Pressure-Sensitive Adhesives: An Introductory Course

Costantino Creton

Abstract

Self-adhesive materials are called, in the adhesives trade, "pressure-sensitive adhesives" (PSAs). PSAs are designed to stick on almost any surface by simple contact under light pressure. This special class of adhesives does not undergo any physical transformation or chemical reaction during the bonding process. Because of this, the rheological properties of the adhesive must be finely tuned for the application, combining a carefully chosen polymer architecture and monomer composition with the proper addition of small molecules called tackifying resins. PSAs are soft, deformable solids and, depending on the formulation, easily form bridging fibrils between two surfaces upon debonding. They are safe to use and easy to handle and thus are increasingly replacing more conventional types of adhesives. In this article, we review both the primary material characteristics of PSAs and the main physical principles that make them work effectively.

Keywords: acrylics, block copolymers, peel, polymers, pressure-sensitive adhesives, tackifying resins.

Introduction

Among the different classes of adhesives, pressure-sensitive adhesives (PSAs) are perhaps the most common type found in consumer products. Self-adhesive tapes and labels of all kinds are ubiquitous in everyday life. However, until recently, the understanding of the materials science and engineering of PSAs and, in particular, the specific role played by the different components in them was very limited outside of the companies involved in their manufacture, and the interested reader had to refer to general technological texts.[1,2] Although PSAs are designed to join two surfaces together, they differ from other adhesives in several ways. First, PSAs are typically used as nonstructural adhesives; they do not compete with epoxies for structural applications. Second, PSAs typically stick to a surface upon contact without any chemical reaction.[3] It is interesting to note that the term pressure-sensitive really should be pressure-insensitive, since PSAs do not need the application of much pressure to stick, and the measured adhesion is then rather insensitive to the compressive pressure applied upon bonding. This property makes PSAs particularly easy and safe to use, since no solvent evaporation or chemical reaction takes place and bonding can be done at room temperature.

Similar to all classes of adhesives, PSAs must be able to form a bond, that is, establish molecular contact (even on a rough surface) and then sustain a minimum level of stress upon debonding. All other classes of adhesives, however, form the bond in the liquid state and then are tested in the solid state, with the transition occurring by chemical reaction, change in temperature, UV irradiation, or another change in the structure of the adhesive. By contrast, modern PSAs are soft, viscoelastic solids that obtain their unique properties simply from the hysteresis of the thermodynamic work of adhesion. That is, there is a difference (adhesion hysteresis) between the energy gained in forming the interactions and the energy dissipated during the fracture of these same bonds. At least for short contact times, the only interface forces active in PSA adhesion are van der Waals forces.[4–6]

In order to possess these unique characteristics, however, the mechanical properties of these adhesives must be much more finely tuned than those of conventional adhesives. It is the goal of this article to give a general picture of the main material requirements for obtaining PSA properties.

Classes of Pressure-Sensitive Adhesives

In practice, as will be developed in more detail in the section on material requirements, all commercial PSAs are based on polymers, mainly coming from three families: acrylics, styrenic block copolymers, and natural rubber. There are also niche markets for silicone PSAs, where low-temperature use or high-temperature stability is required and cost is not an issue. Historically, the first PSAs were rubber-based. They remain the cheapest to produce and also the simplest to formulate, since they are typically compounds of natural rubber and a low-molecular-weight tackifying resin, miscible with the rubber in approximately equal proportions. Earlier versions were not cross-linked, but today a cross-linking step is generally performed to avoid flow.

Acrylic PSAs provide more latitude for optimization and formulation. They are typically random copolymers of a long side-chain acrylic (n-butyl acrylate or 2-ethylhexyl acrylate) with a low glass-transition temperature T_g, a short side-chain acrylic such as methyl acrylate to adjust the T_g, and acrylic acid to improve adhesion and optimize elongational properties (i.e., their mechanical response to deformation in uniaxial extension). Small-molecule additives such as tackifiers can be included, essentially to adjust the T_g and optimize dissipative properties, but they are not necessary for a useful acrylic PSA. As for natural rubber PSAs, a cross-linking step (electron-beam or UV irradiation), once the adhesive has been coated, is generally used to prevent creep.

