

## New Perspectives in Polymer Adhesion Mechanisms — Importance of diffusion and molecular bonding in adhesion\*

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### Abstract

This paper reviews new perspectives in polymer adhesion mechanisms. Both reptation theory and related experiments have demonstrated the existence of either self-diffusion or interdiffusion of rubbery polymers at the interfaces. Thus, adhesive strength, green strength, and tack of elastomeric adhesives can be at least partially explained on the basis of the diffusion mechanism. Besides diffusion, the adsorption mechanism plays a major role in achieving molecular contact. Without molecular contact, polymer molecules can not attain adequate diffusion or physical adsorption at the interface through van der Waals attraction. When the molecular distance is less than 4 Å, chemisorption can take place due to molecular interaction. Thus, both physisorption and chemisorption are important in enhancing adhesion. In addition to the above mechanisms, we shall mention briefly the mechanisms of mechanical interlocking, chemical bonding, and electronic adhesion.

### 1. Introduction

The adhesion of a polymer depends greatly on its physical state.<sup>1,2</sup> Thus, it is difficult to generalize about an adhesion mechanism without referring to its physical state because the viscosity of a polymer varies a great deal as it transforms from rubbery to glassy state. On the basis of Buche-Cashin-Debye's equation, the molecular diffusion constant  $D$  can be expressed as a function of viscosity and other parameters:<sup>3</sup>

$$D \eta = (A \rho k T / 36) (R^2 / M), \quad (1)$$

where  $\eta$  is the bulk viscosity;  $A$  Avogadro's number;  $\rho$  the density;  $k$  the Boltzmann's constant;  $T$  the absolute temperature;  $M$  the molecular weight; and  $R^2$  the mean square end-to-end distance of a single polymer chain. The physical state of the polymer determines which major adhesion mechanism is operative. Polymer adhesion can be subdivided into rubbery polymer-rubbery polymer adhesion ( $R$ - $R$  adhesion), rubbery polymer-glassy polymer adhesion ( $R$ - $G$  adhesion), and rubbery polymer-nonpolymer adhesion ( $R$ - $S$  adhesion). Diffusion, which depends to a great extent on the physical state of a polymer, is actually a limited selective process. Thus, diffusion of rubbery polymers can take place at the interface, but diffusion of a glassy polymer at a viscosity of  $10^{13}$  poise or a diffusion constant of  $10^{-21}$  cm<sup>2</sup>/sec appears to be nearly impossible. On the other hand, physical adsorption is common to all three types of the above adhesion systems.

Since 1971, polymer physics has taken a new turn with a remarkable observation by P. G. de Gennes<sup>4</sup> that there is a correspondence between self-avoiding random walks and the phase-transition properties of an  $n$ -vector model of ferromagnetism for  $n = 0$ . (In the  $n$ -vector model,  $n$  denotes the number of degrees of freedom of electron spins;  $n = 1$  corresponds to the usual Ising model.) Subsequently, this discovery opened a new path for polymer physicists to apply powerful scaling<sup>5</sup> and renormalization group methods to solve polymer problems, e.g., entanglement in polymer solutions<sup>6</sup> and melt,<sup>7</sup> diffusion,<sup>8,9</sup> welding (or healing),<sup>10</sup> and adsorption at the interface.<sup>11,12</sup>

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In recent years, in addition to theoretical developments, for example., reptation<sup>4</sup> and "tube" theories,<sup>13,14</sup> there have been many new analytical techniques,<sup>15</sup> including electron-induced x-ray fluorescence, NMR field gradient method, forced Rayleigh scattering (FRS), forward recoil spectrometry (FRES), photon correlation spectroscopy, Rutherford back scattering, small-angle neutron scattering (SANS), etc. All of these techniques have been used to verify theoretical predictions about polymer dynamics. In comparison to the '60s, we now know more about diffusion, welding, polymer interfaces, adsorption, chemical bonding, and other mechanisms related to adhesion.

For an historical review of adhesion mechanisms published in the literature, the readers should consult a review by Huntsberger,<sup>16</sup> two articles by Kinloch,<sup>17</sup> and a recent account by Allen.<sup>18</sup> In the following, we shall summarize briefly some of the major developments on polymer adhesion mechanisms in recent years and some of the studies that are still in progress. Our emphases will be on diffusion and molecular bonding mechanisms.

## 2. Diffusion Mechanism

Voyutskii<sup>19</sup> first proposed that diffusion was the major driving force for polymer autohesion and heterohehion. The parameters for diffusion are contact time, temperature, polymer type, molecular weight, and viscosity. Some of these parameters have been related in Eq. (1). However, some of them may also be related to the kinetics of wetting as discussed in the next section on physical adsorption. Thus, there were doubts about the validity of the diffusion theory of adhesion. Since the introduction of the reptation theory, there have been many publications devoted to self-diffusion and interdiffusion in polymer solutions and melts.<sup>15</sup> Here, we briefly discuss the application of the reptation theory to diffusion and the difference between the original diffusion (macroscopic) theory and that derived from the reptation theory.

