TECHNOLOGY OF PRESSURE-SENSITIVE ADHESIVES AND PRODUCTS
Handbook of Pressure-Sensitive Adhesives and Products

Fundamentals of Pressure Sensitivity

Technology of Pressure-Sensitive Adhesives and Products

Applications of Pressure-Sensitive Products

© 2009 by Taylor & Francis Group, LLC
Contents

Preface ................................................................................................ vii
Editors .............................................................................................. xi
Contributors ................................................................................... xiii

1 Pressure-Sensitive Raw Materials
   István Benedek ........................................................................... 1-1

2 Rubber-Based Pressure-Sensitive Adhesives
   José Miguel Martín-Martínez .................................................... 2-1

3 Block Copolymer-Based Hot-Melt Pressure-Sensitive Adhesives
   Yuhong Hu and Charles W. Paul .............................................. 3-1

4 Polysisobutene-Based Pressure-Sensitive Adhesives
   Norbert Willenbacher and Olga V. Lebedeva ............................ 4-1

5 Acrylic Adhesives
   Paul B. Foreman ....................................................................... 5-1

6 Silicone Pressure-Sensitive Adhesives
   Shaow B. Lin, Loren D. Durfee, Alexander A. Knott, and Gerald K. Schalau II ...................................................... 6-1

7 Hydrophilic Adhesives
   Mikhail M. Feldstein, Parminder Singh, and Gary W. Cleary 7-1

8 Role and Methods of Formulation
   István Benedek ........................................................................... 8-1
Contents

9 Silicone Release Coating Technology  
Loretta A. Jones and Randall G. Schmidt ........................................ 9-1

10 Manufacture of Pressure-Sensitive Products  
István Benedek ........................................................................ 10-1

11 Pressure-Sensitive Adhesives Based on Polyurethanes  
Zbigniew Czech and Rudolf Hinterwaldner ................................. 11-1

Appendix: Abbreviations and Acronyms ........................................A-1
Since their introduction almost a century ago, pressure-sensitive adhesives (PSAs) have been successfully applied in many fields. They have experienced an astonishing growth rate, and their installed manufacturing and converting capacity has also sharply increased. However, a specific engineering technology for PSAs, surprisingly a special science, appears to be lacking. The application of PSAs requires a thorough knowledge of basic rheological and viscoelastic phenomena. Therefore, there is a need to investigate and summarize the most important features of PSA technology and explain the phenomena scientifically.

Based on our experience in both scientific activity and industrial areas, as well as on the special knowledge of outstanding scientists and technologists as contributors, we have addressed all aspects of 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 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. Fundamentals of Pressure Sensitivity discusses the fundamentals of pressure sensitivity, whereas Technology of Pressure-Sensitive Adhesives and Products and Applications of Pressure-Sensitive Products focus on its practice.

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 pressure-sensitive materials at all stages of the life of an adhesive joint: during 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.

Based on various aspects of macromolecular science and physics described in Fundamentals of Pressure Sensitivity, in Technology of Pressure-Sensitive Adhesives and Products the main aspects of pressure-sensitive technology are described, including the raw materials, equipment, and technology required to formulate and manufacture PSAs and to construct and manufacture PSPs.
Applications of Pressure-Sensitive Products describes the main classes and representatives of PSPs, their competitors, end-uses, application domains, and application technologies, and their tests.

Chapter 1 of this book “Pressure-Sensitive Raw Materials,” is a short presentation of the chemical basis of PSAs, allowing further discussion regarding the details of each class of raw materials or PSA formulation. Although the main synthesis of the pressure-sensitive raw materials (elastomers and viscous additives) is the subject of exhaustive works specializing in macromolecular chemistry and technology, advances in the in-line manufacture technology of PSAs demand discussion of the synthesis and technology of pressure-sensitive raw materials. The monomers used, the polymerization technology, polymer analogous reaction-based technology, and the formulation of off-line manufactured PSA raw materials are described in comparison to in-line synthesis. The major basic products of pressure-sensitive formulation, that is, the elastomers (random, alternative, and block copolymers), the viscoelastic materials (e.g., acrylics and other vinyl polymers, silicones, etc.), and additives, are briefly presented, allowing their detailed discussion in Chapters 2 through 9 of this book. As suggested many years ago by Benedek in Pressure-Sensitive Adhesives Technology (Dekker, 1996), and as discussed in Section 1.3, the science and practice of PSPs reveal that they are composite materials. This means that their construction plays an equivalent role with their constituting materials.

The specific features of rubber-based PSAs are examined in Chapter 2 of this book, “Rubber-Based Pressure-Sensitive Adhesives.” Natural rubber-based PSAs were the first self-adhesive products used for the manufacture of PSPs. Although natural rubber is self-adhesive, most elastomers must be mixed with plasticizers and tackifiers (i.e., formulated) to display usable pressure sensitivity. The special structure of common elastomers, their high, so-called rubberlike elasticity, related to their partially cross-linked structure allowing strain hardening, offers a large range of modalities (tackification, plasticization, cross-linking, filling, etc.) for their formulation. This chapter deals with the specific features of rubber-based adhesives, allowing their comparative examination.

The description of block copolymer-based hot-melt pressure-sensitive adhesives is the subject of Chapter 3 of this book. As discussed in Chapter 1, developments in macromolecular chemistry allowed the synthesis of rubber- and plasticlike polymers. Such so-called thermoplastic elastomers (TPEs) have a partially cross-linked structure like common elastomers, which imparts elasticity. In this case, the partially cross-linked structure (segregation) is based on physical, thermally unstable bonding, which makes the thermal, plasticlike processing of such elastomers feasible. Advances in macromolecular chemistry and technology allowed the synthesis of a broad range of TPEs based on various monomers and with different build-ups. In Chapter 3 the distinctive features of the mechanical and adhesive properties of styrene–diene-based block copolymers are considered and compared with the properties of PSAs of other classes. The synthesis methods of styrene–diene block copolymers with different structures (e.g., linear, radial, tapered, etc.) are described. Star- and oligomer-modified star polymers and multiblock polymers are examined in comparison with olefin- and acrylate-based block copolymers. Tackification, based on selective compatibility, is investigated (see also Chapter 8). The features of block copolymers, that is, their mechanical properties (tensile strength, creep, etc.) and adhesive properties (tack, peel resistance, and shear resistance) are investigated. Processing and limitations in use are also discussed.
Preface

Polysisobutene-based pressure-sensitive adhesives are evaluated in Chapter 4 of this book. In the range of elastomer-based PSPs, polysisobutene (PIB)-based PSAs constitute a special class, with an old and large application field. Owing to their classic synthesis, which allowed the manufacture of various, well-characterized products, PIBs were used for pressure-sensitive tapes in different end-use domains (see also Applications of Pressure-Sensitive Products, Chapter 4). Owing to their systematic investigation (including macromolecular chemistry and physics and contact mechanics), their application performance characteristics can be easily related to their fundamental aspects; that is, they serve as model compounds. The role of high- and low-molecular-weight PIB fractions in adhesive performance is described, along with the impact of molecular weight distribution, chain entanglements, $M_c$ (cross-linking), etc. The advantages and drawbacks of PIB adhesives, compared with other PSAs, are also discussed.

Chapter 5 of this book, “Acrylic Adhesives,” describes the most important viscoelastic polymers used for PSAs. Acrylic copolymers were the first class of synthetic polymers used for PSAs. Acrylics are also available as solvent-based, water-based, and 100% solids. Acrylics are also supplied as acrylic rubbers and thermoplastic elastomers. Owing to their very large monomer basis, their copolymerizability by various procedures (which include in-line technology-required radiation-induced polymerization), their built-in pressure sensitivity (which can be easily regulated by tackification, cross-linking, etc.), and their excellent aging and physiological properties, acrylics remain the main class of pressure-sensitive raw materials. In this chapter the relationship between the monomer composition of acrylic polymers and their adhesive behavior is discussed. Synthesis and the tools to control performance, that is, macromerization, radiation-induced and chemical curing, and tackification, are also described. Water- and solvent-based adhesives are examined in comparison.

Chapter 6 of this book is focused on silicone pressure-sensitive adhesives. Silicones are a special class, with an old and large application field. Owing to their classic synthesis methods can be used to incorporate different monomers in polysiloxane, and due to the regulation of the organic–inorganic ratio in the polymer and other macromolecular characteristics, fine-tuning of the adhesive properties is possible, which leads, ad absurdum, to nonadhesive and adhesive products (see also Chapter 9 of this book).

Hydrophilic adhesives are the subject of Chapter 7 of this book. In the first part of this chapter, the major types of hydrophilic adhesives and bioadhesives are described. As demonstrated in Chapter 10 of Fundamentals of Pressure Sensitivity, at a molecular level, pressure-sensitive adhesion of polymer materials requires a balance between a high value of cohesion energy and a large free volume. This fundamental factor underlies the Corplex technology for development of new adhesive materials through the blending of nonadhesive polymer components. In such adhesives the high cohesion energy results from the formation of either hydrogen or electrostatic bonds between functional groups of two complementary polymer chains (noncovalent cross-linking of the polymers in the blend). The large free volume results from either the location of the reacting functional groups at the ends of the oligomer chains or the plasticization of the interpolymer complex. Such hydrogels (their construction and performances) are
examined in comparison with other hydrogels. The practical aspects of the use of such hydrophilic PSAs are also discussed in Applications of Pressure-Sensitive Products.

In Chapter 8 of this book, the role and methods of formulation of various raw material classes (presented in previous chapters) are discussed. Pressure-sensitive adhesives are based on elastomers mixed with viscous components (e.g., tackifiers and plasticizers), which impart them with pressure sensitivity, or allows regulation based on control of glass transition temperature and elasticity modulus. Other physical or chemical procedures (e.g., filling and cross-linking) affect pressure sensitivity as well. Such design modalities are the subject of formulation. This chapter describes the role of formulation and the methods of formulation to introduce the reader to the detailed discussion of adhesive raw materials must be mixed with various other components to achieve the manufacture and application properties of the PSA. The role of formulation is to ensure the adhesion-related characteristics (e.g., tack, peel resistance, and shear resistance), end-use-related characteristics (e.g., water, temperature, and environmental resistance), and the technology-related performances, including coatibility of the PSA and convertability of the PSP. Such requirements are fulfilled using various formulation methods (e.g., tackification, cross-linking, filling, and special chemical or technological additives).

Silicone release coating technology, discussed in Chapter 9 of this book, constitutes a principal component of PSPs. Generally, PSPs are temporarily laminated, whereas delamination is allowed by using a dehesive, release-coated carrier material (liner) to protect the adhesive-coated carrier material and to allow its processing as a continuous web. Although various release coatings were developed on very different chemical bases, silicone-based release coatings are the sole materials with an almost general usability. In this chapter the functioning, grades, build-up, manufacture, and coating technology of silicone-based release coatings are discussed.

Chapter 10 of this book describes the manufacture of pressure-sensitive products. Using the raw materials presented in Chapters 1 through 9 and the principles of formulation discussed in Chapter 8, PSAs are manufactured and processed in PSPs. Such technology comprises the manufacture of web-components (e.g., adhesive, release, and carrier), the manufacture of the web, that is, the coating of the carrier with the PSA (using various methods), and conversion of the pressure-sensitive web (laminate) into a finished web-like or discrete PSP (e.g., label, tape and protective film) by means of various overcoating (e.g., lamination, printing and lacquering) and confectioning procedures (e.g., slitting, cutting, die-cutting, perforating and folding). The principles of these technologies and the required equipment are also described.

Chapter 11 of this book discusses advances in pressure-sensitive adhesives based on polyurethanes.

This book serves as a practical aid to manufacturers, converters, and those involved in the design and use of PSAs.

We were pleased to see the participation of scientists and industrial experts in very different areas of the field working 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. Platè, invited him to join A.V. Topchiev Institute
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.
Contributors

István Benedek
Pressure-Sensitive Consulting
Wuppertal, Germany

Gary W. Cleary
Corium International, Inc.
Menlo Park, California

Zbigniew Czech
Department of Chemical Organic Technology
Szcecin University of Technology
Szcecin, Poland

Loren D. Durfee
Dow Corning Corporation
Midland, Michigan

Mikhail M. Feldstein
A.V. Topchiev Institute of Petrochemical Synthesis
Russian Academy of Sciences
Moscow, Russia

Paul B. Foreman
National Starch and Chemical
Bridgewater, New Jersey

Rudolf Hinterwaldner
Hinterwaldner Consulting and Partner GbR
Kirchseeon, Germany

Yuhong Hu
National Starch and Chemical
Bridgewater, New Jersey

Loretta A. Jones
Dow Corning Corporation
Midland, Michigan

Alexander A. Knott
Dow Corning S.A.
Seneffe, Belgium

Olga V. Lebedeva
Institute for Mechanical Process Engineering and Mechanics
University of Karlsruhe
Karlsruhe, Germany

Shaow B. Lin
Dow Corning Corporation
Midland, Michigan

José Miguel Martin-Martinez
Adhesion and Adhesives Laboratory
University of Alicante
Alicante, Spain

Charles W. Paul
National Starch and Chemical
Bridgewater, New Jersey

Gerald K. Schalau II
Dow Corning Corporation
Midland, Michigan

Randall G. Schmidt
Dow Corning Corporation
Midland, Michigan

Parminder Singh
Corium International, Inc.
Menlo Park, California

Norbert Willenbacher
Institute for Mechanical Process Engineering and Mechanics
University of Karlsruhe
Karlsruhe, Germany

© 2009 by Taylor & Francis Group, LLC
1

Pressure-Sensitive Raw Materials

1.1 Off-Line and In-Line Synthesis of Pressure-Sensitive Raw Materials

Off-Line Synthesis of Pressure-Sensitive Raw Materials • In-Line Synthesis of Pressure-Sensitive Raw Materials

1.2 Basic Products for Pressure-Sensitive Adhesives

Elastomers • Viscoelastomers • Viscous Components • Comparison of PSAs on a Different Chemical Basis

1.3 Pressure-Sensitive Products as Composites

Pressure-Sensitive Products as Composites on a Macromolecular Scale • Pressure-Sensitive Products as Composites on Macromolecular and Macroscopic Scale • Pressure-Sensitive Products as Composites on a Laminate Scale

References

Fundamentals of Pressure Sensitivity focuses on the fundamental aspects of pressure sensitivity and Technology of Pressure-Sensitive Adhesives and Products and Applications of Pressure-Sensitive Products are practice related. Technology of Pressure-Sensitive Adhesives and Products discusses the manufacturing technology of pressure-sensitive adhesives (PSAs) and products (PSPs), including their chemical basis (raw materials) and engineering technology. Applications of Pressure-Sensitive Products describes the application domains and end-use technology of the main PSPs.

