Adesivi

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Introduction

Yet, with adhesives and sealants all around us, with applications extending back to at least biblical times, and with many examples of outstanding adhesion in nature

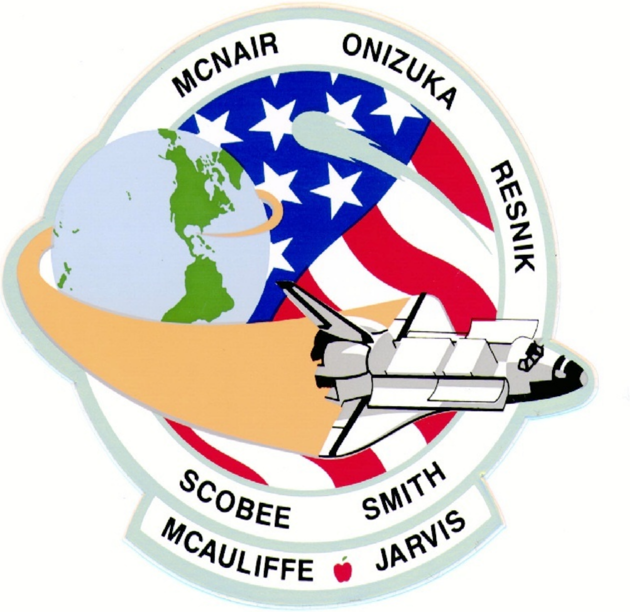
(e.g., barnacles and ice on roads), why are there so many failures when we try to "engineer" the use of adhesives or sealants in practice? Why does it seem as if we must resort to trial and error, if not a bit of luck or magic?

Introduction

Examples of catastrophic disasters such as the 1986 Challenger space shuttle sealant problem and the 1988 Aloha Airlines 737 fuselage peeling apart in flight unfortunately also invade the history of adhesives and sealants. Perhaps no other class of materials or technology is so essential yet so ripe for potential misadventure.

Introduction

STS-51-L was a space shuttle mission by NASA using the Space Shuttle Challenger, launched January 28, 1986. The seven-member crew was killed 73 seconds after lift-off because of an O-ring seal failure in the booster system. Since it was near the Max Q region of the ascent phase, the vehicle quickly disintegrated and the entire crew was killed. It was also the 25th Shuttle mission and the 10th Challenger mission.



Introduction

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On April 28, 1988, Aloha Airlines Flight 243 Boeing 737 (N73711) interisland flight from Hilo Airport to Honolulu International Airport carrying 89 passengers and 6 crew members experienced rapid decompression when an 18 feet section of the fuselage roof and sides were torn from the airplane. One flight attendant (Clarabelle Lansing) was forced out of the airplane from the pressure difference and is presumed dead. Several passengers sustained life-threatening injuries including instances of massive head wounds. The aircraft declared an emergency and landed at Kahului Airport on Maui with slight difficulty. Noise created by the rush of air rendered vocal communication useless and the crew had to use hand signals during landing.

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Materiali non tradizionali

Ing. Nicola Scuor

Introduction

Adhesives and sealants are often made of similar materials, and they are sometimes used in similar applications. These materials have comparable processing requirements and failure mechanisms, and the fundamentals of how they work are similar. Therefore, adhesives and sealants are often considered together. However, different specifications and test methods apply to adhesives and sealants, and most often they are designed to perform different functions.

Introduction

Adhesive: a substance capable of holding at least two surfaces together in a strong and permanent manner.

Sealant: a substance capable of attaching to at least two surfaces, thereby, filling the space between them to provide a barrier or protective coating.

Adhesives and sealants are often considered together because they both adhere and seal; both must be resistant to their operating environments; and their properties are highly dependent on how they are applied and processed.

Introduction

Adhesives and sealants also share several common characteristics:

- They must behave as a liquid, at some time in the course of bond formation, in order to flow over and wet (make intimate contact with) the substrates.
- They form surface attachment through adhesion (the development of intermolecular forces).
- They must harden to carry sometimes continuous, sometimes variable load throughout their lives.
- They transfer and distribute load among the components in an assembly.
- They must fill gaps, cavities, and spaces.
- They must work with other components of the assembly to provide a durable product.

Introduction

Structural adhesive is a term generally used to define an adhesive whose strength is critical to the success of the assembly. This term is usually reserved to describe adhesives with high shear strength (in excess of 7 MPa) and good environmental resistance. Examples of structural adhesives are epoxy, thermosetting acrylic, and urethane systems. Structural adhesives are usually expected to last the life of the product to which they are applied.

Introduction

Non-structural adhesives are adhesives with much lower strength and permanence. They are generally used for temporary fastening or to bond weak substrates. Examples of non-structural adhesives are pressure sensitive films, wood glue, elastomers, and sealants.

Introduction

Sealants are generally chosen for their ability to fill gaps, resist relative movement of the substrates, and exclude or contain another material. They are generally lower in strength than adhesives, but have better flexibility. Common sealants include urethanes, silicones, and acrylic systems.

Introduction

Both adhesives and sealants function primarily by the property of adhesion. Adhesion is the attraction of two different substances resulting from intermolecular forces between the substances. This is distinctly different from cohesion, which involves only the intermolecular attractive forces within a single substance. The intermolecular forces acting in both adhesion and cohesion are primarily van der Waals forces.

Introduction

Joints fail either adhesively or cohesively or by some combination of the two.

Adhesive failure is an interfacial bond failure between the adhesive and the substrate. Cohesive failure could exist within either the adhesive material or the substrate. Cohesive failure of the adhesive occurs when stress fracture within the adhesive material allows a layer of adhesive to remain on both substrates (i.e., the attachment of the adhesive to the substrate is stronger than the internal strength of the adhesive itself, and the adhesive fails within its bulk). When the substrate fails before the adhesive and the joint area remains intact, it is known as a cohesive failure of the substrate.

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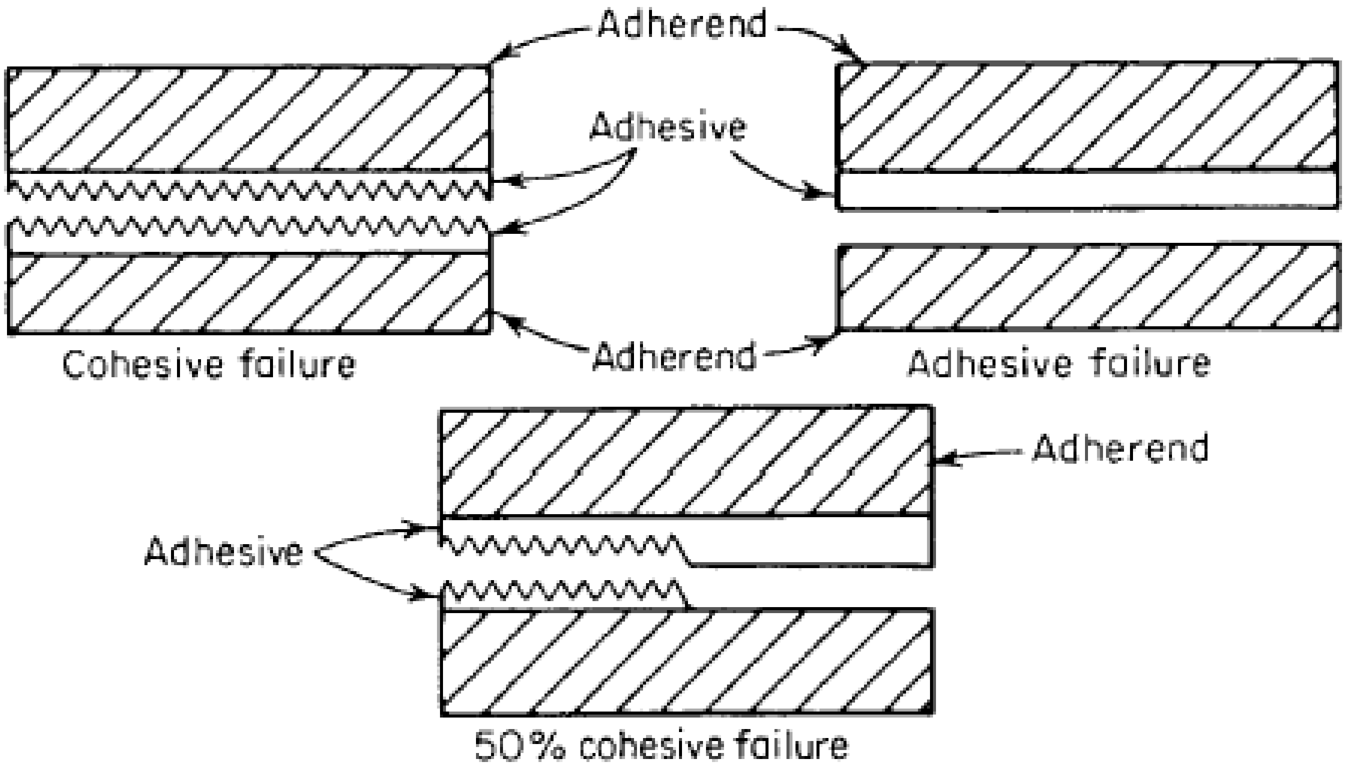

Introduction

The substrate is the material to be bonded. The area between the adhesive and substrate is referred to as the interphase region. This interphase region is a thin region near the point of adhesive—substrate contact. The interphase region has different chemical and physical characteristics than either the bulk adhesive or the substrate. The nature of the interphase region is a critical factor in determining the properties and quality of an adhesive bond. Different from the interphase is the interface, which is contained within the interphase. The interface is the plane of contact between the surface of one material and the surface of the other. The interface is often useful in describing surface energetics. Between the adhesive and substrate there can be several interfaces composed of layers of different materials. Sometimes a primer is used with adhesives or sealants. A primer is applied to a surface prior to the application of an adhesive or sealant, usually for improving the performance of the bond or protecting the surface until the adhesive or sealant can be applied. The joint is the part of the assembly made up of substrates; adhesive or sealant; primers, if present; and all associated interphase regions.

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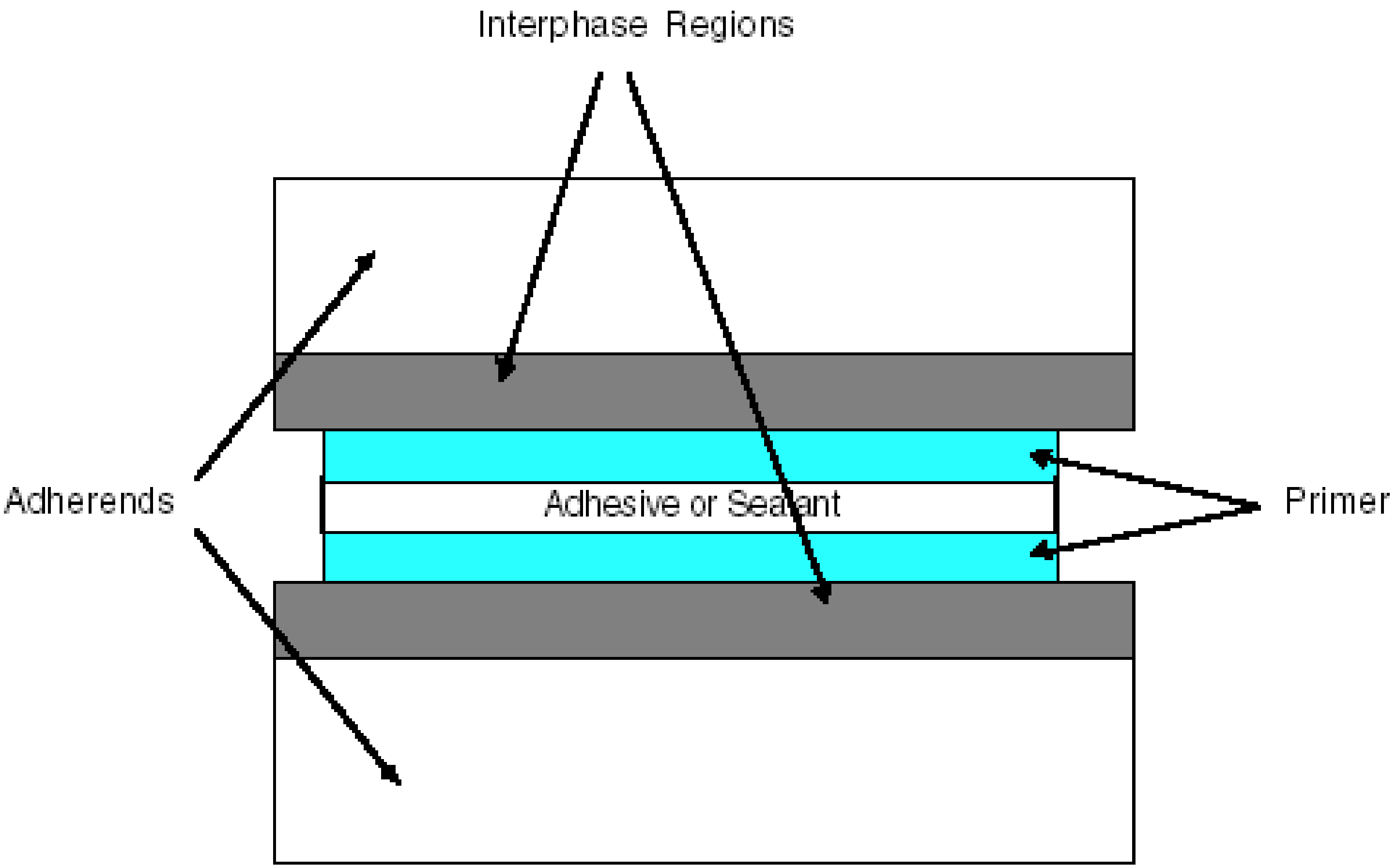

Introduction

The quality of the resulting application will depend on many factors, some of which are very entangled and complicated. One of the principal factors in the success of either an adhesive or sealant is adhesion. The following table lists some of the external and internal factors that influence adhesion. An understanding of how these factors affect adhesion will determine the success of the bonding or sealing operation.

Knowledge of production processes, economics, and environment and safety factors is also important.

Introduction

Factors Influencing Selection of an Adhesive or Sealant

Stress

•Tension: forces acting perpendicular to the plane of the adhesive. Not commonly encountered in bonding thin plastic or metal sheets, leather, cork compositions, etc.

•Shear: forces acting in the plane of the adhesive. Pure shear is seldom encountered in adhesive assemblies; substantial tension components are usually found

•Impact: Minimum force required to cause the adhesive to fail in a single blow. May be determined in tension or shear. Measures brittleness

•Peel: stripping of a flexible member fastened with adhesive to another flexible or rigid member. Stress is applied at a line; test loads are expressed in pounds per inch width. Commonly used angles of peel in tests are 90° for relatively stiff and 180° for flexible members

•Cleavage: forces applied at one end of a rigid bonded assembly which tend to split the bonded members apart. Can be considered as ‘‘peel’’ of two rigid members

•Fatigue: dynamic—alternate loading in shear or tension-compression. Static—maximum load sustained for long periods of time in tension or shear; tests are also used to determine creep

Introduction

Chemical Factors

- External: effect of chemical agents such as water, salt water, gasoline, by hydraulic fluid, acids, alkalies, etc.
- Internal: effect of substrate on adhesive (i.e., exuded plasticizers in certain plastics and rubber); effect of adhesive on the substrate (crazing, staining, etc.)

Exposure

- Weathering: combined effect of rainfall, sunlight, temperature changes, type of atmosphere
- Light: important only with translucent substrates. Effect of artificial or natural light, or ultraviolet
- Oxidation: usually tested by exposure to ozone with the joint either unstressed or stressed, in which case deterioration is faster
- Moisture: either adhesive or substrate may be affected by high humidity or wet conditions. Cyclic testing with alternate moist and dry conditions can be valuable. May cause dimensional changes
- Salt spray: important only in coastal or marine atmospheres. Possible corrosion of substrate should also be considered

Introduction

Temperature

- High: normal atmospheric variations may be encountered, or exceptional conditions. Bond strength may be affected by reactions in adhesive or substrate; decomposition or changes in physical properties of adhesive are important
- Low: may cause crystallization or embrittlement, detected by strength test. Cyclic testing with low or high temperatures may detect lack of durability

Biological Factors

- Bacteria or mold: usually warm, humid tropical conditions. Can affect bond strength, and cause emission of odor or discoloration
- Rodents or vermin: adhesives of animal or vegetable origin may be attacked by rats, cockroaches, etc.

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Working Properties

•Application: brushing, spray, or knife-spreader application characteristics are usually determined by trial and error. Consistency or viscosity may be adequate indications. Mechanical stability of emulsions and dispersions, and foaming tendency, can be important for machine application

•Bonding range: minimum drying or solvent-reactivation time before suitable bond can be obtained. Maximum allowable time before assembly. Permissible temperature range with heat activated adhesives

•Blocking: tendency of surfaces coated for storage before assembly to adhere under slight pressure, or changes in humidity or temperatures

•Curing rate: minimum curing time, and effect of overcuring. May be determined as a shear or tensile-strength vs. curing-time curve at a specific curing temperature

•Storage stability: physical and chemical changes in original unapplied state as a result of storage for extended time periods at representative storage temperatures

•Coverage: area of bond that can be formed with unit weight or volume of adhesive; expressed as pounds per 1,000 ft of bond line, or square feet per gallon. Depends on method of application; dimensions of work or of adhesive-coated area in relation to part size may affect coverage

Introduction

Anyone intending to use adhesives or sealants faces the formidable tasks of selecting the correct materials and determining proper processes. The adhesive or sealant must flow onto the substrate surface and then change from a flowable liquid to a structural solid without creating harmful internal stresses in the joint. The substrate surface must have previously been cleaned and, possibly, prepared specially for maximum adhesion. The joint geometry must be correctly designed with regard to the materials selected and to the expected loads to avoid undesirable local stresses that could lead to early and premature failure. Also, the physical and chemical characteristics of the joint (adhesive/sealant, substrates, and interphase regions) must be understood and forecast in relation to the expected operating environment.