### 2.1. Viscoelastic properties of polymers

For a linear, flexible polymer, the viscoelastic properties<sup>7</sup> display a certain characteristic (relaxation) time  $\tau$ , which increases rapidly with the molecular weight  $M$ , (or equivalently with the number  $N$  monomers per chain). Thus,

$$\tau = \tau_0 N^a, \quad (2)$$

where  $\tau_0$  is a microscopic time (of the order of  $10^{-10}$  sec in melts) and  $a$  is an exponent of the order of 3.2-3.4. Since  $N$  is generally in the range of  $10^4$ - $10^5$ , the time  $\tau$  may be extremely long (minutes). Thus when  $t > \tau$ , the chains appear to be tied up in knots. Conversely, when  $t < \tau$ , the chains flow.

As the molecular weight further increases passing a critical point,  $M_c$  (or  $N_c$ ), the entanglement of flexible chains takes place. The steady-flow viscosity  $\eta$  at low shear rate abruptly increases at  $N_c$  as shown in Fig. 1:<sup>20</sup>

$$\eta \propto N, (N < N_c) ; \quad (3)$$

$$\eta \propto N^{3/4}, (N > N_c) . \quad (4)$$

Generally,  $N_c$  is between 300 and 600 in an undiluted polymer (or melt).

## 2.2. Theories of self-diffusion

The self-diffusion of polymers<sup>8</sup> in concentrated and undiluted solutions has been described by at least three theories: entanglement coupling, reptation, and cooperative. We shall mention the first two theories.

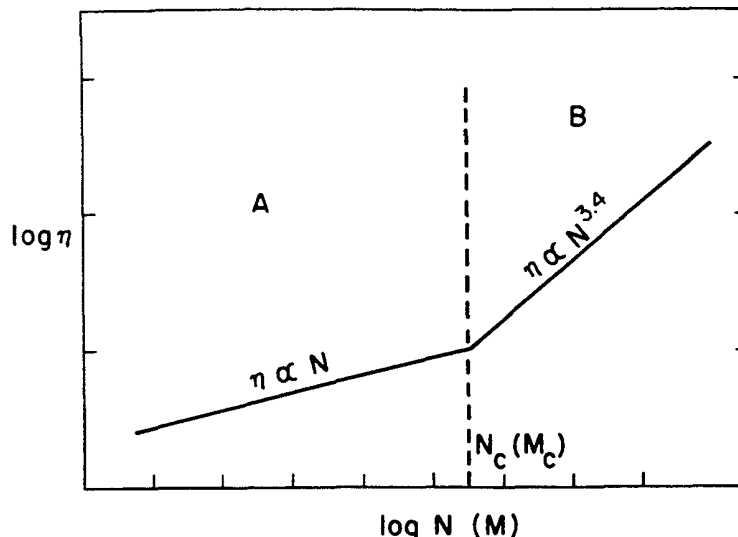


Fig. 1. Variation of the steady-flow viscosity with degree of polymerization  $N$  for a linear polymer in solution at fixed polymer concentration ( $c \gg c^*$ , the overlap concentration). (From J. Klein, *Macromolecules*, 11, 853 (1978)).

In the entanglement coupling theory,<sup>8</sup> the self-diffusion constant  $D_s$  is related to  $N$  on the basis of the free draining concept as

$$D_s \propto N^{-1} \quad (5)$$

It was postulated that above a critical value of  $N$  ( $N > N_c$ ) coupling of chains takes place, resulting in an increase in the frictional drag. As a result, the viscosity increases as shown in Fig. 1, but the self-diffusion decreases. However, the original theory did not consider the spatial or the topological constraints along the contour of a polymer chain when it is heavily penetrated and surrounded by other chains.

On the other hand, the reptation theory proposed by de Gennes<sup>4</sup> assumes that a flexible chain diffuses in a fixed three-dimensional mesh of obstacles which the chain could not cross (Fig. 2). Thus, the chain would be topologically constrained to move by a curvilinear, or snake-like motion alone. This motion was named as reptation (derived from "reptile"). One can visualize that the flexible chain is reptating by a Brownian diffusion within a "tube" surrounded by obstacles, but motions proceed perpendicular to the axis if the tube is blocked. For a chain made from  $N$  monomers of size  $a$ , the coefficient of the curvilinear diffusion,  $D_t$ , along the tube is

$$D_t = \frac{kT}{\eta a N}, \quad (6)$$

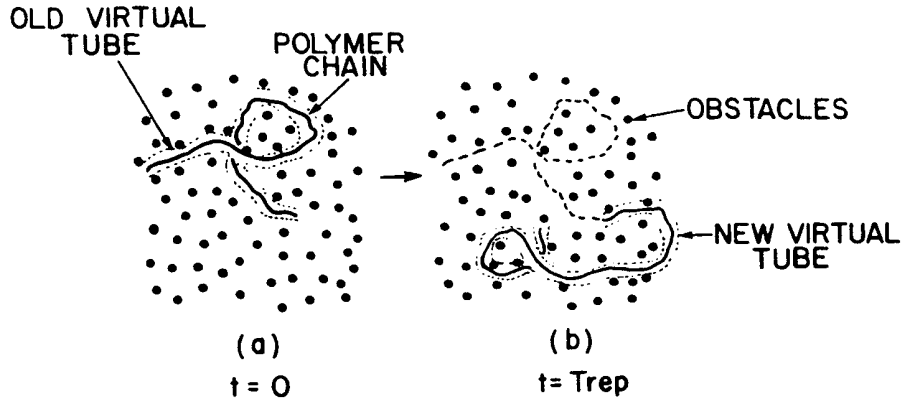


Fig. 2. Schematics of reptation of polymer chains.

where  $\eta$  is the viscosity or the monomer-monomer friction coefficient.