Special raw materials allow the design, formulation, and manufacture of PSAs and PSPs. Their chemical basis was described in detail in our previous works [1–4]. The fundamentals of pressure sensitivity, based on this chemical and macromolecular basis, were discussed in Fundamentals of Pressure Sensitivity according to the most important features of adhesive science. Interfacial and rheologic processes as the main features of pressure sensitivity were described in Fundamentals of Pressure Sensitivity, Chapter 1. Viscoelastic behavior as a principal characteristic of rheology in the course
of the bonding and debonding processes was discussed in *Fundamentals of Pressure Sensitivity*, Chapter 4, and correlated to viscoelastic windows in *Fundamentals of Pressure Sensitivity*, Chapter 5. Transition zones in adhesive joints and the durability of adhesive joints are discussed in *Fundamentals of Pressure Sensitivity*, Chapters 3 and 9. The role of diffusion in adhesion and the molecular fundamentals of pressure-sensitive adhesion were first discussed by Feldstein in Ref. [5]. Now advances in this field are described by Creton in *Fundamentals of Pressure Sensitivity*, Chapter 2. Pressure sensitivity was interpreted as a material property and a process by Feldstein and Creton in Ref. [6]. They continue to evaluate progress in this field in *Fundamentals of Pressure Sensitivity*, Chapters 2 and 10. The significance of relaxation for adhesion is explained in *Fundamentals of Pressure Sensitivity*, Chapter 11.

Advances in the theory of pressure sensitivity allowed the science-based design and formulation of PSAs to replace empirics. The design and formulation of PSAs constitute the subject of our previous works [7–9]; the manufacture of PSAs and PSPs was also described by us in detail in Refs [4,10,11]. The above references are books, that is, they are available, and they cover data from research and literature searches in the whole domain of pressure sensitivity, which is very large. It is not the aim of this treatise to repeat these data; this book presents only the essentials. Chapters 1, 8, and 10 possess a general character that allows the correlation of subjects in other special chapters in these books.

As mentioned previously, the technology of PSAs and PSPs is the subject of this book. Technology generally includes the raw materials and the manufacturing process of the products. Actual PSA technology was founded on basic knowledge in material science and engineering, as discussed in *Fundamentals of Pressure Sensitivity*. The aim of this first chapter is to serve as a short guide, which allows the systematic and detailed discussion of the advances in pressure-sensitive raw materials described by specialists in the following chapters. This is a short presentation of the chemical basis of PSAs, allowing further discussion of the details of each raw material class used in the formulation of PSAs. Although the main synthesis of pressure-sensitive raw materials (elastomers, viscoelastomers, and viscous additives) is the subject of exhaustive works specializing in macromolecular chemistry and technology, advances in the in-line manufacturing technology of PSAs (especially in the development of radiation curing and web-finishing technology) impose a basic discussion of the synthesis and manufacturing technology of pressure-sensitive raw materials. In the following sections the monomers used, the polymerization technology, the technology based on polymer analogous reactions, and the formulation of off-line manufactured PSA raw materials are described in comparison with in-line synthesis.

### 1.1 Off-Line and In-Line Synthesis of Pressure-Sensitive Raw Materials

The manufacture of pressure-sensitive raw materials and adhesives can be carried out off-line or in-line. As illustrated in Figure 1.1, both technological modalities include various chemical technologies. Generally, off-line synthesis yields pressure-sensitive raw materials or PSAs; in-line technology leads to simultaneous PSA and PSP manufacture.
As illustrated in Figure 1.2, off-line synthesis (1) allows polymer-based PSA formulation to be coated (2) and (if necessary) transformed (mainly by cross-linking) in PSP. Formulation is necessary because, generally, off-line synthesis yields PSA components only, that is, macromolecular raw materials that are not pressure sensitive or not pressure sensitive enough; therefore, they must be formulated, that is, mixed with other micro- or macromolecular compounds.

This is the subject of formulation. In-line manufacture of the adhesive consists of simultaneous coating and curing (3) or postpolymerization (4) of the adhesive–raw
materials. In this case, first a special “ready-to-coat” mixture of polymerizing and cross-linking monomers, oligomers, or polymers (e.g., radiation-cured hot melts) is prepared and applied on a temporary or definitive carrier material. Such a reaction mixture is transformed after coating in the ready-to-use adhesive or PSP. This post coating synthesis of the PSA must be carried out by the converter. The base polymeric raw materials for in-line synthesis are supplied by off-line synthesis. Off-line as well as an in-line synthesis was described in detail by Benedek in Refs [12,13]; therefore, the next sections provide only a summary presentation to allow the detailed discussion of the chemical basis of PSAs in the following chapters by specialized scientists.

1.1.1 Off-Line Synthesis of Pressure-Sensitive Raw Materials

Off-line synthesis of PSAs is the common way to produce PSAs. Such products can be macromolecular compounds with ready-to-use or ready-to-formulate adhesive properties or ready-to-postpolymerize reaction mixtures (monomer or polymer based), manufactured and supplied by the chemical industry to be formulated or coated in-line, that is, to convert them to a PSP. The raw materials and the technology used to transform them into macromolecular compounds with ready-to-use or ready-to-formulate pressure sensitivity are the main parameters of off-line synthesis. Owing to the wide use of synthetic elastomers domains other than that of PSAs and to the existence of a sophisticated chemical synthesis–technology, off-line synthesis, that is, the manufacture of macromolecular compounds by polymer specialists, remains the decisive part of the production of pressure-sensitive materials. The raw materials and the technology used for them are the main parameters of off-line synthesis. Table 1.1 presents the main raw materials (monomers, oligomers, polymers, and additives) for off-line- and in-line synthesis of PSAs.

**TABLE 1.1 Main Raw Materials for Off-Line and In-Line Synthesis of PSAs**

<table>
<thead>
<tr>
<th>Raw Materials</th>
<th>For Off-Line Synthesis Grade</th>
<th>For In-Line Synthesis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monomers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Common</td>
<td>Vinyl</td>
<td></td>
</tr>
<tr>
<td>Polyfunctional</td>
<td>Diene</td>
<td>—</td>
</tr>
<tr>
<td>Special</td>
<td>Photosensitive</td>
<td></td>
</tr>
<tr>
<td>Oligomers</td>
<td>Acrylic</td>
<td></td>
</tr>
<tr>
<td>Special</td>
<td>Photosensitive</td>
<td></td>
</tr>
<tr>
<td>Polymers</td>
<td>Acrylic, diene</td>
<td></td>
</tr>
<tr>
<td>Special</td>
<td>Photosensitive</td>
<td></td>
</tr>
<tr>
<td>Additives</td>
<td>Inorganic</td>
<td></td>
</tr>
<tr>
<td>Cross-linking agents</td>
<td>Organic</td>
<td></td>
</tr>
<tr>
<td>Technological additives</td>
<td>Surfactants</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Thickeners</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Stabilizers</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Solvents</td>
<td></td>
</tr>
</tbody>
</table>
1.1.1.1 Raw Materials for Off-Line Synthesis

The raw materials for PSA synthesis as a function of the advances in macromolecular chemistry were discussed in detail by Benedek in a previous book [14]. The glass transition temperature ($T_g$) and modulus of elasticity as the main parameters of pressure-sensitive design and formulation, as a function of the macromolecular characteristics (i.e., molecular weight and its distribution, comonomer content, molecular structure, sequence length and distribution, compatibility, cohesive strength/free-volume-balance, etc.), were described by Benedek in Ref. [15]. The $T_g$ and the modulus are the main rheologic parameters of pressure-sensitive materials. As illustrated by the examples given in Table 1.2, regulation of the glass transition temperature during polymer synthesis and by formulation of the same polymers allows the decisive changes in rheology that permit use if the materials in quite different applications, for example, as a “soft” PSA or as a “hard” carrier material for PSAs. Owing to continuously increasing requirements in the end use of PSPs, especially in labeling, the values of $T_g$ for common PSAs have changed as a function of raw material development. Some years ago, a typical PSA had a $T_g$ of about $-40^\circ$C; in fact, common acrylic PSAs possess a $T_g$ range of $-40$ to $-60^\circ$C.

Although polymerization and polymer analogous reactions remain the main modalities for off-line synthesis, recent advances in macromolecular chemistry allowed the synthesis of PSAs by simultaneous cross-linking and tackification, leading to hydrophilic, biocompatible polymers [5,6,16] (see also Fundamentals of Pressure Sensitivity, Chapter 10, and Chapter 7 in this book).

Monomers are the most important raw materials for polymerization and polymer modification. The choice of monomers, polymerization procedure, and additives decisively affects the performance characteristics of the PSA [14].

1.1.1.1.1 Monomers for Off-Line Synthesis

The most important (vinyl and acrylic) monomers for macromolecular compounds used for PSAs were discussed in detail by Benedek in Refs [13,14], taking into account their polarity and functionality, as well as their influence on the physical and chemical properties of the polymer. Advances in the use of the main monomers are discussed by Hu and Paul in Chapter 3 (monomers for block copolymers), by Willenbacher and Lebedeva in Chapter 4 (monomers for isobutene-based polymers), by Foreman in Chapter 5 (acrylic monomers), by Lin in Chapter 6 (monomers for silicone-based adhesives), and by Jones

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Glass Transition Temperature (°C)</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyvinyl chloride, plasticized</td>
<td>$-40$–$0$</td>
<td>Carrier, PSA</td>
</tr>
<tr>
<td>Polyvinyl chloride</td>
<td>$+75$–$+105$</td>
<td>Carrier</td>
</tr>
<tr>
<td>Poly(ethylene–VAc)</td>
<td>$-10$–$+15$</td>
<td>PSA, carrier</td>
</tr>
<tr>
<td>PP</td>
<td>$-11$</td>
<td>Carrier</td>
</tr>
<tr>
<td>PP, amorphous</td>
<td>$-14$</td>
<td>PSA</td>
</tr>
</tbody>
</table>
and Schmidt in Chapter 9 (monomers for silicone-based release materials). The main classes of monomers (e.g., softening, hardening, polar, and reactive compounds), the influence of carboxy functionality on adhesion, cohesion, cross-linking, and dispersion stability of the PSA, the built-in cross-linkable functional groups, hydrophilic monomers for water-soluble compositions, stabilizing hydrophilic comonomers, and some special comonomers were also described by Benedek in Refs [13,14], where screening formulations for synthesis of water-based acrylic PSAs were also provided and the influence of the choice of comonomers on polymer properties as well as on the properties of the dispersed polymeric system were investigated. The choice of special monomers used for water-soluble acrylic PSAs and the influence of chain length, chain branching, and monomer polarity on adhesive performance characteristics was investigated by Czech [17]. A global view of the parameters of molecular construction of PSPs was given by Benedek in Ref. [4], where the macromolecular basis (monomers, molecular weight, branching, etc.) for PSAs, as well as for the carrier material for PSPs, was described in detail.

The choice of monomers imposes the polymerization procedure (i.e., free-radical, ionic, etc., mechanism), and technology (i.e., solvent-based, water-based, etc.) affects the choice of additives, which influences the polymerization technology and rate of polymerization, the dispersion properties (e.g., particle size, stability and viscosity, and polymer properties) and determines the adhesive and end-use properties of the pressure-sensitive raw materials and the PSA. Special formulations (monomers and additives) are required for removability, water solubility/resistance, and other special properties (see also Chapter 8). Copolymerization of polyalkylacrylates with hydrophilic monomers to improve hydrophilicity is described by Feldstein, Singh, and Cleary in Chapter 7. Advances in free-radical polymerization are discussed by Hu and Paul in Chapter 3.

1.1.1.2 Additives for Off-Line Synthesis

Off-line synthesis supplies elastomers with or without self-adhesivity, pressure-sensitive viscoelastomers, and viscous components used to impart pressure sensitivity to the elastomers or to improve (regulate) pressure sensitivity. Such compounds can be considered special additives. Tackifiers and plasticizers used as viscous components to impart and regulate the adhesive properties will also be described by Benedek in Chapter 8. The special aspects of the tackification of block copolymers are discussed by Hu and Paul in Chapter 3. Other micromolecular, chemical, and technological additives are included in PSA raw materials during their synthesis. Chemical stabilizing agents (e.g., antioxidants, UV-protecting agents, etc.), and physical stabilizing agents (surface active agents, protective colloids, solubilizers, etc.) are included as well. Such compounds are used as postsynthesis formulating components for PSAs (see Chapter 8).

1.1.1.2 Technology of Off-Line Synthesis

Off-line synthesis is carried out by polymerization or polymer-analogous reactions [12,13]; it also includes the off-line modification of the synthesized polymers by chemical reactions (e.g., grafting, cross-linking, and depolymerization) and, in part, physical procedures (see formulation by mixing in Chapter 8). Thus, in some cases ready-to-use (i.e., ready-to-coat) PSAs are manufactured and do not need further formulation (see Chapter 8); in other cases, adhesive formulation is imposed by technological or
end-use requirements [18] (see Chapter 8). Therefore, the technology for off-line synthesis must cover polymer modification by grafting, cross-linking, depolymerization, and (partially) formulation as well (see also Chapter 3). Table 1.3 illustrates the various steps of the manufacture of PSAs (and PSPs) carried out off-line or in-line by the chemical industry or by converters. Polymer synthesis and the technology of off-line synthesis are described by Foreman in Chapter 5.

