

---

# 9 Wood Adhesion and Adhesives

Charles R. Frihart

## CONTENTS

9.1	General	256
9.2	Wood Adhesive Uses	258
9.3	Terminology	259
9.4	Application of the Adhesive	260
9.4.1	Adhesive Application to Wood	260
9.4.2	Theories of Adhesion	261
9.4.3	Wood Adhesion	265
9.4.4	Wood Surface Preparation	265
9.4.5	Wood Bonding Surface	266
9.4.6	Spatial Scales of Wood for Adhesive Interaction	268
9.4.7	Wetting and Penetration in General	270
9.4.8	Wetting, Flow, and Penetration of Wood	271
9.5	Setting of Adhesive	274
9.5.1	Loss of Solvents	274
9.5.2	Polymerization	276
9.5.3	Solidification by Cooling	277
9.6	Performance of Bonded Products	278
9.6.1	Behavior Under Force	278
9.6.2	Effect of Variables on the Stress—Strain Behavior of Bonded Assemblies	281
9.6.3	Bond Strength	282
9.6.4	Durability Testing	285
9.7	Adhesives	286
9.7.1	Polymer Formation	287
9.7.2	Self-Adhesion	288
9.7.3	Formaldehyde Adhesives	289
9.7.3.1	PF Adhesives	291
9.7.3.2	Resorcinol and Phenol—RF Adhesives	292
9.7.3.3	UF and Mixed Urea Formaldehyde Adhesives	293
9.7.3.4	MF Adhesives	296
9.7.4	Isocyanates in Wood Adhesives	298
9.7.4.1	Polymeric Diphenylmethane Diisocyanate	299
9.7.4.2	Emulsion Polymer Isocyanates	301
9.7.4.3	Polyurethane Adhesives	301
9.7.5	Epoxy Adhesives	302
9.7.6	Vinyl Acetate Dispersion Adhesives	304
9.7.7	Bio-Based Adhesives	305
9.7.7.1	Protein Glues	306
9.7.7.2	Tannin Adhesives	307
9.7.7.3	Lignin Adhesives	308
9.7.8	Miscellaneous Composite Adhesives	308

9.7.9 Construction Adhesives .....	309
9.7.10 Hot Melts .....	309
9.7.11 Pressure Sensitive Adhesives .....	310
9.7.12 Other Adhesives .....	311
9.7.13 Formulation of Adhesives .....	311
9.8 Environmental Aspects.....	312
9.9 Summary .....	313
References .....	313

## 9.1 GENERAL

The recorded history of bonding wood dates back at least 3000 years to the Egyptians (Skeist and Miron 1990, River 1994a), and adhesive bonding goes back to early mankind (Keimel 2003). Although wood and paper bonding are the largest applications for adhesives, some of the fundamental aspects leading to good bonds are not fully understood. Better understanding of these critical aspects of wood adhesion should lead to improved wood products. The chemistry of adhesives has been covered in detail (Pizzi 2003a—f); however, the fundamentals of adhesive mechanical performance are not well understood. This chapter is aimed at more in-depth coverage of those items that are not covered elsewhere. It will touch briefly on topics covered by other writers and the reader should examine the recommended books and articles for more details. Many of the books on adhesives and adhesion are long and complicated, but a brief but thorough book exists (Pocius 2002). Adhesives are designed for specific applications, leading to thousands of products (Rice 1990). Petrie has broken adhesives into 20 groups of synthetic structural, 11 groups of elastomeric, 12 groups of thermoplastic, and 6 groups of natural adhesives (Petrie 2000). Brief has summarized the vast number of markets for adhesives (Brief 1990).

Understanding how an adhesive works is difficult since adhesive performance is not a single science, but the combination of many sciences. Adhesive strength is defined mechanically as the force necessary to pull apart two substrates that are bonded together. Mechanical strength is dependent upon primary and secondary chemical bonds and interlocking of the polymer chains in the adhesive, wood and adhesive-wood interphase. Thus, both chemical and mechanical aspects of bond strength, and the interrelation of the two factors are all important. Because adhesive strength is a measurement of failure, the process determines where the localized stress exceeds the bond strength under specific test conditions. One concept is to illustrate the bonded assembly as being a series of links representing different domains with the failure occurring in the weakest link (Marra 1980). However, the bondline is actually more a continuum than discrete links. The localized stress is usually very different from applied stress due to stress distribution and concentration (Dillard 2002). It is generally preferred that the adhesive bond be stronger than the substrate so that the failure mechanism is one of substrate fracture.

There are generally three steps in the process of adhesive bonding. The first is usually the preparation of the surface to provide the best interaction of the adhesive with the substrate. Even though a separate treatment step may not be used in some cases, the knowledge of material science (surface chemistry and morphology) is important for understanding this interaction. Preparation of the surface can involve either mechanical or chemical treatment or a combination of the two. In some cases, the adhesive is modified to deal with problems in wetting of the surface or contamination on the surface. Surface analysis techniques are often more difficult on wood than other materials due to the complex chemistry and morphology of the wood.

The second step is that the adhesive needs to form a molecular-level contact with the substrate surface; thus, it should be a liquid so that it can develop a close contact with the substrates. This process involves both the sciences of rheology and surface energies. Rheology is the science of the deformation and flow of matter. Surface energies are influenced by both the polar and nonpolar components of both the adhesive and the substrate. Improving the compatibility by altering one or both components can lead to stronger and more durable bonds.

The third step is the setting, which involves the solidification and/or curing of the adhesive. Most adhesives change physical state in the bonding process, with the main exception being pressure sensitive adhesives that are used on tapes and labels. The solidification process depends on the type of adhesive. For hot melt adhesives, the process involves the cooling of the molten adhesive to form a solid, whether this is an organic polymer as in some craft glues, or an inorganic material as in the case of solder. Other types of adhesives have polymers dissolved in a liquid, which may be water (e.g., white glues) or an organic (e.g., rubber cement). The loss of the solvent converts these liquids to solids. The third type of adhesive is made up of small molecules that polymerize to form the adhesive, for example, super glues or two-part epoxies. Most wood adhesives involve both the polymerization and solvent loss methods. Understanding the conversion of small molecules into large molecules requires knowledge of organic chemistry and polymer science.

Once the bond is prepared, the critical test is the strength of the bonded assembly under forces existing during the lifetime of the assembly. This involves both externally applied forces and internal forces from shrinkage during the curing of the adhesive and differential expansion/contraction of the adhesive and substrate during environmental changes. Understanding the performance of a bonded assembly requires knowledge of both chemistry and mechanics. Often the strength of a bonded assembly is discussed in terms of adhesion. Adhesion is the strength of the molecular layer of adhesive that is in contact with the surface layer of the substrate, such as wood. The internal and applied energies may be dissipated at other places in the bonded assemblies than the layer of molecular contact between the adhesive and the substrate. However, failure at the interface between the two is usually considered unacceptable. Understanding the forces and their distribution on a bond requires knowledge of mechanics.

An appreciation of rheology, material science, organic chemistry, polymer science, and mechanics leads to better understanding of the factors controlling the performance of the bonded assemblies; see Table 9.1. Given the complexity of wood as a substrate, it is hard to sort out why

TABLE 9.1  
Wood Bonding Variables

Resin	Wood	Process	Service
Type	Species	Adhesive amount	Strength
Viscosity	Density	Adhesive distribution	Shear modulus
Molecular weight distribution	Moisture content	Relative humidity	Swell—shrink resistance
Mole ratio of reactants	Plane of cut: radial, tangential, transverse, mix	Temperature	Creep
Cure rate	Heartwood vs. sapwood	Open assembly time	Percentage of wood failure
Total solids	Juvenile vs. mature wood	Closed assembly time	Failure type
Catalyst	Earlywood vs. latewood	Pressure	Dry vs. wet
Mixing	Reaction wood	Adhesive penetration	Modulus of elasticity
Tack	Grain angle	Gas-through	Temperature
Filler	Porosity	Press time	Hydrolysis resistance
Solvent system	Surface roughness	Pretreatments	Heat resistance
Age	Drying damage	Posttreatments	Biological resistance: fungi, bacteria, insects, marine organisms
pH	Machining damage	Adherend temperature	Finishing
Buffering	Dirt, contaminants Extractives PH Buffering capacity Chemical surface		Ultraviolet resistance

some wood adhesives work better than other wood adhesives, especially during the more severe durability tests. In general, wood is easy to bond compared to most substrates, but it can be harder to make a truly durable wood bond. A main trend in the wood industry is increased bonding of wood products as a result of the fewer old growth trees and more engineered wood products.

## 9.2 WOOD ADHESIVE USES

Because adhesives are used in many different applications for bonding wood, a wide variety of types are used (Frihart and Hunt 2010). Given the focus of this book on composites, the emphasis will be more on adhesives used in composite manufacturing than on those used in product assembly. Factors that influence the selection of the adhesive include cost, compatibility with the assembly process, strength of bonded assembly, and durability.

The largest wood market is the manufacturing of panel products, including plywood, oriented strandboard (OSB), fiberboard, and particleboard. Except for plywood, the adhesive in these applications bonds small pieces of wood together to form a wood-adhesive matrix. The strength of the product depends on efficient distribution of applied forces between the adhesive and wood phases. The composites (strandboard, fiberboard, and particleboard) have adhesive applied to the wood (strands, fibers, or particles); then they are formed into mats and pressed under heat into the final product. This type of process requires an adhesive that does not react immediately at room temperature (pre-mature cure), but is heat activated during the pressing operation. Given the weight adhesive (2-8%) compared to the product weight and relatively low cost of wood, adhesive cost is an issue. In addition, since the wood surfaces are brought close together, gap filling is not an important issue, but over penetration can be. On the other hand, for plywood, the surfaces are not uniformly brought in such close contact, requiring the adhesive to remain more above the surface. Light-colored adhesives are important for some applications, but many of these products have their surfaces covered by other materials. Most of the adhesives used in wood bonding have formaldehyde as a co-monomer, generating concern about formaldehyde emissions. Dunky and Pizzi have discussed many of the commercial issues relating to the use of adhesives in manufacture and the use of wood composites (Dunky and Pizzi 2002). Recently, formaldehyde emissions have become an important issue (Frihart 2011, Williams 2010).

For laminating lumber and bonding finger joints, the adhesive can either be heat or room-temperature cured. The cost of the adhesive has become more critical as the thickness of the wood decreases from glulam to laminated veneer lumber and parallel strand lumber (Stark et al. 2010). Color is sometimes an issue, but moisture and creep resistances are more important because these products are usually used in structural applications.

Adhesives used in construction and furniture assembly usually have long set times and are room-temperature cured. Furniture adhesives are light-colored, low-viscosity, and generally do not need high moisture resistance. On the other hand, construction adhesives generally have a high viscosity and need some flexibility, but color and moisture resistance are less important issues.

The movement away from solid wood for construction to engineered wood products has increased the consumption of adhesives. A wooden I-joist can have up to five different adhesives in its construction; see Figure 9.1. The wood laminates that form the top and bottom flanges may be finger joined with a melamine—formaldehyde (MF) adhesive and glued together with a phenol—resorcinol-formaldehyde adhesive. The OSB that forms the middle part (web) is often produced using both phenol—formaldehyde (PF) and polymeric diphenylmethane diisocyanate adhesives to bond the strands. The I-joist is produced by attachment of the web to the flange and bonding of the web sections together using emulsion—polymer isocyanate. Each of these adhesives has different chemistries, are bonded under different conditions of time, temperature, and pressure to a variety of wood surfaces, and are subjected to different forces during use. Thus, it is not surprising that a simple model for satisfactory wood adhesion has been difficult to derive.

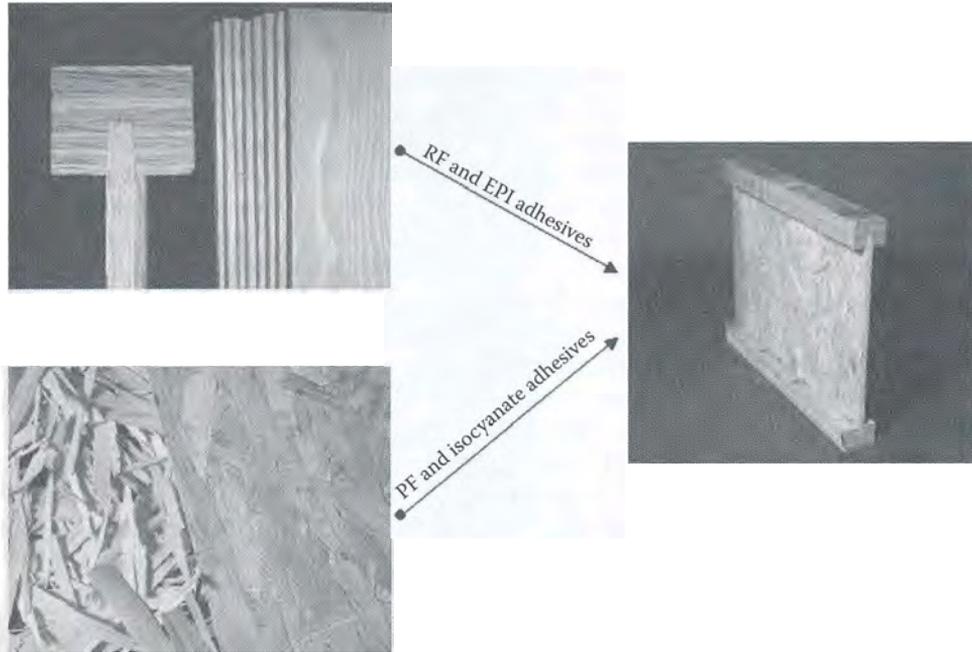
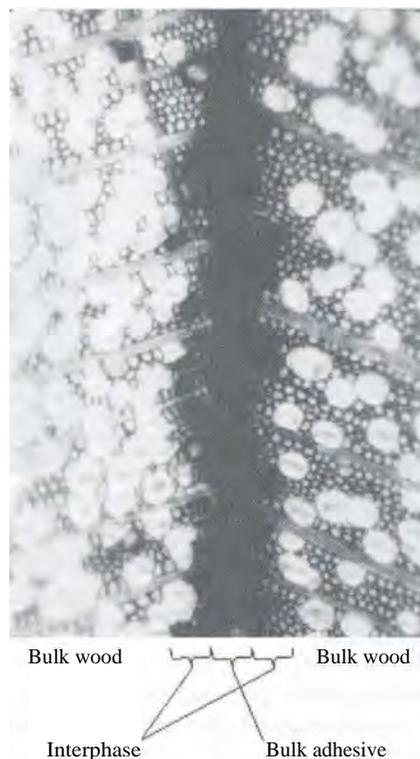


FIGURE 9.1 The importance of adhesives is illustrated by the need for different adhesives to make the flange by the bonding of laminate pieces and the oriented strandboard from the flakes and the final I-joist by attachment of the strandboard to the flange.