At each instant, the ends of the chain find their ways randomly among the obstacles formed by other chains, and progressively define a new tube. The time required to recover completely the conformation of the initial tube is the reptation time,  $T_{rep}$  such that

$$D_t T_{rep} = L_t^2, \quad (7)$$

where  $L_t = [(N/N_e)^2 N_e a^2]^{1/2}$  is the curvilinear length of the tube, and  $N_e$  is the average number of monomers between two entanglements. For a common polymer,  $N_e$  is a phenomenological parameter equal to  $\approx 100$ . The average diameter of the tube is therefore  $(N_e a^2)^{1/2}$ . From the above two equations, one can deduce that

$$T_{rep} = N^3. \quad (8)$$

Since the tube has a random conformation, the experimentally determined diffusion coefficient in a given direction is not  $D_t$  but rather  $D_s$  (self-diffusion coefficient) such that

$$D_s T_{rep} = R_G^2 = N a^2, \quad (9)$$

which is the random walk of step time  $T_{rep}$  and of step length equal to the radius of gyration of the chain,  $R_G$  ( $\sim N^{1/2}$ ), thus

$$D_s \sim N^{-2}. \quad (10)$$

This diffusion process is very slow and experimental measurements reveal that for  $a \sim 3 \times 10^{-8}$ ,  $N \sim 10^3$ ,  $D_s \sim 10^{11} \text{cm}^2/\text{sec}$  (for most rubbery polymers). In the melt, Klein and Briscoe<sup>21</sup> were able to obtain a  $D_s \sim M_w^{-2 \pm 0.1}$  for a polymer of large polydispersity ( $M_w/M_N \sim 20$ ). This result is very close to the value predicted by the reptation model.

The power law in  $N^{-2}$  for  $D_s$  is a characteristic of the reptation model and is rather well verified experimentally, although refinements of the model are required to take into account the fact that the topological constraints imposed by other chains are not fixed.<sup>20</sup>

### 2.3. Self-diffusion coefficient

Though the diffusion model predicts very well the time-dependence of the rehealing experiments, there are still many unanswered questions, such as the absolute value of  $D$ , the roles of chain-ends and of molecular weight, the influence of the relaxing fibrils derived from the fracture event, and the nature of the physical links. The relationships of  $D$  to viscoelastic and structural parameters still rely on the macroscopic formulation such as the Buche-Cashin-Debye's equation<sup>3</sup> as in Eq.(1), which was derived from the free draining model for both entangled and nonentangled systems. For example, Klein *et al.*<sup>21</sup> determined the  $D_s$  for polyethylene ( $M_w = 11,000$ ) at 176°C to be  $3.7 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ . In contrast, the  $D_s$  calculated from Eq.(1) is  $1.4 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ . The agreement between the experiment and the calculated value of  $D_s$  is rather good.

### 2.4. Interdiffusion, healing, and welding

Through diffusion, the cracks in a polymer can be healed, and two different parts of a polymer can be rejoined or welded together. The interdiffusion of polymer chains across the interface requires the polymer to be mutually soluble or similar in the solubility parameters and the polymer chains to have sufficient mobility. In all cases, the polymers should achieve a molecular contact before diffusion can take place. In the following, we shall discuss briefly the application of the reptation model to the healing and welding processes.

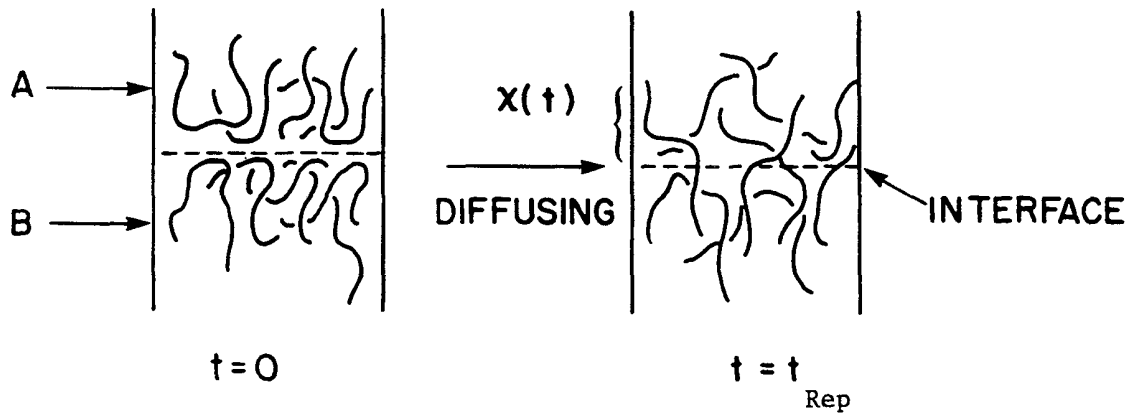


Fig. 3. Interdiffusion across the interface.