PSAs based on styrenic block copolymers are the latest type to have come on the market. They are generally blends of styrene-isoprene-styrene (SIS) triblocks and styrene-isoprene diblocks compounded with a low-molecular-weight but high-T_g resin based on C_5 rings that is miscible with the isoprene phase but immiscible with the styrene phase. It is important to note that a tackifying resin is a necessary component for this class of PSA.[7–10]

In order to obtain usable PSA properties, the proportion of styrene in the compounded PSA must be on the order of 4–12%, the molecular weight of the styrene block must be above 10–11 kg/mol to stay immiscible with the isoprene phase, and the weight fraction of polymer in the blend must typically vary between 25%

and 45%. Because of the use of mutually immiscible blocks, these PSAs are really nanophase-separated, with styrene domains dispersed in an isoprene matrix. These styrene domains provide physical cross-links, which give these PSAs a superior resistance to creep.

How Do They Work?

For many years, the mechanisms by which PSAs adhere to almost any substrate remained rather mysterious. Companies proceeded mostly empirically from formulation to application, using a variety of trade tests designed to closely match the conditions the PSA would be subjected to in a particular application but the results of which could not be easily transported to another. The usual recipe one could use was that the PSAs should have an elastic modulus below a certain threshold called the Dahlquist criterion[11] and a large value of the viscous component of the elastic modulus to dissipate energy upon debonding.[12] Furthermore, due to the complicated nature of the materials (something between a solid and a liquid), few academic studies went beyond making correlations between a specific molecular structure and a macroscopic property. It is chiefly thanks to a BASF scientist, Albrecht Zosel, that a mechanistic approach was developed toward the understanding of PSA adhesion.[5,13,14]

Like all adhesives, PSAs work because the separation of two surfaces requires a certain amount of energy dissipation. This energy dissipation can be readily measured with a peel test, but early experiments quickly showed that the peel force depended on peel velocity, peel angle, and adhesive thickness, implying a strong coupling between geometry and mechanical properties. Zosel developed a simple test in which a cylindrical flat-ended probe is indented into a thin layer of adhesive and subsequently removed, as schematically described in Figure 1. The force and position of the probe are continuously recorded during the test, and the entire curve can be analyzed. The distinctive plateau observed after the maximum force peak shown in Figure 1 was clearly identified as being caused by the formation of fibrils during detachment.[13] Only those PSAs displaying high peel forces showed the formation of these fibrils. However, the molecular parameters controlling the first peak and the mechanism responsible for the drop in the force were only elucidated much later, when a probe tester fitted with a video camera was developed. The real-time observation tool showed that the force peak was due to the formation of cavities growing from the
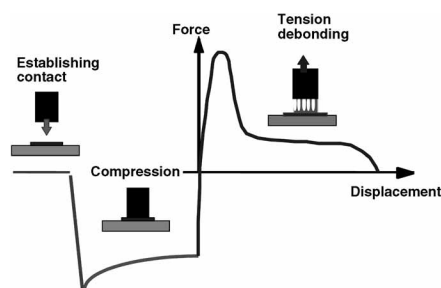

Figure 1. Schematic illustration of a tack test performed with a cylindrical, flat-ended probe.

interface with the probe into the bulk of the layer, as shown in Figure 2.[15] The widespread presence of cavities caused the force to drop, and if the cavities did not coalesce, the walls between these cavities became the fibrils observed by Zosel. It therefore became obvious that the debonding mechanism was rather complicated and could be divided into stages: initiation by cavitation, cavity growth, and finally fibril formation and stability.[15] Several years of further studies[6,9,16–20] provided, little by little, a more complete picture of the main controlling factors: the first peak of stress was due to a process of cavity growth in a rubbery elastic medium and therefore was chiefly controlled by the elastic modulus of the adhesive; sub-

stantial cavity growth along the interface, followed by a coalescence process only occurred on low-adhesion surfaces; and finally, the formation of fibrils was only possible if coalescence of the cavities did not occur. The final elongation of the fibrils at detachment was directly related to the elongational properties of the adhesive, as discussed by others in the interpretation of peel test results.[21–24] Given this general picture of how PSAs work, let us now consider what the key material requirements are to control the debonding mechanisms.

