MOLECULAR DESIGN OF INNOVATIVE ADHESIVES AND PRODUCTS

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Adhesion is traditionally defined as the phenomenon where surfaces of contacting materials are held together by interfacial forces.1. Adhesion may result from the attraction of electrical charges, molecular forces due to the polarizability of molecules, or from specific acid–base interactions of functional electron-donating and accepting groups at the adhesive–substrate interface, respectively. Pressure-sensitive adhesion is defined as the capability of soft viscoelastic polymers to form strong adhesive joints with substrates of any chemical nature under application of a light external pressure (e.g., pressing by a finger) to the adhesive film over a very short contact time (1-5 s).

Over the past years, diverse theories have been proposed to explain the driving forces and mechanisms of adhesion. Best known are the adsorption, diffusion, mechanical interlocking, and electronic theories of adhesion. More recently, it has become generally accepted that, while the adsorption theory has the widest applicability, each of the others may be appropriate in certain circumstances. None of these theories, however, can be regarded as most insightful and adequate in describing the strength of pressure-sensitive adhesion.

Originally, pressure-sensitive adhesion was described rather empirically, but later the importance of the rheological behavior of pressure-sensitive adhesives (PSAs) gained wider recognition. The designation "pressure-sensitive adhesion" attributes the behavior of PSAs to their rheological nature and the contribution of shear deformation under compressive adhesive-bonding, and adhesion strength can be predicted from rheological behavior of the PSAs in the linear domain. Time–temperature equivalence, a typical feature of rubber-like polymers, applies to all PSAs, indicating that they are viscoelastic materials. Moreover, cohesive and interfacial types of adhesive debonding also relate to the linear elastic properties of the PSAs. The techniques used to measure adhesion and tack, such as peel test, probe tack, and loop tack, largely rely on measuring the mechanical energy required to break the adhesive bond, albeit a bond made under rather unfavorable conditions, namely short contact time and low pressure. In the course of adhesive bond failure, many PSAs undergo large tensile deformations and form separate fibrils as shown in Figure 1. The energy expended in deformation and fibrillation of the adhesive film constitutes by far the largest part of the total mechanical energy required for adhesive debonding and dominates the energy of interfacial interaction.



FIGURE 1. Micrographs of adhesive debonding in the course of probe tack (acrylic PSA, A) and peel tests (hydrophilic PSA based on PVP–PEG blend (B). The intact adhesive layer of 0.25 mm thickness is seen in panel B as a light band at the border between the backing film and the substrate.

It is, therefore, no wonder that frequently there is no correlation between the values of the thermodynamic energy of adhesion (calculated using the surface energies of an adhesive and a substrate) and the strength of an adhesive joint measured by probe tack or peel tests. PSAs made of the same material and demonstrating similar values of surface energy, but possessing different supramolecular structures, frequently give different strengths of adhesive joints with a standard substrate. Hence, the large and dominant contribution of deformation of an adhesive material during the debonding process renders impossible prediction of adhesive strength based only on data regarding interfacial interactions.

The contribution of interfacial interactions to the total work of debonding of PSAs by a peel test is often around 1% but can be as low as 0.05% for a PSA with specific supramolecular structure, while the major part of the total work of adhesive joint failure is due to the work of viscoelastic deformation of the adhesive material during failure of the bond. In other words, the strength of an adhesive joint evaluated by the probe tack and peel tests characterizes the viscoelastic properties of the adhesive material, rather than the tack.

DUALISM OF PSA PROPERTIES

Pressure-sensitive adhesion is a complex and multiform phenomenon, where tack (adhesive bond-forming property) is a necessary component, but not sufficient by itself. To establish a good adhesive contact at the molecular scale with the substrate under light compressive force (typically 1–10 Pa), a PSA should behave as a liquid, easily spreading onto the substrate surface and forming perfect adhesive contact. While in the process of adhesive contact breaking up, high cohesive strength and elasticity become more important and these are characteristic features of solid materials. A certain degree of elasticity is required to provide a high level of dissipated energy in the course of adhesive bond failure. That is why all PSAs are viscoelastic, rubber-like polymer materials. PSAs exhibit glass transition temperatures, T_g , ranging between -10 and -113 °C, and elastic storage moduli G_0 in the range 0.01–0.1 MPa. Such carefully adjusted viscoelastic behaviors are difficult to realize in *de novo*. Rational design of novel PSAs with tailored performance properties, therefore, requires knowledge of molecular structures responsible for viscoelasticity of the constituent polymers.

TOWARD A MOLECULAR UNDERSTANDING OF PSAs

Which molecular structures dictate pressure-sensitive adhesion of polymers and polymer composites?

Indeed, if we look at existing PSAs from the chemical point of view we could notice that they exhibit markedly dissimilar chemical compositions and structures, including natural and several synthetic rubbers, for example, polyisobutylene (PIB), styrene-isoprene/butadienestyrene triblock polymers (SIS, SBS), acrylic block copolymer-based hot melt adhesives, polyalkylacrylates, ethylene-vinylacetate copolymers, poly(vinyl alcohol) ethers, silicone, and polyurethane-based PSAs. The differences in chemical compositions of PSAs signify that the answer to this fundamental question should be sought in polymer physics rather than in polymer chemistry. A first step in answering questions regarding molecular and structural characteristics required for pressure-sensitive adhesion is to develop a model PSA having rather simple chemical composition, which will allow establishment of quantitative structure-property relationships (QSPR). A fundamental problem arising from QSPR analysis, however, lies in the fact that pressure-sensitive adhesion is a macroscopic property of viscoelastic polymers that involves numerous processes at the molecular level, which is separated from the macroscopic level by the microscopic and even nanoscopic scales. Bridging the gap between molecular structure at the nanoscopic level and macroscopic physical properties of PSA polymers is, therefore, a great challenge.

Model PSA system designed to elicit molecular structures responsible for pressure-sensitive adhesion

Our earlier research established that blends of high molecular weight (MW), glassy poly(N-vinyl pyrrolidone) (PVP, Mw = 1,000,000 g/mol; Mn = 360,000 g/mol) with liquid poly (ethylene glycol) (PEG, Mw ¹/₄ 400 g/mol) demonstrate excellent pressure-sensitive adhesion. (Figure 2). PVP has been shown to be easily soluble in low-MW PEG, yielding single phase homogeneous blends. It is well known that miscibility of polymer blends results most frequently from a specific favorable interaction between the macromolecules.36

In this case, miscibility attributed to interactions between the proton donor OH end groups on PEG with the PVP electron donors. Such interactions are confirmed by Fourier transform infrared (FTIR) spectroscopy. A schematic view of the proposed structure of the PVP–PEG complex is illustrated in Figure 3. Here PEG acts as an H-bonding reversible crosslinker of longer PVP macromolecules and as a spacer between the PVP chains.

Commonly, novel PSAs are produced by chemical synthesis or modification of initially tacky polymers. However, in case of PVP-PEG H-bounded complex after mixing



FIGURE 2. Chemical structure of PVP (left) and PEG (right). m = 10,000; n = 9-10.



FIGURE 4.Peel adhesion of PVP–PEG blends as a function of PEG concentration and content of absorbed water (percent water absorbed per 100% PVP + PEG).



FIGURE 3.Schematic of supramolecular network structure of the stoichiometric H-bonded PVP–PEG complex.

two initially untacky components high adhesion appears in blends with PEG content in a narrow range around 36 wt % (Figure 4). This finding is of critical industrial importance because it is evident that innovative PSAs can be also obtained just by physical mixing of nonadhesive polymers. We postulate that common properties determined for the PVP-PEG complex and conventional adhesives might be of particular importance for their adhesive behavior. The structure and properties of the model PVP-PEG adhesive system, as affected by blend composition and content of absorbed water, have been studied thoroughly. The interaction mechanism and molecular structure have been investigated using FTIR spectroscopy, differential scanning calorimetry (DSC), wide angle Xray scattering (WAXS), and water sorption techniques. The stoichiometric composition of the PVP-PEG H-bond network complex has been established from the relationship

between T_g and the degree of hydrogen bonding in blends. The phase state of PVP–PEG blends has been examined with DSC. Free volume in PVP–PEG blends has been evaluated by positron annihilation lifetime spectroscopy (PALS). Interdiffusion and PVP–PEG miscibility have been characterized using optical microinterference techniques, while self diffusion of polymer components and absorbed water has been studied using pulsed field gradient (PFG) nuclear magnetic resonance (NMR). Rheological (mechanical) properties have also been characterized in detail. Relaxation properties of model PVP–PEG PSAs have been studied on withdrawal of bonding pressure. All structures and properties have been related to adhesion as evaluated by peel and probe tack tests.

Micromechanics of model PVP-PEG PSA debonding

Fracture mechanics of adhesive debonding of PVP–PEG PSA during the peel test [Fig. 1 (B)] involves dramatic stretching and fibrillation of the adhesive layer, when the length of the extended fibrils is 10–20 times greater than the thickness of the intact adhesive layer. Fibrils are located throughout the entire width of the adhesive film at nearly equal intervals, implying that the mechanism of fibril nucleation is not random and that the adhesive material is spatially arranged into a three-dimensional network. The entire layer of the adhesive is subjected to elongational flow in the fibrils, providing resistance to detaching stress and energy dissipation.

Failure occurs closer to the substrate surface than to the backing film. This means that the locus of failure is miscellaneous but tending to cohesive. Viscoelastic deformation of the adhesive in extension is a major energy consuming mechanism for all PSAs, as is adhesive fibrillation and the cohesive mode of failure.

For typical PSAs, the microscopic mechanisms involved in detachment of an adhesive film from a flat probe can be commonly divided in four parts (see Figure 5):

- 1. homogeneous deformation before the peak of the probe tack stress–strain curve, σ_{max} ;
- 1

FIGURE 5. Direct observation of debonding mechanisms and the force *vs.* strain curve during the probe tack test for a PVP blend with 36 wt % PEG at a debonding rate of 1 μ m/s.

2. cavitation in the bulk of the adhesive

film or at the probe/film interface, around σ_{max} ;

3. rapid lateral growth of cavities during the steep decrease in nominal σ ; then, if there is a plateau in the "stress–strain" curve, slow growth of these cavities in the direction parallel to the tensile direction; and finally

4. elongation of the walls between the cavities (fibrillation).

General features of the stress–strain curve obtained in a probe test of a PSA are characterized typically by three parameters:

- maximum stress, σ_{max} ;
- maximum extension, *E_{max}*; and
- work of separation per unit area, W_a , defined as the integral under the stress-strain curve multiplied by the initial thickness of the layer h_0 .

The mechanical work to break the adhesive bond, W_a , includes the contributions of viscoelastic deformation and structural transformation of the adhesive under the applied tensile stress in the course of the debonding process. The presence of the maximum in the stress–strain curve coincides with the onset of cavitation occurring in the adhesive material. The cavities originate under a nearly hydrostatic tensile stress, at sites of pre-existing defects (for example, microscopic bubble), when the hydrostatic pressure inside the cavity exceeds the tensile modulus of the bulky

adhesive, *E*. That is why the σ_{max} value relates usually to the value of *E*. The next stage of the debonding process is the formation of a foamy oriented supramolecular structure, corresponds to appearance of a plateau in the stress–strain curve. The walls between neighboring cavities grow thinner gradually and elongate at approximately constant nominal tensile stress. Thus, the value of the plateau stress is a characteristic of the strength of stretching fibrils. This final stage of the debonding process is associated with fibrillation.