### 9.3 TERMINOLOGY

Confusion can be caused if there is no clear understanding of the terminology; this chapter generally follows that given in the ASTM Standard D 907-11 (ASTM International 2011a). *Adhesive joint failure* is "n—the locus of fracture occurring in an adhesively-bonded joint resulting in a loss of load-carrying capability" and is divided into interphase, cohesive, or substrate failures. *Cohesive failure* is within the bulk of the adhesive, while *substrate failure* is within the substrate or adherend (wood). The least clear failure zone is that occurring within the *interphase*, which is "a region of finite dimension extending from a point in the adherend where the local properties (chemical, physical, mechanical, and morphological) begin to change from the bulk properties of the adherend to a point in the adhesive where the local properties equal the bulk properties of the adhesive." Figure 9.2 shows the various regions of a bonded assembly. The bulk properties are the properties of one phase unaltered by the other phase.

The *assembly time* is "the time interval between applying adhesive on the substrate and the application of pressure, or heat, or both, to the assembly." This time can be "closed" with substrates brought into contact or "open" with the adhesive exposed to the air; these times are important for penetration of the adhesive and evaporation of solvent. *Set* is "to convert an adhesive into a fixed or hardened state by chemical or physical action, such as condensation, polymerization, oxidation, vulcanization, gelation, hydration, or evaporation of volatile constituents." *Cure* is "to develop the strength properties of an adhesive by chemical reaction." Note that cure is only one way for the adhesive setting step. However, because cure is a function of how it is measured, there is no universal value for an adhesive. Separating partial cure from total cure is important because they usually have very different properties, and in most bonded products, total cure is not usually obtained after long after the product is assembled while partial cure can allow the product to be handled for the next stage of manufacturing. *Tack* is "the property of an adhesive that enables it to form a bond of measurable strength immediately after the adhesive and adherend are brought into contact under low pressure." Tack is important for holding composites together during layup and pre-pressing.



**FIGURE 9.2** A transverse scanning electron microscope image of a resorcinol bond of yellow-poplar, showing the zones of bulk wood, interphase region, and bulk adhesive.

A *structural adhesive* is "a bonding agent used for transferring required loads between adherends exposed to service environments typical for the structure involved" (ASTM International 2011a). For wood products, structural implies that failure can cause serious damage to the structure and even loss of life (Frihart and Hunt 2010), while semi-structural adhesives need to carry the structural load, but failure is not as disastrous, and nonstructural adhesives typically support merely the weight of the bonded product.

Other terms are used in different ways that can also cause confusion. The term *adhesive* can refer to either the adhesive as applied or the cured product. On the other hand, a *resin* is often used to refer to the uncured adhesive, although the ASTM defines a resin as "solid, semisolid, or liquid, usually organic material that has an indefinite molecular mass and, when solid, usually has a softening or melting range and exhibits a tendency to flow when subjected to stress" (ASTM International 2011a). Thus, a cross-linked adhesive is not a resin, but the adhesive in the uncross-linked state may be. Glue was "originally, a hard gelatin obtained from hides, tendons, cartilage, bones, etc. of animals," but is now generally synonymous with the term adhesive.

## 9.4 APPLICATION OF THE ADHESIVE

### 9.4.1 ADHESIVE APPLICATION TO WOOD

The first step in bond formation involves spreading the adhesive over the wood surface. The physical application of the adhesive can involve any one of a number of methods, including using spray, roller coating, doctor blade, curtain coater, and bead application technologies. After the adhesive application, a combination of some open and closed assembly times is used depending on the specific bonding process. Both give the adhesive time to penetrate into the wood prior to bond formation,

but the open assembly time will cause loss of solvent or water from the formulation. Long open times can cause the adhesive to dry out on the surface causing poor bonding because flow is needed for bonding to the substrate. In the bonding process, pressure is used to bring the surfaces closer together. In some cases, heat and moisture are used during the bonding process, both of which will make the adhesive more fluid and the wood more deformable (Kretschmann 2010).

For any type of bond to form, molecular-level contact is required. Thus, the adhesive has to flow over the bulk surface into the voids due to surface roughness that exist for almost all surfaces. Many factors control the wetting of the surface, including the relative surface energies of the adhesive and the substrate, viscosity of the adhesive, temperature of bonding, pressure on the bondline, and so on. Wood is a more complex bonding surface than what is encountered in most adhesive applications. Wood is very anisotropic because the cells are greatly elongated in the longitudinal direction, and the growth out from the center of the tree makes the radial properties different from the tangential properties. Wood is further complicated by differences between heartwood and sapwood, and between earlywood and latewood. Adding in tension wood, compression wood, and slope of grain increases the complexity of the wood adhesive interaction. The manner in which the surface is prepared also influences the wetting process. These factors are discussed in later sections of this chapter and in the literature (River et al. 1991), but for now we will assume that the adhesive is formulated and applied in such a manner that it properly wets the surface.

#### 9.4.2 THEORIES OF ADHESION

Adhesion refers to the interaction of the interface between adhesive and adherend. It must not be confused with bond strength. Certainly if there is little interaction of the adhesive with the adherend, these materials will detach when force is applied. However, bond strength is more complicated because factors such as stress concentration, energy dissipation, and weakness in surface layers often play a more important role than adhesion. Consequentially, the aspects of adhesion are a dominating factor in the bond formation process, but may not be the weak link in the bond breaking process.

It is important to realize that, although some theories of adhesion emphasize mechanical aspects and others put more emphasis on chemical aspects, chemical structure and interactions determine the mechanical properties and the mechanical properties determine the force that is concentrated on individual chemical bonds. Thus, the chemical and mechanical aspects are linked and cannot be treated as completely distinct entities. In addition, some of the theories emphasize macroscopic effects while others are on the molecular level. The discussion of adhesion theories here is brief because they are well covered in the literature (Schultz and Nardin 2003, Pocius 2002), and in reality, most strong bonds are usually due to a combination of the concepts listed in each theory.

In a mechanical interlock, the adhesive provides strength through reaching into the pores of the substrate (Packham 2003). An example of mechanical interlock is Velcro; the intertwining of the hooked spurs into the open fabric holds the pieces together. This type of attachment provides great resistance to the pieces sliding past one another, although the resistance to peel forces is only marginal. In its truest sense, a mechanical interlock does not involve the chemical interaction of the adhesive and the substrate. However in reality, there are friction forces preventing detachment, indicating interaction of the surfaces. For adhesives to form interlocks, the adhesive has to wet the substrate well enough so that there are some chemical as well as mechanical forces in debonding. For a mechanical interlock to work, the tentacles of adhesive must be strong enough to be load bearing. The size of the mechanical interlock is not defined, although the ability to penetrate pores becomes more difficult and the strength becomes less when the pores are narrower. It should be noted that generally mechanical interlocks provide more resistance to shear forces than to normal forces. Also, many substrates do not have enough roughness to provide sufficient addition to bond strength from the mechanical interlock. Roughing of the substrate surface by abrasion, such as grit blasting or abrasion, normally overcomes this limitation.

If the concept of tentacles of adhesive penetrating into the substrate is transferred from the macro scale to the molecular level, the concept is referred to as the diffusion theory (Wool 2002). If there are also tentacles of substrate penetrating into the adhesive, the concept can be referred to as interdiffusion. This involves the intertwining of substrate and adhesive chains. The interface is strong since the forces are distributed over this intertwined polymer network (Berg 2002). However, the concept can also work if only the adhesive forms tentacles into the substrate. For this to occur there has to be good compatibility of the adhesive and substrate. This degree of compatibility is not that common for most polymers. When it does occur a strong network is formed from a combination of chemical and mechanical forces.

The other theories are mainly dependent upon chemical interactions rather than truly mechanical aspects. Thus, they take place at the molecular level, and require an intimate contact of the adhesive with the substrate. These chemical interactions will be discussed in order of increasing strength of the interaction (Kinloch 1987). The strengths of various types of bonds are given in Table 9.2, along with examples of some of the bond types in Figure 9.3. It is important to remember that the strength of interaction is for just a single interaction. To make a strong bond these interactions need to be large in number and evenly distributed across the interface.

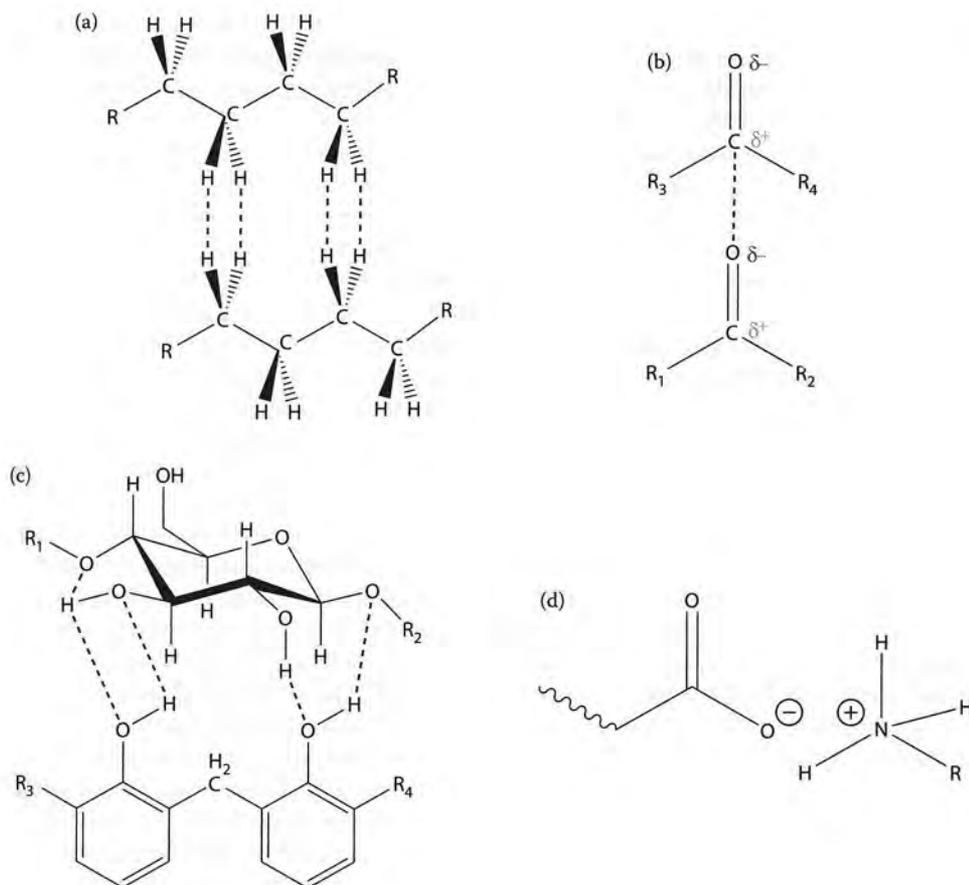
The weakest interaction is the London dispersion force (Wu 1982a). This force is the dispersive force that exists between any set of molecules and compounds when they are close to each other. The dispersion force is the main means of association of nonpolar molecules, such as polyethylene (Figure 9.3). Although this force is weak, where the adhesive and the adherend are in molecular contact, the force exists between all the atoms and can result in appreciable total strength. The ability of the gecko to walk on walls and ceilings has been attributed to this force (Autumn et al. 2002).

The other types of forces are generally related to polar groups (Pocius 2002). The weakest are the dipole—dipole interactions. For polar bonds, there is a separation of charge between the atoms; this process creates a natural, permanent dipole. Two dipoles can interact if positive and negative ends of the dipole match up with the opposite ends of another dipole. The strength of this interaction depends

**TABLE 9.2****Table of Bond Strengths from Literature Bond Types and Typical Bond Energies**

Type	Bond Energy (kJ mol <sup>-1</sup> )
Primary bonds	
Ionic	600-1100
Covalent	60-700
Metallic, coordination	110-350
Donor-acceptor bonds	
D <sub>2</sub> O—acid—base interactions (i.e., up to a primat { ..... } up to 1000 ..... ionic bond)	
Lewis acid—base interactions	Up to 80
Secondary bonds	
Hydrogen bonds (excluding fluorines)	1-25
Van der Waals bonds	
Permanent dipole—dipole interactions	4-20
Dipole-induced dipole interactions	Less than 2
Dispersion (London) forces	0.08-40

Source: Adapted from Fowkes, F.M. 1983. *Physicochemical Aspects of Polymer Surfaces*. Vol. 2, 583-603. Plenum Press, New York; Good, R. J. 1967. *Treatise on Adhesion and Adhesives, Volume 1: Theory*, 9-68. New York: Marcel Dekker; Kinloch, A. J. 1987. *Adhesion and Adhesives Science and Technology*. London: Chapman & Hall; Pauling, L. 1960. *The Nature of the Chemical Bond*. Ithaca, NY: Cornell University Press.



**FIGURE 9.3** Examples of various types of bonds, including (a) dispersive bonds between two hydrocarbon chain, such as exist in polyethylene, (b) a dipole bond between two carbonyl group, such as in a polyester, (c) hydrogen bonds between a cellulosic segment and a PF polymer, and (d) an ionic bond between an ammonium group and a carboxylate group.

on proper alignment of the dipoles, which is not difficult for small molecules in solution, but can be very difficult between two chains because they have constrained translation and rotation (Wu 1982a). A variation of this concept is the dipole-induced dipole, but this interaction is usually weaker than the permanent dipole interaction and also suffers from the same alignment problem in polymers.

