

Adhesion and surface forces in polymer tribology—A review

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Abstract: Polymer tribology is a fast growing area owing to increasing applications of polymers and polymer composites in industry, transportation, and many other areas of economy. Surface forces are very important for polymer contact, but the real origin of such forces has not been fully investigated. Strong adhesive interaction between polymers leads to an increase in the friction force, and hence, the asperities of the material may be removed to form wear particles or transfer layers on the counterface. The theory of polymer adhesion has not been completely elucidated yet and several models of adhesion have been proposed from the physical or chemical standpoints. This paper is focused on the research efforts on polymer adhesion with emphasis on adhesion mechanisms, which are very important in the analysis of polymer friction and wear.

Keywords: friction; dynamics; joint clearance; numerical models; impact; durability

1 Introduction

The fundamentals of tribology are based on mechanics, surface physics, and chemistry [1–3]. For tribological applications of polymers, the dynamic contact interaction is crucial, and contact adhesion and deformation are affected by roughness, hardness, and surface forces [4–8].

The behavior of polymers in the bulk is dependent on their viscoelastic properties [9, 10]. Contact pressure, velocity, and temperature are the main parameters affecting the performance of polymers at friction. These factors determine the formation of the real contact area, coefficient of friction, and wear of the contacting bodies [4, 11–14].

It is generally accepted that friction is mainly governed by two types of interaction: deformation and adhesion. Derjaguin [15] was the first to discuss both factors in his model of friction. Subsequently, this concept was developed further by Bowden and Tabor, along with their co-authors [1, 9] in Cambridge (UK), and by Kragelskii et al. [16] in Moscow (Russia).

Nowadays, these ideas are receiving both experimental support and theoretical justification in many research papers [2, 17–19]. However, the basic problem in this regard is the difficulty in distinguishing deformation and adhesion components [16, 20–22]. Accordingly, the relevant discussion is ongoing [2, 7, 8, 23, 24].

Theories involving the Lennard–Jones potential are prominent as they are based on the assumption that attraction and repulsion forces act between approaching single charged particles, and hence, forces of electrostatic origin become equal at equilibrium distance. The theory proposed by Lifshitz [25] is more general and accordingly, attraction occurs owing to the overlapping electromagnetic fields of the surfaces in contact. There are several simplifications widely used in polymer surface science, facilitating the estimation of the specific surface energy [26–28].

Owing to rapid progress in nanotechnology, the understanding of the surface contact of polymers has become a fundamental issue for further development of new polymer-based materials and their applications.

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2 Adhesion phenomenon

The adhesion force is defined as the maximum force required for separating contacting surfaces. There is a dual opinion on the nature of adhesion [1, 29–32]. First, it is defined as the attraction resulting in the formation of bonds between solids. Second, adhesion is considered as the force necessary to rupture interface bonds when bodies are separated. The complicated nature of adhesion has been studied extensively [6–8, 33]. Further, the surfaces forces—attractive and repulsive ones—operate between the atoms or molecules of mating surfaces. These forces neutralize each other at some equilibrium separation h_0 . If the distance between the surfaces is $h < h_0$, the repulsive force is dominant; otherwise, if $h > h_0$, the attractive force is dominant.

It is generally accepted that a polymer surface operates with a counterbody mainly through van der Waals and electrostatic interactions (see Figs. 1(a) and 1(b)). The orientation, ionic dispersion, induction, and hydrogen intermolecular bonds may be generated within the polymer interface.

A hydrogen bond is formed at very short distances between polymer molecules containing the functional groups OH, COOH, NHCO, etc. The hydrogen atom of the molecule can be linked with an electronegative atom of other polymer molecules. Under favorable conditions, two contacting molecules are bonded together by a common electron, providing a strong and stable combination [34].

Owing to the direct interaction of contacting polymer surfaces, physisorption and direct molecular bonding coexist within the real contact spots as shown in Fig. 1(c). The adsorption of polymer molecules occurs because molecular bonds are formed owing to the existence of energy instability in the contact interface.