The term  $x(t)$  has been defined by de Gennes<sup>22</sup> as the thickness of the interdigitated region, which can be expressed as:

$$x(t) \approx R_G \left( \frac{t}{T_{rep}} \right)^{1/4}, \quad (11)$$

where  $R_G = (La)^{1/2}$  is the coil size, when  $t < T_{rep}$ ,  $x(t)$  is smaller than  $R_G$ . For non-polar (or apolar), compatible polymers, the thickness of the interfacial zone is in the range of 10 nm. In this short distance regime, where the reptation model applies, the macroscopic diffusion equations developed by Vasenin<sup>23</sup> for adhesion appear to be inapplicable. This is one of the major advances in the diffusion theory related to adhesion, since the reptation model enters into the picture.

## 2.6. Interdiffusion coefficient

Interdiffusion or mutual diffusion between two compatible polymers, e.g., PMMA and PVF<sub>2</sub> (polyvinylidene fluoride), was studied by Wu *et al.*<sup>24</sup> In this case, the two diffusion coefficients and rates are unequal, and  $D_i$  is proportional to  $N^{-2}$ . In addition, the interfacial thickness  $x(t)$  grows by  $t^{1/2}$ , hence

$$x(t) \sim N^{-1} t^{1/2} . \quad (12)$$

This formulation is in agreement with the reptation model. Furthermore, the adhesive bond strength  $\sigma(t)$  at the interface can be calculated to be

$$\sigma(t) \propto t^{1/4} N^{-1/4} . \quad (13)$$

## 2.6. Tack and green strength

The application of the reptation model to adhesion is not limited to the adhesive bond strength at the interface. The reptation model can also be used to describe tack and green strength of elastomer or rubbery adhesives.<sup>25</sup>

Tack<sup>26</sup> is the ability of two materials to resist separation after bringing their surfaces into contact for a short time under a light pressure. There are two types of tack: autohesive tack from a pair of similar materials and adhesive tack from a pair of dissimilar materials. On the other hand, the green strength of an elastomer is its resistance to deformation and fracture before vulcanization. We shall discuss tack and green strength on the basis of diffusion mechanism. It is well known that not all types of diffusion can result in the enhancement of adhesion. Only the diffusion involving polymer entanglement can improve tack and green strength.

From microfracture criteria, tack in the uniaxial tension in the absence of a large stress is identical to  $\sigma(t)$  in Eq.(13). Thus, tack is

$$\sigma(t) \sim t^{1/4} N^{-1/4} . \quad (14)$$

and the green strength is

$$\sigma_{\infty} \sim N^{1/2} . \quad (15)$$

From Eqs. (14) and (15), it is clear that tack is a function of contact time, but green strength is not. In fact, the above two relations were obtained independently in 1958 by Forbes and McLeod<sup>27</sup> as shown in Fig. 4.

## 2.7. Adhesion of unvulcanized elastomers

Recently, Ansarifar *et al.*<sup>28</sup> studied the adhesion of unvulcanized elastomers. The self-adhesion of all the elastomers except natural rubber and polybutadiene was found to be time-dependent over the time scales covered, reaching the cohesive strength if sufficient contact time was allowed. The mutual adhesion for some pairs of dissimilar materials (all immiscible) also increased appreciably with time, approaching the cohesive strength of the weaker elastomer. In some cases, it appears that a limited interdiffusion (near the interface) may lead to strong mutual adhesion. However, in one case polar interactions, to be discussed later, are believed to be the cause for the strong mutual adhesion.

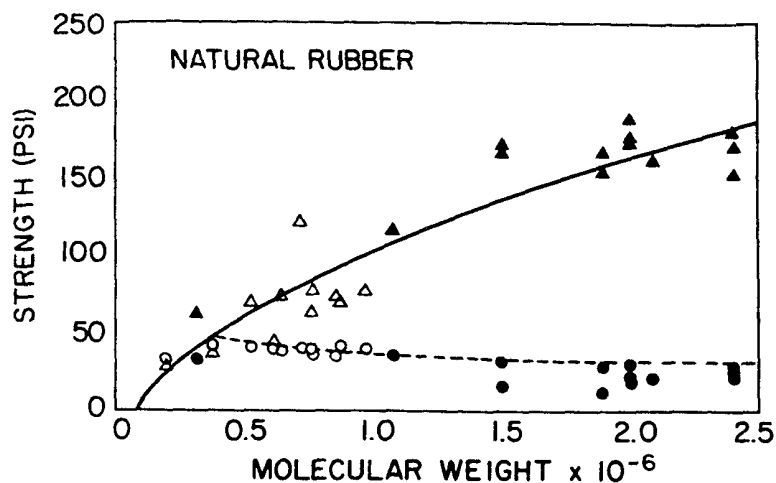


Fig 4. Tack (circles) and green strength (triangles) as a function of  $M_v$  for fractionated samples of natural rubber (data of W.G. Forbes and L.A. McLeod, *Trans. Inst. Rubber Ind.* 30 (5), pp. 154-174 (1958)). The green strength was evaluated at an uniaxial test speed of 26 cm/min at 25°C, and the tack was evaluated at a contact time of 30 s for each sample. The solid lines are the calculated values based on the cited equations in the text. (From R. P. Wool, *Rubber Chem. Technol.* 57, pp. 307-319 (1984)).