Strongest of the secondary interactions is the hydrogen bond formation. This type of bond is common with polar compounds, including nitrogen, oxygen, and sulfur groups with attached hydrogens, and carbonyl groups. This type of bond involves sharing a hydrogen atom between two polar groups, and is extremely likely with wood and wood adhesives because both have an abundance of the proper polar groups. Almost all wood components are rich in hydroxyl groups and some contain carboxylic acid and ester groups. Both of these groups form very strong internal hydrogen bonds that give wood its strength, but are also available for external hydrogen bonds. All major wood adhesives have polar groups that can form internal and external hydrogen bonds. Many bio-based adhesives depend heavily on hydrogen bonds for their adhesive and cohesive strength. Many synthetic adhesives are less dependent upon the hydrogen bond for their cohesive strength because they have internal cross-links, but most certainly form hydrogen bonds to wood. One limitation of the hydrogen bond is its ability to be disrupted in the presence of water. Water and other hydrogen bonding groups can insert themselves between the two groups that present in the hydrogen bond. This

process softens the inter-chain bonds so that they are less able to resist applied loads. Thus, a material that adsorbs and absorbs water, like wood, loses some of its strength when it is wet. The same is true of the adhesion between the wood and the adhesive—it is certainly possible that hydrogen bonds weaken enough to serve as a failure zone.

An interesting aspect of secondary bonds (dispersive, dipolar, and hydrogen bonds) is that after disruption, they can reform while fractured covalent bonds usually do not reform. The reformability of hydrogen bonds has been known about for a long time, but recent work has indicated that it can be an important part of wood's ability to maintain strength even after there is some slippage of the bonds (Keckes et al. 2003), and this process has been referred to as "velcro" mechanics (Kretschmann 2003). The role of this process in allowing the adhesives to adjust and maintain strength as the wood changes dimensions is not well understood, but reformability of hydrogen bonds could play a significant factor.

Strong bonds can be formed from donor–acceptor interactions. The most common of these interactions with wood–adhesive bonds are the Brønsted acid–base interactions. Some acid–base interactions of cations with anions are possible in adhesion to substrates. Wood contains some carboxylic acids that can form salts with adhesives that contain basic groups, such as the amine groups in MF, protein, and amine-cured epoxy adhesives.

Generally, with most materials, the strongest interaction is when a covalent bond forms between the adhesive and the substrate. However, for wood adhesion, this has been an area of great debate, because of the difficulty in determining the presence of this bond type given the complexity of both the adhesive and the wood and the difficulty of generating a good model system. Because wood has hydroxyl groups in its three main components—cellulose, hemicellulose, and lignin—and many of the adhesives can react with hydroxyl groups, it is logical to assume that these reactions might take place. However, others contend that the presence of large amounts of free water would disrupt this reaction (Pizzi 1994a). More sophisticated analytical methods were unable to definitely answer this issue (Frazier 2003). Recently, two-dimensional nuclear magnetic resonance spectroscopy proved that even isocyanate adhesives did not yield covalent bond formation under typical bonding conditions (Yelle 2011a,b).

It is commonly assumed that the strongest interaction will control the adhesion to the substrate. This overlooks the fact that the adhesion is the product of the strength of each interaction times the frequency of its occurrence. Thus, covalent bonds that occur only rarely may not be as important to bond strength as the more common hydrogen bonds or dipole–dipole interactions. Hydrogen bonds may be less significant under wet conditions than other bonds if the water disrupts these bonds. It is more important to think about forming stronger adhesion, not by a single type of bond, but by a large number of bonds of different types. Another point to consider is that the adhesive can adhere strongly to a surface and still not form a strong bond overall, due to failure within either the adhesive or the adherend interphase.

One model of adhesion that is generally not related to the bond formation step, but is observed during bond breakage, is the electrostatic model. This model assumes that adhesion is due to the adhesive or the adherend being positive while the other is the opposite charge. It is unlikely that such charges generally exist prior to bond formation, and therefore cannot aid in adhesion; however, they can occur during the debonding process.

Another model that has limited applicability to most cases of adhesion is deep inter-diffusion, which involves polymers from the adhesive and adherend mixing to form a single, commingled phase. Although it is unlikely that the wood will dissolve in the adhesive, it is quite likely that some of the adhesive molecules will be absorbed into the wood cell walls. This one-way diffusion can form one of several types of structures that more strongly lock the adhesive into the wood. This is one type of penetration, and it will be covered in Section 9.4.8. In many cases, the strength of this penetration could be as strong as covalent linkages.

Most of these adhesion models play not only a role in bond formation, but also aid the bonded assembly in resisting the debonding forces. The important part to remember is that, depending on the origin of the forces, the stresses can be either concentrated at the interface or dispersed throughout the bonded assembly. If the forces are dispersed, then the force felt at the interface may be quite small.

It is often asked which model of adhesion is correct. This question assumes that there is only a single factor dominating the interaction of the adhesive and the substrate. In reality, there is often a combination of factors that play a role to some degree. The general rule is that the more of each mode of adhesion existing at the interface, the greater the bond durability.

#### 9.4.3 WOOD ADHESION

The comprehension of wood adhesive bonds requires both an understanding of the uniqueness of the wood structure for bond formation and an understanding of the modes of stress concentration and dissipation during environmental changes. Because adhesive strength is a mechanical property, the polymer properties of the adhesive, wood, and wood-adhesive interphase regions, are covered in the following sections. Macroscopic generalizations are difficult in the sense that wood is a nonhomogenous substrate. The adhesive needs to interact with many different types of bonding surfaces. In softwood, large longitudinal tracheids opened by vertical transwall cleavage are the main part of the surface, but parenchyma cells, various ray cells, and resin canals that are also exposed to the adhesive are also bonding surfaces with different properties. Opening the resin canals distributes resin across the surface that interferes with bonding. In hardwood, small fiber cells and large vessels form the main bonding surface, with rays and other cells also being involved. The vessel elements are split open, while the fiber cells are split in the middle lamella. Although generally for bonding studies the sapwood is used, in actual products there can be considerable amount of heartwood, which is harder to bond. Adding to the complexity, the wood can have juvenile, tension and compression wood. Adhesion studies use samples that are mainly tangential with a small slope of grain, only tiny knots, and no splits, but in commercial wood these factors are less controlled.

Most observations of adhesive interaction with wood are concentrated on scales of millimeter or larger (Marra 1992). However, the wood—adhesive interaction needs to be evaluated in three spatial scales (millimeter, micrometer, and nanometer) (Frazier 2002, Frihart 2003, 2006). The millimeter or larger involves observations by eye or light microscopy. The use of scanning electron microscopy allows observations on the micrometer or cellular level and smaller. On the other hand, the size of the cellulose fibrils, hemicellulose domains, and lignin regions are on the nanometer scale. The nanometer level is also the spatial scale in which the adhesive molecules need to interact with the wood for a bond to form. Tools, such as atomic force microscopy, developed for making observations on the nanoscale can be difficult to use with wood because its surface is rough on the micrometer scale.

To understand the adhesive interaction with the wood, we need to consider in more detail the aspects of surface preparation, types of wood surfaces, and spatial scales of wood surfaces. This provides the appropriate background for discussing the adhesive bonding as the steps of wetting the surface and solidification of the adhesive. The wood—adhesive interaction is important for the ultimate strength and durability of the bonded assembly.

#### 9.4.4 WOOD SURFACE PREPARATION

On the larger scale, wood is a porous, cellular, anisotropic substrate. It is porous in that water and low molecular weight compounds will be rapidly absorbed and move through the wood. The elongated cells of varying size and shape with the differences between the radial and tangential directions lead to the wood being very anisotropic. A simple model cannot be developed because of the large differences between wood species in the chemistry and morphology of the wood surfaces. The cell types and sizes are dramatically different between hardwood and softwood. The individual species in each of these classes vary considerably in their ability for liquids to penetrate, the amount of extractives, as well as the distribution of the various cell types. Even within a species, there is the problem of earlywood versus latewood, sapwood versus heartwood, and juvenile, compression, and tension wood having distorted cell structures. The earlywood cells with the thinner walls should be

easier to bond because of a more accessible lumen. The sapwood of a species is generally considered easier to bond than the heartwood due to changes in the extractives. The juvenile, compression, and tension wood all have distorted cell structures that should weaken the wood adhesive interphase region. To simplify the discussion, the emphasis will be placed on the wood that meets the selection criteria for standard testing.

The surface preparation has been shown to have a large effect on the quality of a wood surface (River et al. 1991). One concern is a weak boundary layer, which is a layer between the bulk materials and the true adhesive—adherend interface that is often the weak link and fails cohesively within that layer (Bikerman 1968, Wu 1982b). A classic example of a weak boundary layer was the difficulty in bonding to aluminum, due to a weak aluminum oxide surface layer, until the FPL etch was developed (Pocius 2002). Stehr and Johansson have broken down the weak boundaries of wood into those that are chemically weak and those that are mechanically weak (Stehr and Johansson 2000). The distinction is that the chemically weak layer involves extractives coming to the surface, while the mechanically weak layer involves a crushed or fractured cell layer. The role of extractives has been widely considered to be a major factor in poor adhesive strength. Certainly, low-polarity, small molecules coming to the surface can hurt the wetting process. However, it is not clear that they are normally a cause of poor bond strength. Chemically weak boundary layers are certainly an issue in oily woods, such as teak, where wiping the surface with solvent to remove the oils will solve most bonding problems. The issue of extractives should not be confused with the more general phenomena of over-dried wood. The latter case also involves chemical alteration of the wood by excessive heating that leads to poor wetting and weaker bonds (Christiansen 1990, 1991, 1994).

Wetting is an important issue, especially since most wood adhesives are water-borne. Water has such a high surface energy that wetting of many surfaces is difficult. Although surfactants can lower surface energy, they are often avoided since they can create a chemically weak boundary layer. The monomers and oligomers in the adhesive can lower surface energies, as can added low molecular weight alcohols. Wetting should be less of an issue with adhesives that have organic solvents or are 100% solids.

Mechanically weak boundary layers can be an issue with wood (River 1994a). The general problem is the crushing or excessively fracturing the wood cells during the surface preparation. Wood cells, especially earlywood, are weak in the radial and tangential direction. Crushed cells are easy to visualize by looking at cross sections microscopically. If the adhesive does not penetrate through the layer of crushed cells, then this layer will generally be the source of fracture under test or use conditions. The best method for preparing a wood surface for bonding is to use sharp planar blades. Unsharpened blades can crush cells and cause a very irregular surface (River and Miniutti 1975). The difference in penetration of an adhesive on well- and poorly planed wood surfaces is shown in Figure 9.4. Abrasively planed surfaces and saw-cut surfaces also suffer from crushed and fractured surface cells. Hand sanding is generally acceptable because it causes less damage to the cells. For laminates, ASTM prescribes that the wood surfaces be planed with sharp blades and then be bonded within 24 h to provide the most bondable surface (ASTM International 2011b), although it is generally recommended to bond surfaces immediately after preparation to provide the most durable bond.

#### 9.4.5 WOOD BONDING SURFACE

The wood-bonding surface varies considerably both chemically and morphologically depending on how the surface is prepared and what type of wood is being used. The morphology is better characterized than the surface chemistry, and will be discussed first. Except for fiber bonding, the desire is to have sufficient open cells on the surface so that the adhesive can flow into the lumen of the cells to provide more area for mechanical interlock. The accessibility of open cells is dependent upon the tree species, types of cells, and method of preparation. When the cell wall is thin in comparison to the diameter of the cell, then there will be more longitudinal transwall fracture.

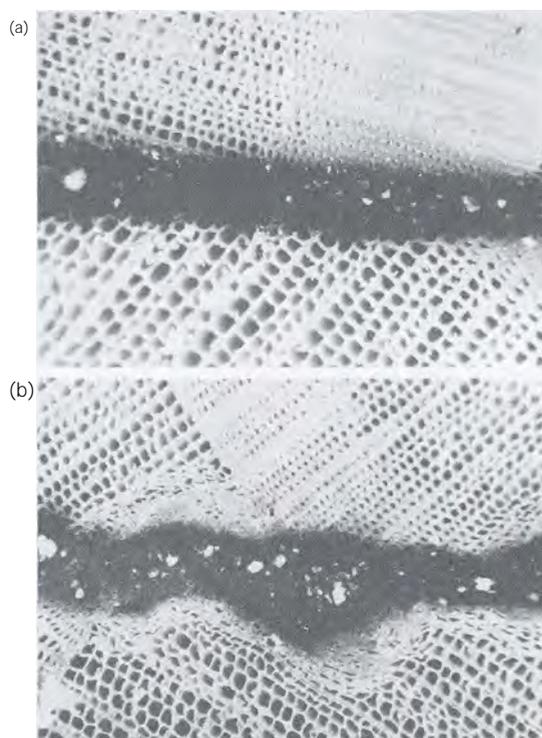


FIGURE 9.4 Bondlines show good adhesive penetration for (a) a sound wood surface, but not for (b) a crushed and matted wood surface.

Hardwood vessels and earlywood cells have thin walls that are easily split to open the lumens to the adhesive for good penetration. On the other hand, hardwood fiber cells and latewood cells have thick walls that are not easy to fracture, so cleavage often occurs more in the middle lamella providing less area for mechanical interlock (River et al. 1991). The open ends of any cells and cracks in the cell walls allow the adhesive to penetrate into the lumens. The differences in the surfaces can be large, by comparing the scanning electron microscopy pictures for southern yellow pine and hard maple (Figure 9.5), with pine having more open cells, while many of the maple's cells are closed.