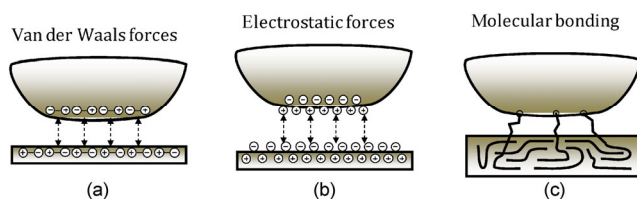


Fig. 1 General types of an adhesion interaction in the polymer interface (adopted from Ref. [35]).

The chemisorption of polymer chains is explained by the appearance of strong chemical bonds at the contact points. Chemical bonds are considerably stronger than intermolecular bonds within the polymer interface.

2.1 Thermodynamic surface energy

The interfacial energy of a polymer is one of the most fundamental parameters characterizing its surface state. Depending on the temperature and molecular weight, polymers can be in liquid or solid state. If two substances interact directly with each other, the molecules of one must come to interplay with the other. In the case of long-chain polymer molecules, some tiles of molecules are adsorbed onto the opposite surface. This is an exothermic process as can be readily represented with a simple thermodynamic argument. The free energy of molecular adsorption dG is written as follows:

$$dG = dH - TdS \quad (1)$$

where dH is the enthalpy, T is the temperature, and dS is the change of entropy. Generally, the energy change, dW , required to increase the surface by the unit area, dA , is proportional to the specific surface energy

$$\gamma = \frac{dW}{dA} \quad (2)$$

The work of adhesion interaction between solids 1 and 2, which is equal to the work of adhesion rupture, is determined by the Dupre formula

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

where γ_1 and γ_2 are the energies required to form the unit surfaces of solids 1 and 2 (their free surface energy) and γ_{12} is the excessive or interfacial energy.

The equation governing the energy balance of microscopic solid/liquid/gas interface is Young's equation

$$\gamma_{sl} = \gamma_{sv} + \gamma_{lv} \cos \theta \quad (4)$$

where θ is the contact angle and subscripts s, v, and l correspond to the solid, vapor, and liquid phases, respectively.

2.2 Electric double layer

In some instances, intrinsic adhesion arises owing to an electric double layer (EDL) formed between materials with dissimilar electronic band structures [36]. These forces are attributed to the free transfer electrons within the polymer interface. The idea of the formation of an EDL at the interface between the surfaces in contact was first advanced by Helmholtz. The mechanisms responsible for the formation of EDL in an interface vary, ranging from direct electron transfer under donor–acceptor interaction to polarization effects. This results in the positive and negative surface charges, that attract each other [20]. However, this approach has a serious disagreement on the magnitude of electrostatic attraction under certain conditions [37]. Some researchers have determined that electrostatic interaction mainly depends on environmental conditions and can significantly influence the contribution to adhesion [38]; others believe that these forces are dominant [39].

The EDL model of contact proposed by Derjagin and Toporov [39] describes the adhesion owing to contact electrification in an EDL appearing at the boundary of two phases in the form of an electric capacitor. In a frame of this theory, for the elastic sphere–plane contact surface, the effective molecular interaction is given by $F_m = AR/6\varepsilon^2$, where ε is the minimal distance of separation of the surfaces (a quantity of the order of a molecular diameter), R is the sphere radius, and A is the Hamaker constant.

Moreover, the elastic compliance follows the Hertz theory. It is evident that repulsion must overcome the interaction arising from the EDL charges in the annular zone around the points of contact. The electrostatic component (F_e) of this interaction is expressed as the derivative of the energy of interaction between the charges on the deformed portion of the spherical particle and the charge on the planar base, and its value is calculated using the Hertz theory. The ratio between the electrostatic component and molecular interaction F_m is proportional to the elastic reaction of the surface and is written as

$$\frac{F_e}{F_m} = \frac{3\pi^2 \sqrt[3]{2}}{2} (1-\nu^2)^{2/3} \sigma^2 \left(\frac{R\varepsilon^2}{AE^2} \right) \quad (5)$$

where ν is Poisson's ratio, E is elastic modulus, and R is the radius of the spherical particle.

Confirmation of the electrical theory of adhesion can be found in the electrification of the delaminated surfaces, luminescence, and characteristic discharge, in addition to the process of electron emission. However, the electrical theory provides a poor explanation for the adhesion of polymers between themselves.