Tensile properties of model PVP-PEG adhesive blends



FIGURE 6. Total work of viscoelastic deformation to break the PVP–PEG film, W_b , ultimate tensile strength, σ_b , and break elongation, eb, as a function of PEG concentration in blends. Extension rate is 20 m/min.



FIGURE 7. Effects of PVP–PEG composition on 180° peel force, *P*, and work of viscoelastic deformation of the adhesive film up to break, *W*_b, under uniaxial extension. Peel and drawing rates are 20 mm/min.

PEG is a good plasticizer for PVP, and addition of PEG results in increased elongation at break (ε_b). According to our experiments, with increasing PEG concentration, the value of ε_b increases linearly (as shown in Fig. 6). For PVP blends containing <36% PEG, the ultimate tensile strength, σ_b , is comparatively high and practically unaffected by PEG content. For PEG concentrations >36%, σ_b declines rapidly with PEG content. The transition from ductile to tight deformation occurs over a fairly narrow range, between 36 - 34% PEG. This range corresponds to the transition from the fibrillar type of adhesive joint failure (36% PEG and higher) to brittlelike fracture without fibrillation.

The area under the stress–strain curve, W_b , which is the total work of viscoelastic deformation required to break the PVP–PEG adhesive blends, correlates well with both peel and probe tack behaviors and reveals a maximum at 36% PEG concentration for the blend demonstrating best adhesion (Fig. 7). An evident correlation between peel adhesion and work of viscoelastic deformation, illustrated in Figure 7, signifies the controlling contribution of viscoelastic deformation to adhesive performance.

Physical significance of correlation between peel adhesion and tensile properties of PVP-PEG model PSA

While the phenomenon of pressure-sensitive adhesion remains comparatively poorly understood, the relation of mechanical properties to polymer molecular structure is much better elaborated. Correlations between the results of peel and tensile tests revealed in Figure 7 are, therefore, useful in gaining molecular insights into pressure sensitive adhesion.

Plotting the values of peel force, *P*, versus the work of deformation to break the PVP-

PEG model PSAs, W_b , as in Figure 8, provides insight into factors governing PSA behavior at the most fundamental, molecular level.

First, the data establish a demarcation line between adhesive and nonadhesive PVP–PEG blends. Both PEG-overloaded (41% PEG) and underloaded (31% PEG) blends demonstrate comparatively moderate adhesive capability, but only the latter blend is a PSA while the former is a tacky liquid. To be a PSA, a tacky material should dissipate appreciable mechanical energy in the course of debonding, and the value of the work of viscoelastic deformation to break the tacky film under uniaxial extension may be taken as a measure of the dissipated energy. This energy (density) should be 60 MJ/m³ or higher.



FIGURE 8. Relation between work of viscoelastic deformation of PVP–PEG model adhesives and SIS-based PSA (Duro-Tak 34-4230, National Starch & Chemical Corp.), and peel force on the PET substrate. Contents of PEG (wt %) are indicated next to symbols.

Second, the linear relationship between peel force and work of deformation, P, holds not only for hydrophilic PVP–PEG PSA, but also for a PSA based on a SIS triblock copolymer. Traditional hydrophobic PSAs demonstrate similar linear relationships between peel adhesion and work of elastoplastic deformation up to break under uniaxial stretching. This linearity could be expressed with following equation:

$$P = kbl \int_{0}^{\varepsilon_{\rm b}} \sigma \cdot d\varepsilon \tag{1}$$

where **b** and **l** are the width and thickness of adhesive film, σ and ε are tensile stress and relative elongational strain, respectively, ε_b is maximum elongational strain of the film at the break, and **k** is a dimensionless constant that takes into account contributions of backing film deformation and interaction between the adhesive and the substrate. If we compare the peel adhesion of various adhesives using the same backing film and a standard high energy substrate, we can assume that $\mathbf{k} = 1$. Assuming further that deformation of the adhesive film in the course of both debonding and uniaxial drawing follows a linear elastic law, $\sigma = \mathbf{E} \varepsilon$, eq 1 can be written as:

$$P = \frac{b l \sigma_{\rm b}^2}{2E} \tag{2}$$

where σ_b is the ultimate tensile strength and E is an approximate tensile modulus of the adhesive material. For PSAs this is not a bad approximation as they usually soften and then harden at large strains. Equation 2 holds for ideally elastic PSAs, while for real PSAs such as the PVP–PEG deviations from this prediction can be of order 20%.22. Equation 2 is similar to the well-known Kaelble equation:

$$P = \frac{b l \sigma_{\rm f}^2}{4E} \tag{3}$$

where σ_f is a critical value of ultimate debonding stress obtained by peeling off the PSA film from a hard substrate with a fixed rate. The similarity of eqs 2 and 3 suggests that the Kaelble equation holds for any type of PSA, including the hydrophilic PVP–PEG. Thus, the rule described by these equations is universal.

FACTORS DEFINING THE PRESSURE-SENSITIVE ADHESION AT THE MOLECULAR LEVEL

Using well-known equations of polymer physics, eq 2 can be further modified to express peel adhesion, P, as an explicit function of the relaxation time, τ , and the self diffusion coefficient, D, of a PSA polymer. Let us assume in the first approximation that a PSA is a viscoelastic material that can be described with a Maxwell model with a single apparent relaxation time, τ , and a microviscosity, η , reflecting monomer–monomer friction. According to the Maxwell model,

 $E = 3 \eta / \tau$, which on introduction into eq 2 yields

$$P = bl \frac{\tau}{6\eta} \sigma_{\rm b}^2 \tag{4}$$

The viscosity of the Maxwell model can then be derived from the classic Stokes-Einstein expression,

$$\eta = \frac{k_{\rm B}T}{6\pi DNa} \tag{5}$$

where k_B is Boltzmann's constant, T is temperature (°K), N is the number of segments of size a in the polymer chain, and D is the self diffusion coefficient of the polymer segment. Substituting eq 5 into eq 4 yields

$$P = b l \frac{\pi N a D \tau}{k_B T} \sigma_{\rm b}^2 \tag{6}$$

Equation 6 is of course only qualitatively illustrative as it is based on some crude approximations. It ignores the existence of the spectrum of relaxation times and assumes validity of the Maxwell model. However, studies of relaxation on withdrawal of bonding pressure have demonstrated two modes, with relaxation times 10–70 s and 300–660 s. These times are associated, respectively, with small- and large- scale mechanisms of strain recovery.

Equation 6 is not useful for quantitative calculations of peel force as a, the presumed size of diffusing a polymer segment, is not measurable. Nevertheless, eq 6 predicts qualitatively the significance of diffusion and relaxation processes, both of which require molecular mobility, for the adhesive behavior of polymers when their debonding is dominated by the formation of fibrils. This eq 6 implies that high molecular mobility of PSA polymer is needed for development of large deformations and large-scale rearrangements of adhesive polymer supramolecular structures in the course of debonding (Fig. 1 and 5). Large deformations and rearrangements of supramolecular structure in the adhesive layer require expenditures of significant mechanical energy, determining the strength of adhesive joints.

According to eq 6, pressure-sensitive adhesion requires coupling of high molecular mobility (D) with long term relaxation processes (τ), and a high cohesive strength of the adhesive polymer (σ_b).

High molecular mobility is a manifestation of large free volume, which is defined as the vacant space between neighboring macromolecules. A fundamental quantity that underlies a high value of the self diffusion coefficient, D, is the free volume fraction, f_v , with

$$D = A \exp(-B/f_{\rm v}) \tag{7}$$

where A and B are positive constants.73. Clearly, D increases with f_{ν} .

Together, eqs 6 and 7 signify that at the molecular level, PSA capability of polymer materials requires both high cohesive energy, as reflected by σ_b , and large free volume. Most commonly, the strong cohesive interaction between macromolecules is associated with reduced free volume, which explains why pressure-sensitive adhesion is a comparatively rare phenomenon. In the model PVP–PEG system, these apparently conflicting properties are reconciled due to the location of reactive hydroxyl groups at the opposite ends of PEG chains of appreciable length and flexibility. High cohesion energy may result from intermacromolecular crosslinking (both covalent and noncovalent, and through entanglements of long chains), addition of tackifiers with high T_g , or to the hydrophobic association of side groups. Large free volume is most prevalent in elastomers with a low glass transition temperature, T_g .

The glass transition temperature relates to the energy of cohesion and free volume by the equation:

$$T_{\rm g} = 0.455 \frac{z \cdot \langle D_0 \rangle}{R} \tag{8}$$

where R is the gas constant, z is the coordination number, which is inversely proportional to the free volume, and D_{θ} is the total interaction energy of atoms forming a polymer segment. In acrylic PSAs containing negatively charged carboxylic groups, increase in free volume may result from electrostatic repulsion of carboxylate anions. In uncrosslinked PIB PSA, cohesive strength is due to a network of long chain entanglements of the high-MW polymer fraction, and to the Van der Waals interactions between nonpolar functional groups. In SIS-based triblock copolymers and other thermoplastic elastomers, cohesion is provided by physical crosslinks of high T_g polystyrene blocks, while free volume is provided by blocks of lower T_g polymers.

The place of PSAs among other rubber-like polymers

As eq 6 predicts, strong adhesion requires a high value of cohesive strength (σ_b), a large diffusion coefficient (D), and a long relaxation time (τ). Although both the diffusion coefficient and the relaxation time are measures of molecular mobility, they vary in opposite directions as molecular mobility increases as a result of transition from glassy polymer to viscous liquid, for example, with the increase of PEG plasticizer content in blends with PVP. Indeed, the longest relaxation times are featured for glasses (years, decades, or centuries), whereas low MW liquids relax almost instantaneously. In contrast, the lowest diffusion coefficients are observed for glasses, while the highest diffusion coefficients are demonstrated in liquids and gases. Thus maximum peel strength, P, relates to the maximum magnitude of the product $D \cdot \tau \cdot \sigma_b$. Evidently, this product achieves its maximum magnitude over a limited range of values of relaxation time and diffusion coefficient, which are intermediate between those inherent for liquids and glasses. Materials exhibiting properties of both liquids and solids are viscoelastic, and all PSAs are viscoelastic materials. Moreover, according to Dahlquist's criterion of tack, PSAs reveal good adhesion when their elastic moduli are between 0.01 and 0.3 MPa. Consequently, all PSAs are viscoelastic and rubber-like.

Summarizing all findings we should answer another question: why do blends of two nonadhesive polymers, PVP and PEG, exhibit pressure-sensitive adhesion? The answer to this question is of fundamental significance for development of innovative PSAs prepared simply by mixing nonadhesive polymers in solution or melt. While this innovative PSA production method is now known to be feasible, the search for nonadhesive polymers capable of serving as parent components remains a challenge.

Properties of polymer blends are usually intermediate between those of the constituent polymers. New properties, untypical of the pure components, arise most frequently from specific

interactions or chemical reactions. In polymer blends, such interaction products are frequently interpolymer complexes. For blended PVP–PEG PSAs, PVP mixing with PEG leads to formation of an H-bonded network complex of nonequimolar stoichiometry. Unblended PVP is glassy and its segmental mobility is essentially frozen. Telechelic PEG chains act as spacers between PVP chains that increase the free volume and molecular mobility of PVP segments between neighboring H-bond network junctions. The longer the crosslinking PEG chain, the greater is the loss in entropy due to fixation of conformation and limitation of PEG chain translational mobility. Dissolution of glassy PVP in liquid PEG is a two stage process. As PVP mixes with comparatively small amounts of PEG, a network complex forms. At higher PEG loadings, OH-groups of excess PEG interact with PVP carbonyls only through single terminal hydroxyl groups, leaving the opposite terminal OH-groups free of H-bonding with PVP. This second stage of PVP dissolution in PEG represents swelling of the network complex in excess PEG. Maximum adhesion is observed at the border between network complex formation and swelling.