Introduction

The end-user should not only be concerned with the performance of the joint immediately after bonding or sealing. The performance of the joint must also be considered throughout its practical service life. Almost all adhesive or sealant systems will undergo some change during their life. These changes could have a profound effect on the strength and permanence of the joint.

Introduction

Unfortunately, substrates and adhesive/sealant materials tend to change due to external influences from the environment. These changes could occur: (i) during formation of the joint; and (i) during aging in service. Not only is the adhesive and substrate subject to change, but the interphase region could be subject to transformation as well. These simultaneously occurring, dynamic processes are one reason why it is so difficult to predict the life of a bonded joint. In some applications, they could result in a catastrophic, premature joint failure.

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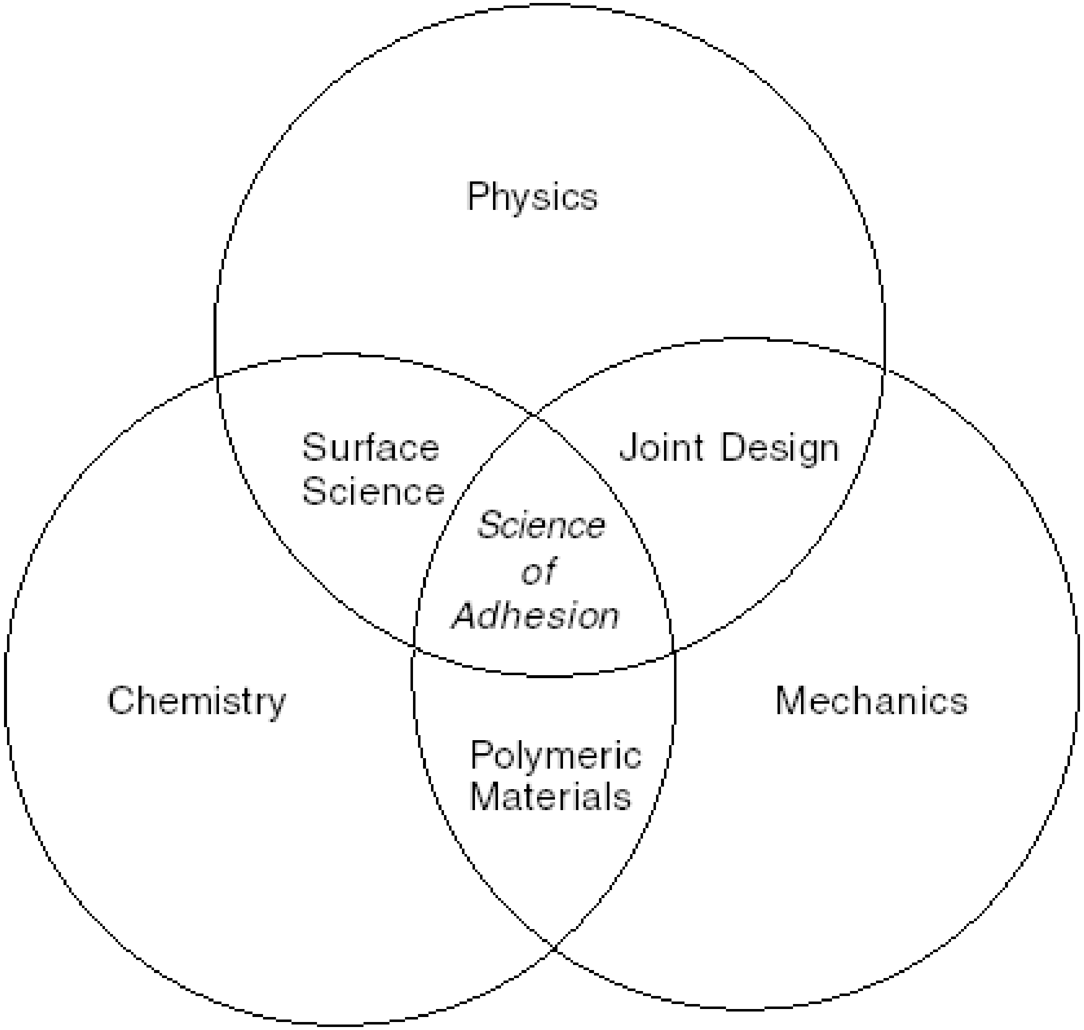

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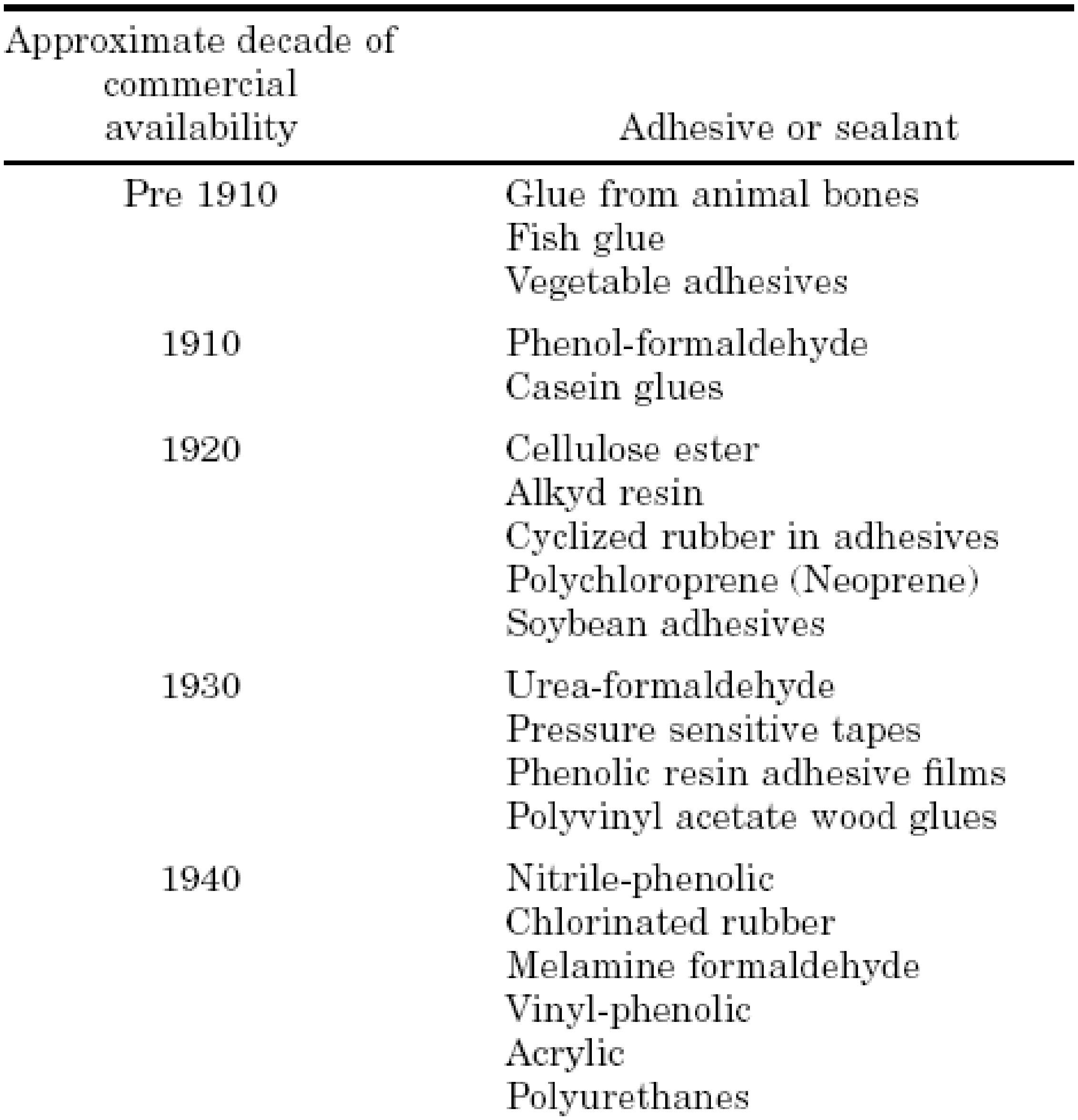

Approximate decade of commercial availability	Adhesive or sealant
Pre 1910	Glue from animal bones Fish glue Vegetable adhesives
1910	Phenol-formaldehyde Casein glues
1920	Cellulose ester Alkyd resin Cyclized rubber in adhesives Polychloroprene (Neoprene) Soybean adhesives
1930	Urea-formaldehyde Pressure sensitive tapes Phenolic resin adhesive films Polyvinyl acetate wood glues
1940	Nitrile-phenolic Chlorinated rubber Melamine formaldehyde Vinyl-phenolic Acrylic Polyurethanes

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1950	Epoxies Cyanoacrylates Anaerobics Epoxy alloys
1960	Polyimide Polybenzimidazole Polyquinoxaline
1970	Second-generation acrylic Acrylic pressure sensitive Structural polyurethanes
1980	Tougheners for thermoset resins Waterborne epoxies Waterborne contact adhesives Formable and foamed hot melts
1990	Polyurethane modified epoxy Curable hot melts UV and light cure systems

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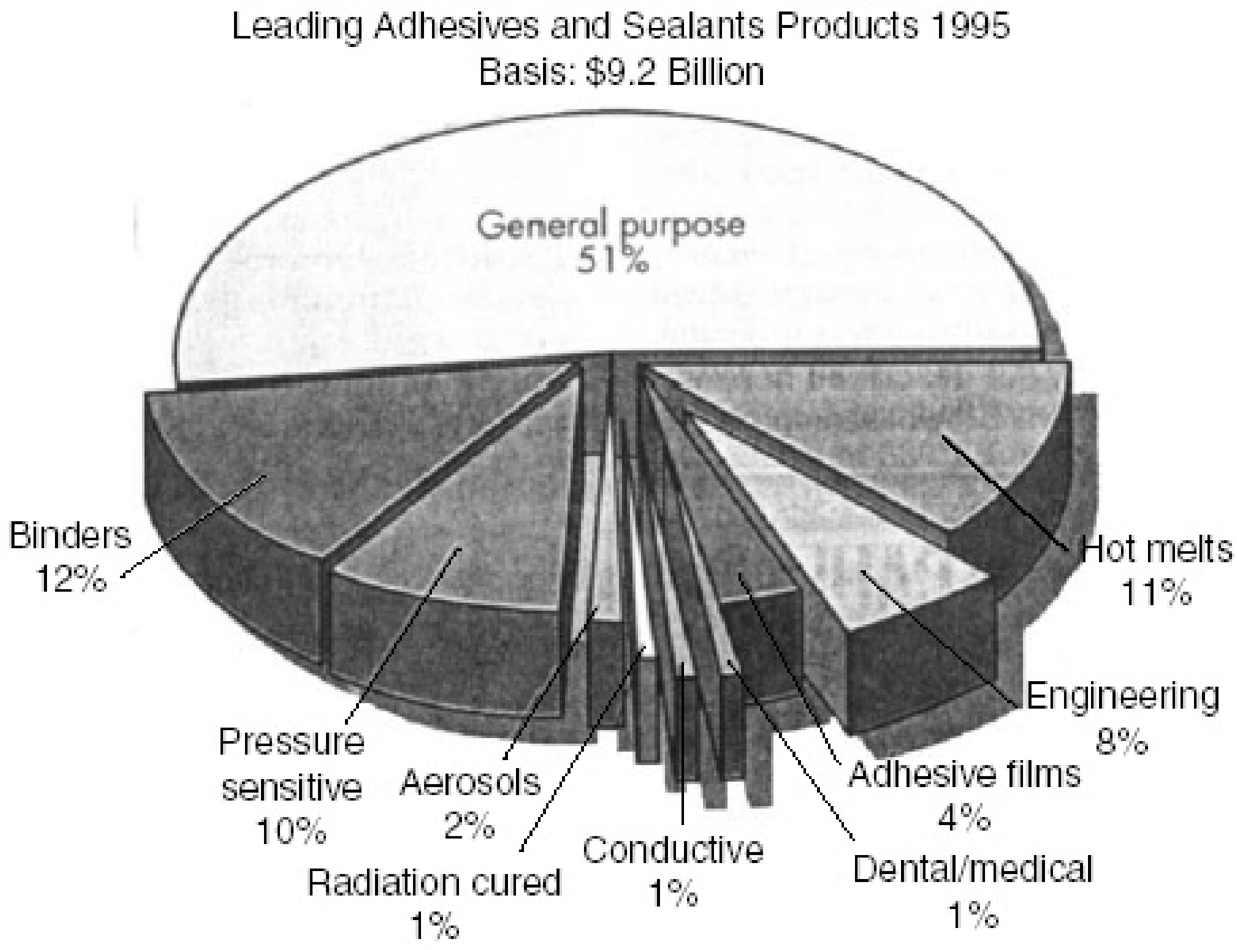

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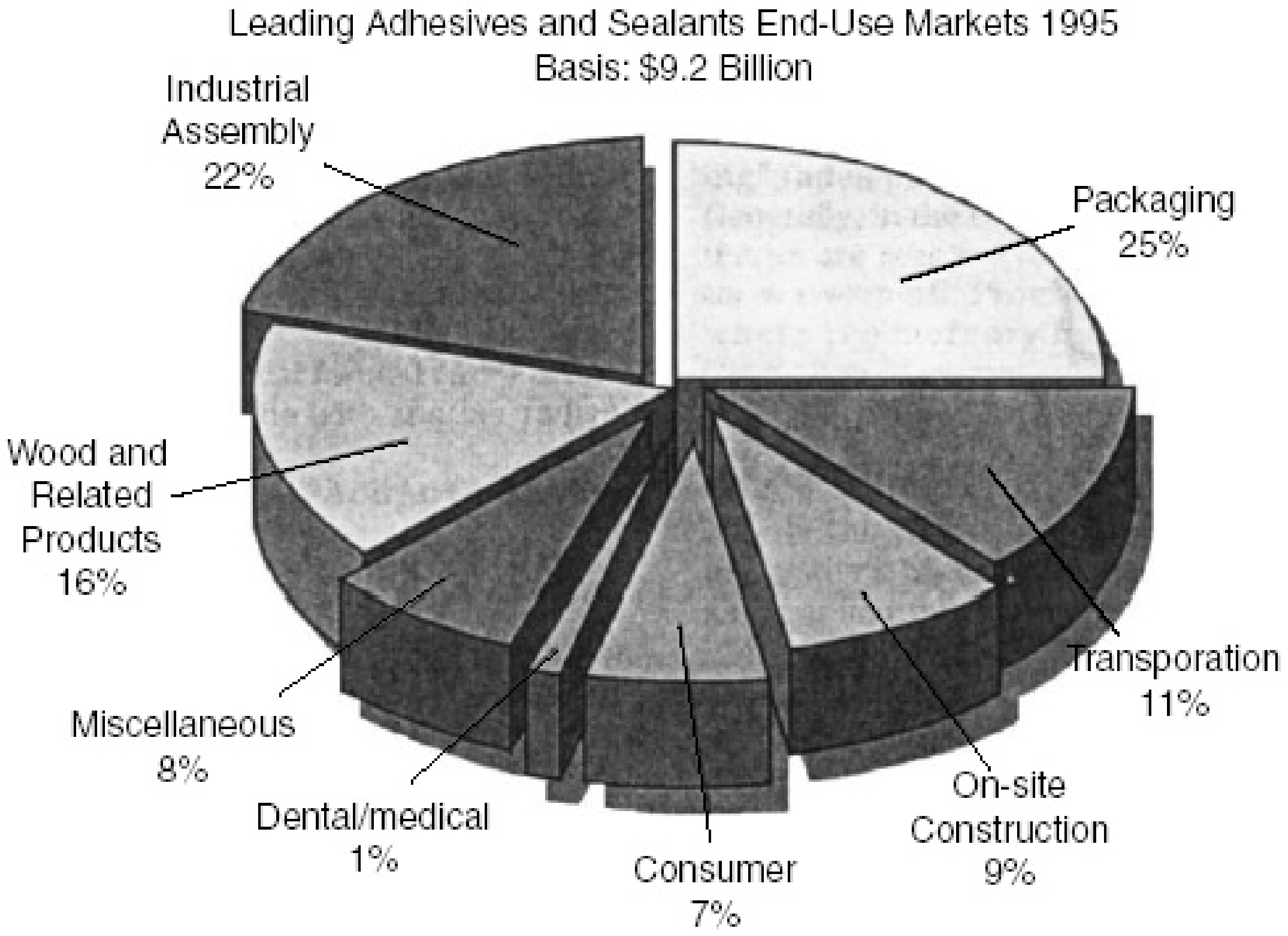
Leading Adhesives and Sealants End-Use Markets 1995
Basis: $9.2 Billion

Introduction

How to choose a joining method?