As can be seen from Table 1.3, with the exception of polymerization of the base raw materials, the other manufacturing steps can be and generally are carried out by converters. A special domain of off-line synthesis focuses on the manufacture of radiation-curable PSA raw materials. The preparation and adhesion performances of UV-curable acrylic PSAs were investigated recently by Kim and coworkers [19,20]. Off-line synthesis of styrene–butadiene–rubber (SBR) copolymers is described by Martin-Martinez in Chapter 2.

Polymerization in an extruder is a special off-line polymerization technology [21] that can be used, for instance, for the manufacture of water-soluble solvent-based acrylic PSAs (see also Chapter 8) that can be UV-light cured in-line. Polymerization in an extruder is a common technology for grafting and can be combined with simultaneous depolymerization in the extruder [22]. The influence of screw speed, acrylic acid and starter amount, and the cross-linking after extrusion polymerization of acrylics were discussed in Ref. [21].

As mentioned previously, a new possibility for obtaining plastomer-based PSAs is given by the manufacture of pressure-sensitive hydrogels [5,6,16]. First discovered as a special case of pressure sensitivity, the N-vinyl pyrrolidone–polyethylene glycol (PEG)-based aqueous blends allowed the synthesis of other PSAs and the reformulation of the theory of pressure sensitivity. As noted by Feldstein and colleagues [23], the general

### Table 1.3 Processing Steps, Materials, and Manufacturers for Off-Line and In-Line Synthesis of PSAs

<table>
<thead>
<tr>
<th>Processing Steps</th>
<th>Off-Line Formulation</th>
<th>In-Line Formulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw materials</td>
<td>Nonreactive Base Polymer</td>
<td>Reactive Base Polymer and Oligomer</td>
</tr>
<tr>
<td></td>
<td>Monomers</td>
<td>Monomers</td>
</tr>
<tr>
<td></td>
<td>Technological additives</td>
<td>Chemical additives</td>
</tr>
<tr>
<td>Common products</td>
<td>Common AC, EVA, SBC-based PSA raw materials</td>
<td>Cross-linkable AC, CSBR, SBC-based PSA raw materials, reactive oligomers; macromers</td>
</tr>
<tr>
<td>Manufacturer</td>
<td>Chemical industry</td>
<td>Chemical industry</td>
</tr>
</tbody>
</table>

© 2009 by Taylor & Francis Group, LLC
applicability of the polyvinyl pyrrolidone (PVP)–PEG model to other hydrophilic polymers and plasticizers follows from the fact that the $T_g$ of PVP-PEG system obeys fairly well Kovács’s equation concerning the additivity of $T_g$. This equation establishes the additional criteria of adhesive capability of a hydrophilic polymer blend, which relates mainly to the physical properties of the plasticizer. Consequently, by mixing the PEG with various complementary high-$T_g$ polymers, similar $T_g$ composition behavior will be obtained, which accounts for adhesion. In Fundamentals of Pressure Sensitivity, Chapter 11, based on the analysis of peel force in the work of viscoelastic deformation of adhesive film up to break under uniaxial drawing, peel resistance is presented as a function of the self-diffusion coefficient, relaxation time, and the cohesive strength of the adhesive polymer. The physical meaning of the derived relationship demonstrates the energy of intermolecular cohesion and free volume as a factor that controls adhesion. The relationships explains why PSAs must be in a viscoelastic state. In Chapter 7 the practice of such hydrophilic polymers is described. At a molecular level, pressure-sensitive adhesion of polymer materials requires a balance between a large value of cohesion energy and a large free volume. This fundamental factor underlies the Corplex™ technology for the development of new adhesive materials by blending nonadhesive polymer components. In Corplex adhesives the high cohesion energy results from the formation of either hydrogen or electrostatic bonds between functional groups of two complementary polymer chains (noncovalent cross-linking of the polymers in the blend). The large free volume results from either the location of the reacting functional groups at the ends of the oligomer chains or the plasticization of the interpolymer complex.

Advances in the synthesis of thermoplastic elastomers will be summarized in this chapter and discussed in detail in Fundamentals of Pressure Sensitivity, Chapter 3, by Hu and Paul.

Principally, off-line synthesis of PSA raw materials presents advantages in comparison to in-line synthesis in that various polymerization technologies (i.e., batch, continuous; water based, solvent based, or 100% solids) with different feed-in modalities of the reaction components and various temperature and hydrodynamic conditions are possible. Feed-in possibilities include tackification during polymerization. As demonstrated, the properties of the polymers synthesized may strongly differ according to such technological changes. For instance, emulsion polymerization of acrylates carried out to complete conversion produces significant amounts of microgels; thus, full conversion must be avoided. Emulsion and suspension polymerization yield different PSA raw materials as a function of the particle size. Carboxylated SBR latexes consist of a mixture of polymer species with linear chains, branched chains, and cross-linked materials. The relative ratio of the species can be controlled by changing the concentration of molecular weight regulators and by varying factors such as conversion, reaction temperature, or polymer particle number. The critical soft monomer (EHA) level in acrylics, which affects failure nature, depends on the polymerization process. The above-listed examples illustrate the importance of the polymerization technology.

In the past decade the solution polymerization of acrylics in recovered solvents to prepare in-line radiation-curable polymers has gained special importance [24].

It is not the aim of this book to discuss polymerization technology; however, in Chapters 2–9, which describe in a detailed manner the main raw materials for PSAs,
the technological aspects of their synthesis and processing (which decisively affect their properties) will be discussed as well. Formulation of off-line synthesized pressure-sensitive raw materials will be discussed in Chapter 8. Polymer analogous reactions (e.g., cross-linking) on off-line synthesized PSA raw materials will also be described (see Chapter 8).

1.1.2 In-Line Synthesis of Pressure-Sensitive Raw Materials

Generally, for the PSA converter the manufacture of the adhesive consists of its formulation, that is, of mixing macromolecular compounds and additives. In certain cases it would be desirable for the adhesive converter to carry out its own polymerization. Such necessity appears for low-volume special products or for adhesives for which formulation is based on the mixing of low-molecular-weight products, oligomers, or prepolymer, and the converting technology of this mixture must supply simultaneously the PSA and the PSP (see Table 1.3). There are also some special cases where the formulation is made to allow the modification of the coated adhesive by postpolymerization. In this case, the last production step of the adhesive, that is, of the off-line synthesis, is an in-line process and represents the simultaneous manufacture of the PSA and PSP. The full or partial postmanufacturing of the PSA is the result of chemical development induced by the trend of solvent-free fabrication. Such formulations with 100% solids include hot melts or radiation-curable reaction mixtures. In-line polymerization, which includes polymerization in situ or postpolymerization, uses special multifunctional monomers or macromers and classic (chemical) or physicochemical polymerization techniques [13]. Polyaddition, polycondensation, or cross-linking is carried out.

Postapplication cross-linking can be considered a special case of off-line synthesis (finishing) of an adhesive. It is proposed to improve shear or to ensure delamination (detachment) after use. Such postcross-linking is achieved using thermal, free radical, or photoinitiated reactions.

Generally, in-line synthesis is based on polymer analogous reactions (which include functionalization and cross-linking of polymers), polymerization, and macromerization [13]. Polymerization can also be limited to the surface of an existing base polymer. Improvement of the reversible work of adhesion can be achieved by grafting polar groups onto the polymer. Surface-treatment procedures also cause polymer analogous reactions (see Chapter 10). Cross-linking required to increase molecular weight and to shift the adhesion–cohesion balance can be carried out through classic, thermally initiated reactions or by radiation-induced reactions (see Section 1.2.2).

1.1.2.1 Raw Materials for In-Line Synthesis

The raw materials for in-line synthesis are monomers or prepolymerized compounds that must be postpolymerized. As illustrated in Figure 1.3, monomer-based off-line synthesis can lead to oligomers or polymers. In-line synthesis can also use monomers as starting materials (this is the old, so-called “syrup” technology, which employs low-viscosity, reactive, and diluting monomers), but oligomer–monomer blends can also be used (in the modified syrup technology) or pure, medium-viscosity oligomers/macromers can
be cross-linked and, finally, reactive high polymers [e.g., cross-linkable acrylics, styrene block copolymers (SBCs), etc.] can also be coated and cured.

The materials used for postpolymerization are common PSAs, PSAs with unbalanced adhesive properties, or nonadhesive oligomers. Such compounds are manufactured by off-line synthesis. Generally, they include macromolecular compounds with a low to medium molecular weight and residual functionality, that is, they can be postpolymerized (or cross-linked). For this process the converter can choose to use either a classic polymerization technology (i.e., thermal, free radical-initiated polymerization, polyaddition, or polycondensation) or a radiation-induced reaction. In some cases this choice is limited by the chemical nature of the (pre)polymer. In certain cases (i.e., acrylic hot-melt development) postpolymerization of an oligomer is a necessity because of the lack of suitable macromolecular compounds (see also Chapter 5).
1.1.2.1.1 Monomers for In-Line Synthesis

In the case of in-line synthesis, the common range of monomers (used for off-line synthesis also) is enlarged by special, radiation-polymerizable monomers and copolymerizable photoinitiators. Raw materials (e.g., monomers and oligomers) for in-line synthesis (radiation-induced polymerization and curing) were described in detail by Benedek in Ref. [24] (see also Chapter 8).

Photoinitiators were described in detail by Do and Kim in Ref. [20]. Generally, they are ethene-unsaturated, ultraviolet (UV)-reactive, functionalized, acrylated, vinylated, allylated, acrylamidated, or vinyloxidated chromophores. Photoinitiators suitable for addition are another new group of compounds with a conventional chemical group on one side, which tends to addition reaction or another kind of reaction with the carboxyl or hydroxyl groups of the polymer chain, and other photoreactive side groups. Oligomeric and polymeric photoinitiators have been developed as well. They do not show yellowing, have less odor, do not migrate, and exhibit low irritancy [13]. Although the classic way is to use external photoinitiators (e.g., benzophenone), built-in, monoethyclically unsaturated aromatic ketones can also be used for radiation cross-linking of polyacrylates. For instance, such a copolymerized photoinitiator can be an acrylic ester with benzophenone terminal groups. The built-in cross-linker makes it unnecessary for the viscoelastomer to contain unsaturated polymerizable bonds (and, therefore, it displays improved aging properties), it does not produce skin irritation, and its UV-induced polymerization is not affected by atmospheric oxygen. Li et al. [25] describe the synthesis of benzocyclobutenone containing polymers for UV light-curable PSAs. Under UV radiation, benzocyclobutenone readily reacts with itself and also with an alcohol to produce an ester; thus, in this case UV-induced cross-linking occurs without an initiator.

Like common, off-line synthesis, photoinitiated in-line polymerization is strongly affected by the choice of monomers. However, this choice is limited because of the rheology and technical requirements, which can be contradictory. Concerning the monomers used for radiation curing, they must fulfill different requirements for the main radiation-induced polymerization procedures, that is, the UV-light-induced and electron beam (EB)-induced polymerization. In particular, UV light-polymerizable monomers require functionalities other than EB-curing ones.

As discussed in detail by Benedek in Ref. [13], formulation for UV light-curable PSAs must allow pronounced molecular mobility. Relatively low cross-linking density and a glass transition temperature lower than $-20^\circ$C are necessary to fulfill such requirements. Ethyl acrylate, butyl acrylate (BA), glycydylmethyl acrylate, and acrylic acid may be used as monomers for prepolymer. To improve the coatability of monomer-based, UV light-induced formulations, thickened monomer mixtures were proposed [20]. In this case, nonreactive or reactive oligomers can serve as thickeners. If the recipe contains reactive oligomers as well, reactive diluents are used to “dilute” them. The term reactive diluent generally refers to an unsaturated ethylene monomer that is miscible with the principal oligomers, which reduces the viscosity of the composition and reacts with the oligomer to form a copolymer. In some cases, the addition of the reactive diluent not only reduces the viscosity of the uncured diluent composition but also increases
the elongation of the cured coating. The polymers synthesized by UV-induced polymerization must possess an elastic network. Therefore, the reaction mixture contains multifunctional monomers as well. The main common multifunctional (cross-linking) monomers and diluting monomers, as well as their influence on the properties of the PSA, were described in detail in Ref. [13]. To improve the coatability of monomer-based, UV light-induced formulations, thickened monomer mixtures were proposed [20]. The difficulties encountered in the use of UV-light or EB-curable systems are similar: high viscosities, air inhibition, and potential pollution from volatile monomers.

The EB is a much higher energy source than UV light and promotes a higher level of cross-linking, so UV light-curable formulations cannot be used unchanged for EB. EB-induced polymerization requires unsaturation; therefore, certain UV-curable formulations are not adequate for EB curing. EB curing supposes the reaction of a vinyl unsaturation with the electrons of suitable energy levels. For instance, 1,2-polybutadiene requires a high radiation dosage for cross-linking. The curing occurs more easily if acrylates are added in the formulation. Better results are obtained with hydroxylated or epoxidized acrylics as curing sites together with ethylhexyl acrylate (EHA) as a monomer. EB-cured formulations are composed of oligomers, prepolymer (50–100%), multifunctional monomers, and additives, or they are based on polymers. In the case of EB-induced curing, where a multifunctional monomer is used, its concentration should be preferably 1–5% bw (in comparison, the effect of diluting monomers used in UV light-induced polymerization is investigated at a level of about 10%). Radiation-curable SBCs are described by Paul and Hu in Chapter 3.