Correlations of adhesion and mechanical properties with free volume in PVP–PEG model PSA

Depth profile of Free Volume Radius in PVP–PEG Model PSA and its significance for Adhesion PALS has been used to characterize the size and content of subnanoscopic free volume in a model PSA based on a stoichiometric hydrogen-bonded network complex of PVP and oligometric PEG. The size and number density of free volume domains in the PVP–PEG blends were determined as functions of blend composition and relative humidity of the surrounding atmosphere, which controls the amount of absorbed water.

With the free volume behavior in model PVP–PEG PSA, we can answer key questions: What values of free volume correlate with high adhesion in the PVP–PEG blends? How does free volume relate to the viscoelastic properties of PVP–PEG model PSAs? Answers to these questions are of fundamental significance since they establish direct correlations between nanoscopic and macroscopic properties of PSA materials.

The high sensitivity of PALS in probing defect properties arises from preferential trapping and localization of positronium (Ps, an "atom" consisting of a positron and an electron) in atomic scale free volumes and holes. Because of the relatively small size of Ps (1.59 Å) and short probe lifetime (nanoseconds), PALS is sensitive to small holes and free volume defects in a size range of 1–20 Å and times of molecular motion from 10^{-10} s and longer. Positron lifetimes (τ_1 , τ_2 , τ_3) and intensities (I_1 , I_2 , I_3) from PAL spectra are attributed to annihilation of parapositronium (p-Ps), positron (P), and ortho-positronium (o-Ps), respectively. The o-Ps lifetime τ_3 , of order 1–5 ns in polymeric materials, is attributed to "pickoff" annihilation with electrons and is used to calculate the distribution of free volume radii, R (Å to nm), based on an established semiempirical correlation for a spherical cavity model, and to estimate the relative free-volume fractions.

Both PEG-400 and absorbed water are good PVP plasticizers. Interestingly, however, while the rise in PEG concentration increases free volume radius and fraction, absorbed water leads to the increase in number density of free volume holes, having no effect on the size of free volume cavities. As is shown in Figure 9, the depth profile of free volume radius in the PVP–PEG-400 PSA demonstrates excess free volume near the surface of the adhesive film (~3.25 Å at ~20 nm into the film) compared with the bulk (3.08 Å at 1.4 lm and beyond). Excess free volume at the surface facilitates substrate



FIGURE 9. Orthopositronium (o-Ps) lifetime s3 and hole size radius versus positron incident energy or depth from the film surface in PVP–PEG blend.

wetting by the PSA polymer under slight bonding pressure, as shear deformation dominates. On the other hand residual free volume in the bulk facilitates dissipation of mechanical energy under detaching force, during which the PSA polymer exhibits large tensile strain and fibrillation. Thus, the depth profile of free volume radius in the PVP–PEG model PSA promotes its pressuresensitive adhesion.

The nanoscopic free volume governs the molecular mobility of the PSA material and it is a key factor underlying deformability of PVP–PEG blends.

Free volume fraction and average free volume radius, along with peel adhesion force, are plotted versus PVP–PEG composition in Figure 10 (A,B), respectively.46 Strongest adhesion is observed at 6.3–7.0% free volume content, and free volume radius varying between 2.95 and 3.08 Å.



FIGURE 10. Effects of PEG content on peel adhesion (P) (A) and average radius of free volume (B) of PVP– PEG model PSA at RH ¼ 50%.

Strength of the adhesive joint is evaluated in terms of maximum debonding stress or probe tack, σ_{max} , and the amount of mechanical energy dissipated during the debonding process, which is known as practical work of adhesion (W_a) and is measured as the area under the probe tack stress–strain curve. These both characteristics of typical PSA are predominantly controlled by cohesive strength.

In PSAs the transition point from a predominantly adhesive to a predominantly cohesive mechanism of debonding occurs at the point of maximum adhesion. While free volume and tensile strain are bulk properties of polymer materials, adhesion is an interfacial phenomenon,

including the contribution of adhesive– substrate interaction forces, which compete with PSA cohesive strength. Values of maximum elongation at break, eb, and free volume fraction are increasing linear functions of PEG concentration, suggesting that nanoscopic free volume, which governs molecular mobility of the PSA material, is a key factor underlying deformability of viscoelastic amorphous polymers, which include all PSAs.

Thus, a unique feature of tensile testing is that it provides a feasible though indirect measurement of free volume,



FIGURE 11. Effects of PEG content on maximum elongation at break and free volume fraction in PVP–PEG model PSAs.

which is embodied in the maximum value of relative elongation at the break of the adhesive film (Fig. 11). Qualitative estimation of free volume from maximum values of relative elongation based on tensile test data can be useful for comparative analysis of the structure and properties of viscoelastic polymers. The tensile modulus of a polymer material, E, is defined as the σ/ε ratio. The ratio $\sigma_{b}/\varepsilon_{b}$ can be interpreted physically as an average modulus of the adhesive material prior to fracture, i.e. the break modulus of the stretched polymer. The quantity σ_{b} is an integral measure of cohesive strength of stretched polymer at the moment of polymer film break. The break modulus of the stretched polymer, defines at the macroscopic level the fundamental ratio of cohesive strength to free volume, which governs not only pressure-sensitive adhesion, but also mechanical properties of polymer materials. It was revealed that the effect of free volume fraction on mechanical properties of viscoelastic polymers is far greater than that of the size of free volume holes. Because failure of adhesive joints involves mainly large strain mechanical behavior of viscoelastic PSA materials, this conclusion may be also reasonably extended to correlations between their adhesion and free volume behaviors.

CORRELATIONS BETWEEN DIFFUSION PROPERTIES AND PRESSURE-SENSITIVE ADHESION IN THE PVP–PEG MODEL PSA

Diffusion Coefficients

Equation 6 predicts that the self-diffusion coefficient of a PSA polymer should be large to promote good adhesion by formation of an intrinsically strong interface between a PSA and a polymer substrate over a contact time of only a few seconds. In addition, **eq 6** demonstrates, the diffusivity of the adhesive polymer contributes to the amount of mechanical energy needed to break the adhesive film in the course of stretching that accompanies the process of adhesive bond fracture (Fig. 1). Sufficiently high molecular mobility, signified by the magnitude of the diffusion coefficient, is necessary to endow the adhesive material with high compliance and the capability to develop a large tensile strain.

Thus, the liquid-like diffusional mobility of PSAs is needed not only to provide deep penetration of the PSA polymer into a substrate under slight bonding pressure, but also to develop large tensile strain of the adhesive layer under a detaching force. The PEG self diffusion coefficient in the PVP-PEG PSA coincides with the border between self diffusion coefficients of elastomers and viscous liquids, $D = 10^{-9}$ cm²/s.

Because debonding occurs after a certain time under application of a fixed tensile force, the time, *t**, required to rupture the adhesive bond characterizes the durability of the joint. Durability of an adhesive joint is a fundamental quantity characterizing pressure-sensitive adhesion.

So, a phenomenological analysis of the relationship between pressure-sensitive adhesion and the molecular mobility of the PSA, outlined by eq 6, suggests that the two important parameters controlling pressure-sensitive adhesion and diffusion are the energy of favorable intermolecular interactions (cohesion) and intermolecular free volume. The difference between adhesion and diffusion is quantitative: adhesion occurs only within a very narrow range of the ratio of cohesion energy to free volume, and in this case, both magnitudes are large. In contrast, diffusion takes place at any value of cohesion energy and free volume.

Relaxation times in PSAs

Diffusion and relaxation represent two sides of the same phenomenon—the molecular mobility of a material. The high diffusion coefficients seen in liquids are always associated with short relaxation times, whereas the low diffusion coefficients in solids relate to longer relaxation times (eq 12). Relaxation is a material response to perturbation of equilibrium structure caused by temperature jump, magnetic impulse or, in the case of pressure-sensitive adhesion, application of mechanical bonding or detaching stress. In the process of adhesive joint failure, relaxation is a driving force directing recovery of equilibrium material structure. During relaxation, macromolecules or their segments change their positions by diffusion, tending to their initial, equilibrium structure. Clearly, the relaxation process involves diffusion as one of the main mechanisms.

Because pressure-sensitive adhesion is a material response to applied mechanical stress, the role of relaxation in providing both good adhesive contact and adhesive joint strength is significant.

However, there is an abundance of information on the relaxation of elastomers, a family to which all PSAs belong, and recognition of the role of relaxation in well-known effects of bonding time and debonding velocity on the strength of adhesive joints. Most recent studies demonstrate that cyclic relaxation of an adhesive can be successfully modeled assuming linear viscoelasticity. Slower relaxation of the adhesive under cyclic loading than in the static regime is the result of memory effects.

Pressure-Sensitive Adhesion as a Three-Stage Process

Adhesion consists of a series of transformations in the structure of the adhesive material under an applied bonding and detaching stress, and it involves the evolution of material structure, geometry (e.g., cavitation and formation of fibrils), and other properties.

The process of making and breaking a PSA bond can be divided into three stages:

(1) adhesive bonding under compressive force,

(2) relaxation on removal of bonding pressure, and

(3) rupture of the adhesive bond under a tensile force.

As illustrated above, the third stage, adhesive debonding, is in itself a four stage process, as evidenced by structural and geometric transformations of the adhesive material in the course of a probe tack test



FIGURE 12. Typical protocol of squeeze–recoil testing of PVP–PEG (36%) adhesive film. Compressive and debonding forces are 0.2 N.

(Fig. 5). The squeeze-recoil test provides a simple but adequate characterization of all three stages (Fig. 12). During stage 1, the adhesive film is compressed between a upper cylindrical rod and a stationary lower plate under a fixed squeezing force, and the deformation, $\Delta h(t)$, of the tested material is registered. Adhesive bonding under a compression is followed by removal, in stage 2, of bonding pressure and relaxation of the adhesive material. Finally, in stage 3 a detaching stress is applied. The process ends when fracture of the adhesive joint occurs (3) at high elongations, via adhesive or cohesive mechanisms.

Because the three stages are applied in succession, it is not surprising that details of the compression and relaxations stages lead to "memory effects" that can affect the debonding process and the value of the practical work of adhesion evaluated with a probe test. The strength of a PSA adhesive joint can be a function of both contact time and contact pressure. It is, therefore, important to discuss mechanisms by which the process of adhesive bond formation contributes to the process of adhesive debonding.

Relaxation Properties of PSAs under Compressive Load during Adhesive Bonding

To evaluate the relaxation properties of adhesives under bonding pressure and adhesion, the probe tack test is most appropriate.

In the probe tack test, adhesive film deformation is kept constant and the probe tack curve can be divided into three portions reflecting successive stages of the process (Fig. 13). The first stage corresponds to adhesivesubstrate joint formation. During this stage, the flat end cylindrical probe approaches the 0.5mm thick adhesive layer with a constant velocity, penetrates 0.1 mm into its depth, and then stops. In the second stage, the adhesive material relaxes under the probe, which is held at constant position over a predetermined contact time, in the range 1–1000 s. During these two stages, the apparatus measures compressive stress. In the third, debonding stage, the probe is withdrawn at a constant rate of 0.1 mm/s, and the force of the probe detaching from the adhesive film and the strain,



FIGURE 13. Typical nominal stress-time curve obtained in the course of the probe tack test. Region I corresponds to probe penetration into the adhesive layer (compression-adhesive bonding), region II relates to compressive stress relaxation during the contact time, and region III represents probe detachment from the adhesive film surface in the course of the debonding process

that is, the height of probe lifting above the adhesive film surface, are recorded. The unique advantage of the probe tack test technique is that it allows simultaneous evaluation of material relaxation properties at the stage of adhesive joint formation and measurement of adhesive bond strength during the same experiment, ideally characterizing the pressure-sensitive adhesion as an uninterrupted process.

