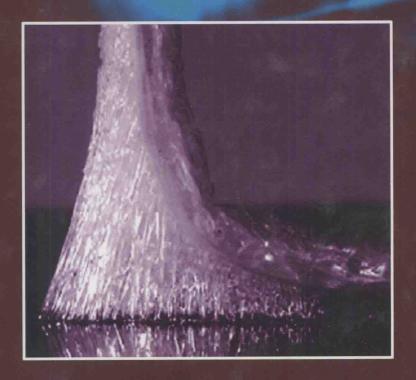
HANDBOOK OF
PRESSURE-SENSITIVE ADHESIVES AND PRODUCTS

# FUNDAMENTALS OF PRESSURE SENSITIVITY



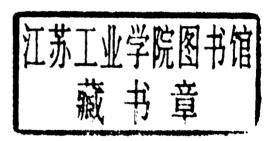
EDITED BY

ISTVÁN BENEDEK Mikhail M. Feldstein



# HANDBOOK OF PRESSURE-SENSITIVE ADHESIVES AND PRODUCTS

# FUNDAMENTALS OF PRESSURE SENSITIVITY



EDITED BY

ISTVÁN BENEDEK Mikhail M. Feldstein



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## **Preface**

In recent years, pressure-sensitive products (PSPs) have reached a maturity that warrants a detailed and critical examination of their science and technology. Based on our experience in both scientific activity and industrial areas, as well as on the special knowledge of outstanding scientists and technologist as contributors, we have addressed all aspects of pressure-sensitive adhesives (PSAs) in the form of a handbook. The huge volume of data accumulated in this field over the past decade presents a delicate problem due to the gap between the fundamentals of pressure-sensitive materials and their practice. The application of PSAs requires a thorough knowledge of basic rheological and viscoelastic phenomena. Adhesive and polymer scientists, however, are not often employed as industrial managers or machine operators. Therefore, a need exists to investigate and summarize the most important features of PSA technology and explain the phenomena scientifically. This book covers the fields of manufacturing, conversion, application and end uses of PSAs using a classic approach to compile a treatise based on the work of various experts, theoreticians, chemists and engineers. The volume and diversification of the data, as well as the boundary between theory and application, imposed the need to impart our treatise in three books.

The destination of this handbook is twofold. On one hand, it is addressed to scientists focusing on the fundamental processes underlying the complex phenomenon of pressure-sensitive adhesion; on the other hand, it is intended for industrial researchers who are involved in the practical application of these fundamentals for the development of various products and specialists working in various end-use domains of PSPs. Fundamentals of Pressure Sensitivity contains a detailed characterization of the processes occurring in PSA materials at all stages of the life of an adhesive joint: its formation under compressive force, under service as the bonding force is removed, and under adhesive bond fracture when the major type of deformation is extension.

Technology of Pressure-Sensitive Adhesives and Products describes particular features of different classes of PSAs, such as rubber–resin-based adhesives, acrylics, and silicones, and presents a discussion of the synthesis of pressure-sensitive raw materials, their formulation, and the manufacture of PSAs and PSPs.

Applications of Pressure-Sensitive Products describes the main classes and representatives of PSPs, their competitors, end use, application domains, application technology, and tests.