### 3. Lifshitz-van der Waals Interactions and Physical Adsorption

As stated in the Introduction, physical adsorption is common to all three types of adhesion systems. For good adsorption and diffusion, wetting is necessary and essential. Wetting and wettability of polymers have been reviewed by Zisman,<sup>29</sup> Mittal,<sup>30</sup> and others. In the past, the efforts have been focused on the thermodynamic aspects of wetting because through wetting the maximum thermodynamic (Lifshitz-van der Waals) work of adhesion  $W_A^{LW}$  can be obtained according to Dupré's Equation,<sup>31</sup>

$$W_A^{LW} = F_{LV} + F_{SV} - F_{SL}, \quad (16)$$

where  $F_{LV}$ , and  $F_{SV}$  are the surface free energy of the liquid and solid, respectively, and  $F_{SL}$  is the interfacial energy. Generally, surface tension  $\gamma$  is used to express surface free energy, thus  $W_A^{LW} = \gamma_{LV} + \gamma_{SV} - \gamma_{SL}$ . Throughout this discussion, we shall put emphasis on  $W_A$  instead of on adhesive strength, which also involves the work of deformation. We do not intend to discuss in detail the Lifshitz-van der Waals interaction in this paper, but recommend readers to refer to recent articles by Good *et al.*<sup>32</sup>

One of the important developments in the wetting studies conducted in the last decade is the kinetics aspect. Several reviews by Marmur,<sup>33</sup> de Gennes,<sup>34,35</sup> and Cazabat<sup>36</sup> should serve to highlight many careful studies carried out in recent years. In the following we shall briefly summarize the important work by de Gennes and his colleagues on the kinetics of wetting and spreading of a nonvolatile liquid or polymer. In addition, Leger *et al.*<sup>37</sup> reported the recent experimental study of dry spreading of polymer liquid on solid surfaces and Cazabat *et al.*<sup>38</sup> highlighted the recent work on the spreading of a liquid drop.

#### 3.1. Young equation

In the Young equation,<sup>39</sup> the surface tension of the liquid,  $\gamma_{LV}$ , the surface tension of the solid,  $\gamma_{SV}$ , and the interfacial tension,  $\gamma_{SL}$ , also represent the three forces by unit length applied on the line of contact. In the case of

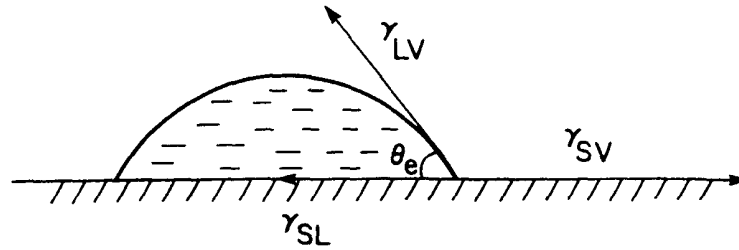


Fig. 5. Contact angle of a sessile drop on a solid surface

partial wetting (Fig. 5), they are related to the equilibrium contact angle,  $\theta_e$ , in the saturated vapor of the respective liquid as follows:

$$\gamma_{LV} \cos \theta_e = \gamma_{SV} - \gamma_{SL} \quad (17)$$

This equilibrium also requires a balance of vertical forces: capillary forces along the contact line ( $\gamma \sin \theta_e$ ), Laplace pressure, and drop weight.<sup>40</sup>

### 3.2. Spreading coefficient

For spreading, another parameter, the equilibrium spreading coefficient,<sup>41</sup>  $S_e = \gamma_{SV} - \gamma_{SL} - \gamma_{LV}$ , appears to be important in classifying liquids that have a tendency to form good films on a given substrate. In general, the larger and the more positive the  $S_e$  the more energy is gained by intercalating a liquid film between the solid and air. Thus,

$$S_e > 0, \text{ spontaneous spreading}$$

$$S_e < 0, \text{ no spontaneous spreading}$$

Though the condition  $S_e > 0$  is necessary for a liquid to spread spontaneously on a solid, it is insufficient to describe the final state of the film. According to Joanny and de Gennes,<sup>42</sup> the final state of the film is controlled by long-range forces existing within the liquid. If one deposits on the solid a liquid film whose thickness is much larger than the range of interaction in the liquid, the energy associated with the creation of the film is that required to form two solid-liquid and liquid-air interfaces; that is,  $\gamma_{SL} + \gamma_{LV}$ .

### 3.3. Complete wetting of polymer melt

The spreading of polymer droplets was studied by Brochard and de Gennes.<sup>43</sup> If the polymer droplet height  $h$  is larger than  $b$ , we are considering a case of  $h \gg b \gg Z$ . Then there will be three regions of the droplet as shown in Fig. 6. The one that is not present in the case of liquid is the "foot," which has been previously reported by Schonhorn, *et al.*<sup>44</sup> The three regions of a polymer droplet are:

- a spherical cap ( $Z(r) > b$ ): Here normal viscous flow takes place, the slip is negligible, and the kinetics follows the Tanner laws;
- a foot ( $b > Z(r) > Z_0$ ): In the foot there are plug flows driven by the capillary pressure, and
- a precursor film ( $Z(r) < Z_0$ ). In this case, it has a plug flow driven by van der Waals forces.