How to choose an adhesive?

Introduction

Each joining application should be considered with regard to its specific requirements. There are times when adhesives are the worst possible option for joining two substrates, and there are times when adhesives may be the best or only alternative.

Introduction

Often, one must consider the time, trouble, and expense that may be necessary to use an adhesive. For example, certain plastics may require expensive surface preparation processes so that the adhesive can wet their surface. Applications requiring high temperature service conditions may call for an adhesive that requires an elevated temperature cure over a prolonged period.

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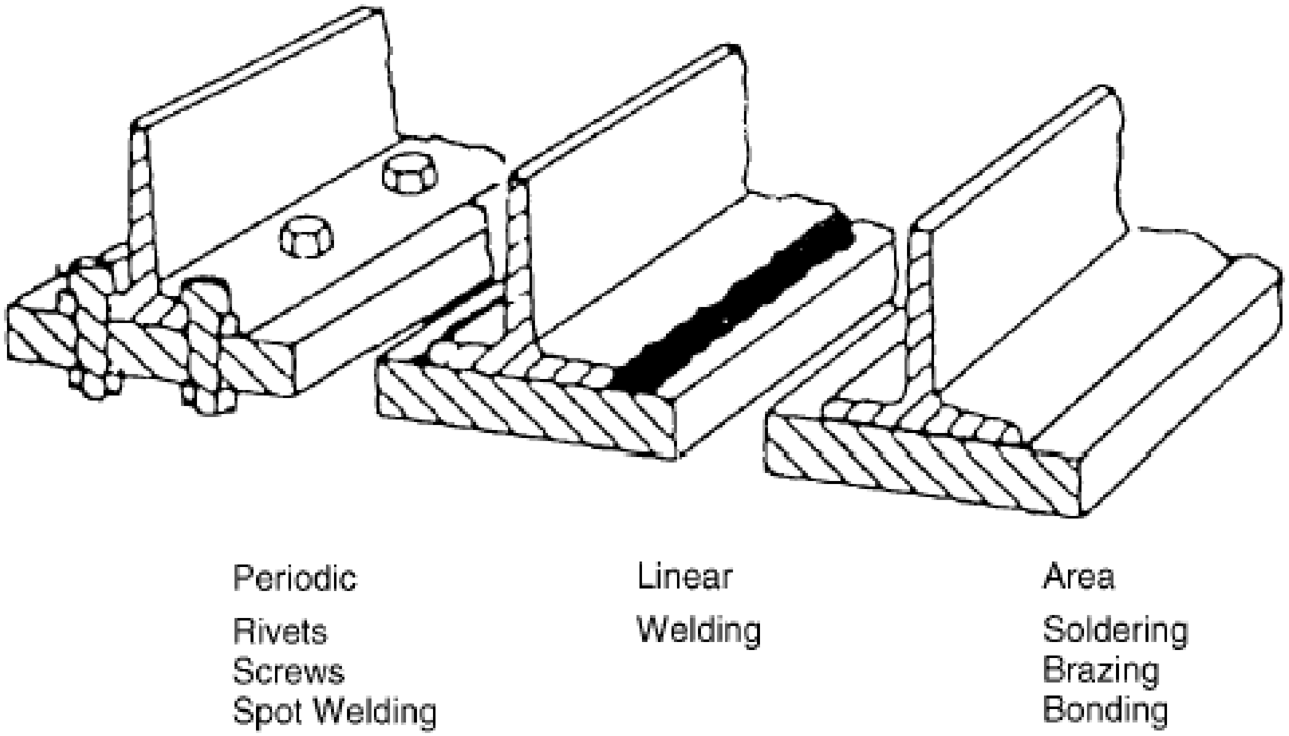
On the other hand, certain applications could not exist without adhesive bonding. Examples of these are joining of ceramic or elastomeric materials, the joining of very thin substrates, the joining of surface skin to honeycomb, and numerous other applications. There are also certain applications where adhesives are chosen because of their low cost and easy, fast joining ability (e.g., packaging, consumer products, large area joints).

Sometimes conventional welding or a mechanical joining process is just not possible. Substrate materials may be incompatible for metallurgical welding due to their thermal expansion coefficients, chemistry, or heat resistance. The end product may not be able to accept the bulk or shape required by mechanical fasteners.

Introduction

A variety of joining methods can be used to provide the assembly function. Alternative joining methods include adhesive bonding, welding, brazing, soldering, and mechanical fastening. All fastening and joining systems, including adhesives, fall into one of three general categories:



Introduction

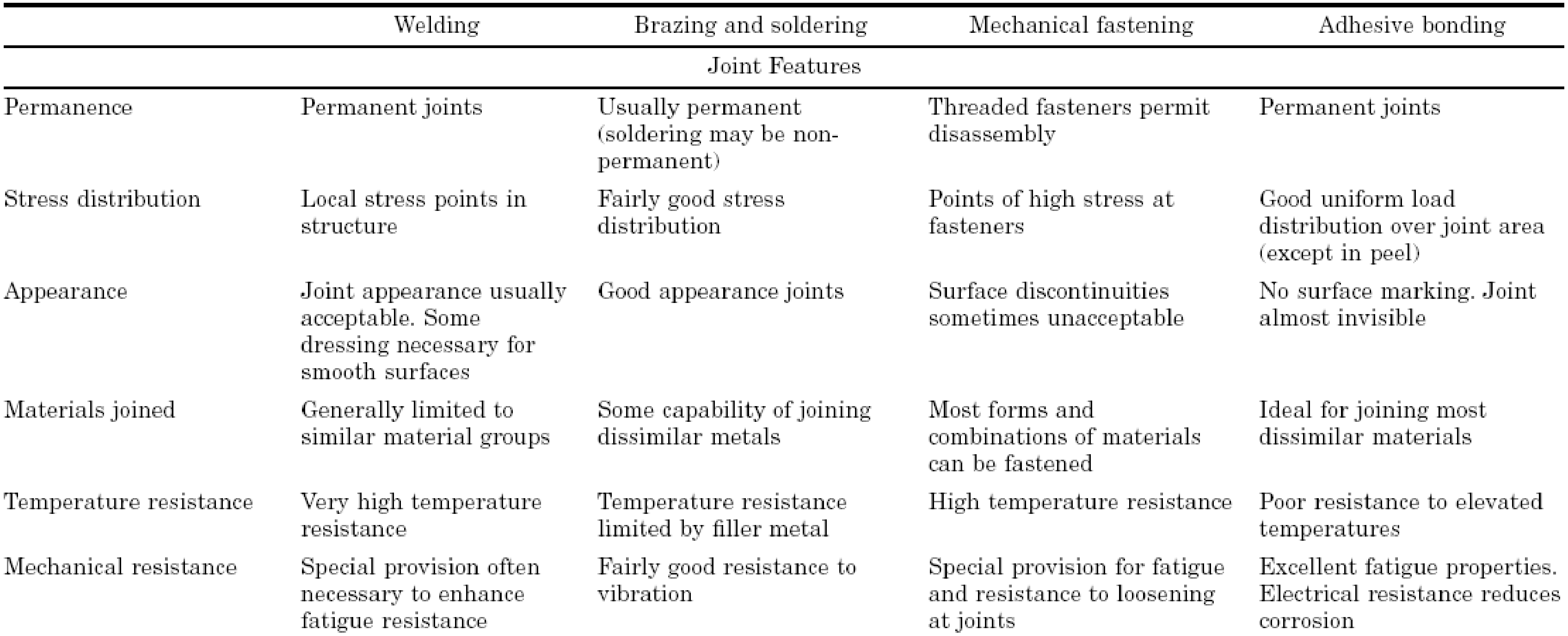
Although adhesive bonding can be successfully employed in periodic or linear attachment applications, the main benefits and advantages are realized when adhesives are used in the “area” attachment designs.

Introduction

In evaluating the appropriate joining method for a particular application, a number of factors must be considered. There generally is no single method of fastening that is obviously the best choice. Some fastening methods can quickly be eliminated from consideration, such as the welding of ceramic substrates or the use of an organic adhesive in an application that will see extremely high service temperatures. Adhesives are usually the proper choice when the substrates are physically dissimilar or metallurgically incompatible materials, thermoset plastics, ceramics, elastomers, thin materials, or very small parts. Adhesive bonding is also generally appropriate when there are large areas to join, or when adhesives can be chosen to provide improvement in manufacturing productivity.

Introduction

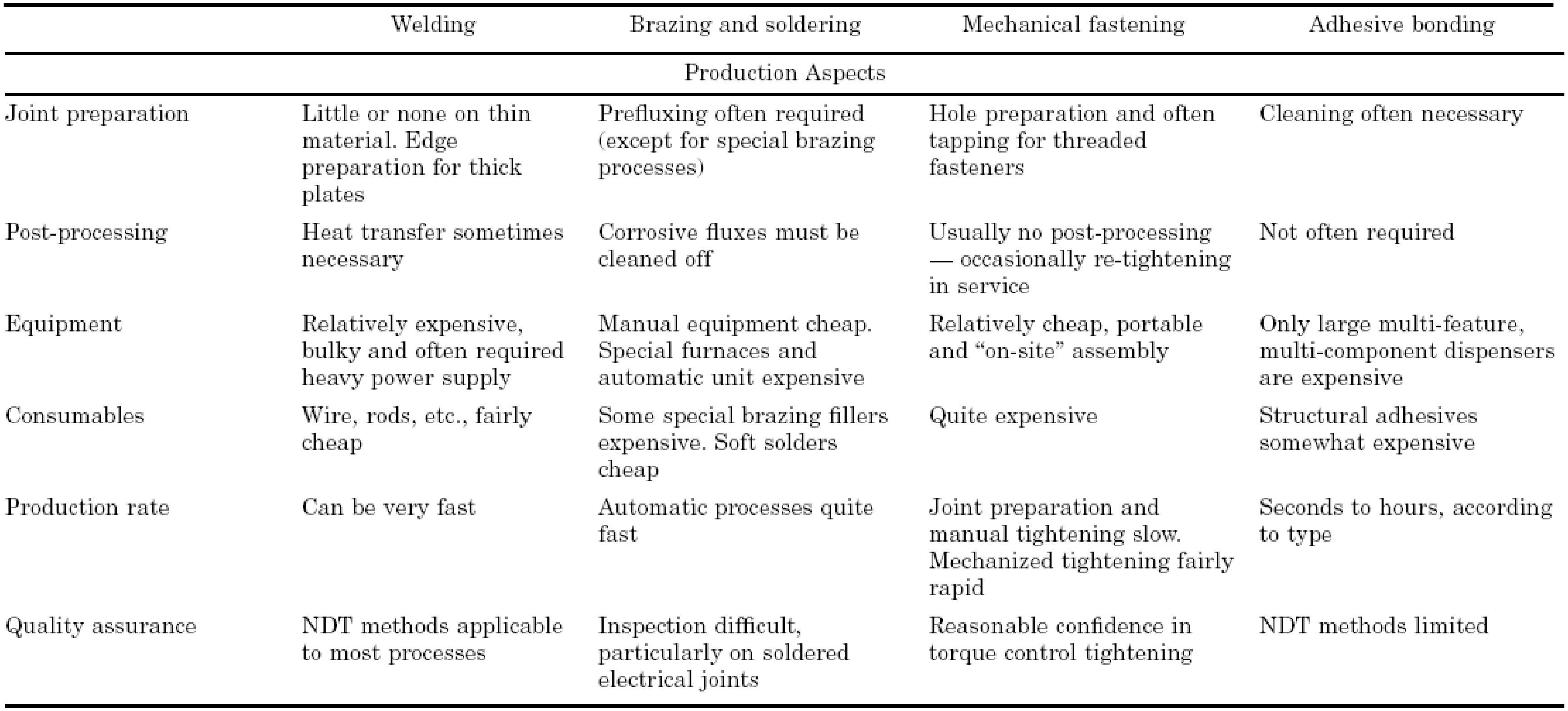
Joining methods process characteristics comparison



	Welding	Brazing and soldering	Mechanical fastening	Adhesive bonding
		Joint Features		
Permanence	Permanent joints	Usually permanent (soldering may be non-permanent)	Threaded fasteners permit disassembly	Permanent joints
Stress distribution	Local stress points in structure	Fairly good stress distribution	Points of high stress at fasteners	Good uniform load distribution over joint area (except in peel)
Appearance	Joint appearance usually acceptable. Some dressing necessary for smooth surfaces	Good appearance joints	Surface discontinuities sometimes unacceptable	No surface marking. Joint almost invisible
Materials joined	Generally limited to similar material groups	Some capability of joining dissimilar metals	Most forms and combinations of materials can be fastened	Ideal for joining most dissimilar materials
Temperature resistance	Very high temperature resistance	Temperature resistance limited by filler metal	High temperature resistance	Poor resistance to elevated temperatures
Mechanical resistance	Special provision often necessary to enhance fatigue resistance	Fairly good resistance to vibration	Special provision for fatigue and resistance to loosening at joints	Excellent fatigue properties. Electrical resistance reduces corrosion

Introduction

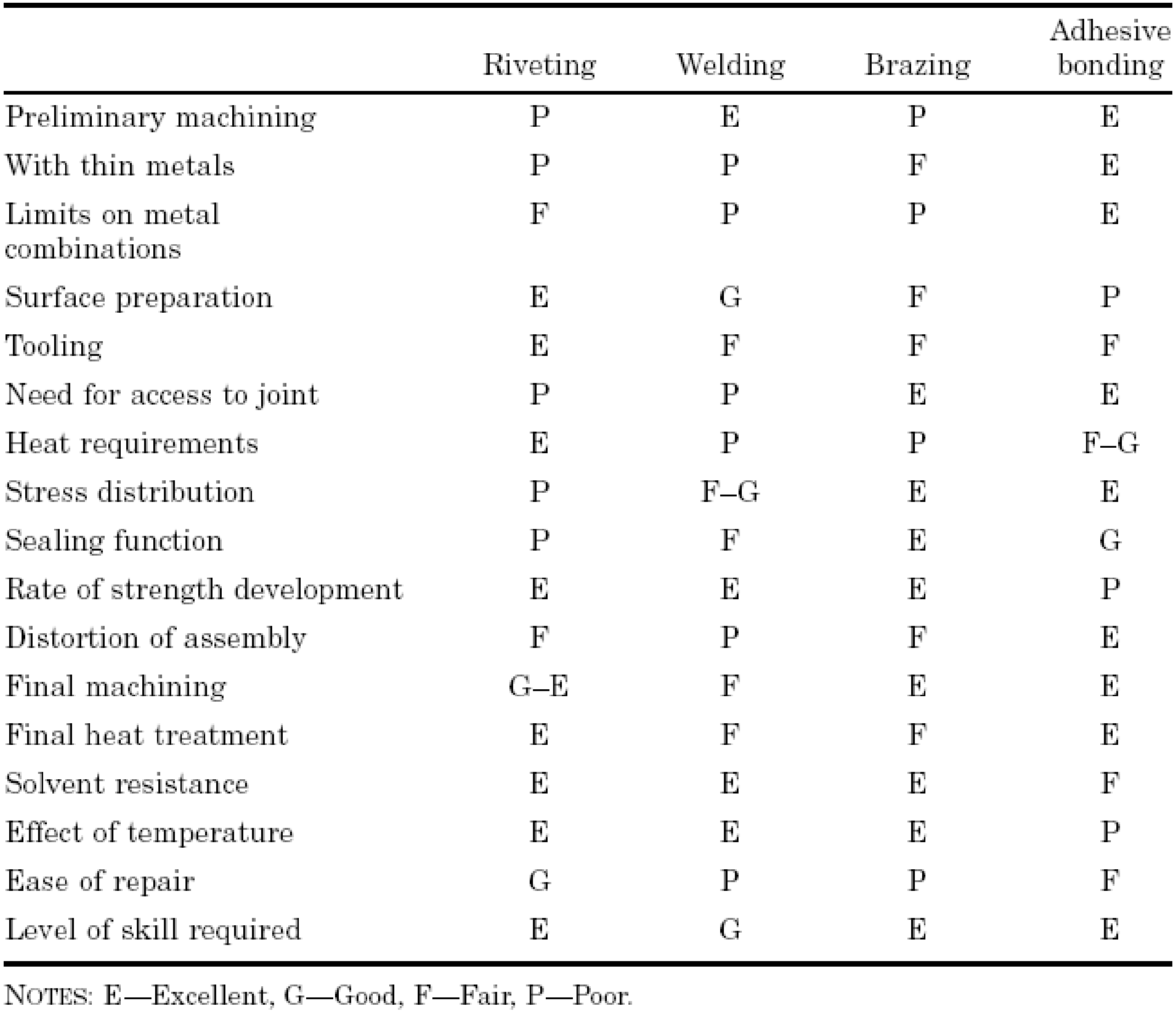
Joining methods process characteristics comparison



	Welding	Brazing and soldering	Mechanical fastening	Adhesive bonding
		Production Aspects		
Joint preparation	Little or none on thin material. Edge preparation for thick plates	Prefluxing often required (except for special brazing processes)	Hole preparation and often tapping for threaded fasteners	Cleaning often necessary
Post-processing	Heat transfer sometimes necessary	Corrosive fluxes must be cleaned off	Usually no post-processing — occasionally re-tightening in service	Not often required
Equipment	Relatively expensive, bulky and often required heavy power supply	Manual equipment cheap. Special furnaces and automatic unit expensive	Relatively cheap, portable and “on-site” assembly	Only large multi-feature, multi-component dispensers are expensive
Consumables	Wire, rods, etc., fairly cheap	Some special brazing fillers expensive. Soft solders cheap	Quite expensive	Structural adhesives somewhat expensive
Production rate	Can be very fast	Automatic processes quite fast	Joint preparation and manual tightening slow. Mechanized tightening fairly rapid	Seconds to hours, according to type
Quality assurance	NDT methods applicable to most processes	Inspection difficult, particularly on soldered electrical joints	Reasonable confidence in torque control tightening	NDT methods limited

Introduction

Joining methods comparison



	Riveting	Welding	Brazing	Adhesive bonding
Preliminary machining	P	E	P	E
With thin metals	P	P	F	E
Limits on metal combinations	F	P	P	E
Surface preparation	E	G	F	P
Tooling	E	F	F	F
Need for access to joint	P	P	E	E
Heat requirements	E	P	P	F–G
Stress distribution	P	F–G	E	E
Sealing function	P	F	E	G
Rate of strength development	E	E	E	P
Distortion of assembly	F	P	F	E
Final machining	G–E	F	E	E
Final heat treatment	E	F	F	E
Solvent resistance	E	E	E	F
Effect of temperature	E	E	E	P
Ease of repair	G	P	P	F
Level of skill required	E	G	E	E

NOTES: E—Excellent, G—Good, F—Fair, P—Poor.

