} + N_B^{-0.5})^2$  with  $N_A$  and  $N_B$  being the degrees of polymerisation for the polymers A and B<sup>(3)</sup>). Obviously, compatibility drops with increasing chain length. For  $\chi_{AB} < \chi_{AB}^{crit}$ , interdiffusion proceeds at the contact face

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• The Saarland University, Gebaeude 22-6, P.O.B.151 150, D-66041 Saarbruecken, Germany

<sup>†</sup>Corresponding author: e-mail: w.possart@rz.uni-sb.de

of polymers A and B thus forming the interphase of intermingled chains of types A and B. That type of interphase plays the key role in the diffusion theory of adhesion introduced by Voyuckij et al. around 1960 (e.g.<sup>[4]</sup>) and improved by other workers (e.g.<sup>[5-8]</sup>). Of course, crystallites or chemical links between the chains in a network hinder the interphase formation.

#### Compatible Polymers – The Diffusion Theory of Adhesion

Compatibility is found if the attractive interaction between segments of A and B is stronger than the interactions A-A and B-B, respectively. This is the thermodynamic force that drives interdiffusion and minimises the free enthalpy of the system. The viscoelastic state is indispensable for interdiffusion since this process is based on the co-operative motion of chain segments. Among the several modes of motion that a polymer chain executes, parts of the generalised Rouse relaxation<sup>[9]</sup> and the reptation of chains (according to deGennes, Doi, Edwards,<sup>[10,11]</sup>) are responsible for creating the interdiffusion layer. The time constant  $\tau_{\text{segment}}^{\text{Rouse}}$  of the Rouse relaxation of a segment between two temporary entanglements scales with  $M_{\text{segment}}^2$  ( $M_{\text{segment}}$  = molecular mass of the segment). The segmental Rouse relaxation is quite fast ( $\tau_{\text{segment}}^{\text{Rouse}} = 10^1 \text{ A}10^2$ ) and results in an interpenetration depth of  $d_{\text{segment}}^{\text{Rouse}} \approx 10^9$  nm. Chain reptation is much slower with  $\tau_{\text{chain}}^{\text{reptation}} \approx 10^5$  since  $\tau_{\text{chain}}^{\text{reptation}} \propto M_{\text{chain}}^3$  but it results in a more extended interpenetration:  $d_{\text{chain}}^{\text{reptation}} \approx 0,8 \cdot R_g \propto \sqrt{M_{\text{chain}}} \approx 10^1$  nm,  $R_g$  is the radius of gyration.

In summary, creating adhesion between two compatible polymers by interdiffusion is a time-consuming process and requires elevated temperatures. If it is well performed, it results in mechanical strength values for the interphase that compare with the cohesive strength of the polymers.

#### Incompatible Polymers

Unfortunately, the majority of polymers is not compatible, i.e. the attractive interaction between segments of A and B is weaker than the interactions A-A and B-B in the bulk. This relative 'repulsion' hampers the interdiffusion. Compared with the 'free' polymer surface, it forces an additional depletion of segments at the contact to the 'hostile' polymer neighbour. This results in an additional loss of conformational entropy because more thermodynamic degrees of freedom are blocked than at the free surface. In turn, the loss of entropy acts now as a new thermodynamic force which produces some segmental interpenetration despite the energetic interaction forces are insufficient. According to Helfand et al.,<sup>[12]</sup> this entropic interdiffusion is called 'conformational relaxation'. It produces an interphase of a width  $d_{\text{AB}}^{\text{conform.relax.}} = 2\lambda(6\chi_{\text{AB}})^{-0.5} \approx 10^9 \text{ A}10^1$  nm with  $\lambda$  being the segment length. This interphase thickness is comparable with compatible polymers. Nevertheless, its mechanical strength is by orders of magnitude lower than for the polymer bulk because the conformational relaxation is completed with only a few diffusing segments.

For technical applications this unfavourable situation is improved by the use of compatibilisers (see e.g.<sup>[13]</sup>). These are block-copolymers with at least one block being compatible only with polymer A and another block being compatible only with polymer B. Hence, the copolymer molecules enrich at the boundary between those two polymers. With an average molecular mass of about 50,000 g/mole per block, each block is mobile enough to penetrate into the polymer that is compatible to it. As the result of this particular type of diffusion, the copolymer molecules form molecular anchors between the incompatible polymers. These anchors are strong enough to

improve the mechanical strength of the interphase considerably.