Material Requirements

From an applications point of view, PSAs need to possess three important properties. First of all, some degree of stickiness: in order to form a good bond on almost any surface, a PSA must be sticky upon simple contact, a property generally called tack. Second, all PSAs are peeled from a surface, either before use or during use, if they are removable: a controlled peel force as a function of peel velocity and precise control of the residue left on the surface are also requirements. Finally, permanent PSAs are subjected to stresses for long periods of time, and creep must be minimized. Each one of these application requirements can only be met with specific material properties, and often commercial formulations are the result of a compromise. The main requirement in terms of molecular structure is that all PSAs must
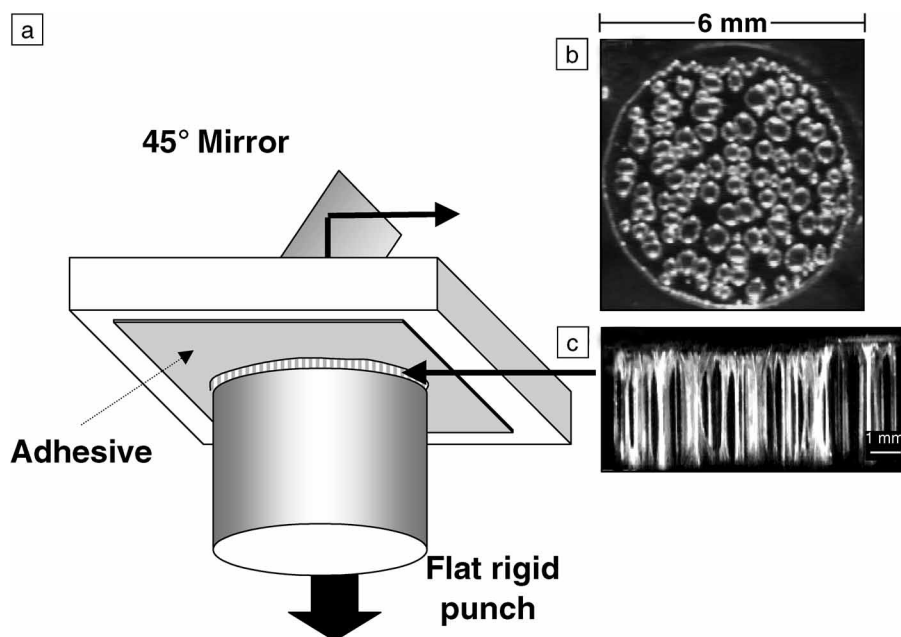

Figure 2. (a) Schematic illustration of a probe test setup, showing possible observation angles for the (b) cavitation and (c) fibrillation processes occurring during debonding of pressure-sensitive adhesives (PSAs).

be based on polymers well above their T_g. Typically, in order to be tacky at a given usage temperature, the T_g of the adhesive must be 25–45°C below that temperature and be as broad as possible to maximize viscoelastic dissipation at the low-modulus end of the glass transition. Differences in properties can only then be obtained with variations in T_g, molecular weight, or molecular architecture and supramolecular structure. In addition, formulation plays a significant part in the optimization of viscoelastic properties, and small molecules are invariably added to the base polymers.

The stickiness to the touch of a PSA is related to its ability to form bridging fibrils when the PSA is pulled away, as demonstrated by a probe test (Figure 2). The required property for obtaining this fibril formation on a standard test surface such as steel is a resistance to fracture by crack propagation. In other words, if failure is initiated by a small crack (at the edge or in the center of the contact area), it should not be able to propagate but rather should blunt.[25,26] If adhesive forces are provided by van der Waals forces alone, this crack blunting, which causes the formation of fibrils, is observed for materials with a Young's modulus E below 0.1 MPa. Such a low modulus puts PSAs in the category of elastomers or gels. As discussed previously, the same requirement of low modulus is dictated by the necessity to form a good bond with a rough surface under a light pressure.[27,28]

If one recalls that the elastic modulus of an elastomer is related to its average molecular weight between entanglements (M_e),[29,30] it becomes clear that suitable elastomers for a PSA application must have a large M_e value.[14] This can be achieved by polymers such as poly(n-butyl acrylate) or poly(2-ethylhexyl acrylate) or by adding miscible small-molecule tackifiers to elastomers such as natural rubber or SIS block copolymers. These tackifiers essentially dilute the entanglement network and lower the modulus of the PSA in the plateau region, as shown in Figure 3. The test frequency was 1 Hz in this figure.[31,32]