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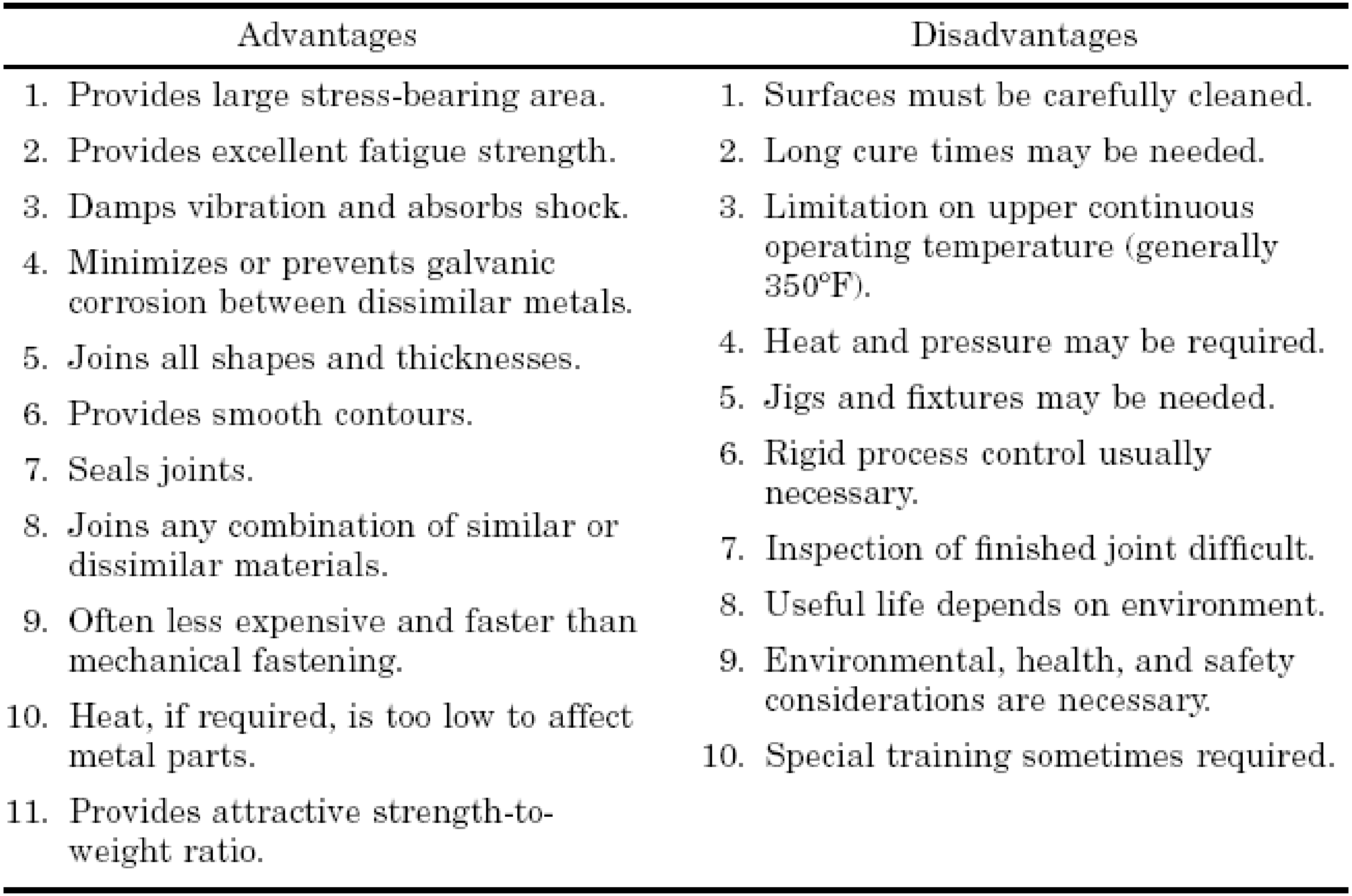
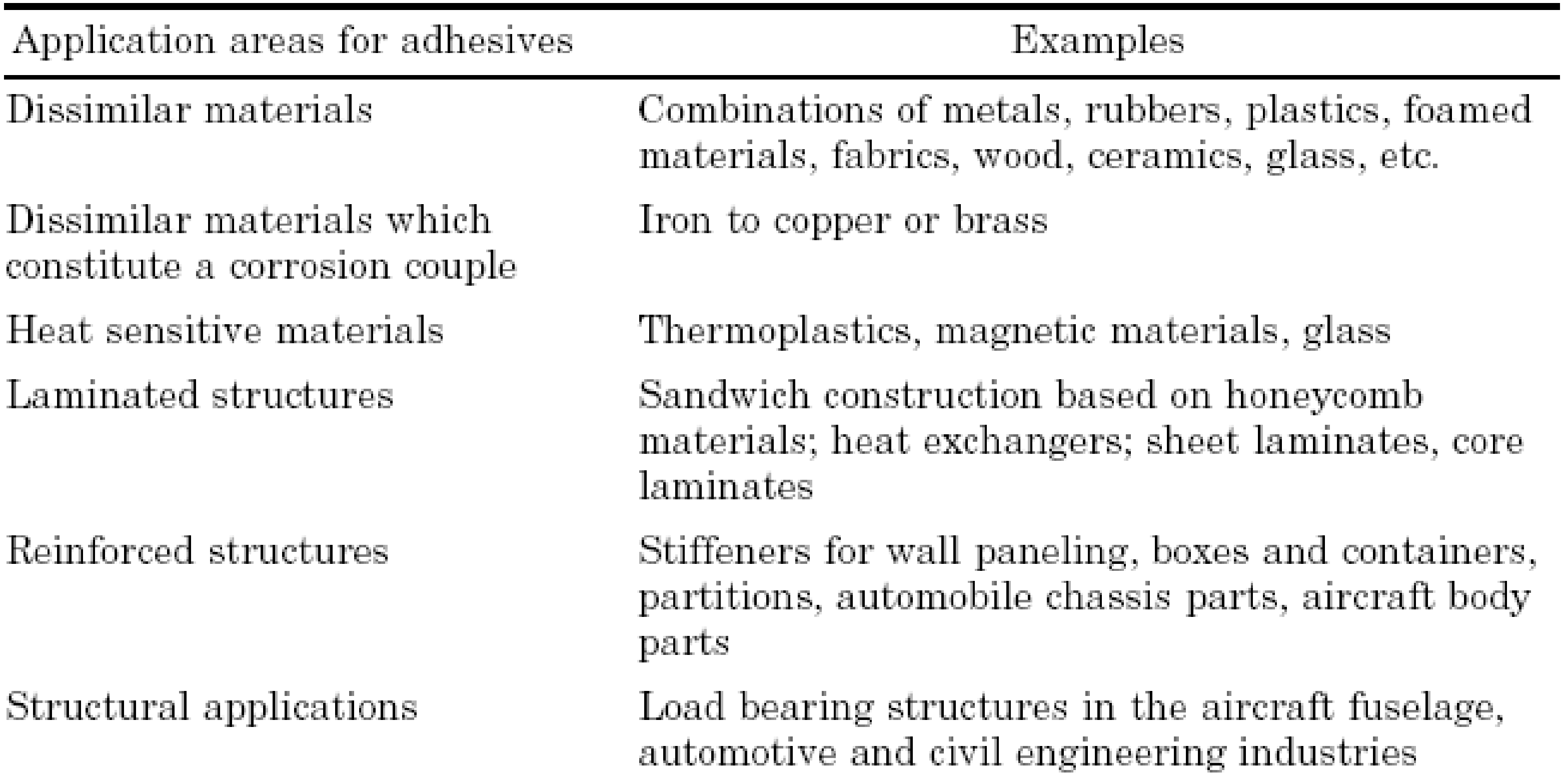
Advantages/disadvantages of adhesive bonding



Advantages	Disadvantages
1. Provides large stress-bearing area.	1. Surfaces must be carefully cleaned.
2. Provides excellent fatigue strength.	2. Long cure times may be needed.
3. Damps vibration and absorbs shock.	3. Limitation on upper continuous operating temperature (generally 350°F).
4. Minimizes or prevents galvanic corrosion between dissimilar metals.	4. Heat and pressure may be required.
5. Joins all shapes and thicknesses.	5. Jigs and fixtures may be needed.
6. Provides smooth contours.	6. Rigid process control usually necessary.
7. Seals joints.	7. Inspection of finished joint difficult.
8. Joins any combination of similar or dissimilar materials.	8. Useful life depends on environment.
9. Often less expensive and faster than mechanical fastening.	9. Environmental, health, and safety considerations are necessary.
10. Heat, if required, is too low to affect metal parts.	10. Special training sometimes required.
11. Provides attractive strength-to-weight ratio.	

Introduction

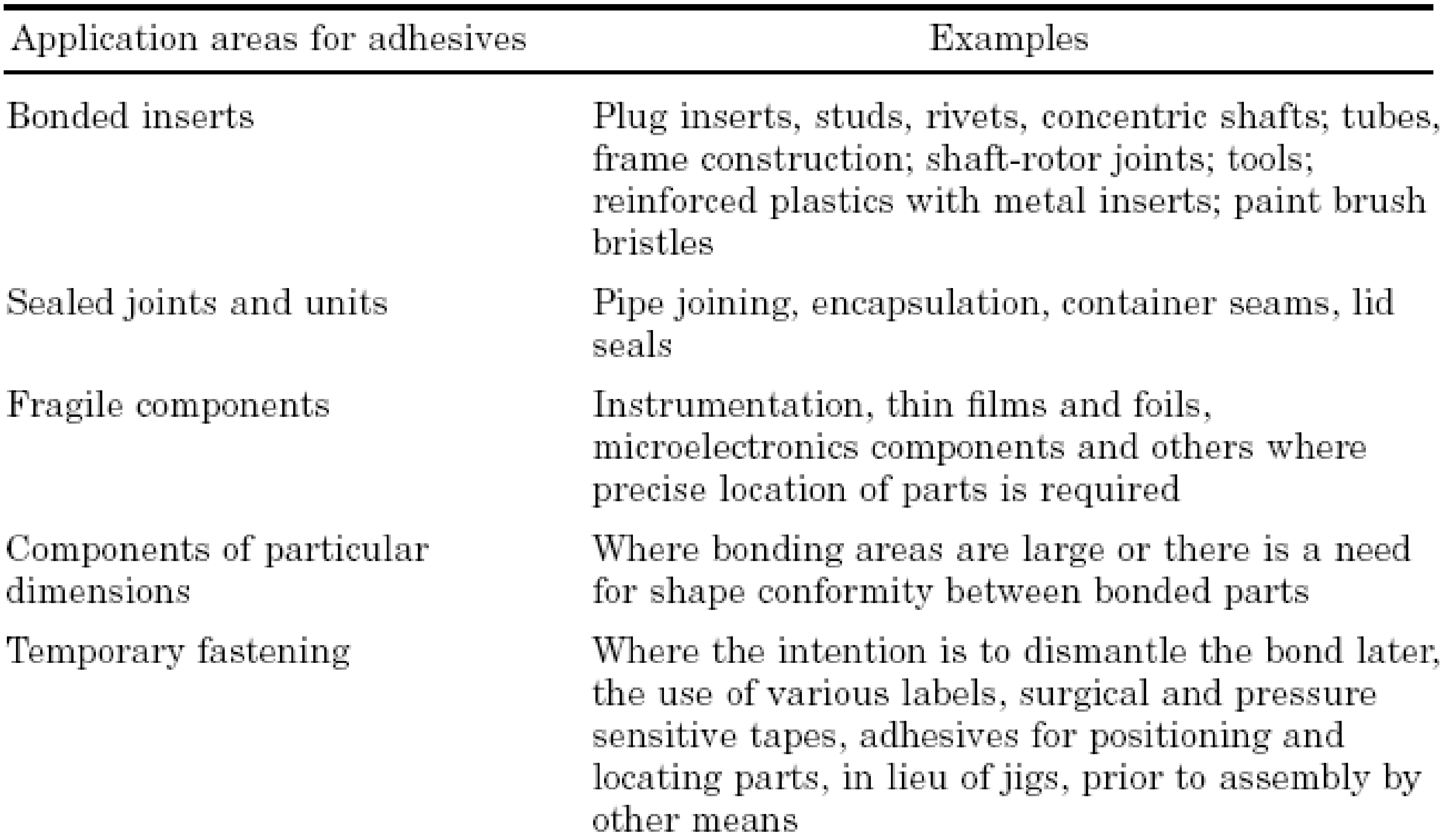
Examples of applications where bonding is a practical method of assembly



Application areas for adhesives	Examples
Dissimilar materials	Combinations of metals, rubbers, plastics, foamed materials, fabrics, wood, ceramics, glass, etc.
Dissimilar materials which constitute a corrosion couple	Iron to copper or brass
Heat sensitive materials	Thermoplastics, magnetic materials, glass
Laminated structures	Sandwich construction based on honeycomb materials; heat exchangers; sheet laminates, core laminates
Reinforced structures	Stiffeners for wall paneling, boxes and containers, partitions, automobile chassis parts, aircraft body parts
Structural applications	Load bearing structures in the aircraft fuselage, automotive and civil engineering industries

Introduction

Examples of applications where bonding is a practical method of assembly



Application areas for adhesives	Examples
Bonded inserts	Plug inserts, studs, rivets, concentric shafts; tubes, frame construction; shaft-rotor joints; tools; reinforced plastics with metal inserts; paint brush bristles
Sealed joints and units	Pipe joining, encapsulation, container seams, lid seals
Fragile components	Instrumentation, thin films and foils, microelectronics components and others where precise location of parts is required
Components of particular dimensions	Where bonding areas are large or there is a need for shape conformity between bonded parts
Temporary fastening	Where the intention is to dismantle the bond later, the use of various labels, surgical and pressure sensitive tapes, adhesives for positioning and locating parts, in lieu of jigs, prior to assembly by other means

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Mechanical advantages

Adhesive bonding does not have many of the disadvantages of other methods. Welding or brazing, useful on heavy-gauge metal, is expensive and requires great heat. Dissimilar metals usually have different coefficients of thermal expansion or thermal conductivities making them more difficult to weld. Some metals have unstable oxides that also make welding difficult. Many light metals such as aluminum, magnesium, and titanium are difficult to weld and are weakened or distorted by the heat of welding. High temperature metallurgical joining methods can cause thin sheets to distort.

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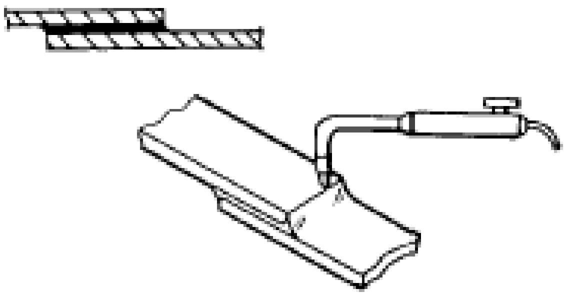
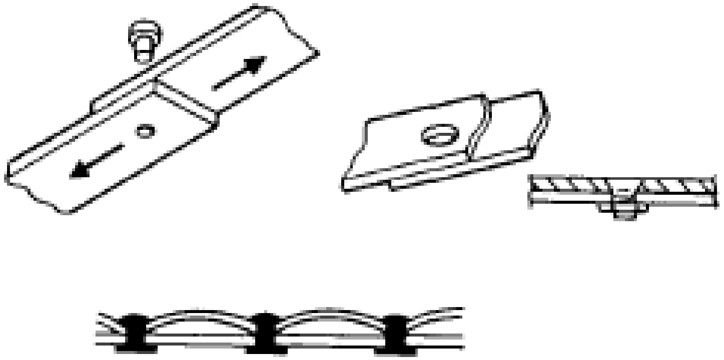
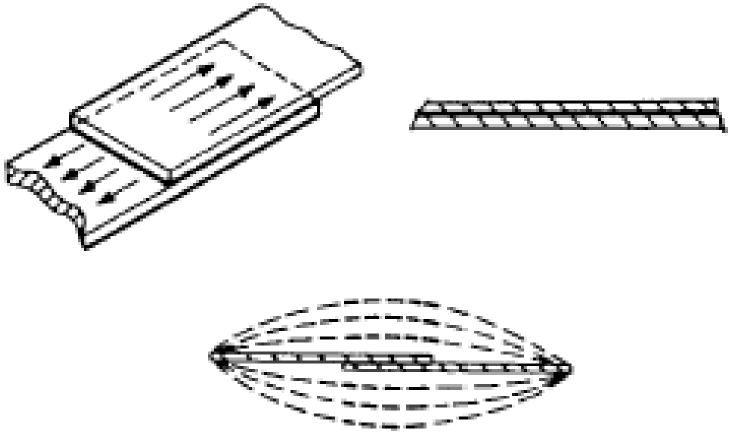


Brazing is an expensive bonding method. Requiring excessive heat, it often results in irregular, distorted parts. Adhesive bonds are always uniform.