1.1.2.1.2 Oligomers and Macromers for In-Line Synthesis

In in-line PSA synthesis on the web, the precise regulation of the polymerization (or curing) as a function of the adhesive raw materials, thickness of adhesive layer, and carrier characteristics is difficult. In the first stage of development (which uses monomer-based formulations), side-reaction products and effects (e.g., residues of unreacted monomers and initiators, carrier damage, etc.) created technical, environmental, and physiological problems. Additional negative technological aspects appeared. The coating of such low-viscosity fluids requires special devices (see Chapter 10). Therefore, macromerization, that is, the use of prepolymerized or polymerized raw materials (reactive oligomers or polymers), and their postpolymerization have been preferred. The polymerization techniques for UV-polymerizable PSAs from thickened monomer blends and from prepolymerized monomer mixtures are described by Do and Kim in Ref. [20]. The manufacture of UV-cross-linkable acrylates is discussed in this paper as well.

Technological reason and insufficient progress in acrylic hot melts forced the development of oligomer-based and macromer-based curable formulations. Macromerization includes the synthesis of a relatively low-molecular-weight polymer and its polycrimerization or cross-linking [13]. The use of macromers is not new. It was developed as graft copolymerization and cross-linking of plastomers. In water-based systems, adhesive modification by macromers is known as well. This method can be considered a development of the use of thickened monomer mixtures. In this case, thickening is carried out with a reactive prepolymer. In the first step, this prepolymer is either a viscous liquid or a solid that can be melted. (For instance, for filled, UV-cured self-sustaining
pressure-sensitive tapes, the monomers may be partially polymerized—prepolymerized—to a coating viscosity of 1–40 Pa · s before the microbubbles are added. In the next step, the prepolymer is blended with additives such as UV-reactive diluents, photoinitiator, and antioxidants to provide a curable PSA. The macromer (polymeric precursor) formulations start from monomer mixtures containing a hard monomer with a high glass transition temperature ($T_g > -25^\circ C$), a soft monomer ($T_g < -25^\circ C$), a tackifying monomer ($T_g < 25^\circ C$), and multifunctional monomers (e.g., pentaerythritol triacrylate). For instance, a mixture of acrylic acid (AA)–BA–diethyl fumarate has been polymerized to a macromer, which can be coated as a hot melt and postcross-linked using EB. Macromerization appeared as a technological need, but it also offers major formulation advantages. It is a new tool to design segregated polymer structures. The raw materials used for macromerization are discussed in detail by Benedek in Ref. [13].

The best known, classic, oligomer-based systems are the polyurethane adhesives and the solventless silicones [26] (see also Chapter 9). Light-curable, functionalized oligomers, based on polyisoprene (PI) and poly(ethene–butene) were developed. They are low-molecular-weight products with special functional groups polymerizable by cationic UV curing. For instance, the product of Shell (EKP-207) is an epoxidized mono-ol, and L-1203 is a mono-ol. Such a product has a primary functionality on one end and epoxidized PI on the other end. Its fully saturated backbone consists of poly(ethene–butene) rubber; its glass transition temperature is $-53^\circ C$. The other polymer, L-1203, is a linear poly(ethene–butene) rubber with a terminal aliphatic primary hydroxy group on one end (see also Chapter 3). Such products were recently tested as mounting adhesives in the automotive industry [27–29]. Epoxidization as method to enhance UV light-induced polymerization ability is used for silicone release as well (see Chapter 9).

The most used prepolymers are acrylates or possess acrylate units as reactive sites. Photopolymerizable radical and cationic polymerizable formulations were developed. Cationic formulations contain carboxylate oligomer, cationic photoinitiator, and a photosensibilizing agent. The free-radical polymerizable formulation is based on urethane–acrylate and contains a urethane–acrylate oligomer, acrylate monomer, ketone photoinitiator, tackifier, thickener, and antioxidant. Low-molecular-weight (less than 5,000 Da) full acrylic oligomers, diluted with reactive monomers, were synthesized in solution polymerization [13]. Based on the need for a cost-effective low-refractive-index material, a hydrogel was developed by Chang and Holguin (see Applications of Pressure-Sensitive Products, Chapter 3) that was easily processed and had good mechanical strength. The formulation included UV-curable PEG acrylate oligomers.

The best known macromer-based products are acrylic warm melts, postpolymerized by UV light. The development of new, low-cohesion acrylic warm melts requires postcross-linking. Therefore, the large-scale application of UV-induced postcuring is enhanced by this raw material development. Such a polymer is, before cross-linking, a highly viscous fluid (at room temperature), which can be processed at 120–140°C (common hot-melt PSAs (HMPSAs) are processed above 170°C) with a viscosity of about 10–20 Pa · s (common HMPSAs have a viscosity of 80 Pa · s); its coating technology is described in Chapter 10.

Such acrylic warm melts were BA acrylate, vinyl acetate (VAc), AA, etc.) with a small amount of UV-reactive comonomer (e.g., unsaturated benzophenone derivative) and
Technology of Pressure-Sensitive Adhesives and Products

with varying contents of 2-hydroxyethyl methacrylate [13]. The photoreactive, solvent-free acrylic PSA is made by a one-pot, two-step reaction that eliminates the gelation problems. Monomers are polymerized by solution techniques to form a high-solids (50–80%) acrylic elastomer. AA or hydroxyalkyl acrylate are used as functional monomers. After polymerization the chain is further functionalized with pendant double bonds, and the pendant hydroxyls are reacted with allyl isocyanate, maleic anhydride, 3-aminopropyl vinyl ether, or 1-(2-isocyanato-1-methylethyl)-3-(1-methylethyl) pentene or by incorporation in the polymer backbone of an unsaturated photoinitiator. Photoreactivity adjustment of the acrylic PSA is achieved by polymerization of unsaturated or additionable photoinitiator with a double bond suitable for polymerization that builds a UV-polymerizable compound with spacers and chromophoric parts, or is polyadditioned on reactive chemical groups (e.g., COOH, OH). Such compound with spacers and chromophoric parts is photopolymerizable [30].

The manufacture and performance characteristics of UV-cross-linkable acrylic hot melts with built-in photoinitiators are discussed in detail by Do and Kim in Ref. [20]. Such monomer-free and double-bond-free acrylic polymers do not cause skin irritation, so they can be used for medical applications (see Applications of Pressure-Sensitive Products, Chapter 4). In the future, macromerization may be used on a large scale. Typical representatives of radiation-curable oligomers and polymers are listed in Table 1.4.

UV light-cross-linkable PSAs and UV light-polymerizable PSAs were investigated comparatively by Do and Kim [20]. Improved curing ability of SBCs was achieved by functionalization of the mid-diene sequence and a mercaptopropionate derivative.

<table>
<thead>
<tr>
<th>Chemical Composition</th>
<th>Reactivity</th>
<th>Commercial Name</th>
<th>Viscosity (Pa·s)</th>
<th>Processing Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrylic oligomer</td>
<td>UV curable</td>
<td>Acronal DS 3429</td>
<td>10–20</td>
<td>120–140</td>
</tr>
<tr>
<td>Polyurethane acrylate oligomer</td>
<td>UV curable</td>
<td>—</td>
<td>10–15</td>
<td>120</td>
</tr>
<tr>
<td>Polyester-acrylate oligomer</td>
<td>UV curable</td>
<td>—</td>
<td>2–10</td>
<td>100</td>
</tr>
<tr>
<td>Poly(ethylene–butene) functionalized oligomer</td>
<td>EB curable</td>
<td>—</td>
<td>20</td>
<td>100</td>
</tr>
<tr>
<td>Styrene block copolymer</td>
<td>UV curable</td>
<td>Kraton LLC</td>
<td>5–80</td>
<td>175</td>
</tr>
<tr>
<td>Epoxidized block copolymer</td>
<td>UV curable</td>
<td>EKP-200, L-1203</td>
<td>80</td>
<td>175</td>
</tr>
<tr>
<td>SIS star block copolymer</td>
<td>UV curable</td>
<td>Kraton EKP 207</td>
<td>Kraton 1320X</td>
<td>70</td>
</tr>
<tr>
<td>Styrene–butadiene–styrene radial block copolymer</td>
<td>EB curable</td>
<td>—</td>
<td>60</td>
<td>175</td>
</tr>
</tbody>
</table>

© 2009 by Taylor & Francis Group, LLC
A complex cross-linking system for an optically clear PSA used as a mounting aid in electronics, which includes various mechanisms, is described by Chang and Holguin in *Applications of Pressure-Sensitive Products*, Chapter 3. Using different chemistries and curing processes, an optically clear adhesive was developed for the needed complex transition from a removable PSA to a permanent PSA and, finally, a structural adhesive for this application. The first stage of product manufacturing utilized ionic cross-linking of the acrylic polymer during the coating and drying phase. The second stage used UV curing for cross-linking the urethane oligomer, which forms an interpenetrating network, and the third stage used thermal curing to completely cross-link the acrylic polymer. Such a typical, curable PSA blend has the following composition: 70.0 pts acrylic PSA (dry weight basis), 30.0 pts aliphatic urethane diacrylate, 1.4 pts benzophenone (photoinitiator), 1.4 pts methdiethanolamine (photoinitiator), 0.6 pts aluminum acetyl-acetonate metal chelate ionic cross-linker, and 0.6 pts methacrylated silane cross-linker.

The formulation of radiation-curable adhesive compositions is discussed in Chapter 8. Foreman et al. used a saturated hydrocarbon macromer [e.g., poly(ethylene–butylene) methacrylate], to create a grafted acrylic–rubber PSA. The rubber phase is compatible with hydrocarbon resins, including fully saturated resins (see Chapter 5).

### 1.1.2.2 Technology of In-Line Synthesis

Based on the experience of radiation curing of thin coatings from printing technology, in-line coating and polymerization of the base monomers (actually a blend of monomers, oligomers, and reactive diluting agents) were carried out to manufacture PSA-coated laminates. The main problems with this (syrup) technology had to do with chemistry, physiology, and rheology. Later, polymerization (with nonreactive polymers) of thickened reaction mixtures was developed. In the next step, advances in macromolecular chemistry allowed macromerization, that is, polymerization of oligomers (mixed with reactive monomers or pure). Thus, radiation-curable warm melts (i.e., polymers with a low softening point and viscosity) and hot melts were manufactured. Their manufacture technology as a high-solids-content polymer solution is described by Benedek in Ref. [24]. Their manufacture technology in an extruder, followed by postcoating, radiation-induced polymerization, is discussed by Czech in Ref. [17]. In a different manner from off-line synthesis, which generally leads to pressure-sensitive raw materials, that is, compounds that must be transformed in a finished PSA by the formulator (except ready-to-use products), in-line synthesis must produce a finished PSA or a finished PSP. Therefore, in this case, formulation is included in polymer synthesis, and formulating additives may interact with the components of the polymerization recipe.

Adhesive formulations for UV light-induced curing and EB curing were developed (see also Chapter 8). The polymerization conditions for UV light-induced and EB-initiated curing are quite different. The UV light-induced photopolymerization of acrylics uses 280–350 nm light, with an intensity of 4 mw/cm² at the surface. The efficacy of UV curing depends on the emission spectrum of the UV lamp, the photoinitiator (its absorption in the emission domain of the lamp), and the transmittance of the UV light-cured layer. The length of polymerization zones and the density of lamps in these zones affect the manufacturing process. Because of the relatively low energy density, the maximum web...
width and running speed of UV-curing lines is limited. Cooling is provided by low-temperature nitrogen gas. The chamber has an atmosphere of nitrogen. Inerting with nitrogen is of no benefit for cationic UV light-induced polymerization, where humidity hinders cross-linking. Although inertization costs about $0.001–0.002/m², inertized UV light systems are preferred because they allow a polymerization yield of 95%. A UV light-curing device is the easiest to add to existing equipment. The capital costs for UV lamps are much lower than for thermal systems and, compared with thermal curing systems, UV systems demand only 1% of the energy consumption. Technological details (equipment) of the UV light-curing system are described in Refs [13,31] and in Chapter 10. The mechanism of UV light-induced photopolymerization and the cross-linking agents and photoinitiators used were described in detail in Refs [13,20,31]. For common PSPs, a comparison of UV-curing displays with EB (and thermal) curing resulted in the following disadvantages: rough paper surfaces are unsuitable and curing is insufficient and not applicable for laminates. Because the adhesive layer absorbs radiation, UV-curable products must have a limited coating weight.

EB curing has the advantage of high coating weights (50–80 g/m²). For pigmented layers it can use a coating weight of 300 g/cm², compared with 50–80 g/m² for UV light-cured systems. UV light-induced curing allows running speeds of 100–200 m/min in comparison to EB-curing lines, at 100–500 m/min. Ozone formation must be avoided by nitrogen injection or by exhausting. EB-induced curing is color blind and dries all compositions with the same speed. It can cure thick films, even through opaque surfaces, but it must operate in a sealed, pressurized chamber using nitrogen or carbon dioxide. Low and no inert gas curing were developed [24]. Hybrid systems with combined UV light/EB or hot air/EB were developed as well [13]. UV/EB cure mechanisms are also used with silicone PSAs, with the advantages of much lower energy requirements and a smaller equipment footprint. Two recent patents describe the use of UV/EB cure with and without thermal activation of the initiator [26]. A silicone PSA composition that uses a thermal/UV dual-cure mechanism to leverage the benefits of UV cure and the properties of thermal-cured silicone PSAs have been described [32]. A comparative examination of UV-induced and EB curing is given in Table 1.5.