viii Preface

The domain of pressure-sensitive materials includes several fields that would be sufficiently autonomous, complex, and large (e.g., bonding-debonding mechanisms, manufacture, equipment, quality assurance) to be described in separate books. Our goal to create a short vade mecum was made significantly easier because of our previous work in this field, which covered almost all aspects of pressure sensitivity and allowed for their detailed discussion. Separate works have discussed special aspects of this waste domain, such as Pressure-Sensitive Adhesives Technology (I. Benedek, Marcel Dekker, New York, 1997) and Pressure-Sensitive Adhesives and Applications (I. Benedek, Marcel Dekker, New York, 2004), which focused mainly on pressuresensitive labels; Development and Manufacture of Pressure-Sensitive Products (I. Benedek, Marcel Dekker, 1999), which describes the whole domain of self-adhesive products, with or without adhesive; and Pressure-Sensitive Formulation (I. Benedek, VSP, Utrecht, the Netherlands, 2000), which gives a detailed discussion of a special, practical segment of pressure-sensitive technology. Advances in PSA materials imposed the need for reediting of these books in cooperation with C. Creton and M.M. Feldstein, allowing a more detailed discussion of the scientific aspects, in Development in Pressure-Sensitive Products (Ed. Benedek, Taylor & Francis, Boca Raton, Florida, 2006), Pressure-Sensitive Design, Theoretical Aspects (Ed. Benedek, VSP, 2006), and Pressure-Sensitive Adhesives and Applications (Ed. Benedek, VSP, 2006). Because these books contained a detailed description of various pressure-sensitive science- and technology-related problems, it was possible to edit our handbook as a lexically constructed work, focused on key problems, which avoids undesired redundancy of aspects described previously in a detailed manner.

In Chapter 1 of this book, "Surface Phenomena on a Solid–Liquid Interface and Rheology of Pressure Sensitivity," rheological characterization of processes occurring in adhesive materials under application of bonding pressure (wetting and spreading flow) is studied as a function of the viscosity of test liquids and viscoelastic properties of a substrate. The rheological response of the PSA material to the application of bonding pressure has been proposed to be characterized in terms of dimensionless parameters, for example, the ratio of the time of adhesive joint formation under bonding pressure to the intrinsic relaxation (or retardation) time. Data are also presented that illustrate the effect of bonding pressure on the change of apparent viscosity and shear rate of a PSA material with time of adhesive bond formation.

Chapter 2 of this book, "Diffusion and Adhesion," is a contemporary, critical reexamination of the diffusion theory of adhesion, in correlation with pressure-sensitive adhesion. When two polymers are not identical and therefore fully miscible, but are partially miscible, they can interpenetrate by a small distance controlled by the thermodynamics of their interaction. In this case, the adhesion energy between the polymer layers depends strongly on the degree of interpenetration at the interface.

In Chapter 3 of this book, "Transition Zones in Adhesive Joints," the structure—morphological classification of transition zones in adhesive joints is presented. The interphase boundary between an adhesive and a substrate is a constituent part of such transition zones. The relationship between the structure and the morphology of the transition zones, with phase diagrams of the adhesive—substrate systems and interdiffusion coefficients, is described. Numerous examples of the structure of

Preface ix

transition zones are presented, including amorphous-crystalline and liquid-crystalline equilibriums.

Chapter 4 of this book, "Role of Viscoelastic Behavior of Pressure-Sensitive Adhesives in the Course of Bonding and Debonding Processes," focuses on the effect of viscoelastic properties of PSAs on their adhesive properties—measured using peeling or probe tack experiments. As demonstrated in Chapter 4, the viscoelastic properties govern, to a large extent, adhesive behavior.

Chapter 5 of this book, "Viscoelastic Properties and Windows of Pressure-Sensitive Adhesives," describes the correlation of the viscoelastic properties of PSAs with industry-standard performance such as peel resistance, tack, and shear resistance. Using a four-quadrant viscoelastic window concept, the possibility of characterizing and aiding in the development of different types of PSAs is further demonstrated.

Chapter 6 of the book, "Probe Tack," is a very illustrative and informative test for adhesion. Structure transformations (cavitation and fibrillation) of adhesive material under a detaching force are discussed. The practical aspects of tack as a common test method for characterization of PSAs and PSPs, as well as its influence on the converting and end-use properties, are also discussed in the other two books.

Chapter 7 of this book, "Peel Resistance," focuses on the measurement of peel resistance as one of the most important characteristics in the evaluation of PSA performance because various factors such as properties of backing materials, surface of the adherend, peeling speed, and test temperature affect peel strength. Much information is provided not only by failure mode detection, but also by drawing up the master curves for peel resistance. The practical aspects of peel resistance as a common test method for the characterization of PSAs and its influence on the converting and end-use properties are discussed in the other two books.