### Polymers on Impenetrable Solids<sup>[14]</sup>

The surfaces of all metals, oxides, salts etc. perform an impenetrable wall for polymer molecules. Therefore, they generally cause a depletion of segments in a contacting polymer due to the loss of degrees of freedom and thus of conformational energy. This undesirable effect has to be neutralised by surface sites that attract local atom groups at the polymer chain—the adhesive groups. If a polymer molecule is flexible enough, it can interact via many of these adhesive groups. Therefore, during the formation of the adhesive contact the macromolecules must be flexible, i.e. in the visco-elastic state. Having a sufficient strength and a sufficient density of interactions between surface site and adhesive group, the deficit in entropy is overcompensated and the specific free energy of adsorption  $\Delta f_{\text{ads}} = A_{\text{contact}}^{-1} \cdot (F_{\text{interphase}} - F_{\text{bulk}}) = \Delta U_{\text{ads}} - T \cdot \Delta S_{\text{ads}}$  will be negative. Only in such a case of 'positive adsorption' the polymer will adhere to the solid. As the adhesive groups are part of the polymer chain, their adsorption affects the conformational state of the chain and in some cases even its entanglement with other chains between solid and polymer bulk. As the consequence, this adhesion may not be considered as a local event between surface sites on the solid and adhesive groups at the polymer chain but it should be treated as a collective phenomenon.

#### Polymer Solutions on Impenetrable Solids

The small-sized solvent molecules make the polymer chains very flexible. Contacting the solution with solids will open the door to a variety of situations.

First, a good solvent is bad for adhesion since the surface sites are unable to

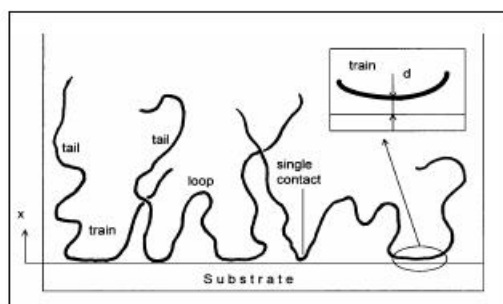
displace the solvate shell that covers the adhesive groups at the polymer chain. Secondly, for a bad solvent, the polymer molecules enrich and increase the segment density even on a non-adhesive solid just in order to avoid contact with the solvent as much as possible. Such a process will not provide good adhesion. On a solid with adhesive surface sites, however, the enrichment of segments supports the formation of adhesive contacts on the segment level and strong adhesion.

As a third case, the solvent molecules may adsorb at the surface sites, too. This compels the chain segments to compete with the solvent molecules for the adhesive sites. For irreversible adsorption of solvent, this so-called 'competitive' or 'preferential' adsorption will obstruct the adhesion. Otherwise, step by step, the macromolecular chains will displace the adsorbed solvent molecules for a simple reason: the adsorbed small solvent molecule occupies just one surface site. The dynamic equilibrium of adsorption and desorption will set it free after some time and a chain segment can attach to the surface site. Since the polymer chain adheres with its segments simultaneously to many sites there is an almost negligible probability of chain desorption and the solvent cannot win the competition.

#### Polymer Melts on Impenetrable Solids

According to Sect.1.2, the visco-elastic polymer will adhere to the solid in case of 'positive adsorption'. The structure of the interphase is determined by the balance of adhesive interactions and segment-segment interactions, see Figure 1.

The trains are responsible for the adhesion. As they contain several adhesive contacts, a weak interaction force per site can provide strong adhesion, too. In case that external forces have torn off parts of the macromolecule, the segment mobility



**Figure 1. Polymer adsorption on a solid. The three chains adsorb in trains while loops and tails are responsible for the entanglement with the polymer bulk (not shown).**

provides a repair mechanism for the adhesion. These dynamics explain the principle of pressure sensitive adhesives in a qualitative manner. The mechanical strength of the whole bond is not only determined by adhesion but it is much influenced by the entanglement of the adsorbed chains with the rest of the polymer. This entanglement has to be performed by the tails and the loops. Therefore, if chains form too long trains a weak boundary layer will be formed despite of excellent adhesion.

## INTERACTION FORCES AND ADHESION

The preceding paragraphs illustrate that the various processes influence each other at the polymersolid contact in a very complex way. As a result, the polymer structure in the interphase is in a delicate dynamic equilibrium. Now, we focus on the nature of local adhesive interactions between the active sites on a solid and the adhesive groups at the macromolecular chain. These interactions are the starting point and keystone for the interphase. Up to now, they cannot be described by a unified theory but by a set of models that will be discussed in the following sections.