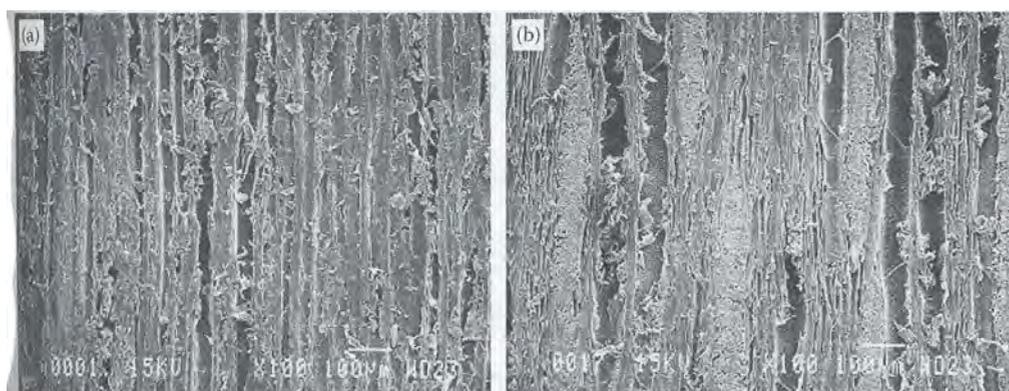


FIGURE 9.5 Scanning electron microscopy pictures of transverse sections of (a) southern yellow pine and (b) hard maple.

The chemical composition of the wood-bonding surface is less well understood because the surface is very hard to characterize. The roughness of the surface, the presence of many different surfaces (lumen walls, middle lamella, and fractured cell walls), and the changes of the surfaces with time, heat, and moisture add to the difficulty. The main components of the wood are the cellulose, hemicellulose and lignin fractions. The interactions of PF and urea-formaldehyde (UF) polymers with cellulose have been modeled (Pizzi 1994b). Although cellulose is the main component of wood, it may not be the main component on the surface. Prior work has indicated that hemicellulose is the main site of interaction with water for hydrogen bonding because of its greater accessibility (River et al. 1991, Salehuddin 1970). The preparation of the wood surface by planing can create many types of surfaces, depending on how the cells fracture, as illustrated in Figure 9.6. If the cell walls are cleaved in longitudinal transwall fashion as desired, then the lumen should be the main bonding surface. The lumen walls are often a large part of the bonding surface, especially for earlywood cells of softwoods, and vessel elements in hardwoods. The lumen walls' compositions can vary from being highly cellulosic, if the  $S_3$  layer is exposed, to highly lignin if they are covered by a warty layer. The middle lamella is also rich in lignin. However, for the most part we do not know when the walls are fractured if the cleavage plane runs through any of the three main fractions or between the lignin-hemicellulose boundary, which may be the weakest link in the wood cellular structure. Complicating this consideration of the bonding surface is that the typical mechanical ways of preparing binding surfaces cause a lot of fragmentation and smearing of the cell wall components. Only by careful microtome sectioning can the clean splitting of the cell walls be observed. Other methods give surfaces that are a lot less intact (Wellons 1983). As can be seen by Figures 9.5 and 9.7, there is a lot of debris on the surface even with sharp planer blades. Hardwood tends to give even more smearing of the surface. Thus, the theory of many open lumens into which the adhesive can flow is not always correct, which may be why the penetration of the adhesive into the lumens is not always that fast.

#### 9.4.6 SPATIAL SCALES OF WOOD FOR ADHESIVE INTERACTION

Wood bonds need to be considered on three different spatial scales: millimeter and larger, micrometer, and nanometer (Frazier 2002, Frihart 2004). The millimeter and larger scale is normally used for evaluating the bonding and debonding processes of wood. The micrometer scale relates to the cellular dimensions. The nanometer and smaller scale correlates to the sizes of the cellulose, hemicellulose,

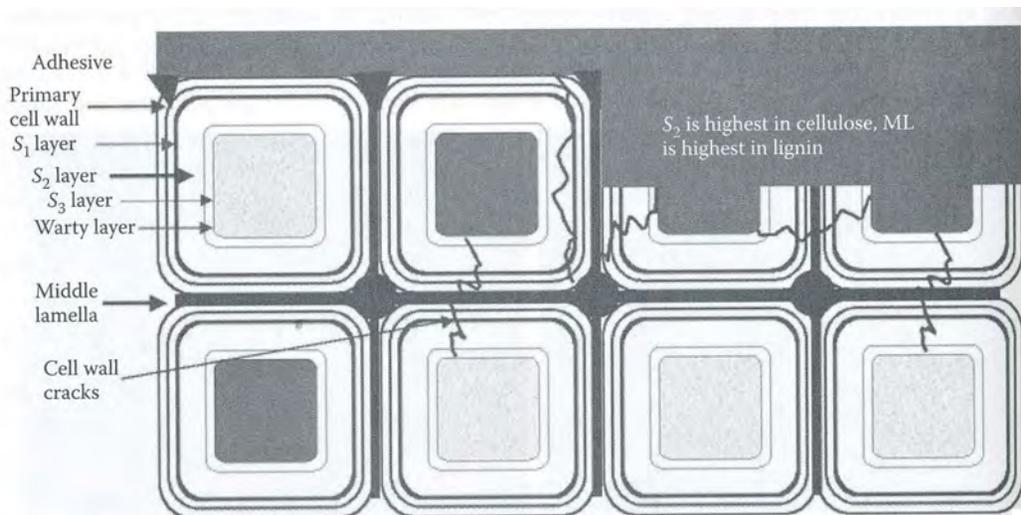


FIGURE 9.6 Illustration of a transverse section of wood showing fracture points  $S_1$  the wood cellular structure and surfaces available with which adhesives can interact, assuming clean fractures are occurring.



**FIGURE 9.7** Scanning electron microscopy of yellow poplar surfaces at four levels of magnification, from (a) to (d) as illustrated by the length bar in each image showing the extensive fracturing of the surface and generation of weakly bonded fragments even with sharp planar blades.

and lignin domains and the molecular interactions of the adhesive with the wood. Each domain size requires different observation methods and has different implications on bonding and debonding processes.

The millimeter and larger scale is the normal method for dealing with both the bonding and the debonding processes. Usually the naked eye or feel by hand touch is used to judge the smoothness of the surface for bonding. On this scale, measurement of the spread by the adhesive across the surface is typically done by contact angles. Normal examination of the adhesive bond failure is generally limited to this scale. This information is valuable for understanding bond formation and failure aspects as the first stage in evaluation of adhesive performance. However, it is important to move on to the smaller spatial scales to gain a fuller understanding of wood bonding.

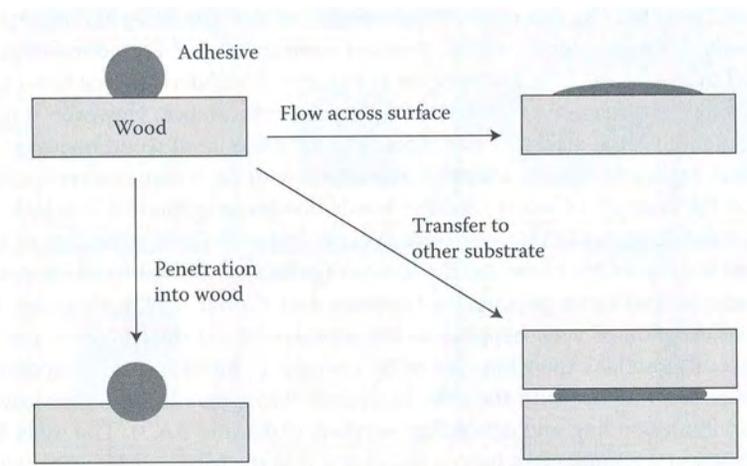
The micrometer scale involves the adhesive interaction with the lumens and cell walls. While the earliest theory on the strength of wood adhesive bonds involves mechanical interlock (McBain and Hopkins 1925), others proposed that there were specific interactions of adhesives of the wood surface (Browne and Brouse 1929). Flow into the lumen of cells is still considered important as judged by many microscopic studies on penetration (Johnson and Kamke 1992). However, there has not been enough consideration of what happens to the adhesive—wood interphase as the cells and the adhesive undergo differential expansion caused by changes in moisture and temperature. Because different adhesives can interact with the cells in diverse ways, these aspects are covered in more detail in the individual bonding and debonding sections (9.4.8 and 9.6.3). The tools for looking at this level of interaction are more complicated because it is at the high end of light microscopy magnification, but it is certainly in the range of scanning electron and transmission electron microscopy (SEM and TEM, respectively).

The nanometer and smaller scale is important because it is the size of the basic domains of wood and of the adhesive—wood interactions (Fengel and Wegener 1984). The size of the cellulose fibrils, the hemicellulose portions, and the lignin networks are in the tens of nanometers. For there to be adhesion, the adhesive needs to interact with the wood at the molecular level; independent of whatever mechanism is involved. The idea of wood adhesion being more than a mechanical interlock was proposed in the 1920s with the concept of specific adhesion as being critical (Browne and Brouse 1929). The problem with understanding this specific adhesion is our lack of understanding of the composition of the wood surface. Although cellulose is the main component of wood, it may not be the main component on the wood surface. If bonding to lumen walls is important, then adhesion to lignin is important since the warty layer present in many species is high in lignin content (Tsoumis 1991). Cleavage in the middle lamella, as may occur with latewood cells, fiber cells in hardwood or fibers prepared for fiberboard, leads to a surface high in lignin content. Until we can better define how the adhesive has to interact with the wood to form durable bonds, this area is still quite speculative. Although instrumental methods, such as atomic force microscopy, surface force microscopy, and nanoindentation can look at surfaces at this scale, they work best when the surface morphology changes only by nanometers while the roughness of the wood surface varies by micrometers.

#### 9.4.7 WETTING AND PENETRATION IN GENERAL

For a bond to form the adhesive needs to wet and flow over a surface, and in some cases penetrate into the substrate. It is important to understand that the terms mean different things even though they sound familiar. Wetting is the ability of an adhesive drop to form a low contact angle with the surface upon contact. In contrast, flow involves the adhesive spreading over that surface in a reasonable time. Flow is important because covering more of the surface allows for a stronger bond. Thus, a very viscous adhesive may wet a surface, but it might not flow to cover the surface in a reasonable time frame. Penetration is the ability of the adhesive to move into the voids on the substrate surface or into the substrate itself. The difference between flow, penetration, and transfer are illustrated in Figure 9.8.

First, we will consider the aspects of wetting, flow, and penetration that are common to most substrates. In the next section, we will discuss how these need to be modified for wood bonding. For a strong bond to form, the adhesive must intimately encounter most of the substrate surface (Berg 2002). With many plastics having low surface energies, this is a significant problem since the adhesive can find it difficult to wet the substrate. An extreme example is the bonding of Teflon, which has



**FIGURE 9.8** Adhesive wetting of wood surfaces, showing the difference between flow, penetration, and transfer. ►

a very low surface energy so that very few adhesives will wet it. In fact, an adhesive applied to the surface forms a bead rather than wets the surface. For bonding to many polyethylene and polypropylene materials, wetting by an adhesive is also a significant problem because of their low surface energies. Thus, a great deal of the literature places emphasis on the measurement of contact angles to determine the wetting of the surface. The contact angle is the angle at the edge of a droplet and the plane of that surface upon which it is placed. Therefore, a material with a high contact angle has poor surface wetting ability. The addition of surfactants or less polar solvents reduces the adhesive's surface energy as indicated by a decreased contact angle. With many plastics, surface treatments such as oxidation by flame or corona discharge are used to increase the polarity and surface energy of the plastic surface to improve its bondability. It is important to remember that most contact angle measurements are equilibrium values, and may not reflect the dynamics of the bonding process well. Another very important property that is closely associated with wetting is flow over the surface. Flow is dependent upon not only the contact angle, but also the viscosity of the adhesive. With a lower viscosity, the adhesive flows better and wets more of the surface.

While flow is movement across the surface, penetration is the movement into the substrate. Adhesives will not penetrate into the bulk of many substrates like metals and many plastics, but penetration is important in the sense of movement of the adhesive into the microcrevices on the surface (Berg 2002). Most surfaces have some degree of roughness, which an adhesive must penetrate. Like flow, penetration is dependent upon surface energies and adhesive viscosity, but it also depends on the size of the capillary or void that it is penetrating. For a strong bond, the adhesive must penetrate into all microscale roughness. A typical problem is a displacement of air, water, or oil on the surface. As discussed in the next section, penetration has a very different meaning for wood, due to its structure.

#### 9.4.8 WETTING, FLOW, AND PENETRATION OF WOOD

Wood bonding faces many of the same issues as discussed in the previous section on general aspects of wetting, flow, and penetration, but there are many characteristics that are unusual about wood that require additional consideration. Wood has a relatively polar surface that allows the general use of water-borne adhesives, although some woods are harder to wet. Examples are some tropical woods that have a very oily nature, such as teak, and wood that has been treated with creosote. Wetting of the surface can be improved by removal of the oily components through solvent wiping, mechanical, or oxidation techniques. In Figure 9.9, the effect of sanding on improving the wetting of yellow birch veneer is illustrated. It has been shown that oxidation of wood surfaces by corona treatment can improve wetting and adhesion for some woods (Sakata et al. 1993). A lot of work has



FIGURE 9.9 Water droplets on yellow birch veneer show the improved wetting by removal of surface contaminants. The photo was taken 30 s after placing three droplets on the surface. The left drop was on an untreated surface, the middle was renewed by two passes of 320 grit sandpaper, and the right drop was renewed with four passes with the sandpaper.

been done on examining the wetting of wood; however, it is not clear what this data means. For example, studies to relate extractives with bonding have not found good correlations (Nussbaum 2001). This may be caused by wetting experiments usually being done with water at room temperature; while most adhesive bonding is done using aqueous solutions of organics with higher temperatures and pressure, all of which improve wetting of surfaces.

Understanding flow over the surface is complicated by the fact that the surface has very macroscopic roughness, and penetration is taking place at the same time. As mentioned in the previous section, penetration generally involves wetting of the micro-roughness. On the other hand, wood's cellular nature allows significant penetration of the adhesive into the substrate. A main complication is that different species of woods have different cellular structures, and therefore, adhesives will penetrate them to different degrees. This leads to problems in trying to achieve uniform penetration when bonding different species of wood, as occurs in OSB production. For a more porous wood, an adhesive can over-penetrate into the wood and not be on the surface for bonding, while the same adhesive on a less porous wood sits on the surface and may not give significant bonding. Thus, adhesives are formulated for different applications given the type of wood, the type of application, and the application conditions. An adhesive that is sprayed onto OSB tends to be much lower in viscosity for better spraying than one that is formulated for spreading on plywood that needs to sit more on the surface. Aspects of formulating adhesives are covered in later sections.