3 Direct measurements of surface forces

The measurement of the molecular forces between solid surfaces is one of the most important challenges in surface science [14, 25]. As the forces are weak and their action radius is short, the measuring instruments should satisfy specific requirements. The first correct measurement of molecular attraction between solids was conducted by Derjaguin and Abrikosova in 1951 [40]. They determined an elegant solution to detect attraction force. An active feedback scheme was realized to stabilize the distance between solids. Subsequently, many other methods have been developed to measure the surface energies of polymers directly. In the following short survey, experimental data on polymer adhesion measured using surface force apparatus (SFA), atomic force microscope (AFM), and contact adhesion meter (CAM) are summarized.

3.1 Surface force apparatus

The surface force apparatus allows direct measurement of the molecular forces in liquids and vapors at the Ångström resolution level [41]. The classical design of SFA contains two crossed atomically smooth mica cylinders between which the interaction forces are measured [42]. One cylinder is mounted to a piezoelectric transducer. The other mica cylinder is mounted to a spring with a known and adjustable spring constant. The separation between the two surfaces is measured optically using multiple beam interference fringes as schematically shown in Fig. 2. In the case of studying polymers, the thin polymer film is deposited on the mica surface.

SFA has been widely used to measure both normal and lateral forces between surfaces in vapors and liquids for many types of materials. Further, SFA is

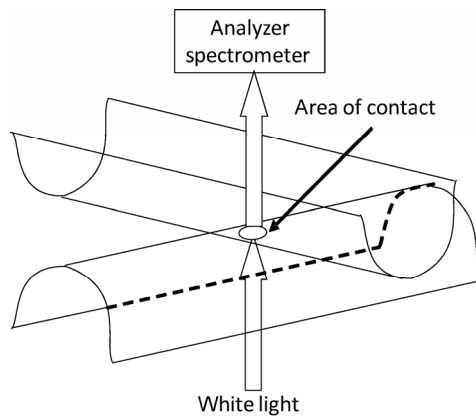


Fig. 2 Sketch of measurement of interfacial forces realized in SFA.

capable of measuring the dynamic interactions and time-dependent interfacial effects. SFA measures forces as a function of absolute surface separation between the contact surfaces. The force sensitivity is ~ 1 nN and the distance resolution is less than 0.1 nm.

3.2 Atomic force microscopy

In recent years, atomic force microscopy (AFM) has been widely used to investigate polymers. The main capabilities of AFM are surface imaging, thickness measurement [43], probing of surface mechanical properties [44], and direct measurement of surface forces using force–distance curve technique [45].

AFM is a powerful device for the investigation of surface properties at the nanoscale [46]. The major application of AFM is the measurement of the tip–sample interaction using force–distance curves. AFM force–distance curves have been used for the study of numerous material properties and for the characterization of surface forces. A force–distance curve directly reflects the relationships between the interfacial tip–polymer interactions and mechanical properties of the polymer. The schematic representation of adhesion measurements is discussed in detail elsewhere [45]. The dependence of cantilever deflection and distance at approaching and retracing is schematically shown in Fig. 3. The jump-off occurs when the adhesion force is overcome by the elastic deflection of the cantilever. The corresponding value of force $F_{\text{pull-off}}$ is assumed to be an adhesion force.

As both attractive and repulsive forces localized over nanometer scale regions can be probed, forces

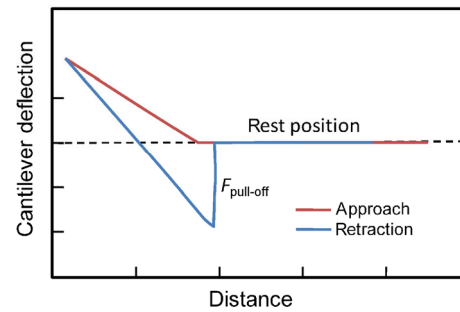


Fig. 3 Schematic representation of an AFM force-displacement curve showing the typical behavior of cantilever at tip–sample interaction.

owing to negative loading of the probe from the van der Waals attraction between the tip and sample prior to contact, or from adhesive forces occurring subsequent to contact can be investigated.