## Thermodynamic Models of Adhesion

The most prominent contributions to this class of models have been made by Zisman et al. (e.g.<sup>[15]</sup>), Fowkes et al. (e.g.<sup>[16]</sup>), Good et al. (e.g.<sup>[17]</sup>) and Neumann et al. (e.g.<sup>[18]</sup>). Basically, they all intend to derive conclusions about adhesion from wetting experiments with a series of testing liquids. The details go beyond the scope of this abstract. In summary, neglecting the experimental problem of contact angle hysteresis all models at least assume that the interfacial free energy is a parameter of a single phase, i.e. of the solid or of the adhesive. However, the Gibbsian thermodynamics for heterogeneous systems shows that any interfacial free energy or interface tension  $\gamma_{AB}$  describe the contact area of two phases (e.g.<sup>[19]</sup>). The thermodynamic equilibrium of the phase boundary, i.e. the interphase in our notation, corresponds to the minimum of the interfacial free energy which depends on the interface tension and on the adsorption of components in the interphase. The models neglect the adsorption although the resulting error cannot be estimated.<sup>[20]</sup> Hence the well-known Dupré equation for the reversible work of adhesion  $W_{adh} = \gamma_{A,v} + \gamma_{B,v} - \gamma_{A,B}$  (with the surface tensions  $\gamma_{A,v}$ ,  $\gamma_{B,v}$  for adhesive and substrate, respectively) turns out to be just an approximation. Due to different additional assumptions, each model could lead to unexpected errors and discrepancies to the real behaviour of contacting phases might appear. It follows from the exact thermodynamic consideration that wetting experiments are neither sufficient for the thermodynamic description of a solid-liquid or a solid-solid interphase nor do they correctly assess the Van der Waals interactions at these phase boundaries.<sup>[21]</sup>

## The Electrostatic Component of Adhesion

In the 40ies and 50ies of the 20<sup>th</sup> century, Deryaguinetal. (see e.g.<sup>[22]</sup>) observed a number of electrical effects during mechanical testing of polymer–solid compounds. They were the first who interpreted these effects as a consequence of the electric double layer (EDL) at the contact. If the contacting phases contain free charges (ions or electrons) that can move freely between them, an EDL will be created during the thermodynamic equilibration of the electrochemical potential at the contact. This holds also for polymers and other insulators. The EDL consists of two space charges of opposite sign each of them located near to the contact in one of the two phases. The energy stored in the electric field between the attracting space charges represents a contribution to the adhesive interaction. The space charge distribution in a polymer adhesive can be deduced from experiments with the help of a physical model derived in previous work.<sup>[23]</sup> According to mechanical testing for appropriate polymer–metal systems,<sup>[24]</sup> the electrostatic component does not seem to provide a major contribution to the fundamental adhesion or to the mechanical strength of bonds with polymer adhesives.

## Chemical Adhesion

All available spectroscopic results show that chemical adhesion mechanisms are based on interactions between the electron systems of adhesive molecule and adherend surface. For both parts, these interactions are very specific. They can be described by the quantum mechanical theory for molecular orbitals including the electronic band structure of the adherend surface. Today, the concept of frontier orbitals<sup>[25]</sup> and the principle of soft/hard acids and bases<sup>[26,27]</sup> are used as qualitative tools for predicting

chemical adhesion.<sup>[28]</sup> So far, serious quantum mechanical calculations were carried out only in few investigations. The majority of chemical adhesion models proposed in literature are deduced from spectroscopic data and need further quantum mechanical verification. It turns out that chemical adhesion is adequately described by electron donor–acceptor interactions which involve several atoms of both partners in many cases. For the following moieties, chemical adhesion mechanisms are described on a variety of oxidised metal surfaces: carbonyl and carboxyl groups (polyacrylates, polyesters, PVAC, ...),<sup>[29]</sup> for the primary and secondary amines in epoxy systems,<sup>[30]</sup> and for the trioxotriazine ring in polycyanurates.<sup>[31]</sup> No such mechanism has been identified for isocyanate systems yet. All known mechanisms are highly selective for their partner sites on the adherend surface. The details of these sites are not revealed so far.

Chemical adhesion bonds force a particular orientation of the adhering molecules on the substrate surface. This could modify the morphology in the interphase of the adhesive and even the polymerisation in reactive systems. Therefore, chemical bonds between adhesive and adherend do not automatically guarantee high mechanical strength for an adhesive bond.

## CONCLUSIONS

Structure and properties (glass transition, density, molecular mobility etc.) of an adhesive interphase can deviate considerably from the bulk. Especially for polymer–polymer interphases in concentrated systems, we have still only few suitable experimental techniques to investigate these processes and effects either on the molecular or on a macroscopic level. Efforts will have to be made to adapt



polymer characterisation methods to this purpose. Today, the interplay of polymer dynamics and adhesive interaction forces cannot be described very precisely. This situation is even worse for crystallising polymers, copolymers and blends.

Our idea about the adhesion mechanisms and about the resulting molecular state of the interphase is still fragmentary and therefore further development is needed. Therefore, the necessary experimental methods do already exist or appropriate surface analytical techniques need to be adapted. Quantum mechanically based methods of molecular modelling have to be integrated into the research concepts. Here, the rapid progress in computing equipment and in software development is giving a very positive impact.

Another crucial question is the measurement of macroscopic properties (e.g. mechanical quantities) for the adhesive interphase and their link to structure and molecular properties. Additionally, the influences of temperature and of diffusing media have to be considered in order to understand ageing phenomena and durability.

All these research efforts are challenging with respect to the intellectual complexity, to interdisciplinary co-operation and to the required financial resources. But scientific advancement will be the key for systematic design of improved adhesive joints in the future.

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