Figure 14 shows compressive stress relaxation curves PSAs formed with SIS, silicone adhesive, and PIB. These curves are well

approximated by a sum of three exponents:



FIGURE 14. Compressive stress relaxation curves for PIB (OppanolV R B15), silicone (BIO-PSAV R 7-4302), and SIS-based (Duro-TakV R 34-4230) adhesives.

1200

1000

800

600

$$G_t = G_{\text{eq}} + \sum_{i=1}^n G_i \exp(-t/\tau_i)$$

where G eq is the equilibrium relaxation modulus and G_i is the modulus corresponding to the relaxation process described by relaxation time τ_i . Three exponential terms suffice, with coefficient of determination (R_2) always between 0.98 and 0.99. The relaxation properties for PSAs were estimated with contact times varying from 1 to 1000 s. Fitted relaxation times and corresponding moduli for various PSAs are summarized in the Table 1.

Adhesive	$G_{ m eq}$ (MPa)	<i>G</i> ₁ (MPa)	τ ₁ (s)	<i>G</i> ₂ (MPa)	τ ₂ (s)	<i>G</i> ₃ (MPa)	τ ₃ (s)
Silicone BIO-PSA® 7-4302	0.025 ± 0.001	0.8 ± 0.02	3.3 ± 0.1	0.5 ± 0.02	21.4 ± 0.8	0.2 ± 0.005	150 ± 5.4
PIB Oppanol B15	0	0.57 ± 0.01	1.2 ± 0.03	0.4 ± 0.01	7.2 ± 0.2	0.07 ± 0.003	48 ± 1.8
PIB Oppanol B12	0	0.2 ± 0.01	1.8 ± 0.04	0.17 ± 0.01	5 ± 0.4	0.02 ± 0.005	35 ± 3.4
SIS DURO-TAK® 34-4230	0.6 ± 0.005	0.2 ± 0.01	5.3 ± 0.3	0.1 ± 0.004	44.5 ± 2.9	0.2 ± 0.004	770.7 ± 56.1
Acrylic Gelva® 3011	0.035 ± 0.001	0.08 ± 0.01	5.1 ± 0.3	0.06 ± 0.002	43.4 ± 3.0	0.05 ± 0.001	355.7 ± 0.3

TABLE 1. Relaxation Times and Moduli of Acrylic (GelvaV R 3011), PIB (OppanolV R), Silicone (BIO-PSAV R 7-4302), and SIS Triblock Copolymer (DURO-TAKV R 34-4230) Adhesives at the Stage of Adhesive Joint Formation under Bonding Pressure

Effects of contact time during bonding pressure on probe tack curves for two typical PSAs, namely the fluid silicone adhesive BIO-PSAV R 7-4302 and the elastic, physically crosslinked adhesive based on SIS, DURO-TAKV R 34-4230, are shown in Figures 15.



FIGURE 15. Probe tack curves of BIO-PSAV R 7-4302 silicone adhesive (a) and SIS (DURO-TAKV R 34-4230) adhesive (b) at various contact times.

Relaxation and adhesive properties of other PSAs, such as PIB, a fluid adhesive with properties similar to those of BIO-PSAV R 7-4302, and acrylic adhesive GelvaV R 3011, which exhibits adhesion and rheological properties similar to those of SIS DUROTAKV R 34-4230 PSA have been evaluated in detail also. Thus, all tested PSAs can be arbitrary classified into the two groups. The first group is composed of PIB and silicone PSA, which relax fully and comparatively rapidly. The second group includes the noncovalently crosslinked adhesives SIS and PVP–PEG, which can store an appreciable amount of mechanical energy during deformation at the adhesive joint formation stage. These adhesives exhibit residual stress after relaxation, corresponding to yield stress of the material.

It is interesting that for this PSA and the acrylic adhesive, two peaks are observed in the section of the probe tack curve corresponding to probe detachment from the adhesive surface (Fig. 15 b). The single peaks (Fig. 15 a) or the first maxima on the curves illustrated in Figure 15 b relate to the onset of the PSA cavitation process and breakup of the adhesive layer into fibrils stretched in the direction of the applied tensile force. The appearance of the second maximum is usually featured in chemically or physically crosslinked PSAs.





FIGURE 17. Slow relaxation times and practical work of adhesion for SIS-based Duro-Tak 34-4230, acrylic Gelva 3011, silicone BIO-PSAV R 7-4302,

FIGURE 16. Effect of contact time on the practical work and two grades of PIB adhesives (OppanolV R B12 and B15). Observation time is 1000 s of adhesion and maximum debonding stresses for the BIOPSAV R 7-4302 silicone adhesive (a) and for the SIS-based DURO-TAKV R 34-4230 adhesive (b). Comparing the data in Figure. 16 with values of the longest relaxation time, displayed in Table 1 for the examined PSAs, demonstrates that achievement of maximum adhesive bond strength requires a contact time comparable with the longer relaxation time, as predicted by eq 6. The compressive stress relaxation curves of adhesive films demonstrate three phases corresponding to fast, intermediate, and slow relaxations. In all cases, achievement of maximum adhesion coincides with the end of the intermediate relaxation period and the onset of slow relaxation. Figure 17 illustrates the correlation between the practical work of adhesion and the longer relaxation times measured for all PSAs examined here. Adhesion appears when τ_3 crosses 50 s, then increases and passes through a maximum (acrylic GelvaV R 3011 PSA) at $\tau_3 = 330-380$ s. Further increase in longer relaxation times results in a gradual decline in adhesion. Good adhesion is assured when the longer relaxation time is in the range 150-800 s.

Many hydrophobic elastomers have been used to produce PSAs, but usually they must be blended with tackifiers and plasticizers to optimize adhesion. In such PSAs, the rubbery polymer provides the elastic component while the low MW tackifying resin and plasticizer constitute the viscous components. Most parent elastomers do not by themselves exhibit proper rheology to be PSAs. Typically, adding a tackifiers raises the glass transition temperature, T_g , lowers the plateau modulus by diluting the chain entanglements of the elastomer, and increases the ratio of viscous to elastic response of the elastomer/tackifier blend, improving both the bond forming and the bond breaking processes. Plasticizers demonstrate similar effects on rheology but cause reduction in T_g . It is, therefore, of particular interest to trace how the formulation process affects the relaxation properties of a composite PSA.

Tack, peel, and shear have all been reported to depend on the relative participation of the two primary molecular mechanisms of deformation: viscous flow, which proceeds by diffusion via free volume, and elastic distortion, which stores free energy. These two mechanisms are characterized by different time scales. Whereas viscous flow requires appreciable time, elastic response dominates at shorter time scales. To appreciate the significance of the relaxation properties for the adhesive behavior of polymers we must study the effects of composition on relaxation and pressure-sensitive adhesion.

We come to the relaxation criteria for pressure-sensitive adhesion, which can be stated in a preliminary form as follows:

1. To be a PSA, polymer compositions preferably possess two retardation times with ranges 10–70 and 300–660 s, respectively.

2. For proper adhesion, the relaxation modulus coefficient G_2 , relating to slower relaxations, is preferably higher than the coefficient G_1 , corresponding to the faster relaxations. Because G1 and G2 reflect relative amounts of energy dissipated, respectively, for predominantly smalland large-scale viscoelastic mechanisms of squeeze-recoil, and because the amount of energy dissipated in the course of the debonding process is the measure of adhesion, this requirement illustrates the dominance of the larger scale mechanism, which requires appreciable molecular mobility, in pressure-sensitive adhesion.

3. Optimum adhesion is achieved as the absolute values of the G1 and G2 moduli range between 0.70–2.20 and 2.5–3.3 MPa, respectively.

Thus, under conditions imitating removal of compressive force on adhesive bond formation, for which the mode of deformation is typically shear, PSAs reveal two retardation times that are separated by about 1 decade. The shorter retardation time defines the rate of release of stored energy due to recovery of conformation of the polymer chains, and show negligible correlation

with adhesion. The longer retardation time (300–660 s) relates mainly to energy dissipating processes and chain entanglements, which are associated with translational movement by self diffusion of polymer segments and entire macromolecules in the course of larger scale structural rearrangements. The longer relaxation time has the most significance for pressure-sensitive adhesion.

Linear Elastic and Adhesive Properties: Validity of Dahlquist's Criterion of Tack

For rational design of novel PSAs or optimization of performance properties of adhesive products, a QSPR is very important. With this purpose in mind, the structure of a PSA is usually varied and its adhesion response is measured. The common method of changing PSA structure is chemical or physical modification of the adhesive material's composition. However, such modification is not always feasible, especially when details of the chemical composition of a PSA of interest are not disclosed by the supplier, for example, for acrylic adhesives. In this case, varying testing temperature may be helpful. Actually, high strength of the adhesive joint requires a proper combination of the contributions of strong intermolecular cohesion energy (E_c) and large free volume fraction (fv). Increase in temperature above glass transition generally results in reduction of intermolecular cohesion energy and in growth of free volume. In this connection, simultaneous measurement of temperature dependence of adhesion strength coupled with viscoelasticity represents a most universal tool for the QSPR investigation. This unique method holds, without exception, for any PSA and does not require knowledge of chemical composition.

When developing novel PSAs, the probe tack test is a most informative and highly illustrative tool that enables not only characterization of an adhesive joint's strength, but also development of qualitative insight into the relative contributions of E_c and f_v to adhesion. When the contribution of E_c dominates that of f_v , the probe tack stress–strain curve has a shape illustrated in Figure 18 by curve 1, which is typical for debonding of solid-like PSAs. This curve is characterized by a sharp maximum at rather low strains and a small area under the stress–strain curve. Adhesive joint failure in this



FIGURE 18. Typical probe tack curves for solidlike PSA (high $E_c:f_v$ ratio, curve 1), liquid-like adhesive (low $E_c:f_v$ ratio, curve 2), and the PSA with optimized adhesion (intermediate value of $E_c:f_v$ ratio, curve 3).

case proceeds through interfacial crack propagation between the probe and the adhesive film surface and is called "adhesive debonding." At the other extreme, when f_{ν} prevails, the probe tack curve is as that shown by curve 2 in Figure 18. This type of adhesive joint failure is characteristic of fluid PSAs, which demonstrate comparatively low cohesion strength, indicated by a lower peak of debonding stress, r, coupled with a relatively high value of elongation, e. In this case, the adhesive joint breaks by cohesive fracture in the bulk of the adhesive layer, and the debonding process is governed by viscous flow. This type of debonding is also called "cohesive debonding," where some residues of adhesive are left on the probe at the end of the test. In between these two cases, when high E_c is accompanied by large f_v , the area under the probe tack curve achieves its maximum value. Debonding proceeds via cavitation and fibrillation of the adhesive layer, which is typical for PSAs with optimized adhesion (Figure 18, curve 3). The $E_c: f_v$ ratio also dictates values of such fundamental quantities of polymers as solubility parameter, glass transition temperature, or elastic modulus, G_{θ} . In this connection, it is of no surprise that adhesive properties of PSAs relate closely to their linear viscoelastic behaviors. This relationship is described by the well known Dahlquist criterion of tack, which stipulates that the shear elastic modulus, G_0 , at a bonding frequency of 1 Hz must be lower than 0.3 MPa for

the layer to be able to form a good adhesive contact with a substrate within a short contact time. If the PSA has an elastic modulus that lies in a range defined by the Dahlquist criterion, then the debonding process is determined by the coupling of bulk and interfacial rheological properties of the material. The Dahlquist criterion of tack holds for all the PSAs, including the typical hydrophobic PSAs based on initially tacky polymers with low T_g , and for the innovative hydrophilic systems, based on nontacky functional polymers capable of forming self assembling complexes with each other, stabilized by hydrogen or electrostatic interpolymer bonds. Another general criterion for pressure sensitivity is that the glass transition temperature of the adhesive should be below ambient temperature, most frequently room temperature. Broadly speaking, the T_g of a PSA should be about 30–70 °C below the room temperature, depending on the base polymer and the added modifiers. This observation implies that all PSAs are viscoelastic rubberlike polymers. Based on this criterion, Chu and Chang have suggested that the first step in designing a PSA is to tailor an adhesive to a predetermined T_g and modulus window.