3.3 Contact adhesion meter

The available evaluations of molecular forces correspond to the sensitivity of an analytical balance. The main problem is that the force increases rapidly with the decrease of the distance between the specimens under testing. Hence, the measurements should be carried out at a very small speed, which cannot be implemented technically using the design of a common balance. Derjaguin et al. [47, 48] proposed to use a feedback balance. This principle was successfully realized in a contact adhesion meter (CAM). This device was designed at Metal–Polymer Research Institute (MPRI), Gomel, Belarus. Figure 4 shows a view of CAM

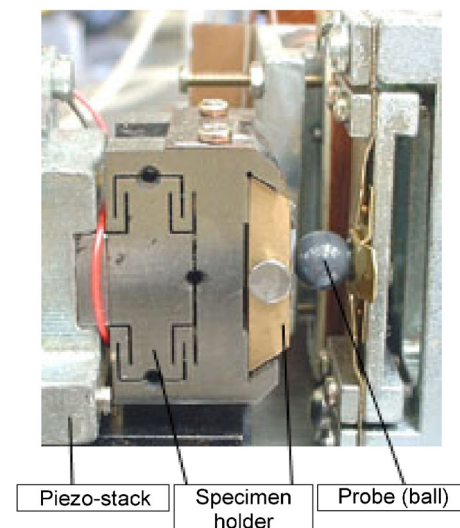


Fig. 4 Photograph of a measure unit realized in CAM device.

detecting unit where the silicon ball and silicon wafer were used in the experiments.

The measurement was realized as follows. The probe is moved toward or away from a surface within the nanometer range using a piezo-stack and the force is registered with a gage fixed on the free arm of a highly sensitive electromagnetic balance. When the probe approaches the surface, the attraction force is recorded. Once the probe touches the test surface, it does not stop and continues moving until a few nanometers are passed. Over this distance, the repulsion force acting between the contacting bodies is recorded.

4 Contact theories considering adhesion

The basics of contact mechanics are used for the explanation of elastic contact and tribological behavior of polymers [31]. The real and nominal contact areas are determined based on solutions to the problems of the theory of elasticity and classical Hertz theory of contact.

Contact mechanics uses two generally accepted theories of adhesion contact involving the surface energy as the measure of attraction between solids. They are the JKR (Johnson–Kendall–Roberts) [27] and DMT (Deryagin–Muller–Toporov) [49] models. Borodich [28] conducted a comparative analysis of these models and concluded that the basis of calculation of adhesion contact of elastic bodies for both models was based on Derjaguin’s idea for the calculation of the total energy in adhesion contact, published in 1934 [50].

4.1 Johnson–Kendall–Roberts model

The Johnson–Kendall–Roberts (JKR) model [27] is based on the assumption of infinitely small radius of surface forces. It is assumed that interactions occur only within the contact area. The elastic contact between a sphere of radius R and half-space is analyzed with the consideration of van der Waals forces operating together with the applied external load. The contact stiffness is resistant to the action of the forces.

The formula for calculating the radius of adhesive contact in the JKR model is

$$a^3 = \frac{3}{4} \frac{R}{E^*} \left(F + 3\pi R\gamma + \sqrt{6\pi R F \gamma + (3\pi R\gamma)^2} \right) \quad (6)$$

where F is the normal load and E^* is the effective elastic modulus.

Therefore, it is apparent that, without adhesion ($\gamma = 0$), the Hertz equation is obtained, whereas if $\gamma > 0$, the contact area always exceeds the Hertzian contact area under the same normal load F .

Only the application of a tensile (negative) load can reduce this radius, and thereafter, the contacting surfaces would be separated at the load corresponding to the conversion of the radicand to zero:

$$F_{\text{pull-off}} = -\frac{3}{2} \pi R \gamma \quad (7)$$

This equation describes the pull-off force required to separate contact bodies. It depends on the specific surface energy γ and is independent of the elastic properties of solids.

4.2 Derjaguin–Muller–Toporov model

The Derjaguin–Muller–Toporov (DMT) model [49] describes the contact of elastic sphere with a rigid half-space. This model is based on the following two postulates: surface forces do not change the deformed profile of the sphere and it remains Hertzian; the attraction force acts outside the contact circle while the contact is under compression by the stresses distributed according to Hertz.

Equilibrium is reached if the deformation is sufficient for the elastic response (restoration of the sphere) F_e to counterbalance the joint effect of the applied external load F and the forces of molecular attraction F_s , i.e.,

$$F_e = F + F_s \quad (8)$$

The DMT model leads to adhesive (tensile) stresses that are finite outside the contact zone but zero inside, resulting in a stress discontinuity at the edge of the contact zone. The relation between the load and approach obtained for the conditions of the DMT model is given as

$$F_e = F - 2\pi \int_0^{\infty} R dh(r) \frac{dV}{dh} \quad (9)$$

where R is the radius of contacting sphere, $h(r)$ is the gap between bodies, and $V(h)$ is the interaction potential.