When joining a material with mechanical fasteners, holes must be drilled through the assembly. These holes weaken the material and allow concentration of stress.



A high strength adhesive bond withstands stress more effectively than either welds or mechanical fasteners.

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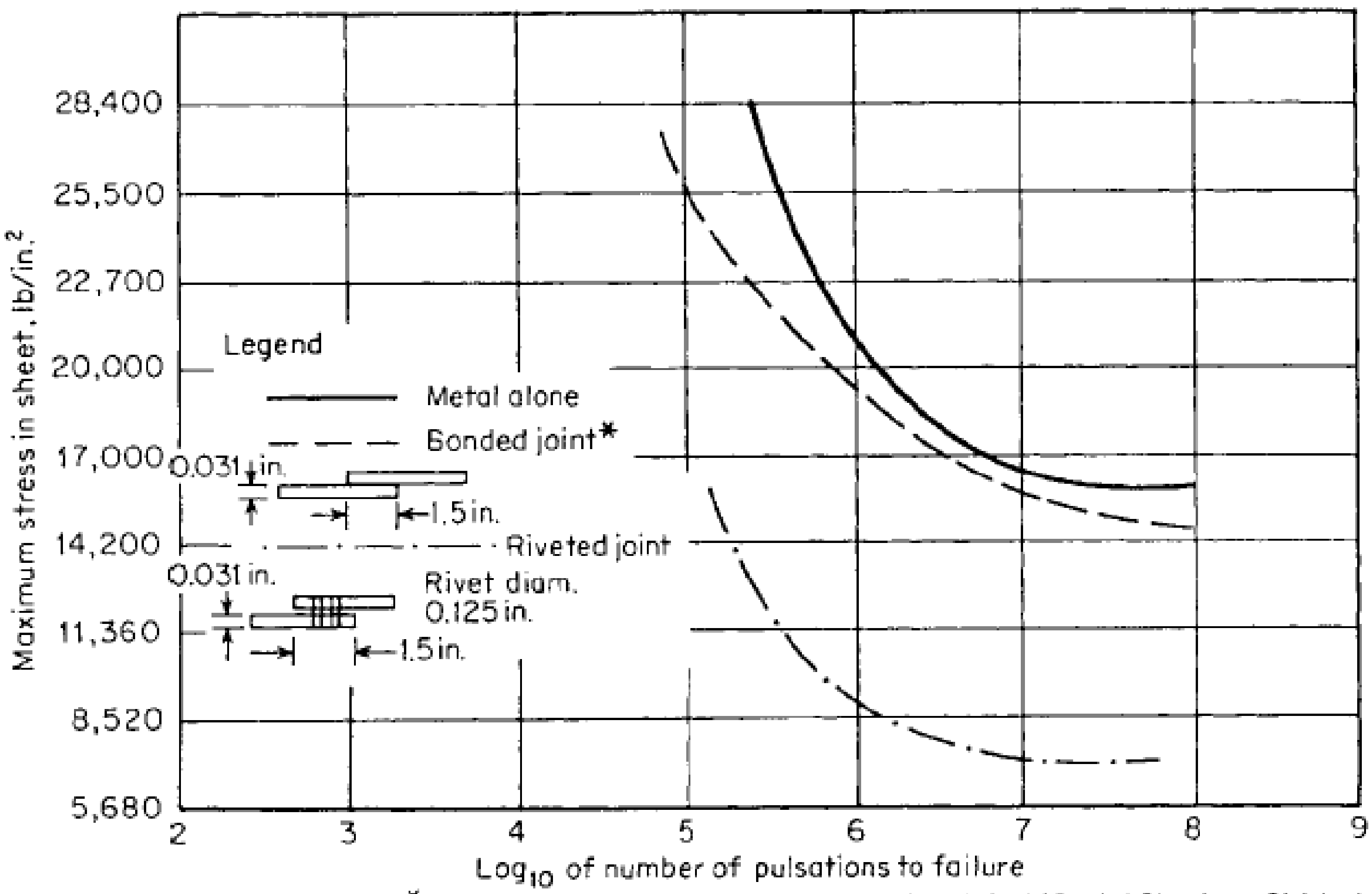

*Modified structural adhesive from CIBA-Geigy Limited (Bonded Structures Division)

Introduction

Design advantages

Adhesives offer certain valuable design advantages. Unlike rivets or bolts, adhesives produce smooth contours that are aerodynamically and aesthetically beneficial. Adhesives also offer a better strength to- weight ratio than other methods of mechanical fastening. Adhesives can join any combination of solid materials regardless of shape, thickness, or mismatch in physical properties such as coefficient of thermal expansion or elastic modulus. Certain substrates may be too thin or too small to weld reproducibly without distortion. Thus, medical products and microelectronics are often assembled with adhesives. Nonmetallic materials, such as plastics, elastomers, ceramics, and many paper products, can be joined together and to one another more economically and efficiently with adhesive bonding than with other methods.

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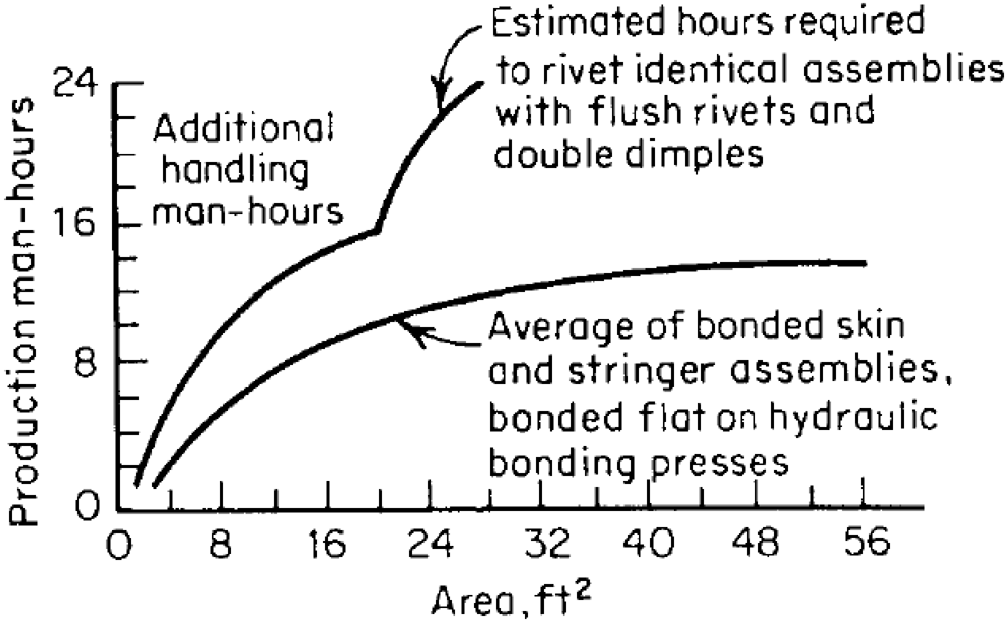
Production advantages

Adhesive bonding is, at times, faster and less expensive than conventional fastening methods. It is well suited for high-volume production or assemblies requiring large bonded areas. As the size of the area to be joined increases, the time and labor saved by using adhesives instead of mechanical fasteners become progressively greater because the entire joint area can be bonded in one operation.



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Other advantages

Adhesives are useful for providing secondary functions as well as the primary function of holding the substrates together. Many designers feel that one of the most valuable characteristics of adhesive bonding is their multi-functional nature. In addition to performing a mechanical fastening operation, an adhesive may also be used as a sealant, vibration damper, insulator, and gap filler—all in the same application. Another property of adhesives that is often advantageous is their ability to function as electrical and thermal insulators in a joint. The degree of insulation can be varied with different adhesive formulations and fillers. Adhesives can even be made electrically and thermally conductive with silver and boron nitride fillers, respectively. Since adhesives usually do not conduct electricity, they prevent galvanic corrosion when dissimilar metals are bonded.

Introduction

Mechanical disadvantages

The most serious limitation on the use of polymeric adhesives is their time-dependent strength in degrading environments such as moisture, high temperatures, or chemicals. Chemical environments and outdoor weathering also degrade adhesives. The rate of strength degradation may be accelerated by continuous stress or elevated temperatures. The combination of continuous stress along with high moisture conditions is of special concern. Certain adhesives will only survive in this environment if their service stress is significantly less than their ultimate strength (e.g., less than 10% of ultimate strength).

Introduction

Mechanical disadvantages

Since nearly every adhesive application is unique, the adhesive manufacturers often do not have data concerning the aging characteristics of their adhesives in specific environments. Thus, before any adhesive is established in production, a thorough evaluation should be made in either a real or a simulated operating environment.

With most structural adhesives, strength is more directional than with mechanical fasteners. Generally, adhesives perform better when stressed in shear or tension than when exposed to cleavage or peel forces. Residual stresses inside the joint can also present serious problems. Such stresses arise from shrinkage due to cure or aging, from different coefficients of thermal expansion between substrates, and from other circumstances.

Introduction

The adhesive material itself should never be used as a structural substrate. Very heavy bondlines with uneven joint thickness result in undesirable concentrations of stresses. Many adhesives cure by an exothermic chemical reaction whose intensity is dependent on the mass of material. Adhesives are generally formulated to cure in thin sections. Therefore, certain epoxy adhesives, when applied in significant bulk, could over-heat due to their own crosslinking reaction and, in fact, burn or degrade when cured in thick sections.

Introduction

Design disadvantages

The adhesive joint must be carefully designed for optimum performance. Design factors include the type of stress, environmental influences, and production methods that will be used. Many rigid adhesives do not work well when external stresses act to peel or cleave the substrates from one another. These stresses can often be reduced or eliminated by careful joint design. Seldom can a joint, which is designed for mechanical fastening, be used successfully for adhesive bonding without revision. Sometimes such revisions result in added expense or manufacturing steps.

There are no standards to guide the user with regard to design limits or to provide a safe design margin. These will depend on the adhesive and substrate, on the production methods, on the specific end-use environment, and on many other factors that are often not foreseen at the time of design development. Therefore, it is very difficult to predict the useful life of a bonded joint.

Introduction

Simple life estimation processes used in other industries are not effective with adhesives because of the numerous and sometimes competing reactions that can take place within a bonded joint. The only effective method of estimating the useful life of an adhesive bond is to test prototypes under environmental conditions that will accelerate the stress on the bond.

Introduction

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Introduction

Production disadvantages

Slow and critical processing requirements of some adhesives can be a major disadvantage particularly in high-volume production operations. Several production concerns must be considered when bonding operations are first projected. All adhesives require clean surfaces to obtain the best results. Depending on the type and condition of the substrate and the bond strength desired, surface preparations ranging from a simple solvent wipe to chemical etching are necessary. Adhesives should never be applied onto other coatings or over other adhesives unless the characteristics of these materials are accurately known. The resulting bond strength will be no greater than the ‘‘weakest link in the chain’’.

Introduction

If the adhesive has multiple components, the parts must be carefully weighed and mixed. The setting operation often requires heat and pressure. Lengthy set time makes jigs and fixtures necessary for assembly. Rigid process controls are also necessary, because the adhesive properties are dependent on curing parameters and surface preparations. The inspection of finished joints for quality control is very difficult. This also necessitates strict control over the entire bonding process to ensure uniform quality. Non-destructive test techniques cannot quantitatively predict joint strength.

Introduction

Other disadvantages

Since the true “general-purpose” adhesive has not yet been developed, the end-user must allow time to test candidate adhesives and bonding processes. Everyone involved in the design, selection, testing, and manufacture of adhesive bonded assemblies should be trained as to the critical requirements and processes. Adhesives are sometimes composed of material that may present personnel hazards, including flammability and dermatitis, in which case the necessary precautions must be considered. Workers must be trained how to handle these materials safely.

Introduction

The following items contribute to a “hidden cost” of using adhesives, and they also could contribute to serious production difficulties:

- The storage life of the adhesive may be unrealistically short; some adhesives require refrigerated storage.
- The adhesive may begin to solidify before the worker is ready.
- The cost of surface preparation and primers, if necessary, must be considered.
- Ease of handling, waste, and reproducibility can be essential cost factors.
- Cleanup is a cost factor, especially where misapplied adhesive may ruin the appearance of a product.
- Once bonded, samples cannot easily be disassembled; if misalignment occurs and the adhesive cures, usually the part must be scrapped.

Introduction

Combining adhesive and mechanical fastening

There are advantages in combining adhesive bonding with mechanical fastening. The combination can provide properties that are superior to either singular method. It is also possible to reduce the number of mechanical fastening steps without sacrificing strength or reliability. When combined with adhesives, mechanical joints can provide fixturing for the adhesive as it cures. In this way, expensive fixturing equipment and the time required to set-up such equipment are not necessary. The curing time is also eliminated as a potential bottleneck to the overall assembly process. The stress distribution characteristic of the adhesive bond also allows the designer the freedom to eliminate thicker substrates or reinforcements that may be necessary with mechanical fasteners alone.

Introduction

The secondary functions of the adhesive, such as sealing, vibration damping, electrical insulation, etc., may also be used to achieve an assembly with greater value. In the automotive industry, for example, adhesives are used in combination with spot welding for joining trunk assemblies. This combination provides sound deadening and sealing in addition to a strong joint. Adhesives can also be combined with fasteners that are designed directly into the part (e.g., snap fit connectors). Here the adhesive eventually assumes the full structural load with the mechanical fastener providing the fixturing as the adhesive cures.

Introduction

General requirements for adhesives

The universal requirements for successful application are:

- Cleanliness of the substrate surface
- Wetting of the substrate surface (intimate contact of the adhesive or sealant on the substrate)
- Solidification of the adhesive or sealant
- Forming a "joint" structure (adhesive or sealant material, interphase regions, and substrates) that is resistant to the operating stress and environment
- Design of the joint
- Selection and control of materials and manufacturing processes.

Introduction

Surface conditions

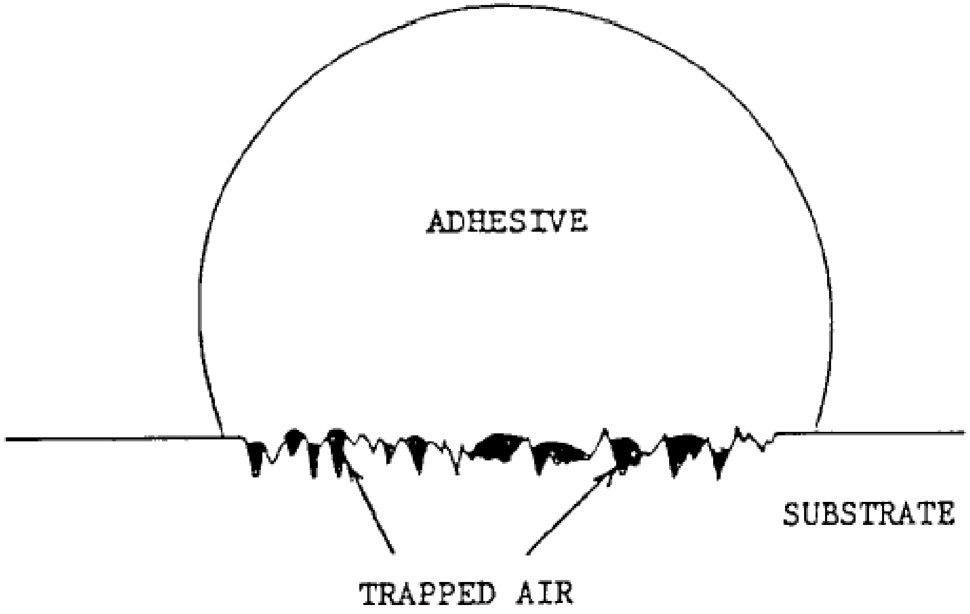
Above all else, one must start with a clean surface. Foreign materials such as dirt, oil, moisture, and weak oxide layers must be removed from the substrate surface, or else the adhesive will bond to these weak boundary layers rather than to the substrate in question. Various surface preparations remove or strengthen the weak boundary layer. These treatments generally involve physical or chemical processes or a combination of both. The choice of surface preparation process will depend on the adhesive, the substrate, the nature of the substrate before bonding, the required bond strength and durability, and the production processes, time, and budget available to the user.