It is now apparent, that the rheological theory, based on considerations of adhesive materials' viscoelastic deformation in the course of adhesive contact debonding, is much more universal than alternatives such as the mechanical interlocking, diffusion, electronic, and adsorption theories, and that it properly relates the strength of adhesive joints to contributions of cohesive strength, high diffusion coefficient, and long relaxation time of the PSA material.

At the most fundamental, molecular level, high strength of PSA joints requires a compromise between two mutually conflicting factors, namely high energy of intermolecular cohesion and large free volume. As comparison of free volume and peel adhesion behaviors in PVP–PEG model PSA has shown, best adhesion is observed when the free volume radius varies between 2.95 and 3.08 Å, and free volume content ranges from 6.3 to 7.0 %. In probe tack curves, if the contribution of interfacial adhesive–substrate interaction dominates that of cohesive strength of the PSA material, then the radius and the relative fraction of free volume govern the value of maximum elongation. Free volume fraction is more important than free volume hole size in controlling the tensile and adhesive properties of PVP–PEG model PSA.

The PVP–PEG model PSA has been prepared by simple mixing of two nonadhesive components: glassy high MW PVP and liquid, short chain PEG. Appearance of pressuresensitive adhesion in blends of these two initially nonadhesive polymers is the result of a stoichiometric hydrogen-bonded nanostructured network complex formation. Because cohesive strength, diffusion coefficient, and relaxation time vary in opposite directions with increase in molecular mobility at the transition from glassy materials to liquids, rheological theory requires that values of these parameters lie in specific and rather narrow ranges of magnitude to make the value of their product, and consequently adhesion strength, as high as possible.

The ratio between high cohesion energy and large free volume, featured for PSAs of various chemical composition and structure, can be expressed in terms of the glass transition temperature, diffusion coefficient, relaxation time, elasticity modulus, and loss tangent. Dahlquist's criterion of tack, which states that the elasticity modulus of a PSA must lie in the range 0.01–0.3 MPa, holds both for traditional hydrophobic PSAs and innovative hydrophilic adhesives based on polymer–oligomer and interpolymer complexes. Glass transition temperatures of PSAs fall in the range between -10 and -115 °C, and the diffusion coefficients should lie on the border between those typical of elastomers and viscous liquids, ~ 10^{-9} cm²/s.

Pressure-sensitive adhesion can be seen as a process of transformation of the structure and properties of the adhesive material under an applied mechanical strain history, including three consecutive stages:

(1) adhesive bond formation under a bonding pressure, when the main type of deformation is shear,

(2) relaxation upon the withdrawal of compressive stress, and

(3) debonding under a detaching tensile force. The third stage, adhesive debonding, is a multistage process itself, including homogeneous deformation under tensile stress, followed by cavitation and fibrillation of the adhesive material. Relaxation mechanisms accompany all stages of the adhesion process and provide links between the stages. In terms of relaxation properties, all PSAs can be classified into two groups: (1) fully relaxing (fluid) adhesives and (2) elastic adhesives that are able to store energy in the course of bond formation and exhibit residual (unrelaxed) stress during contact.

As predicted by eq 6, strong adhesion requires a compromise of the values of cohesion energy, diffusion coefficient, and relaxation time of PSAs. It is, therefore, not surprising that a direct correlation between the practical work of adhesion and values of slower relaxation times has been established for the examined PSAs. During adhesive bonding under applied pressure, adhesion appears with the rise of slow relaxation times values above 50 s and increases, passing through a maximum at $\tau_3 = 330-380$ s. A further increase in slow relaxation time results in a gradual decline in adhesion. Good adhesion occurs when the slow relaxation time varies in the range of 150–800 s.

As with any useful theory, the described molecular approach not only explains the mechanisms underlying adhesion phenomenon, but also possesses predictive value. Insights gained into the molecular structures responsible for the occurrence of pressure-sensitive adhesion opens the door to the molecular design of new PSAs with optimized performance properties by blending nonadhesive polymers bearing complementary functional groups capable of forming hydrogen or electrostatic bonds to one another.

APPLICATION OF MOLECULAR THEORY OF PRESSURE SENSITIVE ADHESION

Our everyday life is inconceivable without pressure-sensitive adhesives (PSAs). Applications of PSAs expand day by day in various areas of industry and medicine. They are widely used as surface protection films, as a component of pressure-sensitive tapes, labels, note pads or automobile trim. In addition, they serve as skin-contact adhesive platforms in medical plasters, wound dressings, transdermal patches, and a variety of other products. PSAs are designed for either permanent or removable applications. Removable PSAs serve to form a temporary bond and ideally can be removed after months or years without leaving residue on the surface of an adherend. Innovative PSAs with tailored properties can be produced by physical mixing of nonadhesive parent polymers bearing complementary reactive functional groups in their recur-ring units and (or) at the opposite ends of their short chains.

The first PSA was natural rubber. The era of modern PSA technology was ushered in during the 1930s with the appearance of synthetic rubbers. The list of currently commercially available elastomers that can be formulated into PSAs is presented in Table 1. Two subsets are differentiated in Table 1: those polymers that are inherently tacky, and those that require modification with tackifiers to meet the Tg and modulus criteria to become a PSA.

Inherently tacky	Need tackification
Polyalkylacrylate	Natural rubber
copolymers	Polyisobutylene (PIB)

TABLE 1. Common PSA polymer classes.

Poly(vinyl ethers)	Styrene-isoprene block copolymers		
Polyalphaolefins	Styrene-butadiene block copolymers		
	Styrene-butadiene random copolymers		
	Polysiloxanes		

As is evident from Table 1, commercially available PSAs are mainly hydrophobic polymers. A common drawback of the hydrophobic adhesives is a lack of adhesion toward wet substrates. Indeed, if an adhesive material is incapable of absorbing water, any accumulation of moisture at the adhesive–substrate interface will render the adhesive untacky. In recent years PSAs have found ever-widening application in transdermal and transmucosal therapeutic systems for con-trolled drug delivery, wound dressings, topical drug plasters, tooth whitening strips, and as skin-contact adhesives for attachment of medical catheters and diagnostic electrodes. Regrettably, hydrophobic PSAs have not yet been applied as broadly as the biomedical community initially hoped it would. The major limiting factor is the lack of adherence toward wet biological tissues that secrete moisture during the lifetime of adhesive joint, a factor that limits long-term wear of adhesive patches on skin. Thus, development of hydrophilic water-absorbing PSAs is vitally important.

As Molecular theory of Adhesion postulate, at the most fundamental, molecular level, cohesive strength is governed by intermolecular cohesion energy. The energy of intermolecular cohesion and the molecular mobility are mutually conflicting properties, as most commonly a stronger intermolecular cohesion lowers the molecular mobility. This explains why pressure sensitive adhesion is a comparatively rare phenomenon.

As the molecular theory of pressure sensitive adhesion predicts, strong adhesion requires a high value of cohesive strength (σ_b), a large diffusion coefficient (**D**), and a long relaxation time (τ) . Both the diffusion coefficient and the relaxation time are measures of molecular mobility, although they do vary in opposite directions as molecular mobility increases in the course of transition from a glassy polymer to viscous liquid, e.g., with the increase of temperature or the content of a plasticizer. Indeed, the longest relaxation times are featured for glasses (years, decades or centuries), whereas low molecular weight liquids relax almost instantaneously. In contrast, the lowest diffusion coefficients are observed for glasses, while the highest diffusion coefficients are demonstrated in liquids and gases. According to Eq. (6), maximum peel strength, **P**, is related to the maximum magnitude of the product $D \sigma_b \tau$. Evidently, this product achieves its maximum magnitude over a limited range of values of relaxation times and diffusion coefficients, which are intermediate between those inherent for liquids and glasses. Materials exhibiting properties of both liquids and solids are viscoelastic and that is why all PSAs are viscoelastic materials. Hence, the molecular theory of pressure sensitive adhesion predicts that adhesion strength goes through a maximum with the change of PSA molecular mobility as an adhesive material composition or temperature is varied.

The molecular theory of pressure sensitive adhesion not only explains the mechanisms underlying adhesion phenomenon but also has predictive power. Here choosing a successful combination of polymers on this basis would provide strong evidence in favor of the theory, with accompanying insights toward molecular design of new PSAs with optimized performance properties. One of such successful example is PVP-PEG H-bounded complex, which demonstrate an excellent PSA. But if we suppose a little change in polymer structure, we will face with another succecceful example of hydrophilic PSA – complex of poly(N-vinyl caprolactam) (PVCL) and poly(N-isoporopyl acrylamide), PNIPAM with liquid poly(ethylene glycol) (PEG,Mw= 400 g/mol) (see Figure 19). Taking into account that poly(N-vinyl caprolactam),PVCL, is a close homologue of PVP (containing respectively seven- and fivemembered lactam rings in side-chains of their backbones), it is logical to expect that blends of PVCL with PEG will also exhibit adhesive properties. At room temperatures the PVP, PVCL and PNIPAM are glassy polymers, demonstrating no tack. Oligomeric PEG-400 is also nontacky viscous liquid, however, their blends are tacky viscoelastic materials. In the recurring units of their backbones both PVP, PVCL and PNIPAM on the one hand, and the PEG on the other hand, contain only electron-donating functional groups and therefore found to be immiscible when PEG molecular weight is higher than 800 – 1000 g/mol.



Figure. 19. Chemical structures of poly(N-vinyl pyrrolidone), poly(N-vinyl caprolactam), and poly(N-isoporopyl acrylamide), and schematic presentation of the corresponding network H-bonded complexes formed with poly(ethylene glycol) oligomer, PEG-400.

Because every PEG chain bears two reactive terminal OH-groups, PEG acts as an H-bonding reversible crosslinker of longer PNIPAm macromolecules and as a spacer between the PVP or PVCL chains. The cohesive strength of this complex is provided by hydrogen bonding between carbonyls in PNIPAm recurring units and both terminal hydroxyl groups at opposite ends of PEG short chains. The large free volume is due to the length and flexibility of PEG crosslinks. In this way, selfassembled PVP-PEG and PVCL-PEG network complexes behave as new individual supramolecular structures and exhibit a tack that is not found in either parent component.