The separation of surfaces occurs at the maximal adhesion force of

$$F_{\text{adh}} = 2\pi R\gamma \quad (10)$$

The DMT and JKR theories predict different adhesion force interactions for identical solids and conditions, which has resulted in long-lasting discussion. Tabor compared the JKR and DMT theories and pointed out their main drawbacks [51] and Maugis proposed a unified model for elastic contacts [52].

4.3 Contact of rough surfaces considering adhesion

In 1940, Zhuravlev published the pioneering work related to contact mechanics, where the statistical approach for describing surface roughness was proposed. He considered a linear distribution of heights of aligned spherical asperities and obtained an almost linear relation between the external load F and real contact area A_r . A historical paper by Zhuravlev has been translated by Borodich [53].

The well-known Greenwood–Williamson model [54] is assumed to predict the real contact area (RCA) of formation of rough solids and local pressure distribution. However, an in-depth analysis indicates that it is impossible to study the contact of polymers unless the molecular interactions between the surfaces are considered [31]. In 1975, Fuller and Tabor published a classic paper on the adhesion between elastic solids and the effect of roughness in reducing the adhesion [55]; it was also concluded that a relatively small surface roughness could completely remove the adhesion interaction. The effect of intermolecular forces can be tentatively assessed using the adhesion parameter proposed by Tabor as follows:

$$\Delta_c = \frac{1}{3\sigma} \left(\frac{9\pi R^{1/2} \Delta\gamma}{8E} \right)^{2/3} \quad (11)$$

where σ is the root-mean-square parameter of asperity distribution and R is the average radius of asperities. The estimation of the adhesion forces shows that the discrete contact is highly sensitive to its adhesion ability [30]. Hence, larger magnitudes of Δ_c can increase the RCA more than 100 times. The relation $\Delta_c < 0.1$ can occur only if at least one of the contacting bodies is

completely elastic. Theoretical and experimental studies have shown that contact is formed by adhesion and surface forces are dominant when $\Delta_c > 0.1$.

The condition $\Delta_c \geq 0.1$ can determine the ultimate mean arithmetic deviations of the equivalent roughness $R_a = (Ra_1 + Ra_2)^{1/2}$ below which the degree of adhesion in the contact should be considered. This correlation is shown in Fig. 5.

A transition region exists above this level when the condition $\Delta_c > 0.1$ is fulfilled only for a certain combination of properties of contact materials. Hence, each specific case requires validation. This analysis indicates that it is impossible to study the contact of any materials at nanoscale unless the atomic and molecular interactions between the surfaces are considered.

5 Experimental results and discussion

Several types of adhesive forces operate within polymer–solid interfaces. A correct analysis of adhesive forces is a crucial challenge in the tribology of polymers [12, 14, 35]. Strong adhesion interaction between the contacting asperities of sliding surfaces is mainly accompanied by the following effects: frictional force is increased and the material may be removed from the surface to form wear particles or transfer layers. The removal of the external load results in a complete or partial restoration of the shape of the surfaces and the corresponding disintegration of the adhesion bonds. This renders it difficult to determine quantitatively the strength of the adhesion interaction for contacting

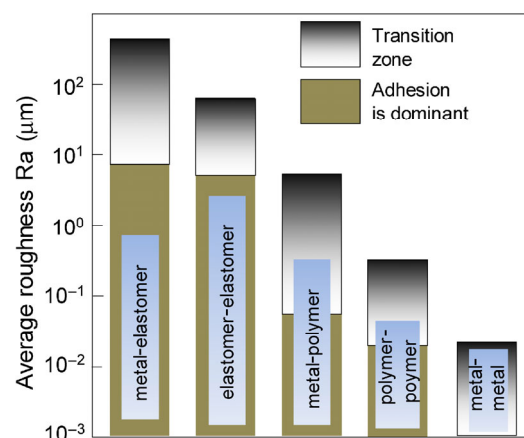


Fig. 5 Influence of adhesion interaction within contact of rough surfaces.

polymers.