### 1.2 Basic Products for Pressure-Sensitive Adhesives

In their first stage of development PSAs were formulated on the basis of natural macromolecular products. Natural rubber (NR) and natural resins were used. Some decades ago, synthetic elastic components (rubbers) and viscous raw materials (tackifiers, plasticizers, etc.) were developed and blended to produce (formulate) the adhesive. Advances in macromolecular chemistry allowed the synthesis of raw materials with built-in viscoelastic properties, that is, pressure sensitivity [e.g., acrylics, VAc copolymers, carboxylated rubber, polyvinyl ethers (PVEs), polyurethanes (PURs), polyesters, etc.]. Some polymers used for PSAs are raw materials for other adhesives or plastics. Their synthesis involves a special chemical/macromolecular technology. It is not the aim of this book to describe the technology. The main basic products used for pressure-sensitive formulation, that is, the elastomers (random, alternative, and block
copolymers) and the viscoelastomers (e.g., acrylics, VAc copolymers, and other vinyl polymers) are briefly presented here, allowing their detailed discussion in Chapters 2 through 8, a description of the role of PSA formulation based on these raw materials (Chapter 8), tackifiers and tackification (Chapters 8 and 3), and the manufacture of PSAs and PSPs (Chapter 10).

### 1.2.1 Elastomers

As discussed in detail in Refs [33–35], PSAs are characterized by special rheology and viscoelasticity (see also Fundamentals of Pressure Sensitivity, Chapter 4). Therefore, their first raw materials were natural and synthetic compounds that display elasticity, that is, their existent elastic network must only be “softened” to achieve pressure sensitivity. NR and some diene-based homopolymers or random and alternative copolymers are such materials. PSAs on a different chemical basis were examined comparatively by Benedek in Ref. [36], rubber-based adhesives were evaluated in comparison to acrylics, and acrylics were examined in comparison to other synthetic polymer-based elastomers. In a similar manner, Chapter 2 deals with the specific aspects of rubber-based adhesives, taking into account the advances in this domain.

---

**TABLE 1.5 Advantages and Disadvantages of UV Light- and EB-Induced Curing**

<table>
<thead>
<tr>
<th>UV Light-Cured Systems</th>
<th>EB-Cured Systems</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Advantages</strong></td>
<td></td>
</tr>
<tr>
<td>Nonexpensive equipment</td>
<td>Adequate for most common PSAs with low cross-linking density and $T_g \leq -20^\circ C$.</td>
</tr>
<tr>
<td>Color blind</td>
<td>Color blind</td>
</tr>
<tr>
<td><strong>Disadvantages</strong></td>
<td></td>
</tr>
<tr>
<td>Need for reactive sites</td>
<td>Need for vinyl unsaturation</td>
</tr>
<tr>
<td>Need for photoinitiator or built-in photosensitive site</td>
<td>—</td>
</tr>
<tr>
<td>Need for special tackifier resins</td>
<td>—</td>
</tr>
<tr>
<td>Need for special stabilizers</td>
<td>—</td>
</tr>
<tr>
<td>For monomer-based formulations, need for thickeners</td>
<td>—</td>
</tr>
<tr>
<td>For monomer-oligomer based formulation, need for diluting monomers</td>
<td>—</td>
</tr>
<tr>
<td>Need for cross-linking monomers 10% bw</td>
<td>For improved efficacy, need for cross-linking monomers 1–5% bw</td>
</tr>
<tr>
<td>Limited running speed</td>
<td>Expensive equipment</td>
</tr>
<tr>
<td>Limited coating weight</td>
<td>Carrier damage</td>
</tr>
<tr>
<td>Anisotropy of the cured PSA layer</td>
<td>—</td>
</tr>
<tr>
<td>UV transparency required</td>
<td>—</td>
</tr>
<tr>
<td>Oxygen or humidity-sensitive, inerting required</td>
<td>Sealed, pressurized chamber required</td>
</tr>
<tr>
<td>Low-energy consumption compared with thermal curing</td>
<td>—</td>
</tr>
<tr>
<td>Rough paper surface inadequate</td>
<td>—</td>
</tr>
<tr>
<td>Not usable for laminate</td>
<td>—</td>
</tr>
</tbody>
</table>
1.2.1.1 Common Rubber-Based Adhesives

Natural rubber-based PSAs were the first self-adhesive products used for the manufacture of PSPs. Although NR is self-adhesive, most elastomers must be transformed into viscoelastomers to display usable pressure sensitivity (i.e., they must be tackified). The special structure of common elastomers, consisting of their high, so-called rubber-like elasticity, which is related to their partially cross-linked structure allowing strain hardening, offers a large range of modalities (tackification, plasticization, cross-linking, filling, etc.) for their formulation [13]. NR and elastomers based on homopolymers and random and alternative copolymers [e.g., diene homo- and copolymers and polyisobutene (PIB)] are the main representatives of this raw material class. NR as a base elastomer for rubber–resin PSAs is described in Chapter 2 by Martin-Martinez. Although they have a molecular structure that imitates NR, stereoregulated synthetic elastomers have only a limited use for PSAs. Screening formulations with such polymers are listed by Benedek in Ref. [13]. Styrene–diene copolymers are discussed in Chapter 2 by Martin-Martinez.

Later, thermoplastic elastomers were developed that are rubber-like and plastic-like polymers. Such so-called thermoplastic elastomers (TPEs) have a partially cross-linked structure like common elastomers, which imparts elasticity. These new, segregated, block copolymer-based thermoplastic elastomers must imitate the multiphase construction and the elastic behavior of NR. In this case, the partially cross-linked structure (segregation) is based on physical, thermally instable bonding, which allows the thermal, plastic-like processing of such elastomers. The first thermoplastic elastomers were based on styrene–diene copolymers. Advances in macromolecular chemistry and technology allowed the synthesis of a broad range of TPEs based on other monomers and with quite different build-up.

Thermoplastic elastomers were discussed in detail in Refs [4,13,25,37]. Advances in their domain will be described by Hu and Paul in Chapter 3, in which distinctive features of the mechanical and adhesive properties of styrene–diene-based block copolymers are considered compared with the properties of PSAs of others classes. The synthesis methods of styrene–diene block copolymers with different (e.g., linear, radial, tapered, etc.) structures are described; star polymers and oligomer-modified star polymers and multiblock polymers are examined in comparison to olefin- and acrylate-based block copolymers. Their tackification, based on selective compatibility, is also investigated (see also Chapter 8). The features of block copolymers, that is, their mechanical properties (e.g., tensile strength, creep, etc.), and their adhesive properties (tack, peel resistance, and shear resistance) are also investigated. Processing and limitations in the use of TPEs are also discussed. The viscoelastic properties and adhesive performance of special block copolymers and their blends [e.g., styrene–isoprene–styrene (SIS) + styrene–isoprene (SI), SIS, SI4 + SI] are examined in Fundamentals of Pressure Sensitivity, Chapter 5, by Chang.

In the range of elastomer-based PSPs, PIB-related PSAs constitute a special class with an old and large application field. Owing to their classic synthesis, which allows the manufacture of various, well-characterized products ranging from liquids to solids, they were used for tapes in different end-use domains (see Applications of Pressure-Sensitive Products, Chapter 4). Owing to their systematic investigation (including the means of
macromolecular chemistry, physics, and contact mechanics), their application performance characteristics can be easily related to their fundamental aspects, that is, they serve as model compounds. Chapter 4 discusses the fundamentals and special properties of PIB adhesives. The rheology, viscoelasticity, and adhesion of PIB-based PSAs are described. The formulation and use of PIB and butyl rubber-based PSAs is discussed by Martin-Martinez in Chapter 2 as well.

1.2.1.2 Special Elastomer-Based Adhesives

Elastomers based on heterocompounds (e.g., acrylics [4,13], PEs [4], PURs [4,13], and silicones [4]) are also used as raw materials for PSAs.

A comprehensive examination of the developments in silicone PSAs is given by Lin et al. in Ref. [26]. Developments in silicone PSAs are discussed in detail in Chapter 6 by Lin. As noted, liquid solventless and high-solids PSA compositions that can be applied using traditional application methods necessitate the use of lower viscosity, more highly functional silicone polymers and MQ resins, which are inherently stable. Thus, the use of silanol-functional, short-chain silicone polymers is largely excluded, leading developers to use additional or UV-curable silicone systems with components containing silicon-bonded hydride with silicon-bonded vinyl or silicon-bonded epoxy or acrylate functionalities. The use of short-chain fluids in PSA applications can provide adequate tack and adhesion, but leads to high-temperature stability and performance issues, which can be overcome through raw material selection or cure methodology [38–40]. Solvent-resistant silicone PSAs were also developed. Eckberg and Griswold [41] determined that tackifying MQ resins undergo facile reaction with fluoroalkylsilanes to provide modified MQ resins compatible with fluorosilicone gums. Fluorinated silicone resin and fluorosilicone gums combine to yield compositions with PSA properties similar to those of conventional silicone PSAs, with the added virtue of resisting solvent attack by hydrocarbon solvents. Noncoupled fluorosilicone PSA compositions have significantly improved solvent resistance, but inferior peel adhesion as a function of the fluoro content of the fluorosilicone gum. Coupled fluorosilicone PSAs can be prepared with peel resistance approaching that of conventional methyl silicone PSAs without sacrificing solvent resistance by proper selection of gum fluoro content and resin/gum (R/G) ratio. These new adhesives may be laminated to conventional silicone release liners to form pressure-sensitive constructions that can be readily packaged and dispensed. Additional details on the basics of silicone PSA synthesis can be found in Refs [42–48]. Sheridan [49] combined the properties of silicone with those of urea block copolymers to build stretchable, releasable constructions that adhere to low-energy surfaces.

The development of full acrylic counterparts of SBCs has been a long sought after goal [50]. Owing to the inherent and adjustable adhesion of acrylics, acrylate block copolymer systems are expected to perform better in terms of durability, resistance to photodegradation, heat resistance, tack, and moisture vapor transmission rate compared with SBCs. Unfortunately, common synthesis methods and polymer topology lead to high-molecular-weight polymers that are not processible as typical hot melts. In the past decade, major advances to gain control over radical polymerization have been realized. Among the new polymerization techniques, the atom transfer
radical polymerization (ATRP) stands out as a very efficient and practical method to prepare (meth)acrylic block copolymers of different architectures. Many examples of polymethacrylate–block–polyacrylate–block–polymethacrylate copolymers prepared by controlled radical polymerization exist in the literature [51]. Some work on the use of formulated acrylic block copolymers as PSAs has been published. These reports essentially deal with linear triblock copolymers based on poly(n-butyl acrylate) (as the central segment), prepared either by atom transfer radical polymerization or by living anionic polymerization [52–55]. Simal et al. [50] used ATRP to prepare a four-branched radial block copolymer in a one-pot, two-step synthesis. Other works used multivalent chain transfer agents [56] and living radical polymerization [57, 58]. Anionic methods have the advantage of better control of polymer architecture [59] and tacticity [60, 61]. Smit et al. [61] synthesized acrylic block copolymers for HMPSAs with methyl methacrylate for the hard phase and a low \( T_g \) monomer with lower polarity (e.g., butyl acrylate) for the soft phase. Such soft polymers are suggested mainly for medical use (see also Applications of Pressure-Sensitive Products, Chapter 4). Developments in acrylic block copolymers are described by Hu and Paul in Chapter 3.

It is well known from the practice of film- and fiber-forming acrylics that due to the associative possibility of the nitrile group in acrylonitrile and the (physically segregated) microdomains in such polymers, improved mechanical characteristics are obtained. It is astonishing that this “block forming” tendency is not yet used in the design of acrylic TPEs. Advances in elastomers and their cross-linking are discussed in Chapter 8.

Thermoplastic urethane elastomers (TPU) have become well-established commercial materials since their inception in the B.F. Goodrich research laboratories in the 1950s. Chemically, TPUs comprise essentially linear polymer primary chains that are segmented in structure. They contain alternating sequences (blocks) of low \( T_g \) (soft) segments and high \( T_g \) (hard) segments, which are joined together end to end with covalent chemical bonds. In the solid polymer the hard segments tend to associate strongly through urethane hydrogen bonding and \( \pi \)-electron attractions. As demonstrated above, such segregated structures (i.e., virtual cross-links of the hard segments) permit valuable thermoforming and solution applications of the tough, strong TPUs. The advantages of PUR elastomers were first used in common laminating and mounting adhesives, but in past decades PSAs were developed as well. Advances in this domain are described in Chapter 11.

**1.2.2 Viscoelastomers**

Polymers with built-in viscoelasticity possess a broader chemical basis for the manufacture of all adhesive classes (i.e., 100% solids, solvent-based, and water-based formulations) than pure elastomers. Some can be used as raw materials for noncoated PSP components. Of these compounds, acrylics are the most used.

Acrylics were developed as a raw material for PSA in the form of elastomers (rubbers) and viscoelastomers. Acrylic copolymers were the first class of viscoelastomers used for PSAs. Random and block copolymers have been synthesized as acrylic rubber. Both can be applied for solvent-based or HM adhesives. A wide range of acrylics is supplied as water-based dispersion. Recently, ready-to (in-line)-use acrylic oligomers were developed
Pressure-Sensitive Raw Materials

Advances in polymer chemistry and technology supplied a large range of viscoelastomers that are usable as pressure-sensitive raw materials, threatening the leading position of acrylics in this domain. Acrylics are available as solvent-based, water-based, and 100% solids. They are supplied as common acrylic rubbers and thermoplastic elastomers as well. Owing to their very large monomer basis, their polymerizability by various procedures (including in-line technology-required radiation-induced polymerization), their built-in pressure sensitivity (which can be, if necessary, easily regulated by tackification, cross-linking, etc.), and their excellent aging and physiological properties, acrylics remain the main class of pressure-sensitive raw materials. Functionalized acrylics can be used for special products. For instance, side-chain fluoroacrylate monomers such as H,\textsuperscript{1}H-pentadecafluoro-octyl acrylate and H,\textsuperscript{1}H-heptafluorobutyl acrylate were used together with a nonfluorinated comonomer (acrylic acid) to obtain low-refractive-index polymers (see Applications of Pressure-Sensitive Products, Chapter 3). UV curing of urethane diacrylate was combined with thermal curing to obtain a structural adhesive used in electronics by Chang and Holguin (see Applications of Pressure-Sensitive Products, Chapter 3). Advances in macromolecular synthesis led to acrylic hydrogels (based mostly on hydroxyethyl acrylate) that are curable chemically or by radiation. Their use in electronics is discussed in Applications of Pressure-Sensitive Products, Chapter 3, by Chan and Holguin. Acrylic hydrogels are examined in comparison with other products in Chapter 7 by Feldstein et al. In Chapter 5, Foreman describes acrylic adhesives.