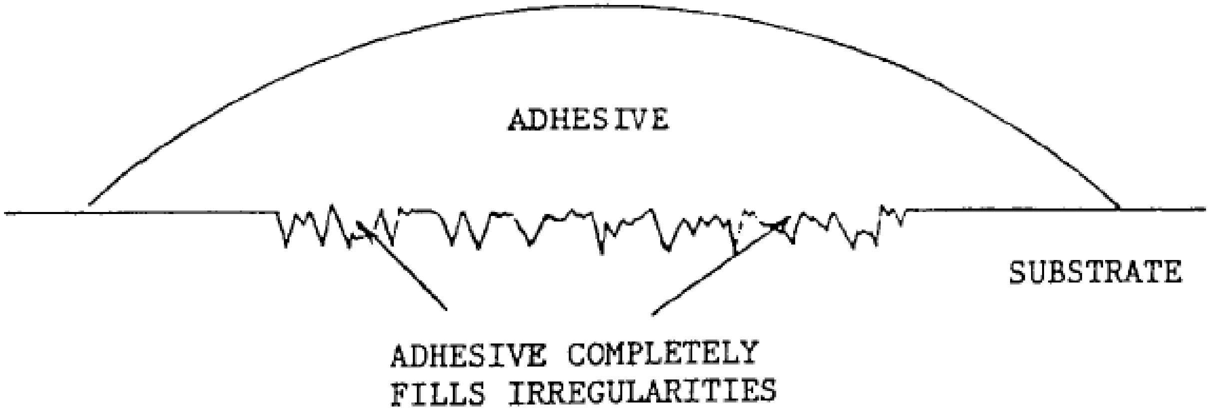
Introduction

Wetting the substrate

Initially, the adhesive must be either a liquid or a readily deformed solid so that it can be easily applied and formed to the required geometry within the assembled joint. It is necessary for the adhesive to flow and then conform to the surfaces of the substrates on both micro- and macroscales. Small air pockets caused by the roughness of the substrate at the interface must be easily displaced with adhesive or sealant. While it is in the liquid state, the material must ‘‘wet’’ the substrate surface. The term wetting refers to a liquid spreading over and intimately contacting a solid surface. One result of good wetting is greater contact area between substrate and adhesive over which the forces of adhesion can act.

Introduction





Introduction

Solidification of the adhesive

The liquid adhesive, once applied, must be converted into a solid. Solidification occurs in one of three ways: chemical reaction by any combination of heat, pressure, curing agent, or other activator such as UV light, radiation, etc.; cooling from a molten liquid to a solid; and drying due to solvent evaporation. The method by which solidification occurs depends on the choice of adhesive. When organic resins solidify, they undergo volumetric shrinkage due to the crosslinking reaction, loss of solvent, or thermal expansion coefficient (contraction on cooling from an elevated temperature cure). In the case of adhesives, it is important that the material does not shrink excessively. Otherwise, undesirable internal stresses could develop in the joint.

Introduction

Forming an impervious joint

Once solidified, the adhesive must have adequate strength and toughness to resist failure under all expected service conditions. To determine the effect of the environment on the performance of the joint, one must consider the adhesive material, the substrate, and the interphase regions that are formed before, during, and after the bonding process. The initial performance and the durability of the joint are strongly dependent on how the substrates are prepared and on the severity of the service environment. The structure and chemistry of the surface region of the parts to be joined and their response to service environments may well govern bond performance. If these surface regions change significantly during processing of the joint or during service life, then the resulting performance characteristics of the joint may also change.

Introduction

Joint design

The adhesive joint should be designed to take advantage of the high shear and tensile strength properties of most materials and to spread the resulting load over as great an area as possible. Although adequate adhesive-bonded assemblies have been made from joints designed for mechanical fastening, the maximum benefits of the adhesive can be obtained only in assemblies specifically designed for adhesive bonding.

Introduction

Selection and control of materials and manufacturing processes

When determining which adhesives are suitable candidates for an application, a number of important considerations must be taken into account. With regard to the controlling factors, the many adhesives available can usually be narrowed to a few candidates that are most likely to be successful. The appropriate manufacturing processes must then be chosen to provide consistent, high strength joints within the allotted time and cost. The exact manufacturing process will depend on many factors including the choice of adhesive and the availability of equipment. However, once chosen, the manufacturing process must be rigidly controlled with regard to the incoming adhesive materials and with regard to the incoming substrate materials. A change in processing parameters could change the degree of stress in the joint, or even the chemical nature of the interphase regions. Should the user decide to change substrate suppliers, he or she should re-verify completely the entire bonding processes. An example is the case of a vulcanized elastomeric substrate such as neoprene. There are many formulations that an elastomer supplier can use to meet a material specification. However, the formulations may contain compounds (e.g., low molecular weight extenders, plasticizers, etc.) that drastically reduce the adhesion of any material to the surface.

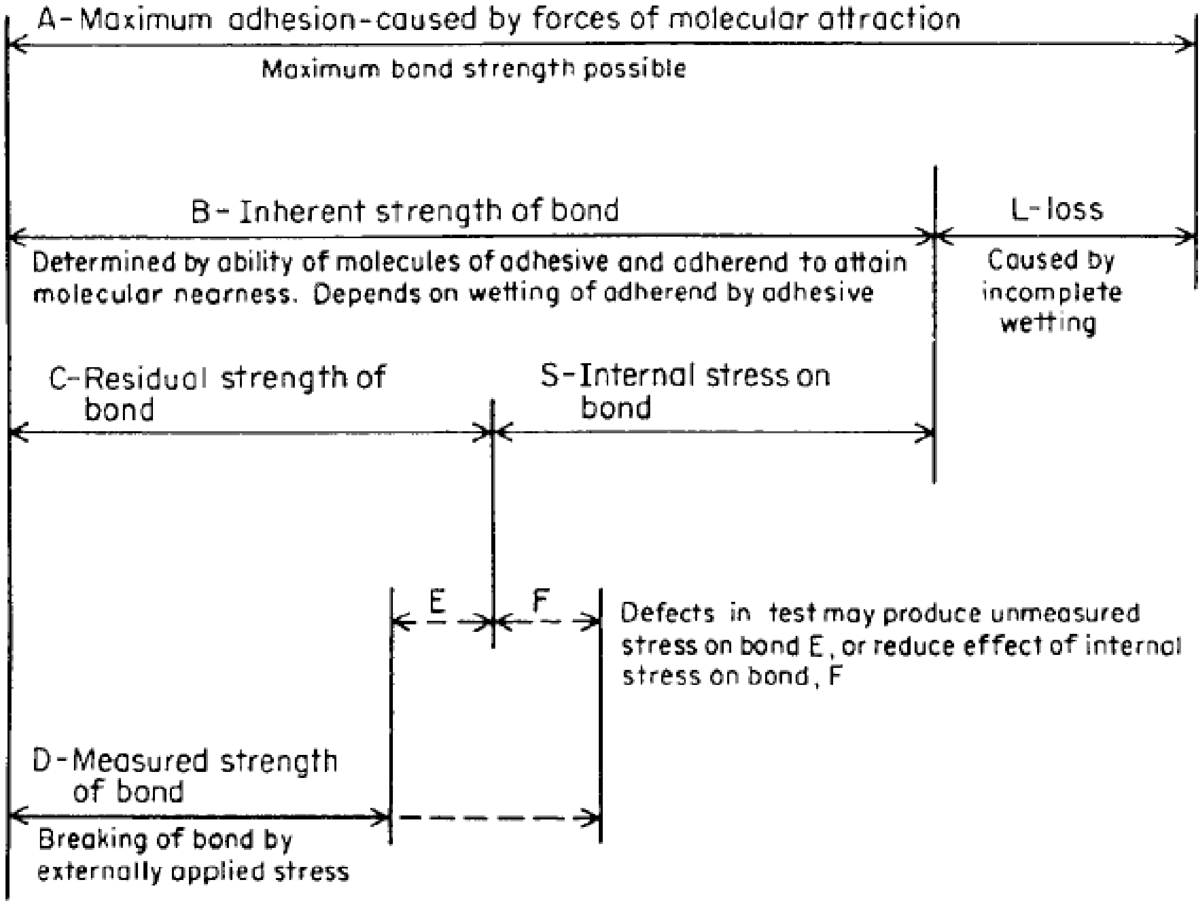
Introduction

Mechanisms of bond failure

Joints may fail in adhesion or cohesion or by some combination of the two. Adhesive failure is an interfacial bond failure between the adhesive and substrate. Cohesive failure occurs when the failure is such that a layer of adhesive or sealant remains on the substrate. When the substrate fails before the adhesive, it is known as a cohesive failure of the substrate. Cohesive failure within the adhesive or one of the substrates is sometime considered a preferred type of failure, because the maximum strength of the material in the joint has been reached. However, failure mode should not be used as a sole criterion for a useful joint. A cohesive type of failure does not necessarily insure a practical or economic assembly or one that will even survive the expected life. The function of the joint is a more important criterion than the mode of joint failure. However, an analysis of failure mode can be an extremely useful guide to determine if the failure was due to a weak boundary layer or improper surface preparation

Introduction

Failure mode	Inference
Adhesive failure (interfacial)	Cohesive strength > interfacial strength
Cohesive failure (bulk)	Interfacial strength > cohesive strength
Adhesives/cohesive (mixed failure mode)	Interfacial strength ≈ cohesive strength



This chart is qualitative, not quantitative, no significance is attached to the relative lengths of the lines, A is always greater than B, and B greater than C

Introduction

Materials used for adhesives

Solid surfaces brought into intimate contact rarely stick to one another, but any liquid placed between them will cause some degree of adhesion. Therefore, almost anything could be used as an adhesive or sealant. However, the nature of the substrate, its surface chemistry, the processing method, and the type of the load and service environment will dictate what material is best to use. Adhesives and sealants are highly formulated materials with many components. They generally have an organic base, although there are some mineral-based adhesives that perform very well in certain applications.

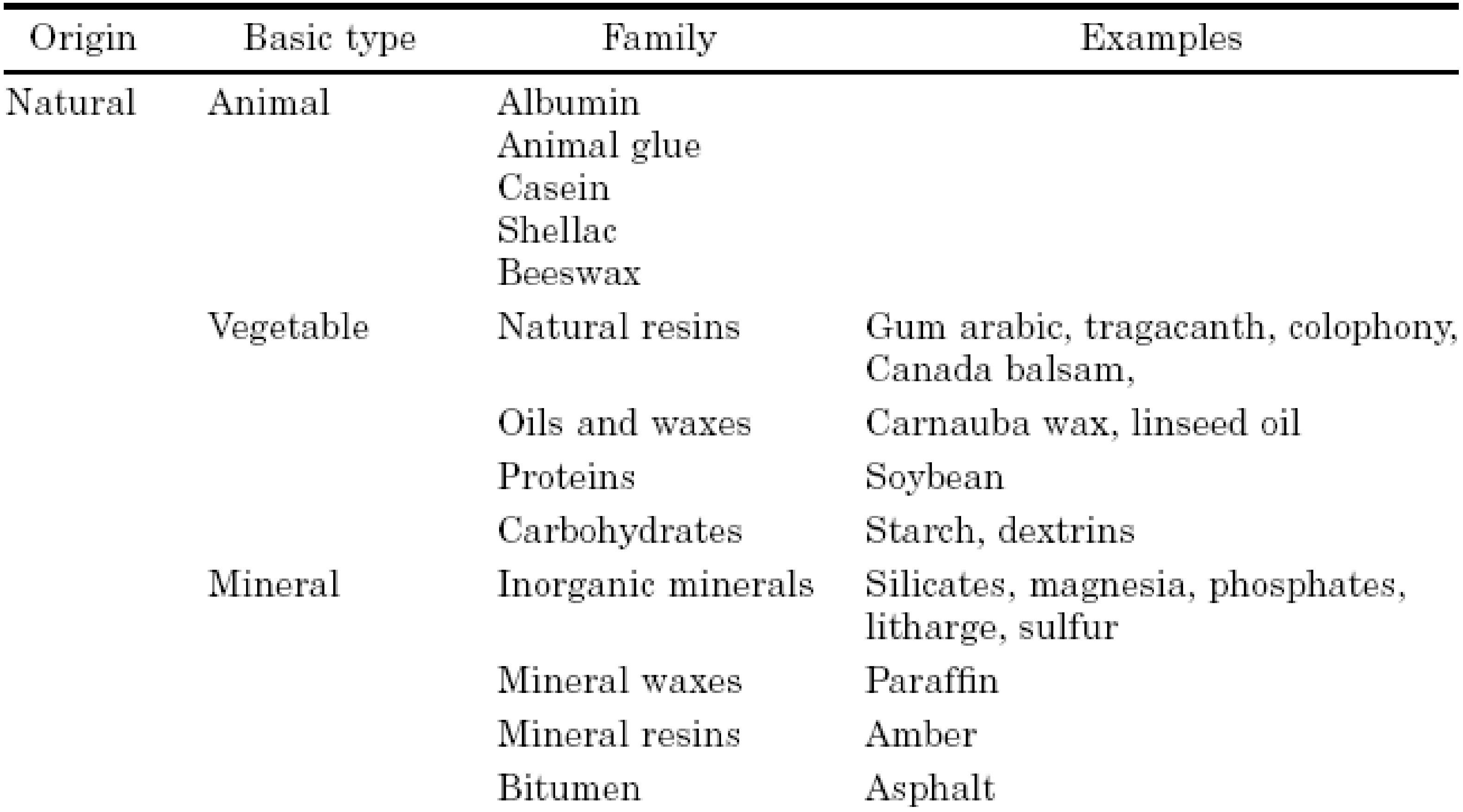
Introduction

For a material to be a potential adhesive or sealant, it must meet three basic criteria. First, the material has, at some stage, to be in a liquid form so that it can readily spread over and make intimate contact with the substrate. Second, the material must be capable of hardening into a solid to withstand and distribute stress. Lastly, the material must resist the environments that it will see during processing and during service.

Introduction

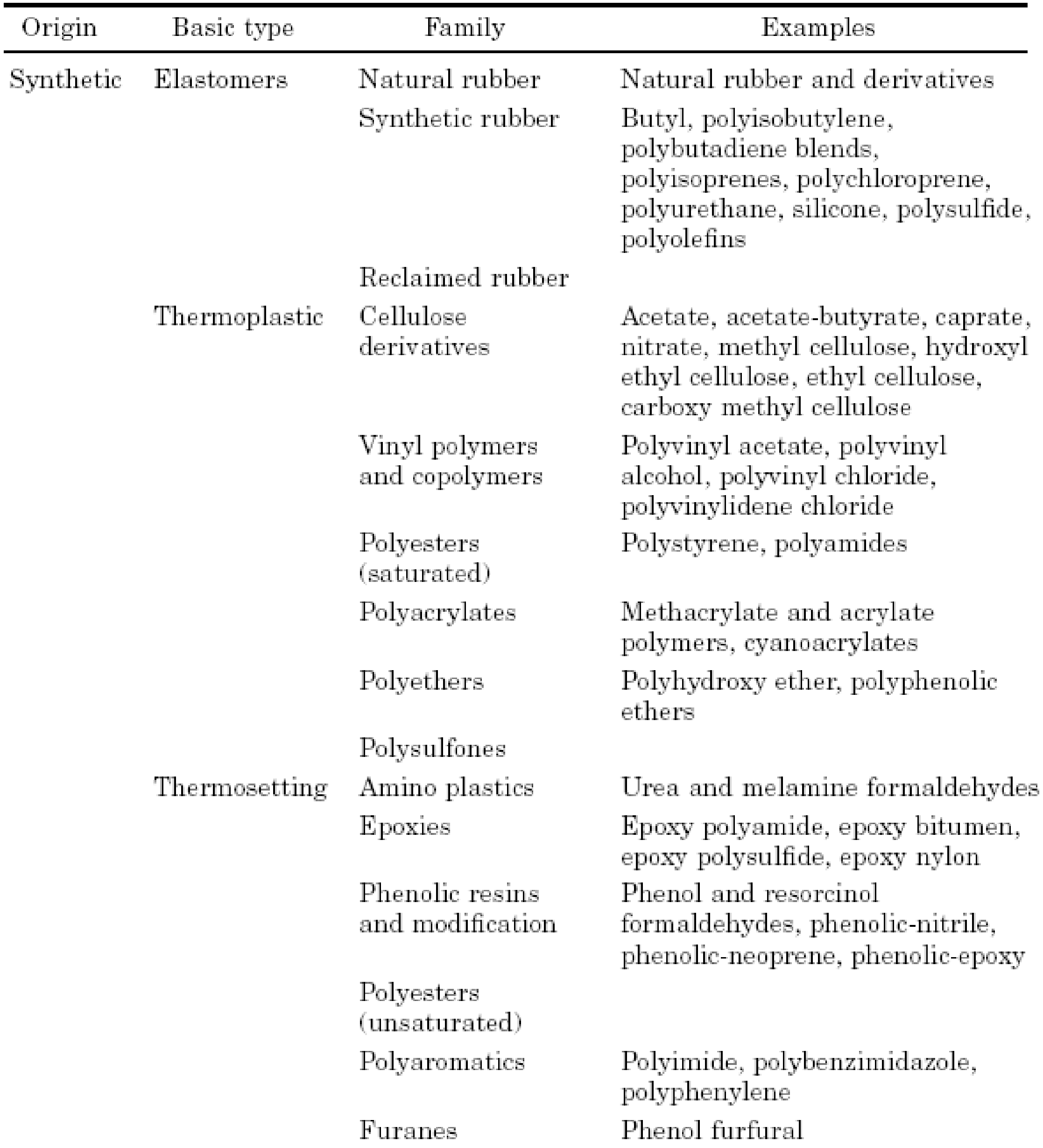
The modern organic materials are all high polymers: long chains of carbon atoms that can form three-dimensional networks. The oldest adhesives and sealants, many that are still used today, are of natural origin. The most common of these are animal glues, starches, and tar or pitch. Naturally occurring adhesives and sealants also include dextrin, asphalt, vegetable proteins, natural rubber, and shellac. Modern polymers are ideal materials to use as adhesives and sealants because they can be applied as low viscosity liquids and, then by various means, hardened into a strong material with relatively good resistance to stress and various environments. This hardening may occur through loss of water or solvent, cooling from the molten state, chemical reaction by crosslinking or curing between the molecular chains, or by polymerizing from the monomer state.