Similar to other PSAs, the PVP– PEG adhesive joints fail by elastic stretching of the adhesive bulk up to a critical value of tensile strain of $\varepsilon = 1000$ – 1500%, where a fracture occurs. The entire layer of the adhesive is thus subjected to elongational flow as fibrils, which provides resistance to detachment and energy dissipation. Thus, viscoelastic deformation of an adhesive in extension is



Figure 20.. Effect of PEG content on probe tack adhesion of PNVAm blends withPEG-400. The amount of absorbed water is 7 wt. %. The PEG concentrationsare indicated in the Figure. Inset: Effect of blend composition on the valuesof the practical work of adhesion, Wa(J/m2), and maximum stress, MPa.A: PVP–PEG blends; B: PVCL–PEG blends.

a major energy dissipating mechanism in the course of adhesive bond failure.

In a probe tack experiment, the maximum stress is generally considered as a measure of tack, the value of plateau stress characterizes the cohesive strength of fibrils, and the area under the stress–strain curve corresponding to the practical work of adhesion (*Wa*) is related to the total amount of mechanical energy needed for adhesive bond failure, and hence is a measure of adhesive strength. As follows from the data in Fig. 20, the curves for 25, 31,and 34 wt.% of PEG-400 in blends with PVP and 30% and40% PEG in blends with PVCL are typical of solid-like PSAs, wherein the contribution of cohesive interaction energy dominates that of free volume. The PVP–PEG blend containing 36 wt.% of PEG-400 and PVCL blend with 50% PEG demonstrate the debonding behaviors typical of PSAs when the contributions of cohesive interaction energy and free volume are properly counterbalanced. As follows from Fig. 20, probe tack adhesion and mechanism of PVP–PEG and PVCL–PEG model PSA debonding can be easily tuned by varying the PSA composition.

Pressure sensitive adhesion is an interfacial property. When the fibrils detach from the probe (or substrate) inter-face rather than failing cohesively, it is described as a "clean detachment". An adhesive (clean) detachment is often preferable over having high tack energy. Insights gained into the molecular structures responsible for pressure sensitive adhesion enable molecular design of new PSAs with optimized performance proper-ties. The fundamental basis for molecular design has been established using PVP-PEG binary blends as a model PSA. Commonly, novel PSAs are produced by chemical synthesis or modification of initially tacky polymers. However, the data presented here show that innovative PSAs can be obtained by physical mixing of nonadhesive polymers bearing complementary functional groups that form non-covalent bonds. Adhesive and mechanical properties of PSA composites can be tuned by changing blend composition, once the function of each polymer blend component is understood. Thus, in the PVP–PEG model PSA, high MWPVP is the most important component that serves as afilm forming polymer (FFP). Short chain PEG is a minor complementary component, which acts as a noncovalent crosslinker, NCC, i.e., as a curing agent. The NCC function is instrumental in forming the 3-dimensional supramolecular network structure and in enhancing the cohesive strength of the PSA. Owing to the low glass transition temperature and a telechelic structure, i.e., due to location of complementary hydroxyl groups at opposite ends of short chains (Fig. 1), PEG also acts as a plasticizer, increasing free volume and reducing Tg. Together, the PVP and PEG build up a PSA with ideally tailored performance properties.

Energy of intermolecular H-bonding and free volume in PVP-PEG PSA

As Eq. (6) has shown, the factor responsible for pressure sensitive adhesion at a molecular level is specific balance between sufficiently strong intermolecular cohesion energy (ΔEc) and large free volume (unoccupied space between neighboring macromolecules). With the ΔEc and free volume behaviors in model PVP–PEG PSA's properly characterized, we can answer key questions: What values of free volume are responsible for high adhesion in the PVP–PEG blends? The answer to this question is of fundamental significance since it establishes direct correlations between nanoscopic and macroscopic properties of PSA material. Mechanisms of intermolecular interactions in the system PVP–PEG–water have been studied by FTIR spectroscopy, which provides unambiguous identification of interacting functional groups in complementary macromolecules. Formation of hydrogen bonds between functional groups is manifested in IR spectra by a shift of their characteristic frequencies toward lower wavenumbers. These results are indicative of strong H-bond formation between the carbonyl bond in the amide group of PVP and the hydroxyl groups at the ends of PEG short chains. It was revealed also that the most stable complexes in the PVP–PEG system are formed owing to the participation of water molecules associated with the PVP monomer units in the first hydration shell. Thus,

absorbed water is not a competitor, but rather assists in the process of PVP–PEG H-bonded complex formation. The formation energies of PVP–PEG–H2O complexes underlie the cohesive strength of PVP–PEG model PSA at the molecular level.

"SMART" THERMOSWITCHABLE PSA BASED ONHYDROPHILIC POLYMER POSSESSING LOWER CRITICAL SOLUTIONTEMPERATURE IN WATER

Despite evident progress in adhesion technology over the last few decades, it remains challenging to produce materials that are sticky on demand. The main challenge is to develop reversibly switchable adhesives that exhibit the ability to trigger adhesion in response to environmental stimuli – pH, solvent, temperature, mechanics and electromagnetic field. Polymers which demonstrate low critical solution temperature (LCST) behavior in an aqueous environment, including poly-acrylamides, polyvinylcaprolactone, polyethyleneglycols, and polypeptides , have been employed to design reversibly switchable adhesives. In this case, the reversible formation of hydrogen bonds is responsible for switching. At room temperature, for example, polyacrylamide chains form hydrogen bonds with surrounding water molecules and adhesion is poor. As the hydrogen bonding becomes weaker with increased temperature while hydrophobic interactions persist through 37–50°C temperature range, such polymers lose their solubility in water at the LCST. Thus, increasing the temperature induces a phase transition (LCST) and leads to a change in adhesion.

The PVCL and PNIPAM demonstrates a LCST and becomes insoluble in water near 37-40°C. As follows from results of our earlier experiments, the PVCL–PEG H-bonded complexes are characterized by much greater stability, a higher density noncovalent network and a higher complexation constant in comparison with PVP-PEG-complexes. It was interesting to investigate how does the LCST affect the adhesion behavior of PVCL-PEG hydrogels in the course of their swelling (upon water addition) and temperature elevation? To answer this question we performed 180°PeelTests, which enabled the control of water content captured by the hydrogel in the course of heating if a water impermeable film is employed as a substrate. The effects of temperature and the amount of absorbed water on the 180°Peel Adhesion of the HMW PVCL with 45 wt.% PEG-400 are illustrated in Fig. 16. As follows from these data, in the temperature range from 20 to 90°C the PVCL-PEG hydrogels containing 10 and 20 wt.% of water exhibit gradual reduction of adhesion with an increase in temperature. In contrast to this behavior, the hydrogels containing 30 wt.% of water and more demonstrate the loss of adhesion in rather narrow temperature ranges. Thus, the PVCL blend with 45 wt.% of PEG-400, containing 30 wt.% of absorbed water, loses its adhesion sharply between 55 and 70°C. The higher the content of absorbed water, the lower the temperature of spontaneous detachment of the adhesive film.

The temperature transitions of the mixing-demixing behavior and the change of adhesion are fully reversible. As an opaque detached adhesive film is removed from warm aqueous solution, it becomes transparent and tacky within1–1.5 min as the result of both cooling and partial evaporation of absorbed water. The fact that the PVCL–PEG-400blends containing 10 and 20 wt.% of water demonstrate only a smooth decrease of adhesion with increasing temperature implies that the amount of absorbed water in these hydrogels is too low to inhibit adhesion. The PVCL–PEG net-work is much denser than the PVP–PEG one, resulting in stronger adhesion. The comparison of PVP–PEG and PVCL–PEG stoichiometric complexes shows that their remarkable adhesive properties is a common feature of the whole class of polyvinyl lactam or even polyvinylamide polymers.

Eq. (6) establishes the direct relationship between adhesion and diffusion transport properties of PSAs. High diffusivity of PSAs favors their strong adhesion and makes them useful as diffusion matrices in transdermal drug delivery systems (TDS). TDS have found increasing applications in pharmacy for controlled delivery of drugs into systemic blood circulation across intact skin with predetermined release rate. In addition, both components of the PVP–PEG PSA have been approved for medical applications and are generally regarded as safe. Currently fivetransdermal patches based on the PVP–PEG PSA with nitro-glycerin, isosorbide dinitrate (ISDN), clonidine, cytisine and phenazepam, known as Nitropercuten, Nisopercuten, Clopercuten, Cypercuten and Phenapercuten, respectively, have been approved for medical applications in Russia following their successful large scale clinical trials. The PVP–PEGPSA has been also employed as adhesive platform in a topical antimycotic drug plaster with chinosol. As an example, for 14 examined drugs with various chemical structures, delivery rates from the hydrophilic PVP–PEG based PSA matrices is higher than hydrophobic PSA matrices and depend on drug solubility in the PSA.

PVP–PEG and PVCL–PEG blends are not unique examples of high molecular weight hydrophilic polymers and short-chain telechelics that form adhesive interpolymer complexes. As has been shown earlier, PVP and PVCL may be replaced by other polymers (PNIPAM), bearing H-bonding recurring units.

FUNDAMENTALS OF INTERPOLYMER AND POLYELECTROLYTE COMPLEX FORMATION

Another example of supramolecular network structures that couple high molecular mobility with intermolecular cohesion strength, are interpolymer complexes (IPCs), in particular polyelectrolyte complexes(PECs).In polymer blends, where formation of an interpolymer complex between macromolecules of a polybase and a polyacid takes place, high cohesion strength is provided by hydrogen, electrostatic, or ionic bonding between macro-molecules that carry complementary reactive groups in recurring units of their main chains, whereas a large free volume can result from the occurrence of loops and other defects in the supramolecular network structure.

Cooperative mechanisms of self-assembling the interpolymer and polyelectrolyte complexes

Basing on their interaction forces, IPC can be divided into four classes i.e., hydrogenbonded complexes, polyelectrolyte complexes (PECs), stereo complexes and charge-transfer complexes. PECs are formed mainly due to long-range Coulomb forces by mixing oppositely charged polyelectrolytes, i.e., by poly-anions and poly-cations. Hydrogen-bonded complexes are formed by a combination of complementary polymers bearing proton-accepting functional groups in their recurring units (polybase) and proton-donating groups (polyacid). The family of such proton-accepting and proton-donating complementary polymers also includes polymers forming either polycations or polyanions upon ionization of the irreactive functional groups. The cooperative mechanism of IPC formation is governed by the entropy factor because as one of the functional groups reacts with a complementary one, the neighboring functional groups in the recurring units have more favorable entropy to form new interchain bindings. Thus, the activation energy is highest for the first intermacromolecular bond formation and becomes substantially lower with an increase of the number of interchain bonds. For this reason, the cooperative reaction between two complementary macromolecular chains advances very rapidly according to the "all-or-none" type principle, like a zipping mechanism as the segments of interacting complementary macromolecules also inter-lock. The zipper effect is the neighboring group effect in the course of cooperative IPC formation. As a result of the cooperative zipper mechanism between complementary macromolecules, e.g., oppositely charged polyelectrolytes, a 1:1 complex stoichiometry can be achieved. The thermodynamics of IPC formation controls

the IPC stability. The enthalpy gain is not very large and only slightly depends on the number of reactive functional groups in polymer chains, because the IPC formation maybe regarded as a kind of substitution reaction between counterions.



FIGURE 21. Schematic representation of the association and aggregation of interpolymer and polyelecrolyte complexes.

A characteristic feature of such IPC formation is their self-assembly into the most energetically stable supramolecular structures. PEC (IPC) formation process follows through three mainsteps or stages (Fig. 21):

(1) primary complex formation,

(2) rearrangement of the primary complex structure intomost energetically stable state,

(3) intercomplex aggregation process, i.e., supramolecular structure formation.

The first step occurs through hydrogen bonding in IPCs or Coulomb forces in PECs. It should be particularly emphasized that Coulomb forces are long-range attractions between cations and anions that can be fairly far apart, whereas H-bond formation requires direct contact between proton-donating and proton-accepting functional groups. Both reactions are very fast.