However, a low elastic modulus, while being necessary for tackiness, is not sufficient for control of the peel force, and therefore two more properties guiding molecular design must be included:
1. For the material to be a useful PSA, the viscous component G'' of the shear modulus at the test frequency must be relatively high (on the order of the elastic component G' for permanent PSAs and ~10–30% of the elastic component for the removable ones). This requirement presupposes a material that will dissipate energy through deformation, causing a moderate to high
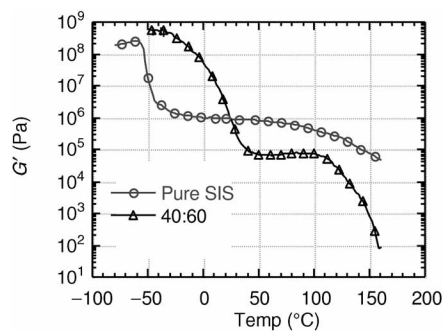
Figure 3. Elastic component of the shear modulus G′ for a pure styrene-isoprene-styrene (SIS) triblock copolymer containing 30 wt% triblock (open circles), and a 40:60 blend of SIS triblock and tackifying resin (open triangles).

peel force. Often, this is achieved by a significant broadening of the G'' peak associated with the glass transition.[9]
2. The PSA must be able to strain-harden at high levels of strain (viscous fluids such as honey or tar are sticky but are not useful PSAs). This property fulfills the typical requirement of an adhesive to fail without leaving a sticky residue on the surface.

Although all PSAs exhibit some degree of strain hardening in elongation, the level of elongational strain where strain hardening sets in and how progressive this strain hardening is are key material parameters in PSA design. For homopolymers and random copolymers, the degree of strain hardening is controlled through a suitable choice of molecular-weight distribution and degree of cross-linking.[33] Experimentally, the optimum degree of cross-linking corresponds approximately to slightly above the gel point: a typical PSA contains about 50–70% of insoluble fraction. The gel point is defined as the degree of cross-linking at which the elastic and viscous moduli are equal over a range of test frequencies. By increasing or decreasing the gel fraction, it is possible to modify the onset of strain hardening and control fibril extension and, therefore, the peel force.

Finally, another property that some PSAs must have is good resistance to a continuous shear force, since many applications, while not being strictly speaking structural, must sustain a moderate level of stress for a very long time. Examples include PSAs used to fasten components inside a digital camera, and the PSA that holds the rear-view mirror of your car in place. This requirement assumes PSAs to be solids and therefore to have no measurable Newtonian viscosity at the usage temperature. Again, this can be achieved

through two main molecular design tools: controlled chemical cross-links or physical cross-links. However, the requirements to maximize resistance to creep are not the same that maximize peel force. In a shear experiment, no fibrils are formed, and the optimum degree of cross-linking is displaced toward more cross-linking than for the peel force. The upper limit in degree of cross-linking is given there by the resistance to crack propagation: if the PSA is too highly cross-linked, it becomes too elastic (as determined by the ratio tan $\delta = G''/G'$ in a rheology experiment), and the adhesion hysteresis is not large enough to cause crack blunting. Therefore, the inevitable presence of a small defect leads to a quick adhesive failure.

Nanostructured PSAs

It is worthwhile to spend a little time discussing the structure and specific properties of PSAs based on block copolymers. These PSAs are widespread in the adhesive-tape industry, essentially because of their ease of production in thin-film form by the hot-melt process (as discussed later in the article). The first studies on their properties date back to the late 1970s.[8,34–36] They are, however, also used because of their unique properties as adhesives.