The adhesion of a surface has strong relation to its wetting [56–58]. A common method of observing surface wetting is to measure the contact angle as the edge angle of the liquid droplet in contact with the solid surface. It indicates the energetic balance between the solid, liquid, and gas phases involved. Contact angles for some polymers are listed in Table 1. One can conclude that their values for certain polymers can significantly vary. The diffusion of long-chain polymers has been the subject of intense research activity in the last decade but the nature of this process is still not clear [8, 59–61].

In the case of low surface energy of solids, high adhesion bonding is usually explained by the contribution of chemical interaction to the adhesion bonding. However, the real origin of “chemical interaction” remains unclear in certain cases. For example, Derulle et al. [62] examined the interaction between elastomeric lens of cross-linked poly(dimethylsiloxane) (PDMS) and a silicon wafer covered with a grafted layer of monodisperse PDMS. It was observed that the work of adhesion was higher than that expected by considering only the surface energy of PDMS. The adhesion energy was measured to be approximately 80 mJ/m², which is higher than the value of 45 mJ/m², the expected value for symmetrical PDMS-PMMS. Generally, segments of PDMS elastomer can be adsorbed onto silica if they find their way to the wafer surface. Accordingly, increasing the grafting density and thereby capping more hydroxyl groups

Table 1 Values of contact angle measured on polymer surface (liquid is water).

Material	Contact angle, θ (°)	Reference
Polytetrafluoroethylene (PTFE)	105, 112	[60, 56]
Polyethylene (PE)	86, 103, 33	[26, 56, 60]
Nylon-6	65	[60]
Polyvinylcyclohexane (PVCH)	29	[26]
Poly-4-methyl-1-pentene (TPX)	26	[26]
Polystyrene (PS)	30, 90	[26, 61]
Polymethylmethacrylate (PMMA)	53	[26]
Polyethylene terephthalate (PET)	38	[26]
Poly-2-vinylpyridine (PVP)	50	[26]
Polyvinylbenzyl chloride (PVBC)	88	[61]

on the silica surface should lead to the decrease of interfacial energy. However, this has not been observed in this experiment.

Mangipudi used SFA to measure the surface energies of PET and PE, and the interfacial energy between them. He also reported the increase in the surface energy of PE from 33 up to 56 mJ/m² after corona-treatment procedure [63]. Tirrell [26] analyzed SFA data on adhesion force and applied the JKR model for the estimation of adhesion contact for polymers. Using SFA, Chen et al. [61] studied the adhesion of glassy polystyrene (PS) and poly(vinylbenzyl chloride) (PVBC) surfaces with various molecular weights. It was observed that cross-linking of high-molecular-weight polymers leads to lower adhesion. The surface energy was approximately 38 mJ/m² for PS and approximately 50 mJ/m² for PVBC. A friction force, relative to the untreated polymers, is usually accompanied by the scission (bond-breaking) that leads to higher adhesion resulting in the surface energy hysteresis of about 13.5 mJ/m². It is associated with the interdiffusion point of view, which supposes that the chains cross the interface and diffuse into the other medium. Selected experimental results on the work of adhesion probed using SFA are listed in Table 2.

Adhesion hysteresis [64, 65] has often been observed in polymer materials. In hysteretic systems such as polymers of low molecular weight, the loading and unloading paths are not the same, as observed for polystyrene-*graft*-poly-(ethylene oxide) (PS-*g*-PEO) [66]. The use of the JKR model for the loading

Table 2 Selected results on work of adhesion measured by means of SFA.

Polymer	Work of adhesion, γ (mJ/m ²)	References
Polyethylene terephthalate (PET)	61	[26]
Polyethylene (PE)	32 (56)	[63]
Polyvinylcyclohexane (PVCH)	28	[26]
Poly-4-methyl-1-pentene (TPX)	21	[26]
Poly-methyl methacrylate (PMMA)	40	[26]
Polystyrene (PS)	44, 38	[26, 61]
Poly-2-vinylpyridine (PVP)	63	[26]
Polyvinylbenzyl chloride (PVBC)	50	[61]
Polydimethylsiloxane (PDMS)	80 (45)	[61]

path yields $\gamma = 37.0 \text{ mJ/m}^2$, which corresponds to the thermodynamic surface energy of the PS-g-PEO film. An analysis of the unloading path yields the adhesion force of $\gamma \approx 47.7 \text{ mJ/m}^2$, resulting in the adhesion hysteresis $\Delta\gamma$ of 10.7 mJ/m^2 . The adhesion hysteresis of PS-g-PEO surfaces is explained mainly by the interdigitation of polymer chains/segments across the contact interface, and the hydrogen bonding between the PEO chains at the polymer–polymer interface should also be considered [67].