Chapter 8 of this book, "Shear Resistance," describes shear resistance as an important factor affecting the performance of PSAs. The main parameters influencing shear resistance and the correlation among shear resistance, peel resistance, and tack are discussed. The practical aspects of shear resistance as a common test method for the characterization of PSAs and PSPs, as well as its influence on the converting and end-use properties, are also discussed in the other two books.

Chapter 9 of this book, "Durability of Viscoelastic Adhesive Joints," discusses the durability of PSA joints under constant detaching stress for a range of PSAs spanning different classes that have been analyzed using a squeezing–flow technique. The approach to the prediction of adhesive joint durability, one of most important characteristics of PSA performance, is proposed. The role of durability in practice is also discussed in detail in *Applications of Pressure-Sensitive Products*.

Chapter 10 of this book, "Molecular Nature of Pressure-Sensitive Adhesion," is based on the analysis of peel force in relation to the work of viscoelastic deformation of adhesive film up to break under uniaxial drawing; a simple equation has been derived that represents peel adhesion as a function of the self-diffusion coefficient, relaxation time, and cohesive strength of the adhesive polymer.

Chapter 11 of this book, "Significance of Relaxation for Adhesion of Pressure-Sensitive Adhesives," examines the phenomenon of pressure-sensitive adhesion that is treated as a three-stage process, involving adhesive joint formation under compressive force,

x Preface

followed by relaxation of the adhesive material as the bonding force is removed, and then debonding as a detaching stress is applied. The mechanisms of PSA deformation at each of these stages are different, and the contribution of PSA relaxation to adhesion is also different. The strength of the adhesive joint requires the contribution of slow relaxation processes, which imply the specific importance of both longer relaxation time and large-scale structural rearrangements in the PSA material for proper adhesion.

We suggest that our readers use the list of abbreviations and acronyms in the end of this book to facilitate the comprehension of various symbols, whenever they are not sufficiently clear. The role of this book is to provide comprehensive and convenient upto-date information for users in both industry and academia.

We were pleased to see the participation of scientists and industrial experts, working in very different areas of the field, on this book. We thank our contributors for their efforts.

The Editors

# **Editors**

István Benedek is an industrial consultant based in Wuppertal, Germany. After exploring his initial interest in macromolecular science, he transferred to the plastics processing and adhesive converting industry as research and development manager, where he has worked for three decades. He is the author, coauthor, or editor of several books on polymers, including Pressure-Sensitive Adhesives Technology (Dekker, New York, 1996), Development and Manufacture of Pressure-Sensitive Products (Dekker, New York, 1999), Pressure-Sensitive Formulation (VSP, Utrecht, the Netherlands, 2000), Pressure-Sensitive Adhesives and Applications (Dekker, New York, 2004), Development in Pressure-Sensitive Products (CRC, Boca Raton, FL, 2006), Pressure-Sensitive Design, Theoretical Aspects (VSP, Leiden, the Netherlands, 2006), and Pressure-Sensitive Design and Formulation, Applications (VSP, Leiden, the Netherlands, 2006), as well as more than 100 scientific research and technical reports, patents, and international conference papers on polymers, plastics, paper/film converting, and web finishing. He is a member of the Editorial Advisory Board of the Journal of Adhesion Science and Technology. Dr. Benedek received his PhD (1972) in polymer chemistry and engineering technology from Polytechnic University of Temeswar.