In most bonding applications, adhesive penetration into the adherend does not occur to any great degree, but penetration is very important for wood bonding. The need for the proper degree of penetration influences both the formulation of the adhesive and the bonding conditions. The proper balance is necessary in that poor bonds will result from either under- or over-penetration. In under-penetration, the adhesive is not able to move into the wood enough to give a strong wood—adhesive interaction. In contrast, with over-penetration so much of the adhesive moves into the wood that insufficient adhesive remains in the bondline to bridge between the wood surfaces, resulting in a starved joint. To solve these problems, the viscosity and composition of the adhesive can be adjusted, as well as the temperature and time for the open and closed assemblies. Some species are known to be more porous compared to other species, leading to complications when bonding mixed species. This is a significant issue for composites that usually use a wide mixture of species and a frequently changing mixture. Using mixed species certainly could lead to both over- and under-penetration and to potentially reduced bond strength. Although it is generally known that proper penetration is important to strong bonds, it is not clear whether penetration into the lumens or the cell walls is more critical.

The penetration of adhesives into wood is most often examined at the cellular level. Some lumens have openings on the surface as a result of slope of grain so that the adhesive can flow into the lumen; this is more likely with larger diameter cells in softwood. In hardwoods, most of the filling of lumens is of the larger vessels rather than the smaller fiber cells. Factors that influence the filling of the lumens can be classified into those that are

- Wood related, such as diameter of the lumen and exposure on the wood surface
- Adhesive related, such as its viscosity and surface energy
- Process related, such as assembly time, temperature, pressure, moisture level

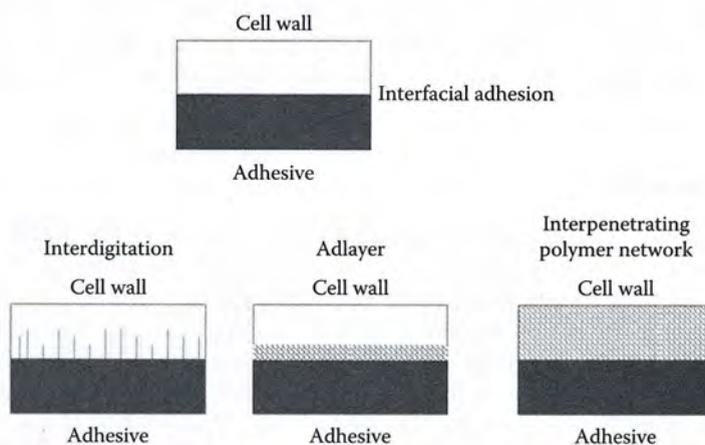
It is normally assumed that the filling of lumens contributes to bond strength. Resin penetration into lumens has been extensively investigated in the wood bonding literature because it is easy to determine by visible light, fluorescence, and scanning electron microscopy. The problem is that these data have not been related to bond strength or level of bond failure. An example, where a filled ray cell contributed to adhesion of a coating after environmental exposure, has been shown by light microscopy (Dawson et al. 2003).

In addition to filling the lumens, an important part of wood adhesion, especially for durable bonds, might be infiltration of adhesive components into cell walls (Nearn 1965, Gindl et al. 2004)

A significant amount of lower molecular weight compounds can go into cell walls due to their ability to swell. These compounds include water, cosolvents, adhesive monomers and oligomers, but not higher molecular weight polymers. Polyethylene glycol molecules of up to 3000 g/mol were shown to penetrate into the transient capillaries or micropores in cell walls (Tarkow et al. 1965). In addition to hydrodynamic volume of an adhesive, its compatibility with the wood structure controls this infiltration. Generally, solubility parameters are widely used to determine the compatibility of adhesives and coatings to interact with surfaces (Barton 1991). Limited studies have been done trying to relate the solubility parameters of the components of wood to its ultrastructure (Hansen and 1998, Horvath 2006), which would then relate to the components' interaction with adhesives.

The observation of adhesive components in cell walls has been shown by a variety of methods. The migration of PF resins into cell walls has been shown using fluorescence microscopy (Saiki 1984), autoradiography (Smith 1971), transmission electron microscopy (Nearn 1965), scanning electron microscopy with x-ray dispersive emissions (Smith and Cote 1971), dynamic mechanical analysis (Laborie et al. 2006), and antishrink efficiency (Stamm and Seborg 1936). For polymeric diphenylmethane diisocyanate, pMDI, the presence of adhesives in cell walls has been shown by x-ray micrography and nuclear magnetic resonance spectroscopy (Marcinko et al. 1998, Marcinko et al. 2001). These and other techniques such as UV microscopy (Gindl et al. 2002) and nano-indentation (Gindl and Gupta 2002) have been used to show the presence of OF and MF (Bolton et al. 1985, 1988), while fluorescence spectroscopy has been used to show epoxy resins in the wall layers (Furuno and Goto 1975, Furuno and Saiki 1988). Because both chemical and mechanical data show the presence of adhesives in cell lumens and cell walls, it is likely that the wood portion of the interphase has very different properties than the bulk wood.

Although it has been shown that adhesive components can infiltrate into cell walls, only in one case has it been claimed to improve bond strength (Nearn 1965). Several models can be proposed as to how these adhesive components may influence bond strength. The simplest is that the oligomers and monomers are simply soluble in the cell walls, but do not react, being too diluted by the cell wall components (Laborie et al. 2006). In this case, they would maintain the cell walls in the expanded state due to steric constraint (bulking effect); thus, the process would reduce the stresses due to less dimensional change. A second model is that the adhesives react with cell wall components and possibly cross-link some of the components, thereby increasing the strength properties of the surface wood cells, as shown in Figure 9.10. A third model is that the adhesives polymerize to form molecular



**FIGURE 9.10** Modes of adhesive interaction within wood cell walls are depicted for true interfacial adhesion with no cell wall penetration, interdigitation of fingers of adhesive penetrating the microchannels, adlayer of cross-linking in the surface cell wall and interpenetrating polymer.

scale fingers of the adhesive in the wall, providing a nanoscale mechanical interlock. The fourth is that they form an interpenetrating polymer network within the wood, providing improved wall strength (Frazier 2002). All of these models have the adhesive reducing the dimensional changes of the surface cells, and therefore reducing the stress gradient between the adhesive and the wood, thereby improving the bond strength, but the degree of improvement should be different.

Knowing that adhesive components do migrate into the cell wall, the next questions is: Are they associated with any specific cell layer or the middle lamella, and are they more in the cellulose, hemicellulose or lignin domains? One study indicates that the isocyanates seem to be more concentrated in the lignin domains (Marcinko et al. 2001). Peeling experiments have shown that an epoxy adhesive gave failure in the S<sub>3</sub> layer while a PF adhesive resulted in failure deeper in the S<sub>2</sub> layer (Saiki 1984).

## 9.5 SETTING OF ADHESIVE

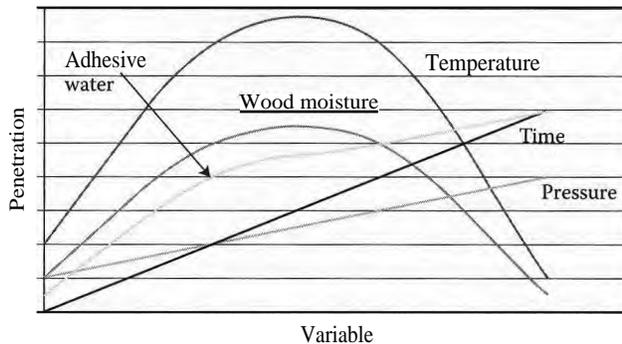
Once an adhesive is applied to wood; the adhesive needs to set for forming an assembly with high strength. Set is "to convert an adhesive into a fixed or hardened state by chemical or physical action, such as condensation, polymerization, oxidation, vulcanization, gelation, hydration, or evaporation of volatile solvent." Although the ASTM terminology uses solvent to refer to organic solvents, this chapter uses it in the more general sense of both water and organics because wood adhesives are usually water-borne. Water-borne adhesives often contain some organic solvent to help in the wetting of wood surfaces. For some of the polymeric adhesives, including polyvinyl acetate, casein, blood glue, and so on, the loss of solvent sets the adhesive. For many others, including the formaldehyde-cured adhesives, the set involves both the loss of water and polymerization to form the bond. For polymeric diphenylmethane diisocyanate, the set is by polymerization. For hot melt adhesives, cooling to solidify the polymer is sufficient. In wood bonding, all of these mechanisms are applicable, dependent upon the adhesive system that is being used.

The original wood adhesives were either hot-melt or water-borne natural polymers (Keimel 2003). These had several limitations in relation to speed of set, formation of a strong interphase region, and environmental resistance. All of the biomass-based adhesives had poor exterior resistance. The use of composites and laminated wood products has greatly expanded with the development of synthetic adhesives with good moisture resistance. Instead of being mainly polymers with limited and reversible cross-links, these adhesives have strong covalent cross-links to provide environmental resistance. In addition, these synthetic adhesives generally cure by both polymerization and solvent loss, leading to a faster setting process. Having multiple modes of set allows both the use of lower viscosity polymers for good wetting and polymers with a higher molecular weight for a faster cure. This combination gives a fast set rate that allows for higher production speeds.

### 9.5.1 LOSS OF SOLVENTS

For many adhesive uses, solvents are a problem because of the nonporous nature of the substrate preventing removal of the solvent by migration into and through the substrate. However, wood is quite effective in allowing solvent to migrate away from the bondline, thus allowing adhesives to set. Of course, this property is very dependent upon the wood species and the moisture level of the wood (Tarkow 1979). It is not surprising that wet wood will less rapidly absorb moisture, thus making it harder for water-borne adhesives to move into the wood. The dynamics of water movement have a large effect on the bonding process. The factors involve penetration of the adhesive into the wood, rate of adhesive cure, flow of heat through composites, and premature drying of the adhesive.

Penetration of the adhesive into the wood is an important part of the bonding process. Green wood is difficult to bond with most adhesives because there is little volume into which the adhesive



**FIGURE 9.11** General effects of conditions on adhesive penetration. The temperature makes the adhesive more fluid until too much causes polymerization. At low wood moisture the water is drawn from the adhesive, while at high wood moisture the water retards the penetration. As the water content of the adhesive increases, the viscosity of the adhesive is lower and penetration increases. Both an increase in bond pressure and a longer time promote adhesive penetration.

can penetrate. (See Figure 9.11 for the generalized effect of bonding parameters on penetration.) At the other extreme, overly dry wood can also be difficult for the adhesive to penetrate because the wood surface is more hydrophobic and therefore harder to wet (Christiansen 1994). Thus, wood with a 4-10% moisture range is typically good for optimum penetration and set rates. The desire is to have the bonded product be near the normal in-use moisture condition to reduce dimensional changes and internal stress (Marra 1992). Although most of the studies on uptake of small molecules into wood have naturally concentrated on water, other solvents are also readily absorbed/adsorbed by wood.

For many of adhesives, cure rate is dependent upon the moisture content. Most bonding processes require the wood to be within a set range of moisture content to get an acceptable set rate. For the adhesive to set, the solvent needs to flow away from the adhesive into the adjoining and further removed cell walls. The sorption of the water into the nearby cell walls allows the formation of the solid, cured adhesive. Many setting reactions involve condensations that give off water; higher moisture levels can retard the reactions as expected by normal chemical equilibrium theory and from limited collisions due to dilution. The amount of water present also alters the mobility of polymer chains during the curing process, which can change the product distribution for the adhesive polymers. On the other hand, many isocyanates depend on a small amount of water to start the curing process. Thus, the isocyanates are most tolerant of higher moisture content of the wood.

A very important issue in the rate of setting is the heat flow through composites or laminates to the bond surface, especially since wood is a good insulator. In composites, water boiling in the wood near the composite surface or added steam helps transfer heat to the core of the composite. Use of core resins that cure at lower temperatures than face resins is important for fast production cycles; fast curing can be accomplished by using higher molecular weight oligomers or adding catalysts to the core resins. Controlling heat transfer and moisture levels is important for fast, reproducible composite production. Isocyanates are less sensitive to higher moisture levels in the core. The ability of resorcinol-formaldehyde (RF) and phenol-resorcinol-formaldehyde to cure rapidly at room temperature favors them over PF resins despite their higher cost where it is difficult to heat the bondline, such as laminated beams. Another way to accelerate cure is to use radiation methods, such as radio frequency curing. Polyurethanes use moisture to cure rather than heat.

With some adhesives, premature drying can be a problem if the open time is too long. This involves too much loss of solvent so that the adhesive does not flow to wet the other surface. Proper control of moisture level and penetration are accomplished by the length of open- and closed-assembly times, as well as adhesive composition.

### 9.5.2 POLYMERIZATION

For a strong bond, higher molecular weight and more cross-linked polymers are needed (Wool 2005). In most cases, adhesives consist of monomers and/or oligomers, which are a small number of monomers linked together. Because adhesives need to have stability prior to application, there needs to be some method for activation of polymerization. This activation can include heat, change in pH, catalyst, addition of a second component, or radiation. Sometimes a combination of methods is used for faster cure. The cure method is closely tied to the process for making the wood product.

Heat is a very common way to speed up polymerization reactions. Most chemical processes are controlled by the transition state activation energy, using the standard Arrhenius equation. The typical factor is that rates of reaction double for every 10°C increase in temperature, but this does not always apply. This means that if the normal reaction temperature is moderate, there will be appreciable reaction at room temperature and a limited storage life of the adhesive for a single component system. Since wood is a good insulator, uniform heating of the adhesive continues to be a problem for many composites and laminates. Incomplete heating gives poor bond strength as a result of incomplete formation of the adhesive polymer. To overcome this problem adhesive producers try to have the adhesive formulation in as advanced stage of polymerization as is possible while still having good flow and penetration into the wood. Having a more advanced resin means that fewer reactions need to take place to obtain the strength properties needed from the adhesive. This balance between the advancement of the resin for fast curing while still having good bonding properties has been optimized by intense study of reaction mechanisms over the years and allows for higher production rates. On the other hand, the understanding of heat and moisture levels within the composites is still being studied to allow further improvement in production rates (Winandy and Kamke 2004).