Taking into account that intermolecular cohesion energy is very high in the course of cooperative IPC formation, our major concern is to reveal the factors making free volume in the IPCs and PECs as large as possible.



FIGURE 22. Schematic representation of a noncovalently crosslinked net-work structure of interpolymer complexes. A: Noncovalent crosslinksconsisting of sequences of hydrogen, electrostatic, or ionic bonds formedbetween functional groups in monomer units of complementary macromolecules. B: The entanglement junctions of long

As has been noted above, strong intermolecular cohesion and the cooperative mechanism of interpolymer polyelectrolyte polymer chains. C: Loopsconsisting of the segments of macromolecules free of interpolymer bond-ing.

complex formation lead to a drastic decrease in the distance between neighboring complementary macromolecules and therefore to reduction of the free volume. Hence, in order to reconcile the strong intermolecular bonding with large free volume, that is a prerequisite of pressure sensitive adhesion, special technological practices should be applied. Fig. 22 presents a schematic illustration of such methods. The scheme shown in Fig. 22 covers the blends of complementary polymers including the interpolymer complexes. High cohesion energy can be provided by the formation of intermolecular hydrogen, electrostatic, or ionic bonds. The bonds crosslink the chains of complementary polymers into three-dimensional network structures. The cohesive strength of the network is controlled by the number and strength of interchain junctions. Two kinds of junctions may be distinguished. Junctions A rep-resent the ladder-like sequences of interchain bonds. Their strength depends on the energy and the amount of these bonds, i.e., on the length of the ladder-like bond sequences. Junctions B emerge due to physical entanglements of macromolecules in the blend. Their number and strength are affected by the polymer concentration in the blend and the chain length (molecular weight). The free volume of interpolymer complexes, along with other defects of the supramolecular network structure, can be produced by loops (C) of unbounded macromolecular chains (Fig. 22). The size and the number of the loops, or their degree of conversion in the cooperative chemical reaction of solidstate interpolymer complex formation, are governed by the content and the strength of topological polymer chain entanglements B. These entanglements con-strain the mobility of complementary polymer chains and hamper the formation of the ladder-like network junctions A. In other words, the topological entanglements of complementary polymer chains B assist in stopping the cooperative process of interpolymer complex formation at an intermediate nonequilibrium stage. Thus, the free volume in the polyelectrolyte blends depends on the specific features of the polyelectrolyte PSA preparation method, rather than the contribution of interpolymer cohesion energy. The major principle underlying the uniformity of such blends is simple: avoiding local supersaturations in the course of complementary polyelectrolyte mixing.

Summing up fundamental mechanisms of IPC and PEC formation, we have drawn following general principles of PSA production:

1. Selection of polymers bearing in their recurring units comparatively weak protondonating and proton-accepting groups;

2. Employment of random copolymers wherein reactive monomer units are diluted with inert units;

3. Mixing the polymers in amounts that strongly deviate from a 1:1 stoichiometric ratio;

4. Using the polymers of disparate chain lengths;

5. Blending the polymers in viscous media: either in concentrated solutions or in melts;

6. Avoiding local supersaturations in the course of polymer mixing;

7. Utilizing the copolymers preferentially forming relatively weaker hydrogen bonds as the materials of choice.

PRESSURE SENSITIVE ADHESIVES BASED ONNONSTOICHIOMETRIC POLYELECTROLYTE COMPLEXES

Mechanisms of intermolecular interactions and the strength of noncovalent bonds in a model polyelectrolyte complex

In our study a model PEC PSA is formed by mixing various ratios of a polybase (e.g., copolymer of N,Ndimethylaminoethyl methacrylate with methyl methacrylate and butyl methacrylate PDMAEMA-co-MMA/BMA,2:1:1), with a polyacid (e.g., copolymer of methacrylic acid and ethyl acrylate, PMAA-co-EA, 1:1) in the presence of triethyl citrate (TEC) as a plasticizer. The



FIGURE 23. Molecular structures of PDMAEMA-co-MMA/BMA polybase, PMAA-co-EA polyacid and TEC plasticizer.

structures of PDMAEMA-co-MMA/BMA, PMAA-co-EA and TEC are illustrated in Fig. 23. In general, an interpolymer complex between a film-forming polymer and a ladder-like crosslinker (LLC) is formed by hydrogen bonding, electrostatic bonding, ionic bonding, or their combination. The ladder-like complexes are reversibly crosslinked due to specific interactions between the functional groups in the complementary macromolecules and thus represent "networks". The component presented in the greatest quantity serves as a film-forming polymer so that the difference between FFP and LLC is a function of their concentration. While the predominant component is typically referred to as a film-forming polymer, the minor component is referred to as a ladder-like noncovalent crosslinker. It must be noted that in further description the model FFP is always a polybase (PDMAEMA-co-MMA/BMA), whereas the model LLC is a polyacid (PMAA-co-EA). FTIR-spectroscopy allows identification of interacting functional groups in polyelectrolyte PDMAEMA-co-MMA/BMA–PMAA-co-EA blends. To evaluate the structure and formation energies of the interpolymer complexes that involve both hydrogen and ionic bonding, quantum chemical calculations have been performed.

According to the quantum analysis of more than 300 polyelectrolyte complex structures examined in the ionic complexes formed with the participation of charged polyelectrolyte

functional groups (ammonium cation and carboxylate anion) are from 4 to 16 times more energetically favorable than the strongest H-bonded complexes of uncharged complementary polybase and polyacid groups. These energies control both the phase state and the cohesive strength of the PSAs based on the polyelectrolyte complexes. The PSAs based on polyelectrolyte complex represent a new generation of water-absorbing adhesive materials. For this reason, the structures including water molecules associated with polymer functional groups were also taken into consideration in the course of the quantum chemical analysis. Molecules of absorbed water are not competitors but rather facilitators for the formation of stable energetically favorable polyelectrolyte complexes. The proton-donating capacity can be significantly improved in the presence of Cl-ions. The Cl-counter ion effect may be appreciably inhibited, if Na⁺ cations are present in the solution.



FIGURE 24. TEM microphotographs of the PDMAEMA-co-MMA/BMA–PMAA-co-EA complex particles in a sol 70:30 (A, top) and gel 50:50 (B, bottom) phases.

The blends of PDMAEMA-co-MMA/BMA polybase with PMAA-co-EA polyacid and a TEC plasticizer exhibit a single glass transition temperature indicating that 20:1 and 10:1 plasticized polybase–polyacid blends are single-phase, whereas the blends of the polybase with larger amount of the polyacid LLC, closer to 1:1 stoichiometry, display signs of microphase separation. The composition behavior of Tg in the PDMAEMA-co-MMA/BMA blends with PMAA-co-EA and TEC demonstrates a predominant contribution of large free volume to the Tg. It is surmised that polyelectrolyte mixing in a solid state or in concentrated solutions, which leads to polymer chain entanglements, favors the formation of loops of unbound polymer chains. Ionization of polyelectrolyte functional groups significantly affects the phase behavior of unblended components but has only a minor impact on the Tg of the blends.

Mixing a polybase with a polyacid in solution, near 1: 1 concentration ratio results in formation of a sol and gel fractions. The sol fraction consists predominantly of a nonstoichiometric complex of so-called "scrambled egg" structure. In contrast, the gel fraction represents a stoichiometric ladder-like network polyelectrolyte complex of a "zipper" structure. Supramolecular structures of nonstoichiometric and stoichiometric polyelectrolyte complexes have been studied with electron microscopy. The nonstoichiometric "scrambled egg" complex in the sol phase exhibits a lamellar structure or spherical-like domains (Fig. 24 A), while a

stoichiometric ladder-like complex in the gel phase forms a well-developed fibrillar network structure that resembles a nanosized web (Fig. 24 B).

The state diagram of polybase–polyacid blends (Fig. 25) reveals areas of partial component miscibility and the formation of a nonstoichiometric complex of "scram-bled egg" structure, which are separated by a field occupied by a ladder-like polyelectrolyte complex of stoichiometric composition. The ladder-like complex is immiscible

with both parent polymers at temperatures below 172°C.Melting of the ladder-like complex and polybase-polyacid miscibility above this critical temperature is thought to be a result of the complex dissociation at high temperatures, when intermolecular hydrogen bonds do not exist any longer. The plasticized polybase-polyacid blends of 20:1 and 10: 1 concentration ratios, that demonstrate pressure sensitive adhesion, relate to the area of the phase diagram which corresponds to the nonstoichiometric poly-electrolyte complex of the "scrambled egg" structure. The stoichiometric ladder-like polyelectrolyte complex in the blends of 1: 1 polybase-polyacid composition ratio with plasticizer exhibits no adhesion.



FIGURE 25. State diagram of polybase PDMAEMA-co-MMA/BMA blends with PMAA-co-EA polyacid in the absence of TEC plasticizer. (I) Mixture of the polyelectrolyte complex with the PDMAEMA-co-MMA/BMA polybase. (II,III) Nonstoichiometric polybase–polyacid complex and (IV) mixture of the nonstoichiometric complex with PMAA-co-EA polyacid. The central zone is occupied by a stoichiometric polyelectrolyte complex of a ladder-like structure (Tm= melting temperature).

Mechanical properties of polyelectrolyte blends

We come now to the macroscopic physical properties of polyelectrolyte PSAs.

Our experimental data shows that the polyacid in the blend with the polybase FFP plays the role of the noncovalent ladder-like polymer crosslinker (LLC), thereby increasing the cohesive strength of the material and decreasing its free volume. The incorporation of even small amounts of the polyacid (PMAA-co-EA; poly-base :polyacid = 10:1) causes dramatic changes in the type of deformation and in the profile of the curve. This type of extension is typical for densely crosslinked rubbers. In this case, the breaking strength of the films increases by a factor of 6.6, while the maximum elongation decreases by a factor of 4.3. Thus, varying the composition of the FFP-LLC blends with plasticizer provides easy tuning of the mechanical properties. The ultimate strength and ductility of the blends are such that they can be useful in many practical applications.



FIGURE 26. Tensile properties of polyelectrolyte complexes. A: Nominal stress–strain curves for uniaxial drawing of the mixture of FFP with 25 wt % TEC plasticizer and the nonstoichiometric polyelectrolyte complex ([FFP]:[LLC] = 10:1) plasticized with the same amount of TEC. B: Effect of plasticizer concentration on tensile stress–strain curves of polyelectrolyte blends (FFP/LLC = 10/1). TEC content is indicated. Drawing rate is20 mm/min.

Adhesion of the PSAs based on nonstoichiometric polyelectrolyte complexes



FIGURE 27. Probe tack curves of the PDMAEMA-co-MMA/BMA polybase (FFP), and its polyelectrolyte complexes with LLC (polyacid, PMAA-co-EA). FFP:LLC = 20:1 and 10:1. The rate of probe detachment

The probe tack profiles (Fig. provide valuable information about mechanism of debonding. Fig. 27 illustrates the effect of LLC is 0.1 mm/s. Corresponding values of the practical work27)of adhesion (debonding energy)theare indicated in the Figure. A: 25 wt % of TECtheplasticizer. B: 35 wt % of TECon the

probe tack curves of the polyelectrolyte complex at two concentrations of plasticizer (25 and 35 wt.% TEC). As follows from the curves, a ladder-like noncovalent cross-linking of FFP (PDMAEMA-co-MMA/BMA polybase) with LLC (PMAA-coEA polyacid) results in a dramatic change in the debonding mechanism, which indicates implies the dominance of intermolecular cohesion over the free volume.