Taylor measured the energies between various polymer layers and crystal 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) [68]. It was observed that the specific surface energy varies depending on the crystallinity of polymers. The influence of the substrate on the adhesion of polymers should also be considered. Ahn and Shull [10, 69] observed that the adhesion of methylated PNBA (m-PNBA), carboxylated PNBA (c-PNBA), and neutralized PNBA (n-PNBA) varies depending on the substrates used. An increase in adhesion is attributed to the acid/base interactions at the elastomer/substrate interface and ionized groups, which can increase the relaxation times of the elastomer, presumably owing to the enhanced segmental mobility of molecules.

The values of work of adhesion calculated from the AFM data are listed in Table 3. Polymer brushes have become an important subject of research [6, 70] owing to their unique ability to change the surface property. They are layers of polymer molecules attached to a surface at one end whereas the rest of the molecule chain extends out of the surface. Densely grafted polymer molecules tend to stretch away from the surface in order to reduce their interaction with other molecules, thus attaining a different conformation than the optimal one for the free polymer molecules

Table 3 Work of adhesion for polymers measured by AFM.

Polymer	Work of adhesion, γ (mJ/m ²)	Reference
Polyethylene (PE)	81	[68]
Polypropylene (PP)	76	[68]
Polystyrene (PS)	92	[68]
Polyvinylidene fluoride (PVDF)	69	[68]
Polychlorotrifluoroethylene (PCTFE)	64	[68]
Polytetrafluoroethylene (PTFE)	58	[68]

in the bulk or solution [71].

Polymer brushes are usually attached to the surface owing to the chemical adsorption of chain ends, resulting in a polymer layer of nanometer thickness [72]. In the case of a functionalized polymer chain, a copolymer layer of nanometer thickness can also be generated on a surface [73–75]. The technique of preparation and deposition of self-assembled molecular layer (SAM) is described in detail elsewhere [76–77]. A comparative analysis of adhesion and friction forces of DDPO₄ (dodecylphosphoric acid ester), ODPO₄ (octadecylphosphoric acid ester), and OTS (octadecyltrichlorosilane) revealed a significant effect of polymer brushes on friction at light loads [78]. Such tailoring may be of utmost importance for controlling the interaction between the polymer brushes and biological systems such as proteins and cells.

Figure 6 shows the typical dependence of adhesion force during approaching and retracting of a silicon ball to the OTS polymer nanolayer obtained using CAM. For DDPO₄ and ODPO₄ SAMs, the initial silicon substrates were covered with Ti or TiO_x interlayers. Polymer nanolayers on metal oxides are of particular interest to biomaterials and biosensors. They allow the tailoring of surface properties. Experimental data on polymer brushes and substrates are summarized in Table 4 [79]. If the characteristics of the adhesion force of the probe are known, the specific surface energy of the polymer nanolayers can be estimated based on the experimental data. The maximal attraction force P_{max} was determined from the experimental curve. The calculation of γ was based on the DMT