As we now understand, SIS block copolymers undergo a microphase separation if the respective blocks are sufficiently long.[37] Compounding the block copolymer with a tackifying resin miscible with the isoprene phase yields a structure of physical cross-links provided by the glassy styrene domains in an elastomeric isoprene+resin matrix. This type of structure gives, at room temperature, a PSA that is very solidlike at low frequencies (absolutely no Newtonian viscosity) while at the same time very viscoelastic at high frequencies. These "nanostructured" materials possess a superior resistance to creep while maintaining a very high peel force and acceptable tack. In terms of molecular design, an important parameter is the ratio between isoprene chains bridging two styrene domains (typically triblocks) and nonbridging isoprene chains (triblocks of SIS in a loop or "hairpin" configuration or diblocks). Large-strain tensile deformation is greatly influenced by this connectivity between domains, and the strain hardening is controlled by the extent and length of the bridges between these styrene blocks,[10,38] as shown in Figure 4. It is also worthwhile to note that there are current efforts to design heterogeneous nanostructured acrylic PSAs using emulsion polymerization to make core-shell particles that retain their original structure once the PSA film is formed.[39,40]

Easy Release of PSAs from Surfaces

An interesting and complementary problem arising from the preparation of PSAs is the issue of protecting the PSA before use. By definition, PSAs are sticky and, therefore, dust particles in the air can easily stick to the surface, making manipulation difficult once the sticky surface is exposed. Adhesive-tape manufacturers solve the problem by adhering the sticky side of the tape to the back surface of the tape in rolls, while adhesive labels normally are sold in contact with a protective film.

How does the back surface of adhesive tape or the protective film of a label work? In this case, it is absolutely necessary not only for the adhesive to peel cleanly from the protective surface but also to retain its properties once it is applied to the target surface. In practice, adhesion must be significantly higher on the back of a tape than on the protective film of a label (otherwise, the tape would unroll under its own weight), and accordingly, different materials are used for both cases. Poly(vinyl carbamates) provide good surfaces for the back side of tapes, while highly cross-linked silicones are used for the protective films for labels.

How does a release coating work? Recalling the section on the mechanisms of debonding of PSAs, the high adhesion comes essentially from the formation of fibrils, so a low-adhesion surface must be able to suppress this fibrillation process. Recent experiments[20] have shown that this lack of fibrillation implies that the multiple cracks nucleating at the interface (Figure 2) no longer blunt but coalesce. Such a coalescence process is shown in Figure 5 for tensile probe test curves of tack. This lack of crack blunting leads to a complete or partial suppression of the fibrillation stage and is therefore a very good way to control a macroscopic adhesion parameter such as the peel force. At a more mechanistic level, separation of the adhesive from the substrate is generally caused by a tensile force applied in the direction perpendicular to the interface. For cavities to coalesce, the lateral crack-propagation velocity must be high relative to the vertical crack-propagation velocity, and this means a low level of instantaneous energy dissipation by viscous flow at the edge of the crack: this is where adhesion is important. Interestingly, surfaces causing high cavity-growth rates and therefore low adhesion have in common a low resistance to interfacial friction.[41,42] This low resistance to interfacial friction requires a high level of molecular mobility of the surface,[43] so that the PSA effectively is adhered to a molecularly fluid but macroscopically solid layer.

Removable adhesives work under the same principle, that is, suppression or at least minimization of the fibrillation stage.

However, in this case, the goal must be achieved by varying the composition and molecular architecture of the adhesive alone. This typically implies a reduction in the value of G'' relative to G' so that crack propagation becomes less dissipative and fibrillation is minimized. Basically, one seeks to obtain the minimization of fibril formation on any given surface.

Manufacturing Adhesives

Although we have focused here on the properties of the adhesives, many requirements in terms of molecular structure or formulation actually stem from the necessity of producing PSA products at high speed and reasonable cost.

PSA films are produced essentially by three methods:

■ From solution by coating and solvent evaporation. This is the more traditional method, but it is now only used where specific performance of solution systems cannot be obtained by other means.

■ From latexes, that is, emulsions of small particles by coating and water evaporation. This is the typical method used for labels based on acrylic polymers.

■ From hot melts. This method implies that the manufacturing is performed without solvent. In order to work, the viscosity must be reasonably low during the coating process and achieve its end-use properties later on through a decrease in temperature
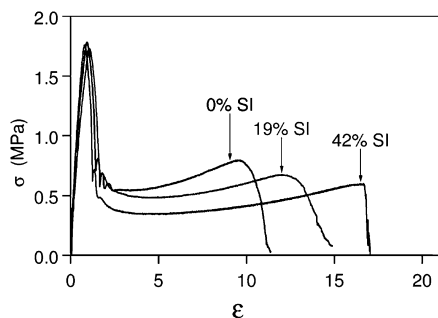