Many of the adhesive polymerization rates are sensitive to pH. This is especially true of the formaldehyde polymers, but the effect varies with the individual type of co-reactant and the different steps in the reaction. For UF resins, the initial addition step of formaldehyde to urea is base catalyzed, while the polymerization of hydroxymethylated urea is acid catalyzed. Thus, UF resins are kept at a more neutral pH for storage stability, but then accelerated by lowering the pH during the bonding process. For PF resins, there is a different pH effect with condensation reactions being faster at high pHs and very low pHs. One issue of concern is how much the pH and neutralization capacity of wood alters the adhesives' polymerization rates near the interface and within the wood. This is complicated by the fact that different woods have different pHs and buffering abilities (Marra 1992).

Another aspect that alters the polymerization rate is the addition of catalysts and accelerators. A true catalyst is one that is not consumed in the process, while an accelerator can be consumed via reaction. A number of accelerators are incorrectly termed catalysts. As mentioned in the previous paragraph, changes in pH can catalyze polymerizations. In some cases, the pH is not changed directly, but compounds are added that can generate acids, such as the ammonium chloride or ammonium sulfate accelerators for UF resins that decompose upon heat to yield hydrochloric acid or sulfuric acid, respectively (Pizzi 2003e). Certain metal ions are known to be catalysts for PF resins. Ortho esters are often described as catalysts for PF resins, but in actuality are consumed in the process, making them accelerators (Conner et al. 2002). A number of compounds have been found to speed up PF curing (Pizzi 1994c). In some cases, co-reactants, such as formaldehyde, have been referred to as accelerators, but in their general use, they serve as hardeners because they become part of the polymer.

Many adhesives are two-part products. Because the components are not mixed together until shortly before the bonding process, each component alone has a good storage life. However, the addition of a second component allows the polymerization to begin. Because the adhesive is applied at ambient temperatures and most of the polymerizations need higher temperatures, setting is slow until the composite or laminate reaches the heated press. Rapid ambient polymerizations

are not desirable because they limit the adhesive's ability to wet and penetrate the wood, and to transfer when the wood surfaces are brought into contact. One area of concern is the uniformity of mixing of two components. Off-ratio mixtures do not form as strong a bond as those at optimum ratio because of the poor stoichiometry. The better the compatibility and more equal the viscosity of the two components, the better the uniformity of the product upon mixing. Most application equipment is designed to give good mixing, but this may not be as true in laboratory testing or during upsets in plant operations. A special type of two-component application is where one component is applied to one surface and the other component to the other surface and has been called a honeymoon adhesive (Kreibich et al. 1998). The two surfaces need to be brought into the proper contact to allow mixing and the two components need to have good mutual solubility for this system to work well.

A common type of cure is those that use water as a reactant in the polymerization process; this type of cure is used for curing of most one-component polyurethanes, isocyanate, and silicones adhesives (Frazier 2003, Lay and Cranley 2003, Parbhoo et al. 2002). The chemistry for the polyurethanes and isocyanates is discussed in a later section. Because these adhesives use water for curing, then water exposure needs to be prevented prior to application. In general, wood contains sufficient moisture to cause curing. In addition, because these reactions use water for curing rather than give it off as in condensation polymerizations, the adhesives are much more tolerant on bonding wood with higher moisture content than are most other adhesives.

Another method of activation of an adhesive is the use of some type of radiation. The use of ultraviolet light and electron beam radiation are common for the curing of coatings, but trying to get light into a wood adhesive bond is more difficult. However, other types of radiation can penetrate wood, including microwaves and radio frequencies, which activate curing by causing heat generation in the bondline to initiate thermal polymerization (de Fleuriot 2004).

### 9.5.3 SOLIDIFICATION BY COOLING

Although hot melts are a small part of the wood adhesive market, understanding the interaction of molten polymers with wood to form a strong durable interface is important for the wood—plastic composite field. Many wood adhesives used by the early civilizations were hot melts (Keimel 2003). Some hot melt adhesives have been used for bonding plastics to wood and are used in some wood assembly markets, such as cabinet construction, edge banding, window manufacturing, and mobile home construction. Because hot-melt adhesives and plastics used for composites are polymeric, they have a limited ability to flow. Heating the polymers above their softening point will allow them to flow. The lower the molecular weight of the polymer and the higher the temperature, the better the flow. However, both of these aspects can reduce the final strength and lengthen the set time. The formulation of the polymer backbone and additives can have a great effect on the set time. In fact, formulation is often used to control the set time so that the adhesive does not solidify before the two components are in place or take so long that extended clamping times are needed. Unlike other adhesives, high viscosities of hot melts limit their ability to penetrate into the wood lumens and flow across the wood surfaces. As the adhesive cools, its viscosity raises rapidly to further limit the wetting. Although the wetting of the wood is limited, there has still been reported flow into lumens (Smith. 2002). Understanding the wood-molten polymer interaction is very critical for making improved wood—plastic composites (Clemons et al. 2012).

Some of the newer hot-melt adhesives are reactive types that allow for better wetting by the adhesive and greater cured strength. Normally, hot melts need to be of high molecular weight for strength, but if the adhesive cures after application, then the initial strength is not such a critical issue. The curing also makes the adhesive a thermoset to eliminate remelting of the adhesive or flow (creep) with time. Some of these products are isocyanates so that they cure by reacting with moisture that is readily available in the wood (Paul 2002). Thus, the combination of modes of set provides benefits that are not available over adhesives with a single mode of setting.

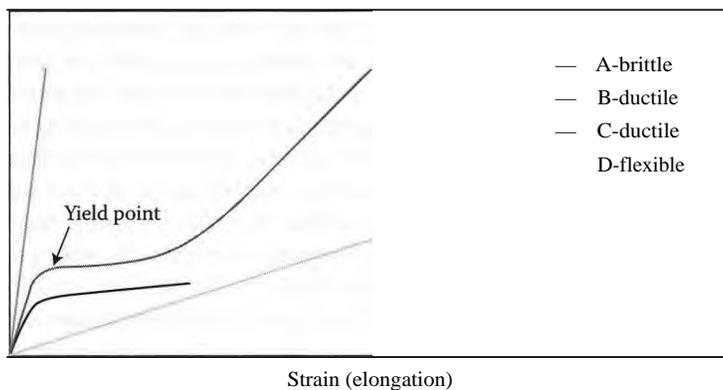
## 9.6 PERFORMANCE OF BONDED PRODUCTS

Because an adhesive is used to hold two adherends together under normal use conditions, it is important to comprehend the properties of an adhesive that allow it to perform this function. The definition of an adhesive is mechanical in nature, making it important to understand the internal and external forces on the bondline and the distribution of those forces across the bonded assembly. Mechanical properties are dependent upon the chemical structure; thus, knowing the structure of the adhesive and interphases helps to understand the adhesive's performance. Bonded assemblies are usually weaker in tension perpendicular to the bondline than in shear or compression because it is easier to pull the chains apart. To understand the performance of bonded products, the structures of the wood adhesive polymers and the mechanical properties of polymers need to be appreciated. Greater strength in the bulk of the adhesive does not necessarily result in more strongly bonded assemblies because the weakest portion may still be in the interphase regions. Another factor is the need to know the forces that the bondline must withstand under normal use conditions. The effect of external forces on the bondline can be analyzed through a variety of standard tests; however, the internal forces are not as clearly determined. There are commonly accepted durability tests, but the forces that are exerted on the bondline during these tests are not well understood. The relationship of mechanical properties that are usually observed on the millimeter scale to the chemical structure that is formed under the nanoscale has to be examined.

### 9.6.1 BEHAVIOR UNDER FORCE

The evaluation of the integrity of a bonded object rests upon understanding the viscoelastic dissipation of energy for each of the components (bulk adherend, bulk adhesive, and adhesive—adherend interphase). A basic test is a stress—strain curve, which shows the response of a material to an applied force, usually in tension. Although the behavior of material can be measured in tension, compression, or shear, tension is usually measured because it is the most likely mode of failure.

Stress—strain data are presented for a variety of material types in Figure 9.12. A very stiff material, such as a nonductile metal or glass, does not elongate (% strain) much before the material breaks; thus, the applied force accumulates as stress until it exceeds the strength of the material, as indicated by curve A. The stiffness or modulus of A is defined as the stress divided by strain at low percent strain usually over the linear region. Plastics are represented by curve B or C in that at some point the elastic limit (when deformation is no longer reversible) is exceeded at the yield point. The



**FIGURE 9.12** General stress-strain data for polymers. The rigid polymers resist applied force and build the stress showing a high modulus (stress/strain) until the material breaks. A ductile material will resist initially but then start to flow at the yield point, with higher molecular polymers showing strain-induced crystallization. The flexible polymer will offer little resistance to the applied force, giving a high elongation.

modulus of B is the linear portion prior to the yield point. The applied force is elastically stored in the plastic prior to the yield point, but stretches inelastically after the yield point. For a lower molecular weight plastic B, at some point on this plateau the applied force exceeds what that plastic can take and the sample breaks. However, a higher molecular weight plastic C will often have a strain-induced crystallization that causes the curve to bend upward again. The last example D represents a rubber that does not store much energy as stress, but the force causes the material to elongate. The modulus in this case is much lower and hard to measure since the initial linear section is short. In addition to the stress, strain, and modulus obtained from these tensile tests, another important piece of information is the area under the curve, which is related to toughness of the material.

For wood-bonding applications, a polymer of type D is not acceptable since there is not enough rigidity in the adhesive. However, type D is excellent for caulking and sealant applications since these materials need to be flexible given the expansion and contraction of buildings. Curves B and C have large areas under the stress-strain curve giving these materials good toughness, especially for impact resistance. Curve C represents plastic used in wood-plastic composites. Some wood adhesives represented by curve B are the poly(vinyl acetate) resins, emulsion polymerized isocyanates, polyurethanes, contact cement, and hot-melt adhesives.

Curve A represents structural adhesives that have low creep, the lack of flow under force. This nonflow characteristic under normal conditions means that bonded products will retain their shape. Most wood adhesives fall into this class, including the widely used UF, PF, RF, and combinations such as melamine-urea-formaldehyde and phenol-resorcinol formaldehyde. The epoxy and fully cured polymeric diphenylmethane diisocyanate adhesives also are members of this class.

The data in these graphs represent the materials at a specific temperature. As the temperature of a material increases it softens so that a class A polymer becomes like B. The transition of going from a glassy (hard and brittle) material to a more pliable one involves going through the glass transition temperature,  $T_g$ . However, there are limits on softening for curable adhesives because they can continue to cure and become more rigid at elevated temperatures and can begin to degrade at some point, thus changing their physical properties.

Knowing the chemical structure of the adhesives allows the prediction of the general mechanical properties, but does not allow the calculation of the specific shape of the stress-strain curve. The curve D polymers are generally linear or branched organics that have low crystallinity. They also include a major nonorganic adhesive and sealant type, the silicone adhesives that are actually poly(dimethylsiloxanes) and their derivatives and copolymers. These materials will creep, that is, flow under an applied force, unless they are cross-linked. The cross-links prevent the polymer chains from continuing to flow past one another. As the number of cross-links increases, the material becomes stiffer, usually resulting in a reduction in the ultimate elongation.

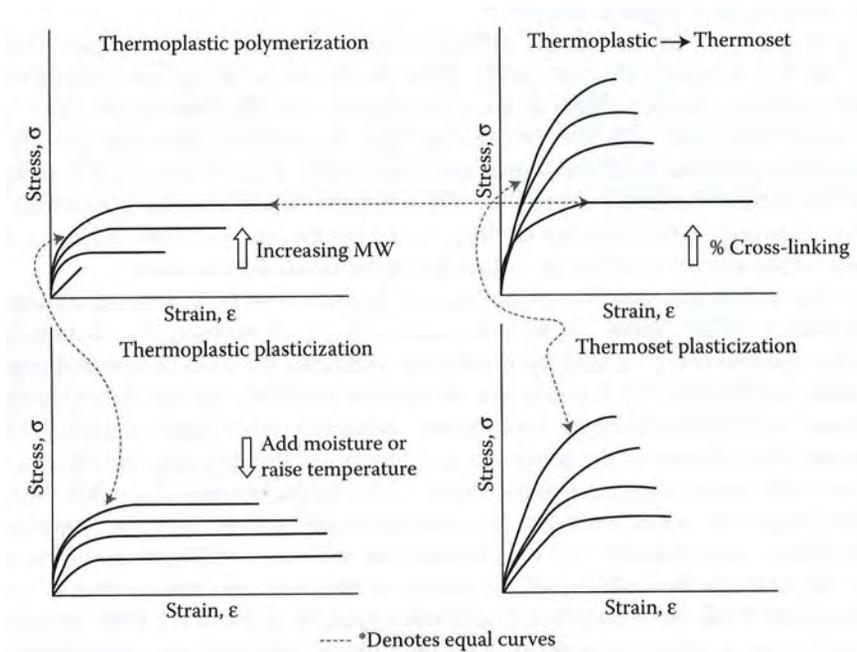
For noncross-linked polymers, the properties are dependent not only upon the chemical structure, but also upon the conditions to which the material has been exposed. As would be expected, the lower the rotational energy around the bond in the backbone, the more flexible and impact resistant the product is. Thus, Si—O—Si bonds provide the most flexibility and are curve D, with C—O—C next, and then C—C—C bonds being the least flexible. Replacement of a linear structure with a cyclic group increases the stiffness of the backbone, and having an aromatic ring provides even higher stiffness. Interchain interactions, such as hydrogen or ionic bonds between chains and the formation of crystalline regions to act as reversible cross-links, usually greatly alter the properties. These interactions reduce chain mobility, and thus increase the stiffness and glass transition temperature ( $T_g$ ) of the polymer. As the stiffness of the backbone increases and the number of cross-links increase, the shape of the curve goes from D to B and eventually A. However, these interactions will be weakened by heat or water exposure, reducing the strength of the polymer. Additionally, the history of the polymer affects its properties. Plastics (curves B and C) generally have a fair degree of crystallinity; this association of the molecules causes a reduction in the mobility of the polymer chains compared to more amorphous polymers. The quantity and structure of the crystalline regions depend very much on how the material solidifies. Fast cooling creates fewer and smaller crystals,

resulting in a less stiff product than does slow cooling (annealing). At the interfaces, the type of adjoining surfaces influences the crystallization of the polymer.