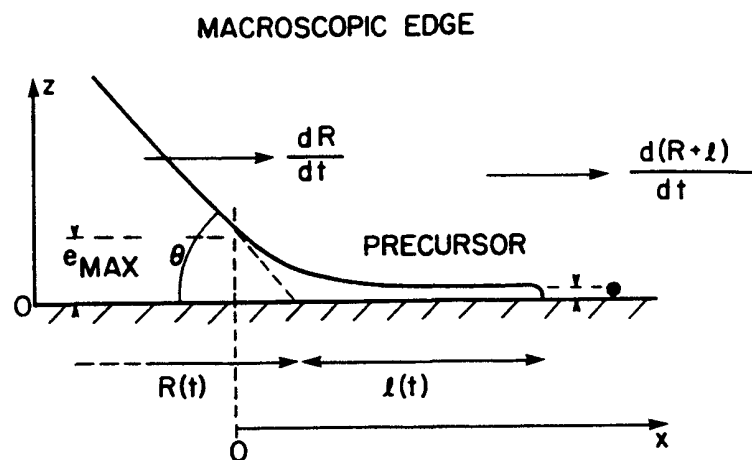


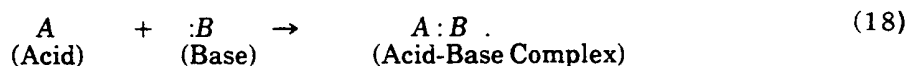
Fig. 6. The precursor film precedes the macroscopic edge of the drop, which advances with the velocity  $U = dR/dt$ . From this edge, the length of the precursor is  $l$ . At the tip, the velocity is  $d(R + l)/dt$ . (From A. Cazabat, *Contemp. Phys.* **28** (4), pp. 347-364 (1987)).

#### 4. Molecular Interaction and Chemisorption

Besides the Lifshitz-van der Waals (LW) interactions, there are short range ( $<0.4$  nm) forces due to the donor-acceptor interaction<sup>45-47</sup> or the acid-base interaction.<sup>48</sup> The role of the acid-base interaction in polymer adhesion has been studied by Fowkes<sup>49-50</sup> and Bolger *et al.*<sup>51</sup> Good *et al.*<sup>52</sup> have examined the role of the interfacial hydrogen bond in enhancing the adhesion through the acid-base interaction. Recently, Lee<sup>53-54</sup> described the molecular bonding mechanism which includes the acid-base interactions. Molecular bonding is in between the van der Waals and chemical bonding. For comparison, physisorption is based on the van der Waals interactions, while chemisorption is established on molecular bonding.

##### 4.1. Enthalpy of the acid-base interaction

Now let us discuss briefly the acid-base interaction, which is the predominant form of molecular interactions. The generalized acid-base interaction<sup>48</sup> can be represented as



This interaction actually involves both covalent (homopolar) and ionic (heteropolar) factors. Thus, Drago *et al.*<sup>55</sup> introduced four parameters for the prediction of the enthalpies of the acid-base interactions. For an A-B pair, the enthalpy or molar energy of the adduct formation can be expressed by the following empirical relation:

$$-\Delta H^{ab} = E_A E_B + C_A C_B, \quad (19)$$

where  $E_A$  and  $E_B$  are the susceptibilities of the acid (A) and base (B), respectively, to undergo the electrostatic interaction, and  $C_A$  and  $C_B$  are those to undergo covalent interaction.

## 4.2. Work of adhesion (the acid-base component)

From the above discussion of the Drago's equation, the work of acid-base interaction for a pair of molecules is simply the acid-base component of the work of adhesion,  $W_A^{ab}$

$$W_{int}^{ab} = W_A^{ab} \quad (20)$$

However, in the case of a solid-solid interaction, the interaction area can be very much localized. Therefore, we need to determine the surface fraction or the population of the interaction  $n^{ab}$  in terms of acid-base pair per unit area.<sup>50</sup> As a result, Fowkes proposed that the work of adhesion,  $W_A^{ab}$ , should be expressed as

$$W_A^{ab} = -fn^{ab}\Delta H^{ab}, \quad (21)$$

where  $f$  is a conversion factor from enthalpy to the free energy, and this factor has been shown by Vrbanac and Berg<sup>56</sup> to be much less than one.

## 4.3. Total work of adhesion

According to Fowkes,<sup>50</sup> when a solid surface involves both the Lifshitz-van der Waals and acid-base interactions, the total work of adhesion should be the sum of the following two components:

$$W_A = W_A^d + W_A^{ab} \quad (22)$$

where the first term is the dispersion component of the work of adhesion between two materials. Later van Oss, Chaudhury, and Good<sup>57</sup> proposed to substitute LW for the dispersion component, because the induced and the polarization components are negligible in the condensed phase

$$W_A^{LW} \approx W_{12}^d, \quad (23)$$

where

$$W_{12}^{LW} = \left( W_{11}^{LW} W_{22}^{LW} \right)^{1/2} = 2 \left( \gamma_1^{LW} \gamma_2^{LW} \right)^{1/2} \quad (24)$$

It is important to note that though the first term can be obtained from the geometric mean, the second term  $W_A^{ab}$  can not be obtained in the same manner. Thus,  $W_A^{ab}$  can only be calculated from Eq. (21), despite the erroneous assumption by others to use the geometric mean approach, instead.