Mikhail M. Feldstein, one of the world's leading experts in the development of new polymeric composites with tailored performance properties that span pressure-sensitive adhesives and other materials designed for medical and pharmaceutical applications, was born in 1946 in Moscow. In 1969 he graduated with honors from M.V. Lomonosov Moscow State University, Faculty of Chemistry, and in 1972 he earned his PhD in polymer science from the same university for the investigation of polyelectrolyte complexes with ionic surfactants and lipids. His early research interests were associated with the mechanisms of the formation and molecular structure of interpolymer complexes. Since 1972 he has worked in the industry of polymers for medical usage as a developer of hydrophilic pressure-sensitive adhesives for skin application in transdermal therapeutic systems and wound dressings. He received international recognition comparatively late: his earliest contacts with colleagues beyond the borders of former Soviet Union date to 1994 only. In 1999, a famous scientist and vice president of the Russian Academy of Sciences, academician Nicolai A. Platé, invited him to join A.V. Topchiev Institute

xii Editors

of Petrochemical Synthesis of the Russian Academy of Sciences, one of the most well-known academic institutes in polymer science. Later that year, Feldstein established long-term and large-scale research cooperation with a leading pharmaceutical company, Corium International, Inc. (CA). In 2005, Feldstein earned his DrSc in polymer science from the A.V. Topchiev Institute of the Russian Academy of Sciences.

Since the second half of the 1990s, Feldstein has focused on the molecular origins of pressure-sensitive adhesion and the interrelationship between adhesion and other properties of polymer blends. Based on gained insight into the phenomenon of adhesion at a molecular level, he has developed the first-ever technology for obtaining numerous novel pressure-sensitive adhesives of controlled hydrophilicity and performance properties by the simple mixing of nonadhesive polymer components in certain ratios. Feldstein is the author of nearly 200 research papers, 7 book chapters, and 25 patents. He is a member of Adhesion Society and Controlled Release Society. Feldstein is also an associate editor of the *Journal of Adhesion*.

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# Contents

Pre	tacevi
Edi	itorsx
Co	ntributorsxii
1	Surface Phenomena on a Solid-Liquid Interface and Rheology of Pressure Sensitivity Oksana A. Soboleva, Alexander V. Semakov, Sergey V. Antonov, and Valery G. Kulichikhin
2	Diffusion and Adhesion Costantino Creton and Régis Schach
3	Transition Zones in Adhesive Joints  Anatoly E. Chalykh and Anna A. Shcherbina
4	Role of Viscoelastic Behavior of Pressure-Sensitive Adhesives in the Course of Bonding and Debonding Processes Christophe Derail and Gérard Marin
5	Viscoelastic Properties and Windows of Pressure-Sensitive Adhesives  Eng-Pi Chang
6	Probe Tack Costantino Creton and Kenneth R. Shull 6-1
7	Peel Resistance Hyun-Joong Kim, Dong-Hyuk Lim, and Young-Jun Park

vi Contents

8	Shear Resistance Sergey V. Antonov and Valery G. Kulichikhin
9	Durability of Viscoelastic Adhesive Joints Sergey V. Kotomin
10	Molecular Nature of Pressure-Sensitive Adhesion  Mikhail M. Feldstein
11	Significance of Relaxation for Adhesion of Pressure- Sensitive Adhesives Mikhail M. Feldstein, Mikhail B. Novikov, and Costantino Creton
App	pendix: Abbreviations and Acronyms
11	T. 1

1

# Surface Phenomena on a Solid–Liquid Interface and Rheology of Pressure Sensitivity

Oksana A. Soboleva M.V. Lomonosov Moscow State University

Alexander V. Semakov Sergey V. Antonov Valery G. Kulichikhin

A.V. Topchiev Institute of Petrochemical Synthesis

1.1	Introduction1-
1.2	Surface Phenomena on a Solid-Liquid
	Interface1-
	Wetting of Solids by Low-Molecular-Weight
	Liquids • Wetting of Solids by Polymer
	Liquids • Wetting of Solids by
	Multicomponent Liquids • Wetting of
	Deformable Substrates (Gels)
1.3	Rheology of Pressure Sensitivity1-13
	Dimensionless Criteria of Pressure-Sensitive
	Adhesive Performance • Rheological
	Properties of Pressure-Sensitive Adhesives
	under Bonding Pressure
Dof	prences 1.2