VAc copolymers are the main competitors of acrylics as raw materials for viscoelastomers and elastomers [4,13]. The first trials of incorporating polar monomers in ethylene [or ethylene–vinyl acetate (EVAc)] copolymers were carried out with acrylates. Unfortunately, faster reacting acrylates (relative to ethylene or VAc) have a tendency toward block copolymerization with vinyl acetate. The disparity in the reactivity ratios between ethylene and acrylates with respect to VAc also limits ethylene incorporation into a terpolymer system. Maleates (or fumarates), on the other hand, do not readily homopolymerize, leading to alternating copolymers with vinyl acetate; this, coupled with a much more favorable reactivity toward VAc and ethylene, enables the production of terpolymers with an increased ethylene content. The two preferred comonomers among EVAc terpolymers for optimal pressure-sensitive performance are dioctyl maleate and 2-ethylhexyl acrylate (2-EHA). The higher molecular weight of dioctyl maleate allows a lower molar fraction, permitting a higher ethylene content. Thus, polymers commercialized by National Starch contain 20% or more ethylene by weight. Acrylic and ethylene copolymers may be incorporated in aqueous EHA-based PSA systems. VAc displays excellent copolymerization ability with a broad range of common and special monomers. The homopolymer of this classic monomer was used on a large scale for common non-PSAs and was the most used and investigated material in this domain. The copolymerization of VAc with nonpolar and polar comonomers (e.g., ethylene, acrylates, maleinates) leads to products with self-adhesivity (see Applications of Pressure-Sensitive Products, Chapter 7), which can be easily regulated by the nature and ratio of comonomers, copolymerization technology, by formulation and application conditions. Thus, VAc are used for PSPs as carrier materials, adhesives, and release materials. Like acrylics, they can lead to rubber-like as well as thermoplastic products. They are used as solvent-based, water-based, and 100% solids.
Chapter 6 describes the silicone-based PSAs as competitors of acrylics. Silicones are a class of heteropolymers that (due to the special nature of the silicone–carbon bond), display valuable application properties. They present increased thermal resistance coupled with positive physiological characteristics (see also Applications of Pressure-Sensitive Products, Chapter 4). Owing to numerous chemical possibilities, various synthesis methods can be used to incorporate different monomers into polysiloxane, and due to the regulation of the organic/inorganic ratio in the polymer and other macromolecular characteristics, it was possible to fine-tune the adhesive properties, leading ad absurdum to nonadhesive products used as release liners (see Chapter 11). Silicone-based adhesives were described in Refs [4,15,26]. Recent advances in this domain are presented by Li in Chapter 6.

As mentioned in Section 1.1.1.2, a special class of PSAs is based on simultaneous cross-linking/plasticizing of common, non-pressure-sensitive plastomers like PVP. In this manner, hydrophilic polymers are manufactured. Hydrophilic PSAs were discussed in detail in Refs [16,62,63]. Chapter 7 describes the advances in synthesis and application of such hydrogels, including bioadhesives.

Urethane derivatives display an increased reactivity and, therefore, are used as monomers (for polymerization, polyaddition, or polycondensation) and as cross-linking agents for various classes of other pressure-sensitive raw materials [4,15,31]. Their polymers form films as well, and such films with excellent thermal and chemical resistance are used as carrier materials for PSAs [4]. PURs as adhesive raw materials were used mostly for common, lamination adhesives, as solvent-based or water-based compositions. Developments in this field allowed the synthesis of block copolymers [24]. Urethane derivatives are used as a release material for PSAs as well [64]. Advances in PUR chemistry supplied new raw materials that can be used for the formulation of PSAs. Developments in this domain are described by Czech and Hinterwaldner in Chapter 11.

### 1.2.3 Viscous Components

The formulation of elastomer–based or viscoelastomer–based PSAs uses viscous components for tackification. Tackier resins and plasticizers are added to the recipe. Tackifiers were described in our previous works [4,24,37]. Advances in chemistry and the use of tackifiers are discussed in Chapter 8. Tackification, especially selective tackification for segregated polymers, is discussed by Hu and Paul in Chapter 3.

### 1.2.4 Comparison of PSAS on a Different Chemical Basis

PSAs on a different chemical basis were compared by Benedek in Ref. [30]. Rubber-based versus acrylic-based PSAs were examined comparatively, taking into account their common and special adhesive properties and stability. Rubber–resin-based adhesives possess excellent tack and peel resistance but remain defensive in shear resistance. Table 1.6 compares the various base polymers used as PSA raw materials.

Acrylic PSAs offer a unique combination of performance advantages relative to hydrocarbon-based rubber–resin adhesives and are used extensively in end-use markets that demand excellent color and clarity, weatherability, durability, and plasticizer migration resistance. Acrylic PSAs also display better specific adhesion properties. Generally, the
### TABLE 1.6  Comparative Examination of the Main PSA Raw Materials

<table>
<thead>
<tr>
<th>Performance</th>
<th>Acrylic</th>
<th>EVAc</th>
<th>NR</th>
<th>SBC</th>
<th>SBR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw materials</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Copolymerizable with various acrylic, vinyl, and diene comonomers</td>
<td>Limited copolymerization</td>
<td>Only polymer analogous reactions and depolymerization possible</td>
<td>Limited comonomer availability</td>
<td>Limited comonomer availability</td>
</tr>
<tr>
<td>Synthesis/ manufacture</td>
<td>1</td>
<td>2</td>
<td>4</td>
<td></td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>Off-line and in-line; free-radical, ionic, etc., mechanism; thermal- and radiation-induced polymerization possible</td>
<td>High pressure required; only off-line free-radical polymerization possible</td>
<td>—</td>
<td>Limited expensive technology</td>
<td>Limited expensive technology</td>
</tr>
<tr>
<td>Formulability</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Compatible with various base polymers and tackifiers</td>
<td>Limited compatibility</td>
<td>Compatible with various base polymers and tackifiers</td>
<td>Limited compatibility with common tackifiers; limited cross-linking ability</td>
<td>Limited compatibility with other base polymers and tackifiers</td>
</tr>
<tr>
<td>Grades</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Monomers</td>
<td>1</td>
<td>2</td>
<td>—</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>Limited choice</td>
<td>—</td>
<td>Limited choice of hard block</td>
<td>Limited choice of styrene derivative</td>
<td>—</td>
</tr>
<tr>
<td>Oligomers</td>
<td>1</td>
<td>4</td>
<td>3</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>No commercial product</td>
<td>Limited choice</td>
<td>Special functionalized products only</td>
<td>No commercial product</td>
<td>—</td>
</tr>
<tr>
<td>Block copolymer</td>
<td>4</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Solvent-based</td>
<td>1</td>
<td>4</td>
<td>1</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>Water-based</td>
<td>1</td>
<td>1</td>
<td>—</td>
<td>1</td>
<td>—</td>
</tr>
<tr>
<td>Hot-melt PSA</td>
<td>4</td>
<td>—</td>
<td>1</td>
<td>1</td>
<td>—</td>
</tr>
</tbody>
</table>

*Note: 1–4 denotes the adequacy of a base polymer to be used as a PSA raw material.*
advantages of acrylic systems include chemical and water resistance, UV and oxidative stability, heat resistance, tack at varying temperatures, and the balance of adhesive and cohesive properties. As noted in Refs [17,20], acryliics are also used in special domains, such as water-soluble adhesives (for splicing tapes, bottle labels, and various medical products; see also Applications of Pressure-Sensitive Products, Chapter 4) or for removable adhesives. Acrylics are the most used monomers, oligomers, and polymers employed for radiation-induced in-line manufacture of PSAs and PSPs (see also Section 1.1).

Rubber–resin adhesives provide a compromise of high cohesive strength for conformance to curved substrates and good tack required in automatic labeling, but they exhibit varying batch-to-batch consistency and can cause staining problems. On the other hand, their high cohesive strength, softness, good anchorage, and high conformance make them absolutely necessary for processing-protection films (see also Applications of Pressure-Sensitive Products, Chapter 4). Low-energy carrier materials and soft, rubber-based PSAs bond fairly well (anchorage), but they are difficult to convert, whereas acrylics convert well, but exhibit low anchorage. Properties that are correlated with the chemical instability of a rubber–resin basis (e.g., temperature and light resistance) and the pronounced liquid character of the rubber–resin mixture (e.g., cold flow and shear sensitivity) remain inferior for rubber–resin PSAs compared with acrylic PSAs (see also Applications of Pressure-Sensitive Products, Chapter 8). Rubber–resin PSAs based on TPEs display inferior cuttability, resistance to migration, and thermal and UV stability in comparison with acrylics (see also Chapter 10 and Applications of Pressure-Sensitive Products, Chapter 8).

Acrylics were compared with other synthetic polymer-based elastomers in Ref. [36]. The tack of unformulated acrylic PSAs is lower than that of tackified, rubber-based PSAs [e.g., EVAc and carboxylated butadiene rubber (CSBR)], but higher than that of other untackified adhesives, except PVEs. Acrylics possess better tack at any coating weight level. The tack of formulated acrylics was examined taking as criterion the ease of tackification, tackifier level and tack level. Acrylics possess good overall compatibility with common tackifiers, which can be fed into as solutions or dispersions to water-based acrylics. A level of 30–40% (by wet weight) tackifier resin is commonly used for acrylics, and a tackifier level of 10–20% suffices for tack improvement of acrylic PSAs. The suggested tackifier level for PSA formulations on different chemical bases (e.g., acrylic, vinyl–acrylic, SIS, SBR, and EVAc) is discussed by Benedek in Ref. [36]. Acrylics need a lower tackifier concentration for maximum tack than CSBR or vinyl acrylics, and the tack maximum (as a function of tackifier concentration) is broader. Generally, the ease of tackification depends on the chemical composition and structure of the polymer. High-molecular-weight acrylic dispersions yield a low tackifying response. The tack level of tackified acrylic PSAs is superior to that of tackified EVAc, but lower than the tack of tackified CSBR (see also Chapter 2 and Ref. [36]).

The special features of water-based acrylic PSAs compared with other water-based PSAs were discussed in Ref. [36]. Generally, water-based acrylic PSAs possess a higher solids content and a higher solids content/viscosity ratio than common CSBR or EVAc dispersions; they also respond better to diluting. Water-based acrylic PSAs exhibit a lower surface tension than common CSBR or EVAc dispersions. On the other hand, water-based acrylics show higher coagulum (grit) than CSBR dispersions, although they display...
better mechanical stability than CSBR. They generate less foam formation than CSBR and EVAc. Water-based acrylics demonstrate better wet-out properties and can be converted at higher speeds than EVAc and CSBR dispersions. Solvent-based acrylics have some special characteristics compared with classic, rubber–resin PSAs. They have a higher solids content (20–30%), and the solids content/viscosity ratio can be adjusted exactly. Generally, special solvents are used [17,21,24,36], and both solutions or dispersions can be produced. In general, if fewer or no plasticizers and antioxidants are used, cross-linking is possible. Cross-linking of acrylics was discussed in detail by Czech in Ref. [31].

As illustrated in Chapter 8, which discusses the role of formulation and the main formulation modalities, softening of the elastomers and viscoelastomers by tackification (and plasticization) and their cross-linking produce macromolecular composites. As described in Chapter 10, the manufacture of PSPs leads to laminates, which are macroscopic composites. That means that PSPs must be evaluated as heterogeneous structures (systems), that is, as multiple composites. In the next section, the multiple composite build-up of PSPs as a whole will be briefly examined.

### 1.3 Pressure-Sensitive Products as Composites

The best known pressure-sensitive raw material (the model compound) is NR. Its build-up illustrates that an adequate balance of the plasticity and elasticity of a macromolecular compound can be achieved by a network structure. Such a network contains rigid, cross-linked parts and flexible, linear parts. The cross-linked part may suffer deformation and the non-cross-linked parts can undergo chain entangling. According to a general concept, such a network is a composite.

Principally, a composite includes a matrix and a reinforcing element. The matrix is the soft (plastic/elastic) continuum that contains a rigid (elastic/plastic) discontinuum. The flow of such a structure is ensured by the matrix; its deformation stability is the result of the interaction of the reinforcing element with the matrix. Bonding needs flow and debonding needs stability against deformation. Such deformation may be plastic or elastic, permanent or temporary.

Recent advances in PSPs lead to composites on a macromolecular level, on a macroscopic level, and on a product construction level. The influence of the composite structure on the PSA was discussed by Benedek in Ref. [33].

#### 1.3.1 Pressure-Sensitive Products as Composites on a Macromolecular Scale

Composites on a macromolecular scale include synthesized and formulated composites. Macromolecular compounds can be built up as a composite or they can be mixed into a composite. Synthesized macromolecular composites contain (like NR) a network structure. “Mixed” macromolecular composites work like filled systems, where the rigid component acts as a filler in a soft macromolecular matrix. Generally, the range of the interchain interactions may differ and, thus, more or less tightly bonded networks are formed. In the case of synthetic macromolecular composites the polymeric network can
be the result of chemical interactions (e.g., chemically cross-linked systems) or physical interchain interactions (e.g., physical association).