Figure 4. Tensile probe test curves of nominal stress ($\sigma = F/A_0$) versus nominal strain [$\varepsilon = (h - h_0)/h_0$, where h and h_0 are the deformed and undeformed thicknesses of the adhesive film, respectively] for three polymer blends. All tests were performed at a probe retraction velocity of 100 μm/s on a 100-μm-thick layer. The percentage of diblock styrene-isoprene in the polymer part of the blend was varied from 0% to 19% to 42%, while the weight ratio of total polymer (diblock + triblock) to resin was kept at 30:70 for all three samples. Note the important effect of the variable amount of diblock on the plateau part of the curve representing the fibrillation process.
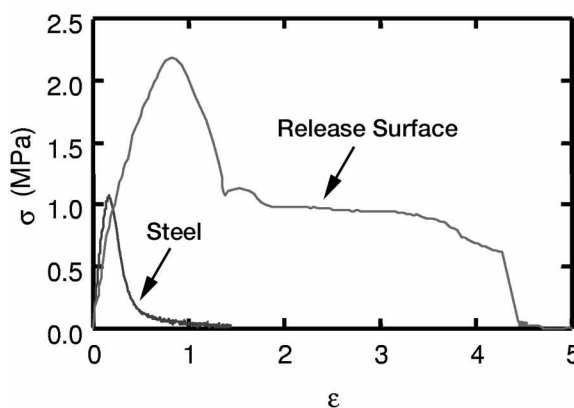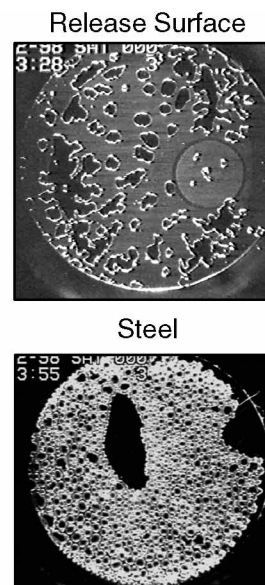

Figure 5. Tensile probe test curves of nominal stress versus nominal strain ("tack") for the same type of PSA as shown in Figure 4, based on a triblock copolymer and a tackifying resin, on two surfaces. The bottom micrograph is polished steel, and the top is a release surface; both have a diameter of 10 mm. Note the very different debonding patterns for both surfaces and the complete absence of a fibrillation plateau on the σ–ε curve of the adhesive on the release surface.

or a cross-linking and polymerization reaction. It is the preferred method for all PSAs based on block copolymers, in which case the phase-separated structure undergoes a "melting" transition when the temperature is raised above the T_g of the styrene phase.

For the reasons explained earlier, the first two coating methods must be followed by a cross-linking step that is normally accomplished either by temperature or radiation. Radiation curing can be performed either by UV exposure, in which case the polymerization and cross-linking proceed simultaneously and suitable photo-initiators must be used, or by electron-beam irradiation, where typically the polymer is already formed. Radiation curing has the distinct advantage over thermal curing of allowing very short reaction times.[44]

Applications

For many people, the quintessential PSA application is adhesive tape or the self-adhesive label. While these applications represent the largest volume of sales, they generally do not require a fine-tuning of properties, and the emphasis is on minimizing production costs. However, a variety of other applications where more finely tuned properties are needed are now widely available. The applications can be roughly divided in three categories based on performance requirements: semi-structural permanent, permanent with no real structural requirement, and removable. Among the applications for removable adhesives, a large industrial application is the temporary protection of surfaces (automobile bodies, windshields, and prefabricated elements used in construction), as illustrated in Figure 6. In this case, the key technical problem is to maintain the easy removability of the protective film and the lack of adhesive residue on the car's surface, even after three months of outdoor aging in harsh conditions. Another important application of removable PSAs is masking tape for painting applications. Finally, one should mention the most consumer-friendly application of PSAs in our opinion, the Post-It note. In this case, a thin layer of adhesive must stick to paper and be easily removable. This requires a particularly low level of adhesion, since the paper fibers are easily ripped apart.