Recently, Huttinger *et al.*<sup>58</sup> proposed a new method to determine the work of adhesion at the solid-liquid interface. The method is based on the above Fowkes method and the classical contact angle technique. Aqueous acidic and basic solutions are used as test liquids in the entire pH range.

## 4.4 New evidences for the acid-base interactions

Lavielle *et al.*<sup>59</sup> investigated the coating of polyethylene terephthalate (PET) with gelatin and found the effect of the acid-base interaction on adhesion. Their results show that PET is amphoteric and its surface can be

treated by flame or microwave plasma to increase the acidity (or polarity). Since gelatin is basic, good adhesion between PET and gelatin can be achieved through the acid-base interaction.

Chehimi *et al.*<sup>60</sup> used XPS to study the acid-base interaction among polymers. For example, an adduct can be formed between poly(methyl methacrylate), PMMA, and pyridine. In this case, PMMA becomes an acid. Thus, the well-known base, PMMA, is actually amphoteric.

For polysaccharides, Spange *et al.*<sup>61</sup> have found that the unmodified cellulose possesses a relatively high acidic strength, and the acetylation of hydroxyl groups tends to reduce the acidic strength.

Kaczinski and Dwight<sup>62</sup> reported the effect of the acid-base interaction on polymeric film adhesion. Four types of functional Teflon surfaces were prepared: two acidic (containing hydroxyl and carboxyl groups), and two basic (containing acetyl and dinitrobenzoate groups). As a result, the carboxylated surface yields a high molar  $\Delta H^{ab}$  with tetrahydrofuran (THF) than the hydroxylated surface. On the other hand, the acetylated surface functions as a base interacting with phenol but not with THF, while the dinitrobenzoate surface is actually amphoteric. The 180° peel test was performed by using the post-chlorinated poly(vinyl chloride) (PVC) as the model acidic adhesive. Thus, the two basic surfaces interacting with the model gave good peel strengths, while the two acidic surfaces interacting with same model had very low peel strengths. The XPS analyses showed that acid-acid pairs produced the interfacial failure, while acid-base pairs caused the cohesive failure of the bulk.

Bonnerup *et al.*<sup>63</sup> studied the coating process of polypropylene (PP)/ethylene-propylene-diene-monomer (EPDM) blended with the chlorinated polyethylene and polyurethane (PUR). The improvement of adhesion between PUR and PP by the chlorinated polyolefin at the interface is credited to the acid-base interaction, as detected by IGC (inversed gas chromatography).

The acid-base interaction of rubbers is somewhat difficult to observe by rolling contact. Roberts<sup>64</sup> used rigid cylinder samples of smooth-surfaces vulcanized rubber which were timed for their rolling descent down an inclined glass track. Sometimes, no clear pattern of the acid-base interaction was detected. On the other hand, some of the results indicated some effect of acid-base interaction. It was concluded that the interactions are not simple, and many of the surfaces appear to be amphoteric. We think that these inconclusive results are partially due to the experimental setup, which does not warrant any molecular contact. Without a close contact of  $<4 \text{ \AA}$ , it is difficult to expect an acid-base interaction to take place.

#### 4.5. Role of chemisorption in adhesion

Since adsorption is believed to be one of the important mechanisms<sup>1</sup> in achieving adhesion, diffusion and wetting are merely kinetic means to attain good adsorption of polymer at the interface. By diffusion and wetting, the polymer molecules can reach an intimate contact that either Lifshitz-van der Waals interaction (long range) or the acid-base interaction (short range) or both may take place. The key for achieving the short range interaction<sup>65</sup> is to keep the molecules within the proximity of  $4 \text{ \AA}$ . Within this range, the molecules can achieve chemisorption in addition to physisorption due to van der Waals interaction.

### 5. Mechanical Interlocking Mechanism

The above discussions on diffusion, wetting, and adsorption are all on the microscopic scale. In the microscopic biological systems, the key-and-lock mechanism has recently been reported by Helm *et al.*,<sup>66</sup> and Jorgensen<sup>67</sup>. For the macroscopic scale, in order to build a strong adhesive joint, mechanical interlocking can be applied, such as the surface treatments of metals, to provide various topographies. Some believe that mechanical interlocking is only a technical means in achieving strong adhesive bonding as in the case of structural adhesives. Others believe that mechanical interlocking is nothing but creating a larger surface contact area for physical adsorption, or a large polymer volume to sustain deformation during the bond-breaking process.

For those interested in mechanical interlocking, one may refer to the papers by Venables,<sup>68</sup> Clearfield *et al.*,<sup>69</sup> Minford,<sup>70</sup> Brockmann,<sup>71</sup> and Kinloch.<sup>17</sup> It is important to point out that though interlocking may, in some cases, affect the intrinsic work of adhesion, its contribution toward the joint strength through high surface rugosity can always be explained by other mechanisms of bond-forming.