As noted in Ref. [10], filled systems are special compositions, where the role of the filler can be played by various components (e.g., crystallites, polymer sequence, or fillers). Multiphase rubbery polymers can be considered elastic networks or filled systems. The stress–strain behavior of such polymers can be adequately modeled by the Mooney–Rivlin equation as an elastic network (considering the trapped entanglements as finite cross-link junctions) or using the Guth–Gold equation relating the stress level (modulus) to the hydrodynamic effects of the styrene blocks considered fillers. Thermoplastic elastomers with segregated structures can be considered filled systems (i.e., composites). They possess a segregated structure on a molecular scale. Their properties depend on their morphology, which is a function of the relative concentration of the components. The morphology of an SBC in its solid-state depends on its polystyrene content. Tackified TPE compositions can be considered diluted systems [37]. In this case the main polymer possesses a segregated composite structure that becomes a multiple composite by “dilution” with the tackifier. According to the filler theory, the polystyrene domains works as a filler dispersed in the continuous polydiene matrix. In this case, the plateau modulus $G^n_0$ is given a function of the density $\rho$, the molecular weight $M_c$, and volume fraction $\Phi$ of the filler,

$$G^n_0 = \left(\frac{\rho}{M_c}\right)RT(1 + 2.5\Phi + 14.1\Phi^2) \quad (1.1)$$

like the elasticity modulus $E$ in the Gooth–Smallwood [65] equation.

$$E = E_0 \left(1 + 2.5\Phi + 14.1\Phi^2\right) \quad (1.2)$$

According to Hu and Paul (see Chapter 3), the styrene hard blocks not only serve as a physical cross-linking agents, but also behave like rigid fillers in a continuous rubbery phase. Therefore, as the concentration of the hard blocks (either styrene block or the high softening point end-block tackifiers) increases, the filler content increases, and the adhesive becomes stiffer. Excessive end-block tackifier will separate from the styrene matrix and form an individual tackifier phase, acting like fillers, which could significantly increase melt viscosity and reduce adhesive tack and clarity.

The composite structure of the tackified compositions is more complex because segregation occurs in the diluted system as well. For instance, as noted by O’Brien et al. [66] by the investigation of tackified SBCs, the subsurface of the PSA demonstrates a spherical morphology characterized by glassy styrene domains in a rubbery matrix. Atomic force microscopy (AFM) images consist of white styrene domains imbedded in a multicolor matrix, suggesting that the rubbery matrix is not composed of a single phase. Rheologic evidence also supports the existence of a two-phase rubber matrix from the bimodal tan $\delta$ (see also Applications of Pressure-Sensitive Products, Chapter 8). The rubbery matrix is likely composed of a tackifier-rich phase and an isoprene-rich phase. O’Brien et al. observed an isoprene–resin phase (a resin-rich phase) and, surprisingly, a second phase composed mostly of isoprene (an isoprene-rich phase). Tse [67] and Class and Chu [68,69] also confirmed the presence of a shoulder at $\sim-40^\circ C$ using...
rheology and transmission electron microscopy in NR-based and SIS-based adhesives. However, the reasons for the existence of the third phase were not clearly explained. Except for the mid-block and end-block phases, there is an additional tackifier-rich phase in SBS tackified with hydrocarbon resins (see Chapter 3). A supramolecular ordering of spherical microdomains embedded in a continuous matrix was established by AFM for a radial acrylic block copolymer by Simal et al. [50]. Differential scanning calorimetry results also suggested that the thermoplastic microdomains are partly miscible with the tackifier. Furthermore, the radial structure of the block copolymer introduces additional chemical cross-links and, hence, produces a dense network that appreciably improves the holding power. This network provides the required cohesion for suitable adhesive performance in PSAs. In contrast, the statistical copolymer has a poor cohesive strength as a result of the low number of temporary entanglements typical for polyacrylates. A two-phase structure exists in silicone PSAs as well. A “resin-rich” phase and a “gum-rich” phase were described by Lin et al. [26]. The composite structure of tackified systems is strongly influenced by their manufacture. According to Kajiyama [70], the phase structure of PSA mixed with a tackifier in the monomer state and solution polymerized was different from that of expected from the phase diagrams of solution-blended systems.

The most important advantage of physically bonded synthetic macromolecular composites is their processibility at high temperatures, where the network dissociates. Evidently, this feature is their main disadvantage as well. Physically built-up networks have principally short and rigid bridges between the chains. To achieve a sufficient reinforcing effect, the macromolecular compound must contain a high level of physically associable component (i.e., a high concentration of long rigid sequences). Such structures are too rigid and not elastic enough. Thus, although such thermoplastic elastomers have a built-in composite structure with a soft matrix, they must achieve a supplemental composite structure based on blends with softening and tackifying components. They must be formulated (see Chapter 8). From the classic point of view, soft mixing components are low-molecular-weight (low or high modulus) compounds (plasticizers or tackifier resins) that reduce the glass transition temperature \( T_g \) of the blend and, thus, improve the fluidity of the macromolecular compound.

Advances in sequential block copolymerization allowed the synthesis of (nonassociable) diblocks, which also work like softening, plasticizing components. Thus, both bulky resins (e.g., monomer-based aromatic resins) and nonassociative copolymers (diblocks) can work as diluents of the physically cross-linked network. They cause less cohesion, less elasticity, and less tack. On the other hand, associative or reactive additives (e.g., tri-blocks, cross-linkers, or tackifiers), which interact with the elastomeric segments of the TPE, can improve the cohesion and elasticity or increase the plasticity (e.g., tackifiers, plasticizers) of the formulation (see also Chapter 8).

The special composite structure of TPEs (see Chapter 3) leads to problems concerning the use of the common adhesive characteristics: shear resistance and tack. Such systems behave as macromolecular composites and display more similarities with filled systems than with elastic networks (see above); the formulation of such systems should differentiate between hardening/elastic reinforcing and softening/tackifying. Principally, for such styrene block copolymers it is possible to improve cohesion with a simultaneous
increase in elasticity (e.g., with triblock or cross-linking agents), to improve cohesion without increased elasticity (with bulky resins or diblocks), to reduce cohesion without increased tack (bulky resins or diblocks), and to reduce cohesion with increased tack (tackifiers, plasticizers). For good cuttability (see Chapter 10 and Applications of Pressure-Sensitive Products, Chapter 8) only increased cohesion without increased elasticity is recommended (using bulky resins, diblocks, or micromolecular bulky fillers). On the other hand, for tackifying and processing-related diluting, softening with a simultaneous increase of tack and peel resistance is preferred. SIS block copolymers with high melt flow rates and a relatively high proportion of diblocks were developed. These low-modulus polymers also promote better die-cuttability of PSAs used in label stock applications. Taking into account the different effects of elastic and nonelastic reinforcing additives, the discrepancies between the shear-adhesion failure temperature values and holding power values can be better understood (see also Fundamentals of Pressure Sensitivity, Chapter 8, and Applications of Pressure-Sensitive Products, Chapter 8). Some years ago, Hamed and Shieh [71] discussed tack as a cohesion-related property. Later, shear resistance was considered as a cohesion- and cuttability-related characteristic [72]. Recent developments in TPEs demonstrate that such generalized assumptions are not valid. The use of shear resistance as an unequivocal index of cohesion or as an index of nonelastic cohesion is incorrect. On the other hand, the use of cohesion as an index of tack is generally not possible. This statement is illustrated by recent advances in the use of the probe tack test method (see also Fundamentals of Pressure Sensitivity, Chapter 6).

1.3.2 Pressure-Sensitive Products as Composites on Macromolecular and Macroscopic Scale

According to Ref. [73], polymer-based nanocomposites are attractive materials because of their unique properties resulting from their nanoscale microstructure. Four representative methods exist to produce nanocomposites: exfoliation-adsorption, in situ intercalative polymerization, melt intercalation, and template synthesis. Emulsion polymerization is the predominant method used in industry to manufacture a large variety of polymers for various uses such as paint, adhesives, and binders.

Some PSAs, such as chemically cross-linked systems, are composites on a molecular and macroscopic level. In such systems, the site of cross-linking, the concentration of the cross-linking sites, and the flexibility of the cross-linked network are the main parameters that influence the final properties of the adhesive. In the range of chemically cross-linked systems, homogeneous, solvent-based adhesives are relatively simple "constructions," but water-based dispersions possess a very complex build-up. The cross-linking of water-based dispersions is a difficult process because of the high reactivity of water as reaction medium. The reaction of the cross-linking agent with the polymer competes with its reaction with the reaction medium (water). The site of cross-linking (i.e., in the particle or on the particle surface) is yet not clear. Recently, investigations by Frazier et al. [74] demonstrated that the cross-linking reaction of poly(vinyl acetate) copolymers using N-methylol acrylamide as curing component occurs on the particle surface.
According to Ref. [75], after being dried the emulsion-based PSA behaves like a filled polymer melt. Although emulsion particles are internally cross-linked to obtain the appropriate viscoelastic behavior, the particles only interact via entangled dangling ends at the interface between particles.

Generally, cross-linking can occur during polymerization or postpolymerization (see Sections 1.1 and 1.2). The polymerization of dienes always leads to partially cross-linked structures. Emulsion polymerization of acrylates carried out to “full” conversion produces significant amounts of microgels inside the particles due to chain transfer to the polymer through hydrogen abstraction [76]. According to Tobing and Klein [77], the main reason for the much lower shear resistance in emulsion-based PSA is discrete microgel morphology, in which the microgels are connected by linear polymer chains by entanglement, in contrast with solvent-borne acrylic cross-linking, as formed after film formation, which resulted in a continuous network morphology. Interlinking of the microgels by covalent bond in the film is needed with the help of a functional monomer (e.g., isobutylmethacrylamide).

In the domain of pressure-sensitive raw materials, styrene–butadiene emulsions are the most important water-based cross-linked systems. A range of various parameters, including the chemical composition (e.g., the styrene content of SBR), the molecular weight, and the sol/gel ratio, describes the adhesive properties of the compound (see also Chapter 2). Because of the corpuscular nature of the particles in water-based systems, gradual cross-linking is possible. Thus, core-shell structures are formed. Spitzer [78–81] investigated the interdependence among polymerization conditions, molecular characteristics, and pressure-sensitive properties of styrene–butadiene latices. For such latices, the balance of the pressure-sensitive properties decisively depends on the glass transition temperature and the molecular characteristics (sol/gel ratio) of the polymer. On the other hand, the maximum peel strength is independent of the gel level and possibly the glass transition temperature [79]. These results indicate that for PSAs in which only the type of the gel differs, the tight gel fraction tends to determine the properties. It is suggested that in such blends the tighter gel is not readily swellable and, hence, poor shear values result. The presence of the “tight” gel promotes adhesive failure as well. In hydrogels (see above) with long-chain cross-linkers (carcass-like cross-linkers) and multifunctional cross-linkers (ladder-like cross-linkers), which lead to tight structures, the same effect of the tight gel on the adhesive properties was reported.

As noted in Ref. [82], a high gel content could compensate for low molecular weight. According to Ref. [76], this was not true for peel behavior.

The strong dependence of pressure-sensitive properties on the rubbery network (gel) characteristics demonstrates that for such polymers the rheologic dynamic mechanical analysis (DMA) data alone do not allow the prediction of pressure-sensitive formulability (see also Applications of Pressure-Sensitive Products, Chapter 8). For such copolymers, formulation based on high polymers only (like formulation for acrylics) is also limited.

The composite structure of the adhesive affects its performance as well. Common, solvent-based PSAs, or HMPSAs, do not contain liquid, low-molecular-weight components in their coated and finished status; water-based formulations (dispersions, solutions, or gels) may include an equilibrium level of water due to the technological additives used...
Technology of Pressure-Sensitive Adhesives and Products

...and the environment resistance (water solubility) of the PSA [36].

Water-based PSAs are composites because of the rest-humidity content of the dried adhesive layer. Although the influence of humidity on the converting properties of PSPs (e.g., guillotine cutting, telescoping by storage, etc.) was evidenced many decades ago [36], progress in this field is lacking. The complexity of such systems as composites increases with mixing. Water-based dispersions can be formulated as blends of various dispersions. For instance, Fabroni and Shull [83] studied the adhesive and mechanical properties of synthesized and characterized acrylic PSAs reinforced with nanoclay. Such acrylic PSAs were synthesized by emulsion polymerization with a nonionic surfactant in the presence of sodium montmorillonite (Na-MMT). This indicates that the tack and peel strength of PSAs demonstrate their maximum values at 1% bw of Na-MMT content. Li et al. [87] reported that ball tack values decreased when the montmorillonite was loaded in the PSA matrix, because the MMT loading increased both the storage modulus and the $T_g$ of PSAs. Patel et al. [88] prepared nanocomposite adhesives based on acrylics and silica or clay. They observed significant peel strength improvement with nanofiller concentration (1–6% bw) and the locus of failure changed from interfacial failure to stick-slip failure for the composites.

Generally, the “composite degree” of PSAs depends on their physical status. As discussed in Ref. [89], the concentration of the adhesive components in the formulated PSA composition decreases as follows.

\[
\text{HMPSA} > \text{solvent-based PSA} > \text{water-based PSA}
\]  

Table 1.7 presents the composite structure of PSPs on a molecular and macroscopic scale. Intramolecular heterogeneity is caused by sequence length, build-up and distribution, molecular weight distribution, and cross-linking, as well as by intramolecular segregation due to cross-linking, crystallization, filler effect, and segregation. Both, intramolecular and intermolecular composite structures affect the adhesive, converting, and end-use performance. The composite structure on a macroscopic scale, characterized by visible phase separation and due to disperse or filled systems, is illustrated. Table 1.8 presents the composite structure of PSPs as a laminated, that is, finished product.