As illustrated in the Probe Tack curves, Fig. 27 amount of adhesive is left on the surface of the probe. The higher the TEC concentration the more the PSA is liquid-like. Thus, the dominance of the cohesive interactions over the free volume is produced by ladder-like cross-linking of FFP that affects the adhesive properties. With an increase in the plasticizer concentration, the maximum stress of debonding increases, passes through a maximum at 35–45 wt.% TEC, and finally declines. The appearance of the plateau in the Probe Tack curves indicates the contribution of adhesive layer fibrillation. The maximum elongation of fibrils tends to increase as the amount of plasticizer increases. The work of adhesive joint failure passes through a maximum at 50–55 wt.% of the plasticizer

It was revealed that the plasticizer hydrophilicity significantly affects the failure mechanism of adhesive joints of the FFP–LLC polyelectrolyte complex. The higher is the plasticizer hydrophilicity, the higher is the adhesion. The work of probe detachment from the adhesive film surface grows as the plasticizer hydrophilicity increases in the sequence: acetyltributyl citrate (ATBC) \approx tributyl citrate (TBC) < acetyltriethyl citrate (ATEC) \approx triethyl citrate (TEC). If the blends with hydrophobic plasticizers (ATBC and TBC) behave as solid adhesives and fail without essential fibrillation of the adhesive layer, the blends of the polyelectrolyte complex with the hydrophilic plasticizers (ATEC and TEC) demonstrate the existence of fibrillation, which is most pronounced in the case of the most hydrophilic plasticizer - TEC.

PDMAEMA-co-MMA/BMA polybase and PMAA-co-EA polyacid are not unique FFP and LLC suitable for the preparation of adhesives based on the mechanism of the ladder-like polyelectrolyte complex formation. The replacement of PMAA-co-EA polyacid by a copolymer of maleic acid with methylvinyl ether (PMAco-MVE) increases adhesion appreciably, implying that the approach illustrated in this research has a general character.

Partial ionization of polybase or polyacid in the blend, achieved with the addition of a strong inorganic acid (HCl) or base (NaOH), also improves the adhesive properties and changes the mechanism of debonding from fibrillar to solid-like (Fig. 46) [343]. The implication of this Probe Tack data is that the adhesive properties are affected by a mechanism of specific interaction between the components of the polyelectrolyte complex (hydrogen or ionic bonding). In turn, the molecular interaction governs the structure of the complex and determines the balance between cohesive energy and free volume. bonding makes the complex more stable (E = 43 kJ/mol). Treatment of PDMAEMA-co-MMA/BMA by HCl in aqueous solutions causes partial ionization of the polybase and the

formation of ammonium cations, which can interact with the carboxyl groups of PMAAco-EA through the exchange reaction:

 $\left(\sum_{\substack{N_{CH_3} \\ CH_3}} + HOOC - \right) \xrightarrow{CH_3} + HOOC - \right) \xrightarrow{CH_3} HOOC - \left(\sum_{\substack{N_{CH_3} \\ CH_3}} + HOOC - \right) \xrightarrow{CH_3} HOOC - \left(\sum_{\substack{N_{CH_3} \\ CH_3}} + HOOC - \right) \xrightarrow{CH_3} HOOC - \left(\sum_{\substack{N_{CH_3} \\ CH_3}} + HOOC - \right) \xrightarrow{CH_3} HOOC - \left(\sum_{\substack{N_{CH_3} \\ CH_3}} + HOOC - \right) \xrightarrow{CH_3} HOOC - \left(\sum_{\substack{N_{CH_3} \\ CH_3}} + HOOC - \right) \xrightarrow{CH_3} HOOC - \left(\sum_{\substack{N_{CH_3} \\ CH_3}} + HOOC - \right) \xrightarrow{CH_3} HOOC - \left(\sum_{\substack{N_{CH_3} \\ CH_3}} + HOOC - \right) \xrightarrow{CH_3} HOOC - \left(\sum_{\substack{N_{CH_3} \\ CH_3}} + HOOC - \right) \xrightarrow{CH_3} HOOC - \left(\sum_{\substack{N_{CH_3} \\ CH_3}} + HOOC - \right) \xrightarrow{CH_3} HOOC - \left(\sum_{\substack{N_{CH_3} \\ CH_3}} + HOOC - \right) \xrightarrow{CH_3} HOOC - \left(\sum_{\substack{N_{CH_3} \\ CH_3}} + HOOC - \right) \xrightarrow{CH_3} HOOC - \left(\sum_{\substack{N_{CH_3} \\ CH_3}} + HOOC - \right) \xrightarrow{CH_3} HOOC - \left(\sum_{\substack{N_{CH_3} \\ CH_3}} + HOOC - \right) \xrightarrow{CH_3} HOOC - \left(\sum_{\substack{N_{CH_3} \\ CH_3}} + HOOC - \right) \xrightarrow{CH_3} HOOC - \left(\sum_{\substack{N_{CH_3} \\ CH_3}} + HOOC - \right) \xrightarrow{CH_3} HOOC - \left(\sum_{\substack{N_{CH_3} \\ CH_3}} + HOOC - \right) \xrightarrow{CH_3} HOOC - \left(\sum_{\substack{N_{CH_3} \\ CH_3}} + HOOC - \right) \xrightarrow{CH_3} HOOC - \left(\sum_{\substack{N_{CH_3} \\ CH_3}} + HOOC - \right) \xrightarrow{CH_3} HOOC - \left(\sum_{\substack{N_{CH_3} \\ CH_3}} + HOOC - \right) \xrightarrow{CH_3} HOOC - \left(\sum_{\substack{N_{CH_3} \\ CH_3}} + HOOC - \right) \xrightarrow{CH_3} HOOC - \left(\sum_{\substack{N_{CH_3} \\ CH_3}} + HOOC - \left(\sum_{\substack{N_{CH_3} \\ CH_3}} + HOOC - \right) \xrightarrow{CH_3} HOOC - \left(\sum_{\substack{N_{CH_3} \\ CH_3}} + HOOC - \left(\sum_{\substack{N_{CH_3} \\ CH_3} + HOOC - HOOC$

Scheme 1. Neutralization reaction of H-bonded interpolymer complex formation between uncharged polybase and polyacid macromolecules.

Presented data illustrate the increase the energy of interpolymer bonding increases



both the energy of intermolecular cohesion and the practical work of adhesion (the area under probe tack curve).

Owing to the formation of three-dimensional network of noncovalent intermolecular bonds, the PSAs based on nonstoichiometric ladder-like polyelectrolyte complexes are partially water insoluble, rubber-like gels capable of absorbing a large amount of water. The swell ratio is a fundamental characteristic of crosslinked polymeric gels that relates to the density of network junctions. The higher the density of a ladder-like network, the lower the swell ratio [345]. As the LLC concentration increases i.e., the FFP: LLC ratio decreases, the ladder-like network gets denser.

Innovative technology of PSA formulation is based on the molecular design of PSA materials and coupling highmolecular mobility with strong intermolecular cohesionoffers products with varying adhesion, mechanical, andwater-absorbing capabilities. This technology provides aconvenient tool for obtaining the desired material per-formance by simply varying the composition of polymerblends. The values of swell ratio and sol fraction can be used as a basis for the classification of novel adhesives in termsof their hydrophilicity. The higher the swell ratio and solfraction values, the higher the hydrophilicity of the adhe-sive and the lower the density of noncovalent cross-linking.



FIGURE 28. Classification guide of pressure sensitive adhesives of con-trolled hydrophilicity and waterabsorbing capability based onpolymer–oligomer and interpolymer complexes.[31], Copyright 2009. Adapted with permission from Taylor & Francis.

The binary blends of PVP–PEG demonstrate SF = 100% and the value of swell ratio tends to be exceptionally high. Conventional hydrophobic PSAs such as acrylic Duro-Tak87-900A and SIS-based Duro-Tak 387 2287 adhesives fall on the other side of the scale of hydrophilicity (SF \approx 0% and swell ratio $\alpha \approx 0.1$). This means that their percentage water absorbency (based on the grams of water absorbed per 1 g of dry material at 25°C and 100% relative humidity) does not exceed 10%.Hydrophilic adhesives fill the range between these two extremes on the scale of hydrophilicity (Fig. 28). The swell ratio scale is used in Fig. 28 to classify the adhesive absorbents of moisture in three broad categories: amphiphilic PSAs based on polyelectrolyte complexes, water swellable but mainly insoluble PSA hydrogels based on ternary polybase–polyacid–telechelic oligomer complexes (PVP–PEG–Polyacid), and watersoluble PSAs (PVP–PEG).

In spite of the fact that chemical compositions of traditional, hydrophobic and innovative hydrophilic PSAs have little in common, the same general factors govern their adhesive and

viscoelastic behaviors. For instance, the Dahlquist criterion of tack holds for all PSA classes, longer relaxation times govern the elasticity and adhesion of different PSAs and similar glass transition temperatures and coefficients of self-diffusion are inherent in a variety of PSAs. The adhesive joint strengths of hydrophilic PSAs fall generally in the range usually found for covalently uncrosslinked hydrophobic PSAs, though they can be somewhat exceeded by covalently crosslinked PSAs and adhesives based on triblock copolymers . While molecular theory of pressure sensitive adhesion predicts correctly the position of the adhesion maximum along the scale of the ratio of molecular mobility to intermolecular cohesive interaction energy, the absolute magnitude of adhesion strength depends also on supramolecular architecture of adhesive material.

CONCLUSION

The time has passed when the efforts of adhesive material designers were solely directed to the achievement of strongest adhesion. The time is ripe for the adhesion scientists to develop innovative materials with a wide and well-balanced spectrum of various and often unprecedented performance properties. Adhesive super-absorbents of moisture, "smart" thermoswitchable and electroconductive PSAs are the typical examples of such innovative materials. Currently they are in well-advanced stage of the development in our laboratory.

Table 11. Functional groups of complementary polymers and oligomers capable of serving as parent components of PSA composites based on polymer–oligomer and interpolymer complexes.

Component 1	Component 2	Bonding Type
СООН	NH ₂ ,NHR,NR ₂	Electrostatic
SO3H	OH, -C-O-C-, -CONH ₂ ,CONHR,CONR ₂	Hydrogen
COO- SO3 ⁻	$-NH_3+, NH_2R+, NHR_2+, NR_3+$	Ionic
PhOHOH	CONH2,CONHR,CONR2 –PhOH—OHCOOH	Hydrogen

Table 11 summarizes the types of major complementary functional groups in numerous polymers and oligomers that are feasible for use as parent components in novel PSA composites. The number of functional polymers suitable as parent components for novel PSAs with tailored performance properties is very large, suggesting that the blending approach, based on molecular design considerations, will lead to significant innovations by the adhesives industry in the coming decades.

The PSAs of controlled hydrophilicity and water-absorbing capacity, as described in the present review, find use in health and personal care as skin contact adhesives, adhesive platforms for tooth whitening strips, and "smart", thermos-switchable, painlessly removable from skin surface super-absorbents of moisture in wound and ulcer dressings. They are also miscible and compatible with numerous low and high molecular weight compounds, leading to a broad spectrum of future commercial products with presently unachieved or unexplored performance properties. Such adhesive innovations include hybrid PSAs based on biomacromolecules. The hybrid PSAs combine the conventional rheological principles of pressure sensitive adhesion with

biospecific mechanisms of cell adhesion, as well as bioinspired PSAs for various medical, household, and industrial applications. The age of rationally designed adhesives is just around the corner.