Among permanent nonstructural PSAs, the main applications are labels in all their forms and packaging tapes. In both cases, the requirement is good adhesion on paper or cardboard, which really means that detachment cannot occur without permanent damage to the surface of the cardboard or to the label. PSAs based on block copolymers have a large segment of the market

Figure 6. Temporary protection of automobile paint and other components is routinely provided by the use of polymer sheets (white areas in photograph) coated with a PSA, thus offering safe adhesion and easy removability without affecting the optical surface quality of the car even after prolonged contact time under outdoor conditions. (Courtesy of tesa AG.)

for tapes, and acrylic water-based polymers dominate the label market. However, high-end labeling applications and, in particular, outdoor applications are dominated by solution acrylics, with their superior resistance to aging.

Finally, double-sided tapes and foams are increasingly used as an alternative to fastening with conventional chemically reactive soft glues. In particular, the microelectronics industry uses a large number of PSA layers for the construction of components.

In this case, the adhesive is often pre-foamed to introduce defects (small bubbles), which, by breaking the confinement without having to nucleate a cavity, have superior strength. Defects introduced throughout the adhesive layer reduce the stress on interfacial defects, which typically fail catastrophically. These are high-end applications where maximizing the resistance to creep of the adhesive under stress is very important. The phase-separated structure of block-copolymer-based PSAs gives them a competitive advantage for this type of application.

Future Trends

PSAs are now increasingly replacing more traditional adhesives because of their ease of use and safe manipulation. Despite the developments of energy-efficient solvent-recovery methods, environmental legislation drives research toward alternative production methods to coating from solution. Water-based acrylic emulsions are widespread for general-use PSAs. However, the presence of surfactants, which are not easy to eliminate,[45,46] and the lesser control that one obtains over the molecular structure, precludes for the moment their access to the most demanding applications. Ongoing research is aimed at improving properties to the same level as solution-cast acrylics.

Along the same lines, an increasingly widespread production method (at least for tapes) is hot-melt, or solventless, technologies. In this type of manufacturing process, the viscosity must be lowered enough for an easy and homogeneous coating without the use of any volatile compound while maintaining properties of the final product. Superior recyclability of this type of product is likely to become important in the future, due to environmental pressures.

From the point of view of end-use properties alone, the future trend for PSAs will be in the direction of heterogeneous polymer structures and also on the incorporation of additional functionalities such as thermal or electrical conductivity or controlled drug release, as in nicotine patches, into a PSA matrix without altering its self-adhesive properties.