## 6. Chemical Bonding Mechanism

Physical adsorption depends on van der Waals interactions, and chemisorption results from the acid-base interaction. Unlike these two interactions, the chemical bonding mechanism is based on the primary covalent bond formed at the interface. Chemical bonding is the strongest form of polymer adhesion. For example, chemical reactions created by coupling agents at the interface have been established. Two recent reviews by Plueddemann<sup>72</sup> and Miller and Ishida<sup>73</sup> should be helpful for those interested in designing strong interfaces through the use of coupling agents.

It is important to note that molecular bonding can lead to chemical bonding. This is especially true for some interactions at polymer-metal interphases.<sup>74</sup>

## 7. Electronic Mechanism

The last, but not the least, is the electronic mechanism. The electronic (or electrostatic) mechanism proposed by Deryagin<sup>75</sup> is especially important in particle adhesion.<sup>76,77</sup> The theory suggests that the surface potentials of the adhesive and substrate differ, charge transfer will take place until the Fermi level is brought into coincidence, and an electrical double layer (EDL) is formed at the interface as in the form of a condenser. Historically, though the electronic adhesion has been claimed to be first investigated by Deryagin, some early work by Skinner, Savage, and Rutzler<sup>78</sup> reported in 1953 was first known to the west and was carried out, presumably, without the knowledge of the Russian work. Skinner<sup>79</sup> actually first laid the theoretical foundation for the electronic adhesion based on the electrical double layer (EDL) theory, despite some errors in the original derivation noted by the Russian school published in English<sup>80</sup> twelve years after Skinner's publication.

There have been at least three controversies surrounding the electronic adhesion theory: 1) the EDL could not be identified without the separation of the adhesive bond, 2) the effect of EDL on the adhesive bond strength was exaggerated, and 3) the Russian school later attempted to encompass the donor-acceptor interaction within the EDL electronic theory.<sup>47</sup> Several works outside Russia have shed new light on the original electronic adhesion theory. We shall attempt to summarize these new developments.

### 7.1. Direct evidence of the electrical double layer

In the past, it was very difficult to prove the existence of an electrical double layer (EDL) without the separation of an adhesive bond. In 1984, an interesting experiment carried out by Possart and Röder<sup>81</sup> used SEM for determining the potential distribution at the polymer-metal interface without separation. The existence of a double layer was thus confirmed. One of the remaining problems is to establish the extent of the EDL and its effect on adhesive bonding.

### 7.2. Work of electrical double layer versus peel work

Then, Possart<sup>82,83</sup> attempted to determine the actual charge density and the work of the electrical double layer without breaking the bond. According to him, the maximum charge moved in the whole measuring interval reached  $2.7 \times 10^{-2}$  C/m<sup>2</sup>. His calculations showed that the electrostatic component of  $W_{el}$  due to EDL was only  $1.71 \times 10^{-3}$  J/m<sup>2</sup>. Here  $W_{el}$  is the interaction energy between the space charges in the undisturbed EDL.

On the other hand, the actual peeling of the LDPE film from the aluminum foil yielded a specific peel work of  $1 \text{ J/m}^2$ , which is about 600 times that of the  $W_{el}$ . Thus, the specific peel energy is much larger than the stored electrostatic energy due to the presence of the *EDL*. This is an indication that the electrostatic component is only a fraction of the total adhesive strength. Thus, this result still can not serve as a definitive proof for Deryagin's hypothesis on the dominant role of *EDL* in adhesion. In 1992, Horn and Smith<sup>84</sup> reported the adhesion between similar and dissimilar materials based on mica and silica and concluded that the adhesion between dissimilar materials is due to the double layer formation. However, recently Horn<sup>85</sup> also attributed their findings to the acid-base interaction. Horn assumed that the electronic mechanism is synonymous to the acid-base mechanism. This may cause further confusion because there is a distinction between these two mechanisms, as discussed in the previous sections of this paper.

In the literature, there has been other work that disputed Deryagin's original claim. Roberts, in his studies of rubber adhesion,<sup>86</sup> indicated that the contribution of the electrostatic component was less than 10%, usually only 0.1-1%.

## 8. Summary

This paper is a brief review about new perspectives in polymer adhesion mechanisms. Among them, we pointed out the importance of diffusion and molecular bonding mechanisms. For the diffusion mechanism, the reptation model has been applied successfully to explain tack, green strength, healing, and welding of polymers. For the adsorption mechanism, new findings related to the kinetics of wetting and spreading of polymer melt provide insights in achieving good molecular contact. If the molecular distance is below 4 Å, chemisorption can take place due to the acid-base (or donor-acceptor) interaction. In general, molecular bonding is in between the van der Waals interaction and covalent bonding. In addition to the above mechanisms, we also briefly mentioned mechanical interlocking, chemical bonding, and electronic adhesion mechanisms. The status of mechanical interlocking and electronic mechanisms is less certain than chemical bonding. In the case of polymer-metal interactions, sometimes molecular bonding can lead to chemical bonding. Furthermore, in the presence of some coupling agents, chemical bonding at the polymer-solid interface has also been reported.

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