The chemical structure and amount of cross-linking play a major role in making an A-type polymer. The backbones usually contain aromatic groups, sometimes cyclic groups, and generally few aliphatic groups, and the polymers tend to be highly cross-linked. Because many wood products are used for structural applications, it is necessary that under applied load most will not exhibit any significant elongation; thus, a high modulus is required. Unfortunately, the same factors that lead to a high modulus generally lead to brittleness in the polymer.

Cross-linking of polymer chains is required to convert a thermoplastic resin to a thermoset resin. The tying of the chains together eliminates the plastic flow of the polymers, which is necessary to eliminate creep over time. Natural rubber was known about for a long time but had little commercial utility because it softened under heat. After much research, vulcanization processes were developed which allowed rubber to retain its deformability, but eliminated the flow. As would be expected at low cross-linking levels, rubber has large segmental mobility, resulting in a very flexible product. As the cross-linking and molecular weight increases, the segments have less mobility, making the product more rigid. Unfortunately at high cross-linking levels, not only does the product become more rigid, it also becomes more brittle.

Figure 9.13 shows some idealized stress—strain curves that demonstrate the effect of increasing polymerization and cross-linking on the properties of different adhesives, and the effect of conditions on the adhesive. For thermoplastics, increasing the molecular weight mainly increases the elongation at break. This means as the adhesive cures, it is able to withstand greater force. The conversion from a thermoplastic to a thermoset will increase the stiffness at some expense of ductility. For both thermoplastics and thermosets, an increase in temperature or moisture will soften the material. However, for thermoplastics this leads to much lower strength, while for thermoset the effect upon failure properties is much less. One consequence of this softening in composite production,



**FIGURE 9.13** Effect of polymer changes on physical properties. For a thermoplastic, increasing the molecular weight leads to increases in both the stiffness and the ductility, while the thermoset loses ductility as it becomes stiffer with higher cross-linking. When the polymers are plasticized or the temperature is raised, both the thermoplastic and thermoset lose stiffness.

both the heat and moisture factors are working against the adhesive as it is trying to hold the material together to resist either a blowout (void in panels caused by steam bubbles) or excessive spring-back (tendency of compressed or bent materials to return to their original state).

Some classes of adhesives are more amenable to changing their properties by altering their formulations than are others. Polyurethanes and polyamide adhesives can go from very flexible to quite rigid depending on the formulation. PF and polymeric methanediphenyl diisocyanate adhesives do not have similar formulation flexibility. For some resins, incorporating flexible segments, which are softer than the main backbone and improve the impact resistance and reduce the brittleness of the polymer, can improve the polymer's properties.

However, the adhesive formulator does have a number of tools for varying the stress—strain behavior of these products. It should be noted that many of these additives are added for other purposes, such as lower cost, reduction of over-penetration, increase of resin tack, and improvement of wet out, but our concern here is how they affect the stress—strain behavior. The additives are divided into the classes of fillers, extenders, plasticizers, and tackifiers, see Section 9.7.13.

Fillers are common additives because they lower the cost, and thus are used at as high a level as possible to make the adhesive more economical. Fillers increase the stiffness of the adhesive, but usually also reduce its elongation and increase its viscosity. At low levels extenders have a small impact on an adhesive's properties, but at high levels they cause decreased elongation and higher viscosity. On the other hand, plasticizers soften an adhesive, resulting in a decreased modulus and  $T_g$ , and an increased elongation. For most wood adhesives the desire is to have a rigid bond; thus, plasticizers are not generally used. Tackifiers are often confused with plasticizers, but provide very different responses in raising the glass-transition temperature while decreasing the modulus. Increase in tack is often desirable with wood adhesives.

### 9.6.2 EFFECT OF VARIABLES ON THE STRESS—STRAIN BEHAVIOR OF BONDED ASSEMBLIES

The discussion, so far, has been on the stress—strain behavior of adhesives under one condition and in tension. It is important to understand what happens to the strength properties under other conditions. For wood adhesives, the two most important variation in conditions are changes in temperature and moisture. Additionally, it is important to consider more than just the cohesive strength of the bulk adhesive and bulk wood. Although the properties of the bonded assembly are a continuum, Marra's weakest link concept is useful in understanding failure (Marra 1980, 1992). Thus, it is important to understand the properties of the interphase, as well as the bulk adhesive and the wood. Applied forces are not going to result in a uniform force throughout the bonded assembly for several reasons (Dillard 2002).

The differences in mechanical properties of the wood, adhesive, and interphase regions imply that stress concentrations are likely to occur in the zone of greatest change, that is, the interphase zone. Additionally, the interphase has the greatest internal stress caused by volume reduction in the adhesive upon setting. With environmental exposure, the interphase has to accommodate the large dimensional changes between the wood and the adhesive. If the applied stresses can be dispersed over the entire volume of the material, then localized stresses are reduced and higher total bond strengths obtained. The ability of the applied forces to be dissipated in certain domains without catastrophic failure can lead to higher bond strengths (the shock absorber approach). On the other hand, high internal stresses can add to the applied force and cause unexpected failure. The stresses can be concentrated such as at a flaw causing early failure (Liechti 2002).

For a bonded assembly, the overall properties are hard to predict because less is known about the properties of the interphase regions compared to the bulk properties of adhesives and adherends. The bulk mechanical properties of many wood species have been well studied (Kretschmann 2010). The bulk properties of many adhesives have also been investigated, but many of the wood adhesives form brittle, inhomogenous films that do not yield good mechanical property measurements. However, the interphase properties change from those of the bulk adhesive to those of the bulk

wood. This change of properties can be gradual or sharp, and it is expected that a more gradual change should be better, as the stress concentration would be smaller. Large internal forces can be generated when the adhesive and the adherend have different responses to environmental changes, such as moisture and heat. The difference in expansion coefficient between metals and adhesives has been well studied as a cause of adhesive failure due to high internal stress. A major issue with wood is the difference in expansion coefficients with moisture changes between adhesives and wood, mainly in the radial and tangential directions. How these expansion differences are handled in the bonded assembly may be very important to its durability. The internal forces can be as significant as the applied forces for bond strength.

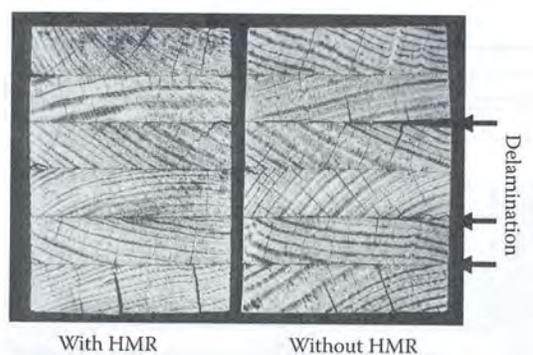
The strength properties of most polymers are sensitive to temperature changes (see Figure 9.13). The increased vibration and therefore mobility of polymers at higher temperatures cause the polymer to be less resistant to applied forces. However, the effect can be greatly influenced by the structure of the polymer. Thermoplastic polymers soften at the glass transition temperature ( $T_g$ ) and eventually flow at the melt transition temperature ( $T_m$ ). Polymers with more cyclic and aromatic character have a lower  $T_g$ . Crystalline segments will limit the effect of temperature until the  $T_m$  of the crystallites is reached. The addition of cross-links, even noncovalent cross-links, such as hydrogen bonds, can improve the resistance to softening at elevated temperatures. Covalent cross-links that exist in many wood adhesives give improved resistance to temperature changes in the bulk adhesive. However, there can be significant differences in the thermal expansion coefficients of the wood and the adhesive causing interphase stresses (Pizzo et al. 2002).

An even greater issue is the effect of moisture changes on bonded assemblies, especially in the interphase region. Some adhesives, like poly(vinyl acetate), lose much of their strength at high moisture levels, as a result of polymer plasticization. UF adhesives are known to depolymerize under high moisture environments, as shown by increased release of formaldehyde (Dunky 2003). On the other hand, wood adhesives, like PF and RF, do not change drastically in their adhesion to wood at higher moisture levels. Wood is known to weaken at higher moisture levels, and to change dimensionally in the radial and tangential directions. When an adhesive does not change dimensionally as the wood swells and shrinks, then stress concentration will occur in the interphase region.

The setting process can generate additional internal forces due to shrinkage of the adhesive. The loss of solvent/water and the polymerization process reduce the volume of the adhesive, while the surface area of the wood stays constant or even increases due to the absorption of water from the adhesive. This difference can cause significant forces that may exceed the strength of the adhesive. Weakness in the bulk of the adhesive UF has been shown to cause cracks in the adhesive (River et al. 1994c); adding flexible groups to an UF formulation reduces this deficiency (Ebewele et al. 1991), especially if those groups are of low to medium molecular weight (Ebewele et al. 1993). In other cases, the forces alone are not sufficient to cause fracture, but may be sufficient to cause fracture when combined with small applied external loads or swelling of the wood as a result of a higher combination of internal and external forces.

### 9.6.3 BOND STRENGTH

Adhesives are used to hold two materials together; thus, the viscoelastic dissipation of internal and external forces is the most important aspect of adhesive performance. The forces that a bond assembly has to withstand depend very much on the type of product and the use of that product. The effects of internal forces are often not considered, but such forces can be very high in wood. The most rigorous test for laminated wood is the ASTM D 2559 cyclic delamination test (ASTM International 2011b). Many adhesives that have strong wood bonds under dry conditions show significant delamination and do not pass this test; however, the extent of the delamination can be reduced by using a hydroxymethylated resorcinol primer (Vick et al. 1998) (Figure 9.14). An interesting aspect of D 2559 is that no external force is applied; swelling and shrinking forces alone



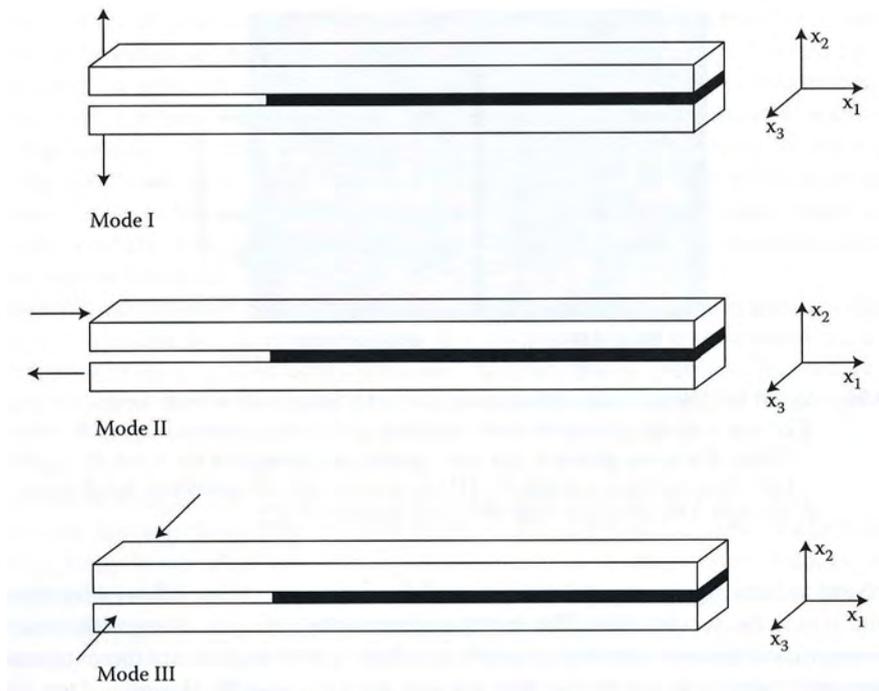
**FIGURE 9.14** ASTM D 2559 causes bond failure, as shown by delamination from the shrinking and swelling of the wood. The test is severe enough to cause cracking in the wood, but an acceptable adhesive gives minimal bondline failure. The same adhesive was used in both specimens, but the wood on the left that was first primed with hydroxymethylated resorcinol (**HMR**) resisted the delamination much better than the untreated wood on the right (Okkonen and Vick 1998) (see Section 9.7.3.2).

cause the bond failures. This test involves cycles of vacuum water soaks, followed by oven drying, with a water boil in the second cycle. The fact that dimensional changes, along with some warping of wood, are sufficient to cause substantial bondline failure shows the power of these internal forces. The problem with internal forces is that they are very hard to quantify. However, a test like the D 2559 may exaggerate these forces since the rapid drying provides sufficient force to cause extensive fracture of the wood, while under normal use conditions the moisture change in the wood is more gradual, allowing stress relaxation of the wood.

The forces on bondlines are divided into three modes: I, II, and III (Figure 9.15) (Liechti 2002). The normal force of mode I is perpendicular to the bond and is the direction in which adhesives are the weakest. On the other hand, the shearing force of mode II is the direction in which the adhesive is the strongest. The torsional forces of mode III are an intermediate test of adhesive strength. All three types of forces are common in bonded wood products. Mode I forces exist in strandboard as it resists springback from its compressed state, internal force of swelling under higher moisture, or applied force in the internal bond test. The mode II force is common in laminated veneer lumber under normal external loading or during swelling under high moisture conditions. Mode III forces exist in plywood as a result of the cross-ply construction.

The performance tests are generally covered by the ASTM and other standards (Frihart and Hunt 2010, River et al. 1991). Normally, the tests tend to be hard to pass to allow safety factors in construction. The general rule with most wood products is to have as much good bonding surface and to have as much of the force in the shear mode as possible. Knowledge of wood bond strength has generally been gained using laminated wood and plywood specimens. Distributing the adhesives as droplets on irregular surfaces of strands or fibers has been more difficult to understand the bonding for strandboard and fiberboard. The issue involves relating the data obtained for laminates and plywood that are normally tested in shear to the internal bond test data for particleboard, strandboard, and fiberboard, that involves mode I forces. Summaries of much of the work on performance testing have already been published (River et al. 1991, River 1994a).