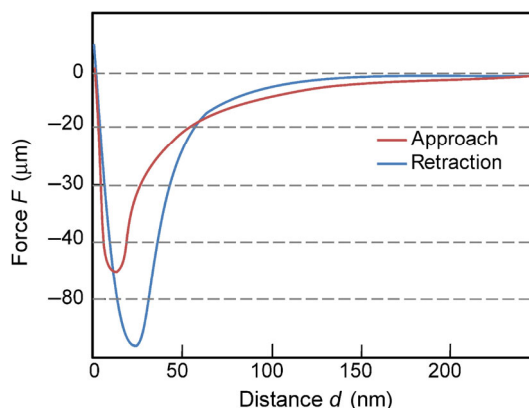


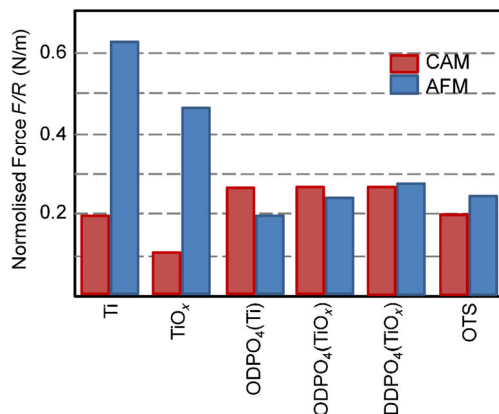
Fig. 6 An example of experimental force–distance curves measured by means of CAM (adopted from Ref. [78]).

Table 4 Adhesion characteristics of polymer brush layers measured by CAM.

Material (substrate)	Attraction force P_{\max} (μN)	Attraction distance h (nm)	Specific surface energy γ (mJ/m^2)
Silicon ball of 1 mm radius			
ODPO ₄ (TiO _x)	99	91	6.7
ODPO ₄ (Ti)	125	121	11
DDPO ₄ (Ti)	67	115	1.6
Epoxilane (Si)	33	92	3.8
OTS (Si)	80	115	3.6
Titanium ball of 1.5 mm radius			
Epoxilane (Si)	38	51	2.9
OTS (Si)	12	50	2.4
ODPO ₄ (TiO _x)	34	14	3.5

theory because the thickness of the polymer layer was very small compared with the radius of contact.

Table 4 also lists the measurement results of the characteristics of force field of coatings on the silicon plate paired with the titanium ball. The calculated values of γ for Si and epoxilane (on Si substrate) specimens are very close to those calculated for the interaction of these specimens with the silicon probe in tests with the silicon ball. All the samples show similar dependence of attraction forces on the distance from the sample to silicon ball. Figure 7 shows the adhesion forces normalized with the radius of the indenter in comparison with similar data obtained with AFM and CAM. The data are consistent except with AFM pull-off force measurements of Ti and TiO_x samples. This difference can be explained by the

**Fig. 7** Comparison of adhesion forces measured with AFM and CAM.

influence of capillary forces and the low hydrophobic properties of the samples. For much bigger size of the indenter of CAM as compared with the AFM tip, capillary forces play a dominant role in the interaction of samples during retraction.

In all the aforementioned examples, the surface adhesion is associated with both physical and chemical contributions of the active chains of polymer molecules. To uniquely distinguish the contribution of given polymer surfaces is an ambiguous task because adhesion interaction slightly depends on the nature of the polymer, but mostly depends on local physical conditions within the real contact, which can activate different types of molecular bonding. The specific molecular activities and certain physical properties of molecular chains more strongly affect the final adhesion force than can be measured using SFA, AFM, or ADM.

Based on the results presented in Tables 1, 2, and 3, we can conclude that the “value” of adhesion interaction still “depends” on the method and device used for measuring adhesion. The confusion in notions, which still plagues scientists, such as the work of adhesion, surface energy, adhesion force, and specific surface energy, influences the conception of adhesion as a physical phenomenon and initiates unnecessary discussions about the veracity of adhesion measurements.

6 Concluding remarks

Significant advances have been made, particularly during the last four decades, in the field of polymer tribology and contact mechanics. Various experimental techniques and theoretical methods have been developed to discover the origin of polymer adhesion.

The classical thermodynamic theory of adhesion cannot be directly applied to polymer systems. According to the experimental results of adhesion of polymers, there are several effects strongly influencing polymer adhesion.

The simplest mechanical approach is to consider interlocking the interaction of surface irregularities on the polymer surface. Other effects are related to the specific molecular activities occurring within the contact area. Cross-linking of the polymer surfaces reduces the adhesion and friction whereas increasing the number of chain ends at the surfaces, via either

scission or addition of short-chain polymers, leads to increased adhesion and friction.

Molecular irregularities also strongly influence the adhesion of polymers. There is partial untwisting of molecules, mutual penetration of polymer molecules resulting in “brush-to-brush” contact, and local cross-linking effect at the interface.

Proper analysis of the adhesion effects in polymer contacts is very important for the fundamentals of polymer tribology owing to the key role played by adhesion in self-lubrication, mass transfer, and wear of polymers and polymer-based materials with increasingly more practical applications in engineering and daily life.

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