### 1.3.3 Pressure-Sensitive Products as Composites on a Laminate Scale

When two materials with different characteristics on a macroscopic level are joined to obtain a multimaterial or composite system, the properties of the composite are a
TABLE 1.7 Composite Structure of PSPs on a Molecular and Macroscopic Scale

<table>
<thead>
<tr>
<th>Parameters of Heterogeneity, Intramolecular</th>
<th>Source of Heterogeneity</th>
<th>Composite Structure Effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sequence length, build-up, and distribution</td>
<td>Reactivity ratios, polymerization mechanism</td>
<td>Intermolecular interactions, reactivity, $T_g$, modulus, fibrillation, processing of PSA, adhesive properties</td>
</tr>
<tr>
<td>Molecular weight distribution</td>
<td>Polymerization mechanism</td>
<td>Reactivity, compatibility, intermolecular reactions, fibrillation, processing of PSA, adhesive properties</td>
</tr>
<tr>
<td>Cross-linking</td>
<td>Monomer reactivity</td>
<td>Reactivity, intermolecular reactions, processing of PSA, adhesive properties</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameters of Heterogeneity, Intermolecular</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cross-linking</td>
</tr>
<tr>
<td>Crystallization</td>
</tr>
<tr>
<td>Filler effect</td>
</tr>
<tr>
<td>Phase separation</td>
</tr>
</tbody>
</table>

Composite on a Macroscopic Scale

<table>
<thead>
<tr>
<th>Visible phase separation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Disperse system</td>
</tr>
<tr>
<td>Filled system</td>
</tr>
</tbody>
</table>
TABLE 1.8  Composite Structure of PSPs on a Laminate Scale

<table>
<thead>
<tr>
<th>Laminate Components as Composite Source</th>
<th>Effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carrier material</td>
<td>Choice of PSA, coating method, drying, coating weight, composite structure of PSA, time/temperature stability of PSA, mutual interactions, anchorage, coating weight, coating weight tolerances, tack, peel, and shear resistance, removability, choice of liner, converting properties, application, build-up of the laminate</td>
</tr>
<tr>
<td>PSA</td>
<td>Choice of carrier material, geometry of carrier, coating method, coating weight, coating image, precoating, pretreatment of carrier, post coating, tack, peel, and shear resistance, removability, water resistance, converting properties, shrinkage, lay-flat, migration, laminate build-up</td>
</tr>
<tr>
<td>Liner</td>
<td>Choice of PSA, coating method, drying, coating weight, composite structure of PSA, time/temperature stability of PSA, mutual interactions, tack, peel, converting and application properties, build-up of the laminate</td>
</tr>
<tr>
<td>PSP Laminate Construction as Composite</td>
<td>Source</td>
</tr>
<tr>
<td>Monoweb</td>
<td>Material, pre- and posttreatment, post- and precoating, lamination conditions</td>
</tr>
<tr>
<td>Multiweb</td>
<td>Carrier and PSA choice, coating methods, lamination conditions, storage, die-cutting</td>
</tr>
</tbody>
</table>

function of the properties of the two basic materials but also, and essentially, of the interaction force between those materials developed in a spatial region along the interface. In reality, no bonding is 100% perfect. Achenbach and Zhu [90] introduced the concept of imperfect interface defined by the interface parameters. Van Dijck et al. [91] developed a simple method for a first approximation of the interaction level between layers in a laminate or an adhesively bonded joint.

PSPs are composites on a laminate scale also. For instance, a label may have a laminated carrier (composite 1) that is coated with an adhesive (composite 2), which is laminated together with a liner (composite 3) to build up the label (composite 4). For this composite, the geometry of the carrier as well as that of the PSA are determinant.
In *Applications of Pressure-Sensitive Products*, Chapter 3, Chang and Holguin describe a special, *in situ* made pressure-sensitive composite based on a curable label construction comprising a curable PSA layer (1–2 μm thick) and curable epoxy layer (0.5–1.5 μm thick) coated onto a transparent carrier film.

The viscoelastic properties of the adhesive (\(\Phi_\text{a} \)) depend on the viscoelastic properties of the bulk adhesive (\(\Phi_{\text{ab}} \)) and on those of the composite adhesive layer (\(\Phi_{\text{com}} \)), or

\[
\Phi_\text{a} = f(\Phi_{\text{ab}}, \Phi_{\text{com}})
\]  

(1.4)

The viscoelastic properties of the bulk adhesive are different from those of the composite material. Generally, the viscoelastic properties of composite solvent-based adhesives are superior to those of the bulk material. The viscoelastic properties of water-based (composite) PSAs are inferior to those of the bulk adhesive. This behavior can be explained by the different nature of the formulation additives (see also Chapter 8).

The influence of the composite structure of the pressure-sensitive laminate on its converting properties was discussed in detail by Benedek in Ref. [92]. The composite structure of the adhesive and the laminate construction of the PSP both affect the stiffness and the cuttability of the PSP. The main components of PSPs are multilayer structures. Their properties are determined by the nature, number, geometry, and mutual interaction of such layers. The classic PSPs are carrier based, where the carrier ensures the mechanical properties of the laminate and the adhesive provides the pressure sensitivity (see *Applications of Pressure-Sensitive Products*, Chapter 1). *Ad absurdum*, the carrier is nondeformable, and the adhesive must be deformable. The development of nonpaper carrier materials provided webs that do not fulfill this statement; they possess deformability and self-adhesivity. Thus, the role of the carrier as a nondeformable, nonadhesive component is not valid.

The modulus of adhesive joints depends on the adhesive’s thickness [93]. In fact, increasing the thickness of the adhesive layer decreases its modulus. This behavior may be explained by the special, multilayer structure of the adhesive and the influence of the surface of the solid-state components. The modulus of the laminate varies close to the interface with the adhesive. The width of this zone depends on the adhesive; for certain adhesives it varies between 0.04 and 0.2 mm [94] (see also *Fundamentals of Pressure Sensitivity*, Chapter 4). However, the thickness (coating weight) of the adhesive would also exert a special influence on the adhesive resistance for PSA laminates. Increasing the coating weight increases the thickness of the mobile middle adhesive layer only (i.e., the cold flow of the adhesive). According to the paradox of Griffith [95], a fiber-like material possesses a much higher strength than the same material in another form. The paradox of tensioning or stressed length influences the effect of the thickness of the adhesive and of the primer as well. The change of the modulus of the constrained PSA in a sandwich structure was taken into account by Kauzlarich and Williams [96]. Another parameter influencing the modulus of plastics is their degree of orientation [4]. No data are available regarding a similar modulus dependence for PSAs.

One should note the dependence of the modulus on the composite structure of the laminate or laminate components. Special attention must be paid to the influence of the humidity on the paper modulus (which may depend on the humidity of the water-based adhesive layer; see above).
For a classic PSP based on a solid-state carrier material and a fluid adhesive, the properties of both components depend on their mechanical characteristics and geometry. The chemical nature, macromolecular characteristics, processing technology, and build-up of the carrier, together with its thickness (geometry), influence its conformability during bonding and its deformability during debonding. The deformability of the carrier during debonding affects the debonding angle, the transfer of the debonding energy, and the thickness of the adhesive (see also Applications of Pressure-Sensitive Products, Chapter 8). Such parameters are determinant for removability. The use of carrier deformability as an instrument to regulate adhesive characteristics was discussed in detail in Ref. [82]. As discussed in Refs [33,36], the laminate construction (build-up, components, and number of components) affects the peel resistance as well.

The thickness of the adhesive expressed as the coating weight \( C_w \) influences its conformability and stress transfer, that is, the bonding and debonding characteristics (tack, peel resistance, and shear resistance) [4,97,98]. The role of coating weight has been studied by several authors [82,99–102] (see also Applications of Pressure-Sensitive Products, Chapter 8).

According to Ref. [102], the effect of the adhesive thickness on the bond strength of adhesive joints is still not perfectly understood. Classic analyses predict that the strength increases with adhesive thickness, whereas experimental results demonstrate the opposite. Various theories have been proposed to explain this discrepancy, such as the theory of Crocombe [103] in 1989, based on the plasticity of the adhesive, but there is a lack of experimental evidence. Crocombe [103] demonstrated that thicker joints have a lower strength with the plasticity of the adhesive. Another theory to explain the effect of the adhesive thickness on the single lap joint strength was introduced by Gleich et al. [104]. The interface stresses that increase with adhesive thickness could therefore justify the fact that thicker joints are weaker. Another earlier theory proposed by Adams and Peppiatt [105] explains the discrepancy by noting that thicker bondlines contain more defects, such as voids and microcracks.

To avoid its influence on the properties of commercial PSPs, the coating weight values are normed (see Applications of Pressure-Sensitive Products, Chapter 8); that is, the coating weight values used in practice are situated in a domain where the dependence of the adhesive properties on the coating weight is minimal and the coating weight tolerances are well defined. The best known correlations concerning the influence of the coating weight on the adhesive properties are determined in such standardized domains.

In practice, the dependence of the peel resistance on the coating weight is complex, and the plot (an S-shape curve) presenting this dependence includes different domains as a function of the adherend surface, carrier material, and adhesive characteristics [36,106] (see also Applications of Pressure-Sensitive Products, Chapter 8). At low, subcritical coating weight values there is no sufficient adhesion; at upper critical coating weight, increased coating weight causes increased peel resistance (term \( C_w \) in the mathematical correlation between peel resistance and coating weight), and over a certain coating weight value, peel resistance does not depend on the coating weight. In practice, according to the (simplified) correlation (Equation 1.5), a reduction in coating weight decreases peel resistance, and at extremes it can lead to a subcritical thickness of the adhesive layer, which does not provide sufficient adhesion. Thus, the dependence of the
Pressure-Sensitive Raw Materials

peel resistance \( (P) \) on the coating weight \( (C_w) \) is not monotonous, but obeys different mathematical laws in various coating weight domains, where changes in bond force as well as bond failure are controlled by the coating weight,

\[
P = f(C_w - k_i)
\]

(1.5)

where \( k_i \) is a constant that describes the critical coating weight \( (C_{wm}) \). In a similar manner, the dependence of peel resistance on the carrier thickness can be described by the following (simplified) correlation,

\[
P = f(F_{m} - k_j)
\]

(1.6)

where \( F_{m} \) is the maximum tensile strength of the (plastic film) carrier material, and the coefficient \( k_j \) takes into account the minimum film thickness required for dimensional stability of the carrier. In the whole domain of variables, the correlation among adhesive thickness, carrier strength, and peel resistance can be written as follows.

\[
P = f[(C_w - k_i), (F_{m} - k_j)]
\]

(1.7)

That means that there is also a critical carrier deformability (i.e., critical carrier strength \( F_{mc} \)). The critical coating thickness (coating weight) value and critical carrier thickness (carrier strength) value together determine the practical usability of a pressure-sensitive laminate. These parameters are correlated.

\[
C_{mc} = f(F_{mc})
\]

(1.8)

Subcritical carrier strength due to subcritical carrier thickness leads to excessive carrier elongation and, thus, causes decreased coating weight. In this manner, the coating weight may also attain its critical value; that is, joint failure occurs.

As a consequence, nondestructive deformation (no break but excessive elongation) of the carrier material (strain) can also lead to a destructive modification of the adhesive joint due to the change in adhesive thickness. As noted by Benedek [36], for monoextrudates with a film thickness of about 35 \( \mu \)m, the critical values, \( F_{m} \) are of 8–9 N; for coextrudates such values are reached at a lower thickness, about 20 \( \mu \)m.

In the above case, in practice, joint failure occurs during delamination. Under static conditions of storage, where no deformation of the carrier material occurs, such PSA (protection) films may work satisfactorily; that is, they adhere to the surface to be protected with the nominal value of adhesion. On the other hand, tests of peel resistance (dynamic use of the joint) can lead to excessive carrier deformation, which means for thin deformable pressure-sensitive laminates there is a difference between their usability and their debonding ability, or testing behavior. Such thin protective films cannot be tested using common test methods (see also Applications of Pressure-Sensitive Products, Chapter 8). In this case, there is a difference between the static and dynamic criterion of usability.

Further investigations are required to optimize the critical carrier thickness as a function of the carrier material and its construction, to optimize the critical carrier...
Technologies of Pressure-Sensitive Adhesives and Products

thickness as a function of the adhesive, to mathematicize the correlation between the mechanical strength of the carrier material and peel resistance, to measure the adhesive and carrier deformation during joint failure caused by carrier deformation, and to elaborate upon an adequate test method for the static test of thin, deformable protective films. For manufacturers the mutual influence of adhesive and carrier thickness limits downgauging of the carrier film or imposes a higher coating weight.

This problem is even more complex because in industrial practice for such thin PSP constructions (most removable protection films), a primed adhesive is used. The adhesive itself is a multilayer construction (see also Applications of Pressure-Sensitive Products, Chapter 1) and, as described by Benedek in Ref. [64], primed constructions use less coating weight. Recently, Carelli et al. [107] examined the adhesive properties of bilayer constructions to optimize the adhesive properties. Because the resistance to crack propagation is mainly an interfacial property, whereas shear resistance is mainly a bulk property of the PSA, they explored the possibility of working with bilayer PSAs, where an interface layer would be softer and more dissipative and the other would be more rigid and less dissipative. “Translated” into industrial language, this is the common use of primers. For instance, isocyanate cross-linked rubber–resin-based PSAs for protection films use the same adhesive as primer, with more cross-linking agent, that is, a more rigid and less dissipative layer. Carelli at al. confirmed the old industrial experience that adhesive properties can be significantly modified using bilayer systems, and the use of a gradient in composition is an option to improve adhesion. Moreover, it offers the possibility of improving removability. In a similar manner, the “old” statement of Benedek [97] concerning the decisive role of the configuration (order of the layers, soft/rigid) was confirmed as well. Industrial practice generally uses a rigid primer combined with a soft adhesive.

**Summa summarum**, PSPs must be discussed as composites on a macromolecular, formulation, and construction level, where the build-up of the components decisively influences the final properties of the product. On a macromolecular and formulation scale, the build-up of network structures (physical or chemical) makes the use of common rheologic notions and DMA questionable. On a manufacturing level, the rheology, mechanical characteristics, and geometry of the adhesive and of the carrier material limit the use of standard test methods and impose the design of PSPs as a construction.

**References**

Pressure-Sensitive Raw Materials


© 2009 by Taylor & Francis Group, LLC
Pressure-Sensitive Raw Materials


© 2009 by Taylor & Francis Group, LLC
82. van Holde K.E. and Williams J.W., J. Polymer Sci., 11, 243, 1953.