Introduction



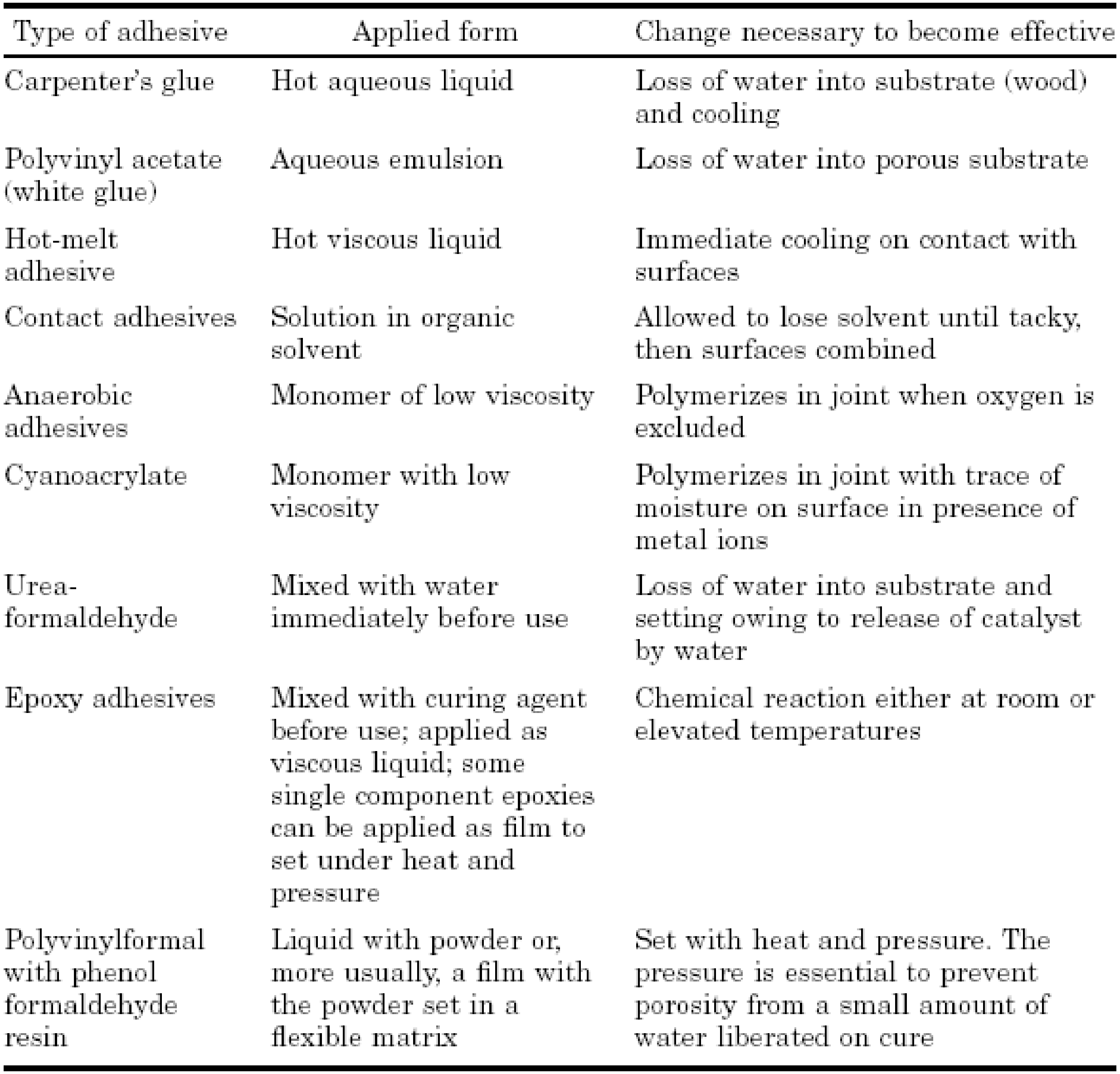
Origin	Basic type	Family	Examples
Natural	Animal	Albumin Animal glue Casein Shellac Beeswax	
	Vegetable	Natural resins	Gum arabic, tragacanth, colophony, Canada balsam,
		Oils and waxes	Carnauba wax, linseed oil
		Proteins	Soybean
		Carbohydrates	Starch, dextrins
	Mineral	Inorganic minerals	Silicates, magnesia, phosphates, litharge, sulfur
		Mineral waxes	Paraffin
		Mineral resins	Amber
		Bitumen	Asphalt

Introduction



Origin	Basic type	Family	Examples
Synthetic	Elastomers	Natural rubber	Natural rubber and derivatives
		Synthetic rubber	Butyl, polyisobutylene, polybutadiene blends, polyisoprenes, polychloroprene, polyurethane, silicone, polysulfide, polyolefins
		Reclaimed rubber	
	Thermoplastic	Cellulose derivatives	Acetate, acetate-butyrate, caprate, nitrate, methyl cellulose, hydroxyl ethyl cellulose, ethyl cellulose, carboxy methyl cellulose
		Vinyl polymers and copolymers	Polyvinyl acetate, polyvinyl alcohol, polyvinyl chloride, polyvinylidene chloride
		Polyesters (saturated)	Polystyrene, polyamides
		Polyacrylates	Methacrylate and acrylate polymers, cyanoacrylates
		Polyethers	Polyhydroxy ether, polyphenolic ethers
		Polysulfones	
	Thermosetting	Amino plastics	Urea and melamine formaldehydes
		Epoxies	Epoxy polyamide, epoxy bitumen, epoxy polysulfide, epoxy nylon
		Phenolic resins and modification	Phenol and resorcinol formaldehydes, phenolic-nitrile, phenolic-neoprene, phenolic-epoxy
		Polyesters (unsaturated)	
		Polyaromatics	Polyimide, polybenzimidazole, polyphenylene
		Furanes	Phenol furfural

Introduction



Type of adhesive	Applied form	Change necessary to become effective
Carpenter's glue	Hot aqueous liquid	Loss of water into substrate (wood) and cooling
Polyvinyl acetate (white glue)	Aqueous emulsion	Loss of water into porous substrate
Hot-melt adhesive	Hot viscous liquid	Immediate cooling on contact with surfaces
Contact adhesives	Solution in organic solvent	Allowed to lose solvent until tacky, then surfaces combined
Anaerobic adhesives	Monomer of low viscosity	Polymerizes in joint when oxygen is excluded
Cyanoacrylate	Monomer with low viscosity	Polymerizes in joint with trace of moisture on surface in presence of metal ions
Urea-formaldehyde	Mixed with water immediately before use	Loss of water into substrate and setting owing to release of catalyst by water
Epoxy adhesives	Mixed with curing agent before use; applied as viscous liquid; some single component epoxies can be applied as film to set under heat and pressure	Chemical reaction either at room or elevated temperatures
Polyvinylformal with phenol formaldehyde resin	Liquid with powder or, more usually, a film with the powder set in a flexible matrix	Set with heat and pressure. The pressure is essential to prevent porosity from a small amount of water liberated on cure

Introduction

Manufacturing processes for adhesives

Adhesives and sealants can be produced in various forms: one and two part liquids, solvent based solutions, water based emulsion, supported or unsupported film, preformed pellets or shaped extrusions, and numerous other forms. An adhesive or sealant formulation will depend on the base material that is the principal part of the formulation and on the requirements of the application. Processes and formulations are often considered proprietary to the adhesive or sealant manufacturer. However, there are formulas and processing methods that are public knowledge due to the tremendous amount of published research on adhesives and sealants.

Introduction

The adhesive base or binder is the primary component of an adhesive that holds the substrates together. The binder is, generally, the component from which the name of the adhesive is derived. For example, an epoxy adhesive may have many components, but the primary material is epoxy resin. A hardener is a substance added to an adhesive to promote the curing reaction by taking part in it. Two-part adhesive systems generally have one part, which is the base, and a second part, which is the hardener. Upon mixing, a chemical reaction ensues which causes the adhesive to solidify. A catalyst is sometimes incorporated into an adhesive formulation to speed-up the reaction between the base and hardener. Certain adhesive bases only need a source of energy to cure. This source may come from ultraviolet light, radiation, etc. In these cases, the adhesive may contain a catalyst but no hardener.

Introduction

Solvents are sometimes needed to disperse the adhesive to a spreadable consistency. Solvents used with synthetic resins and elastomers are generally organic in nature, and often a mixture of solvents is required to achieve the desired properties. There must be some way for the solvent to escape the joint after the adhesive is applied and the assembly is made. Thus, solvents are generally only used in applications where passages are available for their escape, such as in the preparation of pressure sensitive coatings or bonding of porous substrates. An ingredient added to an adhesive to reduce the concentration of base material is called a diluent. Diluents are principally used to lower the viscosity and modify the processing conditions of some adhesives and sealants. Reactive diluents chemically react with the base material during cure, become part of the product, and do not evaporate as does a solvent. Non-reactive diluents are much like solvents and could leach out of the adhesive or sealant during its life.

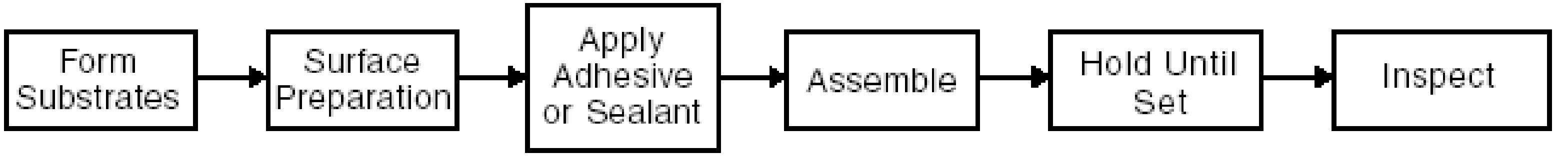
Introduction

Fillers are relatively non-adhesive substances added to the adhesive or sealant to improve their working properties, strength, permanence, or other qualities. Fillers are also used to reduce material cost. By selective use of fillers, the properties of an adhesive or sealant can be changed tremendously. Thermal expansion, electrical and thermal conduction, shrinkage, viscosity, and thermal resistance are only a few properties that can be modified by the use of fillers.
A carrier or reinforcement is usually a thin fabric or paper used to support the semi-cured adhesive composition to provide a tape or film. The carrier may also serve as a bond-line spacer and reinforcement for the adhesive.

Introduction

End-use processes

The manufacturing methods used in producing an assembly will also determine the initial degree of adhesion and service characteristics of the joint. A typical flow chart for the adhesive bonding or sealing process is shown below:



Introduction

Adhesive bonding

Adhesive bonding is somewhat unique in that there are numerous processes available. Certain methods even use the substrate itself as an adhesive. These are known as solvent welding and thermal welding. Heat or solvent can be applied in some manner to the substrate to turn part of the material into a liquid. This liquefied material then acts as the adhesive or sealant, filling in the gap at the joint and solidifying on cooling from the melt or by loss of solvent. The substrate in essence becomes the adhesive.

Adhesion

Theories of adhesion

There is no unifying single theory of adhesion on which to accurately model all interactions that take place between the adhesive and the substrate. The existing theories of adhesion presented provide methods by which one can rationalize practical observations. They are generally useful in understanding why adhesives stick and why, at times, they fail. Adhesion theories allow us to make predictions and even obtain a qualitative realization of joint strength.

Adhesion

Forces involved

The forces involved in holding adhesives and sealants to their substrates or in holding adhesives and sealants together as a bulk material arise from the same origins. These same forces are all around us in nature. To understand what is happening in an adhesive or sealant joint, we must first understand the forces that bind atoms and molecules together.

Adhesion

Adhesive and cohesive forces

Bond strength is not only the result of adhesion forces. Other forces contribute to the strength of a joint. For example, molasses may have good adhesion, but it is a poor adhesive or sealant. Its failure is usually cohesive. Cohesive strength of an adhesive or sealant is at least as important as its adhesive strength. Like a weak link in a chain, the bond will fail at the place where the intermolecular forces are the weakest. Adhesive forces hold two materials together at their surfaces. Cohesive forces hold adjacent molecules of a single material together. Adhesive or sealant joints may fail either adhesively or cohesively.

Adhesion

Adhesive and cohesive forces - examples

Adhesive failure is failure at the interface between adherend and the adhesive. An example would be the peeling of cellophane tape from a glass surface if the adhesive film separates cleanly from the glass. Cohesive failure is failure within the adhesive or one of the adherends. Cohesive failure would result if two metal substrates held together with grease were pulled apart. The grease would be found on the two substrates after the joint failed. The grease would have failed cohesively. Another example of cohesive failure is if two wooden panels were bonded together with an epoxy adhesive and then pulled apart. Most likely, the resulting failure would show that particles of wood fiber were left embedded in the adhesive. In this case, the wood or adherend failed cohesively.

Adhesion

Adhesive and cohesive forces

Adhesive or cohesive forces can be attributed to either short or long range molecular interactions. These are also referred to as primary or secondary bonds. The exact types of forces that could be operating at the interface are generally thought to be the following:

- **van der Waals forces**
- **Hydrogen bonding**
- **Ionic, covalent, or co-ordination bonds**

Adhesion

Adhesive and cohesive forces

Short-range molecular interactions include covalent, ionic, and metallic forces. Covalent forces result from chemical reactions such as provided by some surface treatments on glass fiber. Welding, soldering, or brazing processes form metallic bonds. However, these forces generally are not at work in the more common, everyday adhesive applications. The most important forces relative to adhesion are the secondary or Van der Waals forces. The exact nature of these forces and their influence on adhesive or cohesive strength are difficult to accurately determine. However, a general awareness of their origin and characteristics assists in understanding why strong bonds form and why they fail.

Adhesion

Type of force	Source of force	Bond energy (KJ/mol)	Description
Primary or Short Range Forces	Covalent forces	60–700	Diamond or cross-linked polymers. Highly directional.
	Ionic or electrostatic	600–1000	Crystals. Less directional than covalent.
	Metallic	100–350	Forces in welded joints.
Secondary or van der Waals Forces	Dispersion	0.1–40	Arise from interactions between temporary dipoles. Accounts for 75–100% of molecular cohesion. Forces fall off as the 6th power of the distance.
	Polar	4–20	Arise from the interactions of permanent dipoles. Decrease with the 3rd power of the distance.
	Hydrogen bonding	Up to 40	Results from sharing of proton between two atoms possessing loan pairs of electrons. Longer range than most polar and dispersion bonds.

Adhesion

Surface energy

The forces holding an adhesive to a substrate or maintaining the cohesive integrity of a solid can be measured as the work necessary to separate two surfaces beyond the range of the forces holding them together. In one case, the surfaces are the adhesive and substrate; in the other, they are like-molecules in the bulk of the material. This force is dependent on the intermolecular forces that exist in the material and upon the intermolecular spacing. It is sometimes referred to as the surface energy, γ.

Adhesion

Surface energy

The certainty that liquids have a surface energy is easily demonstrated by the fact that a finely divided liquid, when suspended in another medium, assumes a spherical shape. In the absence of gravitational distortion of shape (i.e., the energy associated with having a surface), the liquid tends to go to its lowest energy state—that of a sphere. The surface energy of a pure liquid is easily obtained because this is simply its surface tension, γ_{LV}.

Adhesion

Surface energy

Surface tension and surface energy are numerically identical for liquids. Surface energy is generally given in units of millijoules per meter squared (mJ/m^2), while surface tension is given in units of dynes/centimeter (dynes/cm) or Newtons per meter (N/m). The surface tensions of organic liquids and of most inorganic liquids rarely exceed the value for water (32 dynes/cm).