## 1.1 Introduction

In accordance with the definition given by the Pressure Sensitive Tape Council, "pressure sensitive" is a "term commonly used to designate a distinct category of adhesive tapes and adhesives which in dry form (solvent/water free) are aggressively and permanently tacky at room temperature and that firmly adhere to a variety of dissimilar surfaces upon mere contact without the need of more than finger or hand pressure" [1]. This definition contains some uncertainties regarding the conditions of formation of the adhesive joint, namely, the exact pressure and duration of its action. It is clear, however, that

because pressure-sensitive adhesives (PSAs) are viscoelastic in nature, these parameters are crucial for their application.

The role of rheological characteristics for PSA performance was realized long ago. The main criterion of pressure sensitivity (Dahlquist's) operates with the rheological parameter (absolute values of elasticity modulus). Attempts have been made [2] to replace this empirical, yet simple and quite reliable criterion with one based on relaxation characteristics. Performance properties of PSAs, especially those related to cohesive strength (e.g., shear resistance), also depend on their rheological behavior. The rheological behavior of adhesive formulations is important for the successful manufacturing of pressure-sensitive products.

To understand how PSAs work, it is necessary to understand not only the properties of the individual components of the adhesive formulation and those of the formulation as a whole, but also the processes that take place upon contact of the PSAs with different types of substrates. The substrates can be solid or viscoelastic. Good interfacial interaction with a substrate is essential for PSA performance. Such interaction is caused by forces of different natures (van der Waals, H-bonding, acid-base, and donor-acceptor interactions) [3–5].

At the macro level, this interaction between PSA and substrate results in a wetting–spreading process. Wetting of the substrate by the adhesive is crucial to establish good contact between them. Wetting is also important in the coating procedure.

In this chapter we will first consider the fundamentals of the wetting–spreading process for simple models (e.g., wetting–spreading of Newtonian liquids on a solid surface). Wetting by polymeric liquids has specific features connected with their high viscosity and elasticity. The viscosity of PSAs upon application is very high. For this reason, spreading (i.e., increase of the wetted surface) proceeds as flow that is governed by the rheological properties. It can be assumed that the rheological characteristics of liquids in thin layers upon wetting should differ from values measured in macroscale by means of conventional rheometers, although the extent of this difference is unknown. To enable the spreading of PSAs onto a substrate's surface, it is necessary to apply external pressure for a definite time depending on the PSA's viscosity and elasticity.

Spreading of multiphase liquids and influence of surfactants will be also discussed in this chapter. Another point of interest to be considered in this chapter is wetting of the deformable substrates, which is important in some specific applications of PSAs.

Finally, we will discuss new rheological approaches highlighting the nature of pressure sensitivity.

## 1.2 Surface Phenomena on a Solid-Liquid Interface

## 1.2.1 Wetting of Solids by Low-Molecular-Weight Liquids

Let us start with the wetting-spreading processes for low-viscosity Newtonian liquids and absolutely rigid supports, such as metallic surfaces.

According to the modern concept [6], spreading of a liquid droplet on a solid surface proceeds through the formation of a primary (or precursor) film. The thickness of this film for different systems is in the range of 0.01– $10~\mu m$ . The existence of the primary film

has been confirmed by various methods (measurement of electric resistance, ellipsometry, optical and electron microscopy, etc.). Several different mechanisms of precursor film formation have been discussed: surface diffusion, evaporation of a liquid with subsequent condensation on a solid surface, and emission of jets due to the difference in capillary pressure inside the drop and in the vicinity of the three-phase (solid-liquid-air) line.

As a rule, in the majority of experiments the secondary spreading (i.e., spreading of a liquid on a surface covered with the precursor film) was studied. Experiments confirmed that the thickness, structure, and composition of the precursor film strongly affected the rate of drop spreading. Kinetic equations of secondary spreading are usually deduced from hydrodynamic models, according to which the spreading rate is limited by the delivery of the liquid to the three-phase line.