Acknowledgments

References

1. D. Satas, in *Handbook of Pressure Sensitive Adhesive Technology,* 2nd ed., Vol. 1, edited by D. Satas (Van Nostrand Reinhold, New York, 1989) p. 940.
2. I. Benedek, *Pressure-Sensitive-Adhesive Formulation,* 1st ed. (VSP, Utrecht, 2000).
3. C. Creton and P. Fabre, in *Comprehensive Adhesion Science,* Vol. 1, edited by D.A. Dillard and A.V. Pocius (Elsevier, Amsterdam, 2002) p. 535.
4. C. Creton, in *Processing of Polymers,* 1st ed., Materials Science and Technology, Vol. 18, edited by H.E.H. Meijer (VCH, Weinheim, 1997) p. 707.
5. A. Zosel, *Adv. Pressure Sensitive Adhes. Technol.* **1** (1992) p. 92.
6. C. Gay and L. Leibler, *Phys. Today* (1999) p. 47.
7. N. Nakajima, R. Babrowicz, and E.R. Harrell, *J. Polym. Sci., Polym. Phys. Ed.* **44** (1992) p. 1437.
8. G. Kraus, K.W. Rollmann, and R.A. Gray, *J. Adhes.* **10** (1979) p. 221.
9. K. Brown, J.C. Hooker, and C. Creton, *Macromol. Mater. Eng.* **287** (2002) p. 163.
10. A. Roos and C. Creton, in *Proc. 25th Annu. Meeting of the Adhesion Society* (The Adhesion Society, Blacksburg, VA, 2002) p. 371.
11. C.A. Dahlquist, *Pressure-Sensitive Adhesives,* Vol. 2, edited by R.L. Patrick (Marcel Dekker, New York, 1969) p. 219.
12. A.N. Gent and J. Schultz, *J. Adhes.* **3** (1972) p. 281.
13. A. Zosel, *J. Adhes.* **30** (1989) p. 135.
14. A. Zosel, *Colloid Polym. Sci.* **263** (1985) p. 541.
15. H. Lakrout, P. Sergot, and C. Creton, *J. Adhes.* **69** (1999) p. 307.
16. I. Chikina and C. Gay, *Phys. Rev. Lett.* **85** (2000) p. 4546.
17. C. Creton and H. Lakrout, *J. Polym. Sci., Part B: Polym. Phys.* **38** (2000) p. 965.
18. A.J. Crosby, K.R. Shull, H. Lakrout, and C. Creton, *J. Appl. Phys.* **88** (2000) p. 2956.
19. A. Chiche, P. Pareige, and C. Creton, *Compte Rend. Acad. Sci.* (Paris) Sér. IV, **1** (2000) p. 1197.
20. C. Creton, J.C. Hooker, and K.R. Shull, *Langmuir* **17** (2001) p. 4948.
21. L. Benyahia, C. Verdier, and J.M. Piau, *J. Adhes.* **62** (1997) p. 45.
22. C. Verdier, J.M. Piau, and L. Benyahia, *J. Adhes.* **68** (1998) p. 93.
23. S.F. Christensen, H. Everland, O. Hassager, and K. Almdal, *Int. J. Adhes. Adhes.* **18** (1998) p. 131.
24. S.F. Christensen, PhD thesis, Technical University of Denmark, 1998.
25. A.J. Crosby and K.R. Shull, *J. Polym. Sci., Part B: Polym. Phys.* **37** (1999) p. 3455.
26. A. Jagota, C.Y. Hui, S.J. Bennison, and J.D. Londono, *Proc. Royal Soc. London, Series A* (2003) in press.
27. C. Creton and L. Leibler, *J. Polym. Sci., Part B: Polym. Phys.* **34** (1996) p. 545.
28. D. Maugis, *J. Adhes. Sci. Technol.* **10** (1996) p. 161.
29. J.D. Ferry, *Viscoelastic Properties of Polymers,* 3rd ed., Vol. 1 (John Wiley & Sons, New York, 1980).
30. M. Doi and S.F. Edwards, *The Theory of Polymer Dynamics* (Oxford University Press, New York, 1986).
31. M. Sherriff, R.W. Knibbs, and P.G. Langley, *J. Appl. Polym. Sci.* **17** (1973) p. 3438.
32. D.W. Aubrey and M. Sherriff, *J. Polym. Sci., Polym. Chem. Ed.* **16** (1978) p. 2631.
33. A. Zosel, *J. Adhes.* **34** (1991) p. 201.
34. G. Kraus, F.B. Jones, O.L. Marrs, and K.W. Rollmann, *J. Adhes.* **8** (1977) p. 235.
35. G. Kraus and T. Hashimoto, *J. Appl. Polym. Sci.* **27** (1982) p. 1745.
36. G. Kraus and K.W. Rollmann, *J. Appl. Polym. Sci.* **21** (1977) p. 3311.
37. F.S. Bates and G.H. Frederickson, *Annu. Rev. Phys. Chem.* **41** (1990) p. 525.
38. A. Roos, PhD thesis, Université Paris VI, 2003.
39. A. Aymonier, E. Papon, J.-J. Villenave, P. Tordjeman, R. Pirri, and P. Gérard, *Chem. Mater.* **13** (2001) p. 2562.
40. J. Mallégol, O. Dupont, and J.L. Keddie, *Langmuir* **17** (2001) p. 7022.
41. N. Amouroux, J. Petit, and L. Léger, *Langmuir* **17** (2001) p. 6510.
42. G. Josse, C. Creton, and M. Dorget, in *Proc. Euradh 2000* (Société Française du Vide, Paris, 2000) p. 165.
43. B.-M. Zhang Newby, M.K. Chaudhury, and H.R. Brown, *Science* **269** (1995) p. 1407.
44. W. Karmann and S. Zöllner, *Eur. Adhesives & Sealants* (12) (1996) p. 3.
45. J. Mallégol, J.-P. Gorce, O. Dupont, C. Jeynes, P.J. McDonald, and J.L. Keddie, *Langmuir* **18** (2002) p. 4478.
46. A. Zosel and B. Schuler, *J. Adhes.* **70** (1999) p. 179.   ☐