F/A ↔ N/m

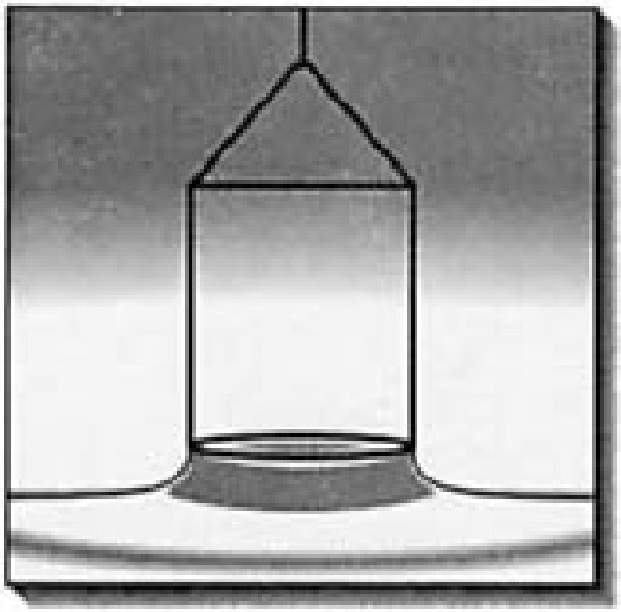
1 dyne = 10^{-5} N

Adhesion

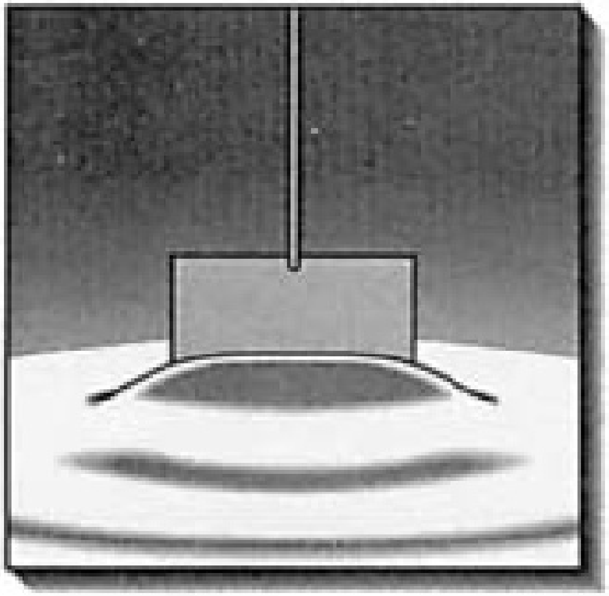
Surface energy

The surface energies of liquids are readily determined by measuring the surface tension with a duNouy ring or Wilhelmy plate. With the duNouy ring, a clean platinum ring is placed under the surface of the test liquid and the liquid is slowly moved downward until the ring breaks through the liquid surface. The force is recorded, and by means of appropriate conversion factors, the surface tension of the liquid is calculated. The Wilhelmy plate is a similar method which measures the force of a liquid on a plate passing through its surface. Another method of measuring surface tension is the ‘‘drop weight/drop volume’’ method. Here, the average volume of test liquid to cause a drop to fall from a carefully calibrated syringe is used to calculate the surface tension of the liquid.

Adhesion



duNouy Ring



Wilhelmy Plate

Adhesion

Surface energy

Whereas, the surface tension of a liquid is a real surface stress, the same cannot be said of a solid surface. With a solid, work is done in stretching a surface and not in forming the surface. For a solid surface, surface energy and surface tension are not the same. Still it is often convenient to refer to γ indiscriminately as either surface energy or surface tension, but it is inaccurate.

Adhesion

Surface energy

It is an easy matter to measure the surface tension of a liquid in equilibrium with its vapor, γ_{LV}, but not to measure the surface energy of a solid. Measurements on high energy solids are mostly made near the melting point; whereas, it is the room temperature properties that mainly concern adhesive studies. Surface free energies of low surface energy solids (i.e., polymeric materials) have been indirectly estimated through contact angle measurement methods.

Adhesion

Surface energy of a solid

$$\delta G = -P\ \delta l + \gamma\ \delta A = 0 \qquad \Longrightarrow \qquad \gamma = P\frac{\delta l}{\delta A}$$

where G is the Gibbs free energy and A is the surface area of the rod:

$$A = 2\pi r^2 + 2\pi r l \qquad \Longrightarrow \qquad \delta A = 4\pi r\delta r + 2\pi l\delta r + 2\pi r\delta l$$

Also, since the volume (V) of the rod remains constant, the variation (δV) of the volume is zero, i.e.,

$$V = \pi r^2 l = \text{constant} \qquad \Longrightarrow \qquad \delta V = 2\pi r l\delta r + \pi r^2\delta l = 0 \Longrightarrow \delta r = -\frac{r}{2l}\delta l\ .$$

Therefore, the surface energy density can be expressed as

$$\gamma = \frac{Pl}{\pi r(l-2r)}\ .$$

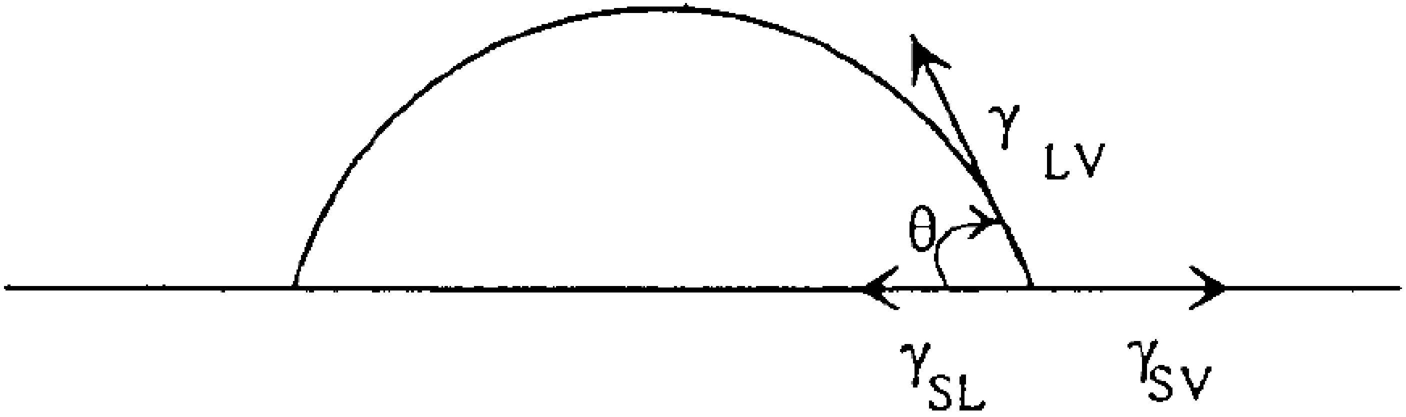
The surface energy density of the solid can be computed by measuring P, r, and l at equilibrium.

Adhesion

Surface energy

In a contact angle measurement, a drop of liquid is placed upon the surface of a solid. It is assumed that the liquid does not react with the solid and that the solid surface is perfectly smooth and rigid. The drop is allowed to flow and equilibrate with the surface. The measurement of the contact angle, θ, is usually done with a goniometer that is simply a protractor mounted inside a telescope. The angle that the drop makes with the surface is measured carefully.

Adhesion



Adhesion

Surface energy

A force balance between the liquid and the solid can be written as:

$$\gamma_{\mathrm{LV}} \cos \theta = \gamma_{\mathrm{SV}} - \gamma_{\mathrm{SL}}$$

where γ_{LV} is the liquid-vapor interfacial tension, θ is the contact angle, γ_{SV} is the solid-vapor interfacial tension, and γ_{SL} is the solid-liquid interfacial tension. This is known as the Young equation after the scientist who originated the analysis.

Adhesion

Surface energy

The γ_{SV} is the solid-vapor interfacial energy and not the true surface energy of the solid. The surface energy is related to γ_{SV} through the following relationship:

$$\gamma_{\mathrm{SV}} = \gamma - \pi_{\mathrm{e}}$$

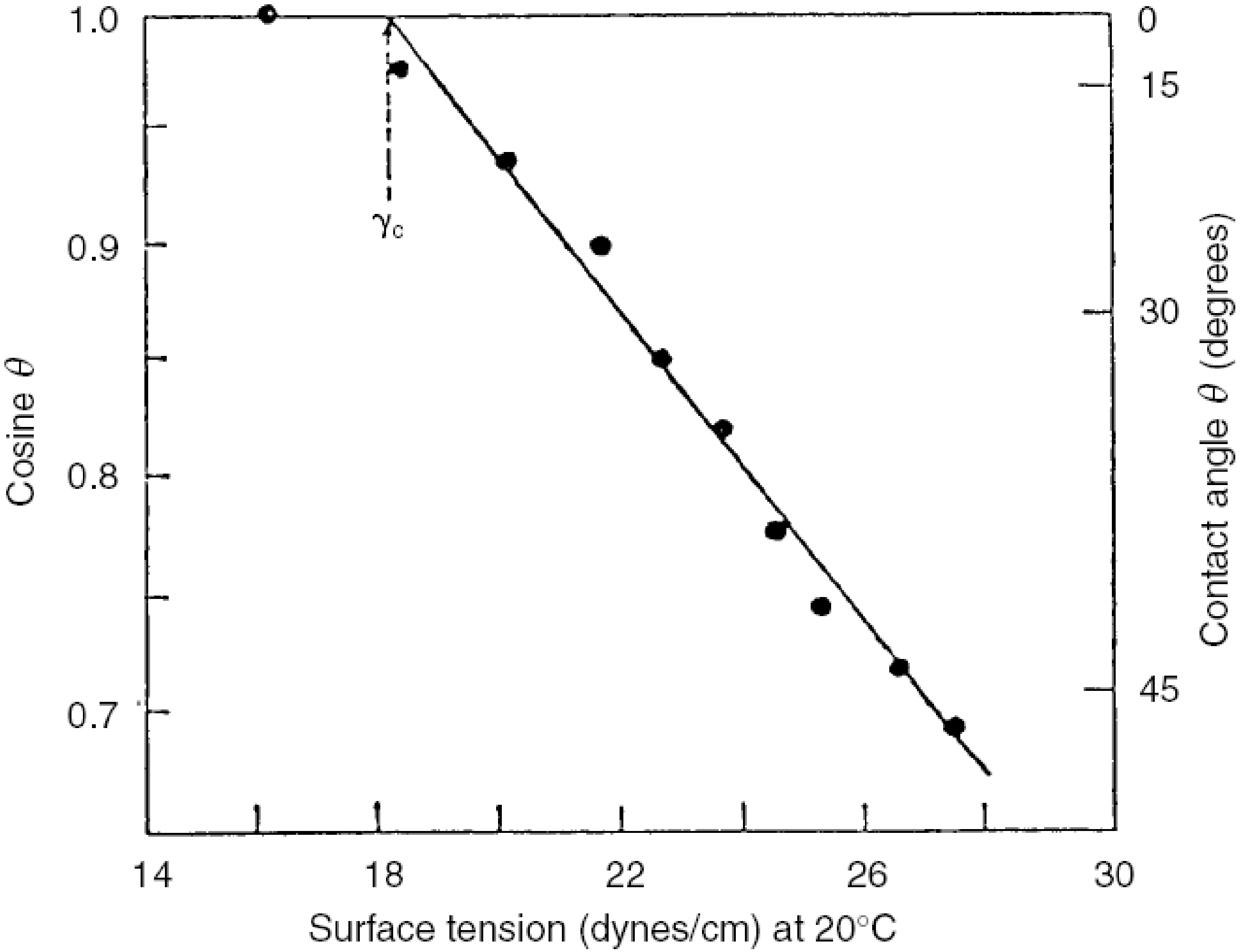
where γ is the true surface energy of the solid and π_e is a quantity known as the equilibrium spreading pressure. It is a measure of the energy released through adsorption of the vapor onto the surface of the solid, thus lowering the surface energy.

Adhesion

Surface energy

A rather simple method of estimating the surface energy of solids was developed by Zisman. Zisman proposed that a critical surface tension, γ_C, can be estimated by measuring the contact angle of a series of liquids with known surface tensions on the surface of interest. These contact angles are plotted as a function of the γ_{LV} of the test liquid. The critical surface tension is defined as the intercept of the horizontal line $\cos\theta = 1$ with the extrapolated straight line plot of $\cos\theta$ against $\gamma_{LV..}$ This intersection is the point where the contact angle is 0 degrees. A hypothetical test liquid having this γ_{LV} would just spread over the substrate.

Adhesion



Zisman plot for determining critical surface tension of polytetrafluoroethylene. Test liquids are n-alkanes.

Adhesion

Materials	Critical surface tension, dyne/cm
Acetal	47
Acrylonitrile-butadiene-styrene	35
Cellulose	45
Epoxy	47
Fluoroethylene propylene	16
Polyamide	46
Polycarbonate	46
Polyethylene	31
Polyethylene terephthalate	43
Polyimide	40
Polymethylmethacrylate	39
Polyphenylene sulfide	38
Polystyrene	33
Polysulfone	41
Polytetrafluoroethylene	18
Polyvinyl chloride	39
Silicone	24
Aluminum	≈500
Copper	≈1000

Material	Surface tension, dyne/cm
Epoxy resin	47
Fluorinated epoxy resin*	33
Glycerol	63
Petroleum lubricating oil	29
Silicone oils	21
Water	73

Adhesion

Critical surface tension is an important concept that leads to a better understanding of wetting.

Adhesion

Work of adhesion and cohesion

If a bulk material is subjected to a sufficient tensile force, the material will break thereby creating two new surfaces. If the material is completely brittle, the work done on the sample is dissipated only in creating the new surface. Under those assumptions, if the failure is truly cohesive where both sides of the broken material are of the same composition, then

$$W_C = 2\gamma$$

where W_C is defined as the work of cohesion.

Adhesion

Work of adhesion and cohesion

Now similarly consider separating an adhesive (material 1) from a substrate (material 2). The energy expended should be the sum of the two surface energies γ_1 and γ_2. However, because the two materials were in contact, there were intermolecular forces present before the materials were split apart. This interfacial energy can be represented as γ_{12}. W_A, the work of adhesion, may be defined by the surface energies of the adhesive and the adherend (Dupre equation):

$$W_A = \gamma_1 + \gamma_2 - \gamma_{12}$$

Adhesion

Work of adhesion and cohesion

This equation could also be represented as:

$$W_A = \gamma_{LV} + \gamma_{SV} - \gamma_{SL}$$

Substitution of the Young equation into the Dupre equation results in the Young-Dupre equation that states:

$$W_A = \gamma_{LV}(1 + \cos\,\theta).$$

Adhesion

Work of adhesion and cohesion

This equation relates a thermodynamic parameter, W_A, to two easily determinable quantities: the contact angle and the liquid-vapor surface tension. For conditions of perfect wetting ($\cos \theta = 1$):

$$W_A = 2\gamma_{\mathrm{LV}} = W_C$$

Adhesion

Bond failure energy

Bond failure energy is composed of two parts: a reversible work of adhesion and an irreversible work of adhesive deformation. Thus, the strength of styrene-butadiene rubber adhesive depends on two components: a viscoelastic energy dissipation term, which is a function of test rate and temperature, and the intrinsic failure energy which agrees closely with the work of adhesion, W_A, when bond failure is apparently interfacial.

Adhesion

Bond failure energy

Much work in adhesion science has centered on the relationship between W_A, the calculated work of adhesion, and practical adhesion, or the real measured adhesion. Ahagon and Gent indicate that practical adhesion can be related to the work of adhesion plus a function describing the energy dissipation mechanisms within an adhesive bond.

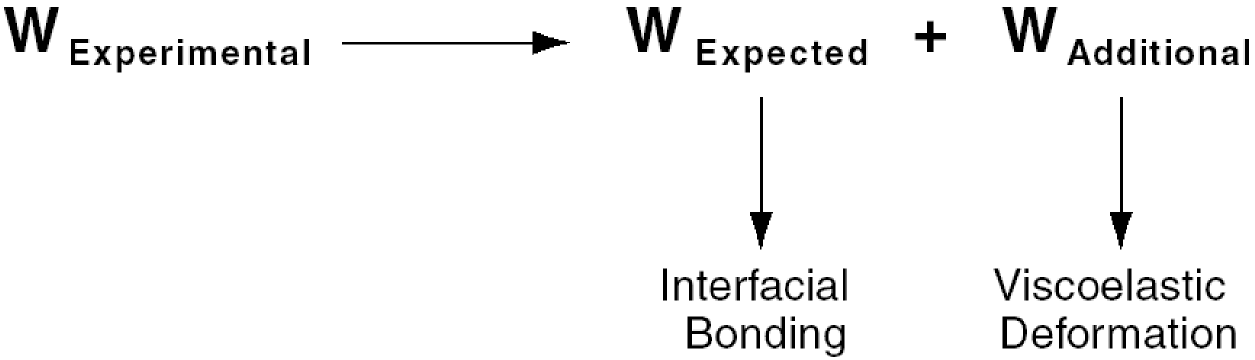
$$\text{Practical Adhesion} = \mathrm{W}_A + f(W_A)\zeta.$$

ζ is a factor related to the viscoelastic properties of the adhesive and, thereby, is related to the mechanical energy absorption characteristics of the joint. This is sometimes related to the amount of energy absorbed by the deformation of the joint.

Adhesion

Bond failure energy

The practical work of adhesion is equal to the theoretical work of adhesion as determined by interfacial effects and to the mechanical work which is absorbed within the joint. Thus, with a completely non-deformable adhesive, interphase, and adherend the practical work of adhesion is equal to the theoretical work of adhesion.



$$W_{Experimental} \longrightarrow W_{Expected} + W_{Additional}$$

Interfacial Bonding

Viscoelastic Deformation

Adhesion

Bond failure energy

It should be realized that the above discussion on forces and work of adhesion is very simplistic and summarizes a great deal to a fault. There are also significant debates over the applicability and direct usefulness of these relationships. However, some conclusions can be derived and are of significant assistance to the user of adhesives and sealants.

Adhesion

Bond failure energy

1. The work of adhesion is at a maximum when the contact angle, γ, equals 0 degrees, that is when the liquid spreads completely on the surface of the solid. This condition implies that there are stronger forces between the molecules of the liquid and the substrate than between the liquid molecules themselves.

2. Adhesion will tend to go to zero as the contact angle increases above 90 degrees.

3. Under conditions of perfect wetting of a surface by a liquid, $W_A = 2\,\gamma_{LV}$. Hence $W_A = W_C$.