The initial stage of the spreading process is controlled by the inertial forces in the drop volume [7]. The spreading rate at the end of the inertial stage  $v_{in}$ ,

$$v_{\rm in} = \frac{dr}{dt} \tag{1.1}$$

where r is the radius of the wetted surface and t is time, can be estimated from Bernoulli's law,

$$\frac{1}{2}\rho v_{\rm in}^2 = \Delta P_{\rm c} \tag{1.2}$$

where  $\rho$  is the density of the wetting liquid and  $\Delta P_c$  is the difference between the values of capillary pressure inside the drop at the beginning and at the end of the inertial stage.

If the drop upon spreading has the shape of a spherical segment,  $\Delta P_c$  can be calculated as

$$\Delta P_{c} = 2\sigma \left(\frac{1}{R_{i}} - \frac{1}{R^{*}}\right) \tag{1.3}$$

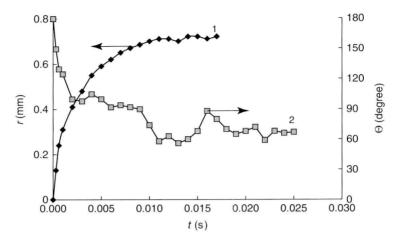
where  $\sigma$  is the surface tension of the liquid and  $R_i$  and  $R^*$  are the curvature radii of the drop surface at the beginning and at the end of the inertial stage of spreading, respectively. It is convenient to express the capillary pressure difference,  $\Delta P_c$ , as a function of the dynamic contact angle  $\Theta$ . For a spherical segment of a constant volume,

$$\frac{R_{\rm i}}{R^*} = \left(\sin^4\frac{\Theta}{2}\left(1 + 2\cos^2\frac{\Theta}{2}\right)\right)^{\frac{1}{3}} \tag{1.4}$$

Expression of the spreading rate in the inertial stage can be derived from a combination of Equations 1.2 through 1.4.

$$v_{\rm in}^2 = \frac{4\sigma}{\rho R_{\rm i}} \left( 1 - \left( \sin^4 \frac{\Theta}{2} \left( 1 + 2\cos^2 \frac{\Theta}{2} \right) \right)^{\frac{1}{3}} \right)$$
 (1.5)

The inertial spreading regime is usually observed upon the contact of drops of low-viscosity liquids (hydrocarbons, water) with solid surfaces at ambient temperature.



**FIGURE 1.1** Dependence of the radius of the wetted area (1) and contact angle (2) on time for water drop spreading on a steel surface.

At the initial stage of the spreading process, the surface of the drop is unstable and the drop height changes unpredictably, which is reflected by a "zigzag" dependence of the contact angle on spreading time. An example of such dependence is illustrated in Figure 1.1 for spreading of the water drop on a steel surface.

The duration of the inertial stage is very short—about  $10^{-2}$  s; therefore, for its registration high-speed shooting [several thousands frames per second (fps)] is needed. At this stage the spreading rate does not depend on the viscosity of the spreading liquid.

With the increased radius of the wetted area and reduction in the height of a drop, the role of viscous resistance in a volume of the drop increases. The inertial stage transforms into the viscous stage [7,8]. According to the hydrodynamic model, we can evaluate the kinetic features of viscous spreading, such as the change in radius of the wetted area r with time, by comparing the driving force of spreading,

$$f_{\rm d} = 2\pi r(\cos\Theta_0 - \cos\Theta) \tag{1.6}$$

where  $\Theta_0$  and  $\Theta$  are the equilibrium and current values of the contact angle, respectively, with the force of viscous resistance,

$$f_{\eta} = \pi r^2 \eta \operatorname{grad} \nu \tag{1.7}$$

(v = dr/dt;  $\eta$  is viscosity). If the spreading drop has the shape of a spherical segment of height h, the whole volume is involved in the spreading process and

$$\operatorname{grad} v = \frac{1}{h} \frac{dr}{dt} \tag{1.8}$$