If the bonded assembly is considered as a series of links in a chain (Marra 1992), the chain will hold unless the force exceeds the strength of one of the links. Thus, the process for making improved adhesives involves understanding what the weak link is, and why it failed. The internal forces influence the strength of the links and thus, they can vary with conditions. For example, if an adhesive, such as uncross-linked poly(vinyl acetate), softens with heat or increased moisture content, then it is likely to become the weak link under hot or wet conditions. Many adhesives give strong bonds to wood under dry conditions so that the wood is the weak link. However, under wet conditions the

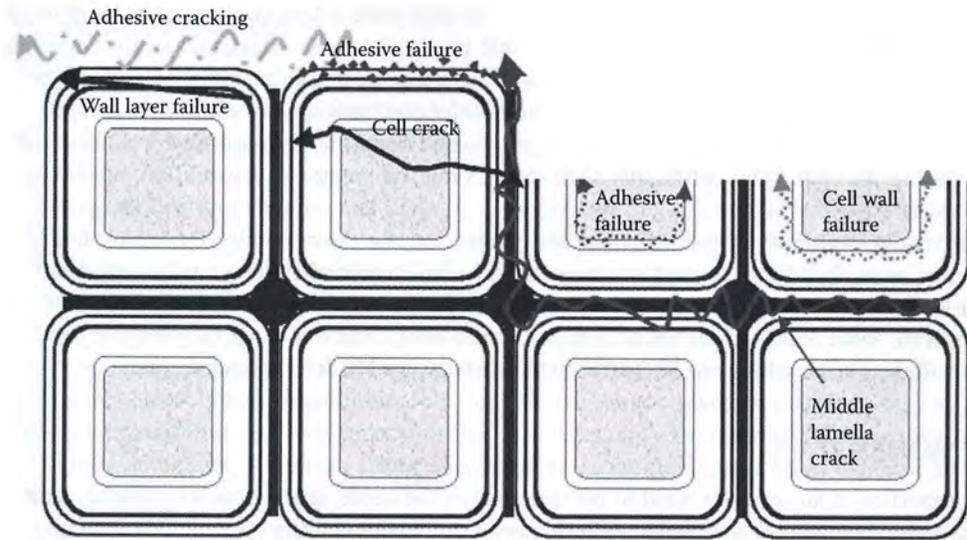


**FIGURE 9.15** The force on the bondlines is often a combination of the three modes of force. Mode I is a tensile force in the normal mode and is usually the one in which the adhesive is the weakest. Mode II is the common shear force and is usually the mode in which the adhesive is the strongest. Mode III is the less common torsional force.

weak link may be in the interphase because of a greater strength loss in this link than in the bulk wood or adhesive. Epoxies exhibit a high percent wood failure when dry, but low wood failure when wet (Frihart and Hunt 2010); thus the conditions cause the weak link to change. Failure analysis has indicated that the weak link for epoxies is the interphase region (Frihart 2003), leading to the need to strengthen the epoxy or reduce the stress concentration in the interphase. Using the chain analogy can also aid in understanding why adhesives do not bond as well to dense wood species. If the strength of the bulk adhesive and the adhesive–wood interphase links are enough to hold 2000 psi and the wood strength is only 1000 psi, then the wood breaks first. If the wood strength is 3000 psi, then the fracture is in the adhesive not in the wood even though the adhesive strength has not changes. This is not to imply that more dense woods may not be harder to bond in some cases, but the data needs to be evaluated by considering the strength of the wood relative to that of the adhesive. An important aspect of this discussion is that the tests of the bonded assemblies are measuring the strength of the bondline and not the adhesive.

To make an improved adhesives and bonded assemblies, it is important to understand where failure occurs. Failures within the bulk wood and bulk adhesive are generally easy to see using the naked eye or microscopy. Failure analysis in the interphase is more complicated, especially for wood. In Figure 9.16, the different types of interfacial failure are illustrated. Understanding failure mechanism is important because it leads to better routes for improving the adhesive to solve the problem. One study showed that PF gave fracture in the  $S_2$  layer while an epoxy gave failure in the  $S_3$  under peel, suggesting that the PF gave deeper penetration of the cell walls (Saiki 1984).

At this time, there is insufficient knowledge to predict how well a new adhesive will hold wood pieces together without testing the bonding with the same type of wood and a similar bonding process that will be used commercially and then carrying out the performance tests. The current



**FIGURE 9.** Failure in the interphase region of wood bonds is complicated. Besides the true interfacial failure that leads to adhesive on one surface and wood on the other, there are a number of other failure zones. The adhesive near the wood may not cure as well, leading to failure in the adhesive near the surface. The adhesive may bond strongly to the wood, but the wood itself may split between layers or within a cell wall layer.

limitations involve in understanding what is necessary about the adhesive—wood interactions to give strong durable bonds. This has been hard to examine because of the complex chemistry and morphology of wood. However, improved analysis will help to shed light on this issue.

#### 9.6.4 DURABILITY TESTING

ASTM defines durability "as related to adhesive joints, the endurance of joint strength relative to the required service conditions" (ASTM International 2011a). Because wood products are used for many years, accelerated tests are used to estimate the long-term performance. A few studies have used field-testing to understand the performance of adhesives under some environmental conditions (River 1994b, Okkonen and River 1996). In addition, for many adhesives, there is in-use experience over many years. Several accelerated tests have been developed that give similar results on durability with the same type of adhesives (River et al. 1991). The key factor that has often been overlooked is that the failure mode must be the same for both long-term use and accelerated test results; thus, it is of paramount importance to extensively validate the accelerated aging tests. If the failure modes are different between normal use failure and an accelerated aging test, then the accelerated test is not likely to always be a reliable predictor of long-term performance.

The most common problem with wood durability is the adhesive's inability to withstand the swelling and shrinking of wood with moisture changes. Most wood products are subjected to temperature and humidity changes, but those in uncontrolled environments are subjected to greater changes. The swelling of wood can subject the bond to mode I, II, or III types of forces depending on the joint design. Swelling has normally been considered on the basis of the macroscopic changes; however, it should be considered also on the basis of the cellular (micrometer) scale. The available data indicate that the swelling of cells usually involves thickening of the cell walls outwards rather than shrinking of the lumen diameter (Skaar 1984). Thus, large forces are exerted on the adhesive at the cell wall edges (Frihart et al. 2004). One study indicates that a phenol—resorcinol—formaldehyde adhesive yields more under wet conditions, but the changes were not as large as the dimensional changes of wood during the wetting process (Muszynski et al. 2002). A key question is

whether durable adhesives stabilize the cell walls so that there is less swelling and shrinking with moisture changes, or whether they are better able to distribute the interfacial strain between the wood and adhesive? Understanding these points is a key to designing more durable adhesives. Another factor that has to be considered is that accelerated tests involve rapid wetting and drying of the wood. These changes can be so fast that the wood structure does not have a chance to stress relax during the tests; thus, artificially high stresses may be created that would not be observed in normal use.

Wood adhesives have to pass other durability tests, but, for the most part, these have not been as difficult. Certainly, adhesives used in structural and semi-structural applications have to resist creep under load. Given the rigid nature of the polymer backbone and the cross-linking, this has not been a significant issue. Wood adhesives also have to resist decay, and therefore, they may be formulated using additives so that fungi do not grow on the surface (ASTM International 2011c).

## 9.7 ADHESIVES

The properties of an adhesive need to not only match the needs of the bonded assembly in its end use, but also needs to be compatible with the wood properties and the bonding process conditions. For wood bonding, adhesives are rigid enough to transfer load between adherends and can be divided into structural, semi-structural, and nonstructural types—see Section 9.3 (River et al. 1991). Although rigidity is often good, adhesives can be too rigid that leads to too much brittleness for some applications.

Wood adhesives can be grouped not only by their structural, semi-structural, and nonstructural use, but also by their permanence and durability. Permanent is more stable than wood under irreversible environmental conditions, while nonpermanent is less stable than wood under irreversible environmental conditions (River et al. 1991). Durable is stronger, more rigid than wood, and more stable under reversible environmental effects, while nondurable is weaker, less rigid than wood, and less stable under reversible environmental effects.

Adhesives need to be compatible with the bonding conditions used commercially. For example, heat-cured adhesives are compatible with the manufacture of panel products for the following reasons:

- They cure slowly at room temperature, allowing time for the wood components to be coated with the adhesive and brought together for assembly.
- The heat and moisture let the wood soften, allowing the adjoining wood surfaces to be brought into close contact.
- Upon heating, the adhesive cures quickly, reducing springback when the pressure is released.

However, a room temperature cure is better for thick laminates because heating the deep layer is more difficult. For manufacturing bonded products, low-cost and rapid setting of the adhesive are important factors, but for construction adhesives, a longer set time, room temperature curing, and easy dispensing from cartridges are important. In many nonwood applications, water-borne adhesives are not used because of poor surface wetting and the inability of the water to move away from the bondline. Neither of these issues is as critical for wood adhesives. However, the penetration of adhesives into wood without over-penetration is important for wood bonding, but not a factor in bonding of most other materials.

To understand the application, setting, and performance of adhesives, some general polymer chemistry and polymer properties are covered below. The specific adhesive discussions refer back to this general discussion. The properties of polymers are controlled by the structure of the backbone and the number of cross-links, if any. In a few cases, such as polyurethanes, domain separation is also an important factor.

### 9.7.1 POLYMER FORMATION

Knowledge about the structure of polymers leads to a better understanding of their properties; the properties of polymers are important both in the bonding process and in the ultimate end use performance of the bonded material. Aspects of polymers that need to be considered include use, class, type, and size.

Different applications require materials of different mechanical properties, with these being greatly influenced by the chemical structure of the polymer. It must be remembered that as discussed in Section 9.6.1, the properties of polymers are greatly influenced by the conditions under which they are measured. For example, most adhesives will tend to soften and therefore are less able to carry a load as the temperature increases. When many adhesives absorb small molecules, including water or other solvents, they will soften and, in some cases, will develop cracks that will expand and ultimately cause failure. In addition, the properties of many polymers change as they age. If a polymer is susceptible to oxidation, over time this can either make the material stiffer or depolymerize the adhesive, making it weaker. Chemicals, such as ozone, acids, and bases can also alter the performance of many adhesives.

Polymer classes are determined by how the polymer is constructed. Some polymers are homopolymers, such as polyethylene used in wood-plastic composites. This means that the polymer (AAA ...) is made up of the same individual monomer units (A). Another common type are those polymers made up of two or more components, such as A and B. One way of putting the components together is a random process where two or more monomer units form the copolymer (AAABAABBAB ...), but there is no specific order to the adjacency of the components. An example of this class is the styrene—butadiene rubber that is used in many sealants and mastics. Another way of putting the components together is an alternating copolymer (ABABABAB). Two components can also be combined by making block co-polymers where there are long stretches of monomer A that are then attached to sections of monomer B. Often the A and B components are not compatible when polymerized, so materials tend to separate into individual domains, with examples being polyurethanes and styrenated block copolymers. While the random and alternating copolymers exhibit the average properties of the homopolymers, the block copolymers often exhibit properties not obtainable with either of the homopolymers. A fourth way of reacting two monomers is a grafting process, in which monomer B is attached along the sides of a polymer A backbone. An example is the reaction of grafting of acrylate polymers onto a polyolefin backbone.

Polymer types can be used to group adhesives with different topology independent of their class. For example, the same polymer type can be either a homopolymer or copolymer. One type is a linear polymer where all the monomer units link with one another like a string of beads. Polyethylene and polypropylene are for the most part linear polymers. A second type has branches of the linear chain; the properties of the polymer change dramatically as the type and degree of branching changes. In going from the linear high-density polyethylene to the slightly branched low-density polyethylene and onto the much more branched very low-density polyethylene, there are changes in melting point, flexibility, and strength. Another type of polymer backbone involves whether the structures are linear aliphatics, such as the case with polyethylene, or whether they are cyclic structures, such as cyclohexane or aromatic rings. The cyclical nature of the monomers makes the polymers much stiffer because they have less ability to rotate around the backbone bonds. Aromatic rings make the adhesives even more rigid due to less rotation in the backbone. Many wood adhesives tend to be made from aromatic compounds, including phenol, resorcinol, and melamine, to produce much more rigid polymers with high glass transition temperatures.

Another type of morphology involves whether the polymer chains are cross-linked (thermoset) or not cross-linked (thermoplastic). Some wood adhesives are thermoplastic, including uncross-linked poly(vinyl acetate) and hot melts. The problem with thermoplastics is that at elevated temperatures or moisture levels, they will flow, leading to creep (flow under load over time) problems. For structural and semi-structural applications creep is very undesirable. Thus the great majority of

wood adhesives are thermoset. The term thermoset is used to indicate cross-linked polymers even though the setting process may not be caused by heat. Hot press adhesives are certainly thermoset because they need heat activation to develop the cross-link. On the other hand, moisture-cured adhesives, such as some polyurethanes and silicones, are cross-linked not by the heat process but by the presence of moisture, but are also considered thermosets.

Another factor in the properties of polymers is their size or molecular weight. This is an area that illustrates the two competing natures that an adhesive needs to exhibit. For bond formation, the adhesive needs to flow and penetrate into lumens well and sometimes cell walls, favoring low molecular weights. However, once the bond is formed, it is desirable that the product has great resistance to flow, which favors higher molecular weight. A higher molecular weight adhesive will tend to set faster because fewer reactions are needed to form the cured product. On the other hand, the higher molecular weight polymer can lead to solubility and stability problems for the uncured adhesive. Thus, in designing polymers to be used as adhesives, a balance is needed between low molecular weight for a good wetting of the wood and higher molecular weight for more rapid set and to resist flow once the bond is formed.

Aside from these obvious differences in formulations, changes in the curing conditions can have an effect on the properties of the resin. It is well known for epoxies that additional heating causes additional cross-linking reactions. An epoxy cured at room temperature becomes a rigid gel so that the remaining unreacted groups are not physically able to find each other. As the epoxy is heated, the mobility of the polymers increases, allowing additional groups to come into physical contact to add more cross-links in the matrix, making the product more rigid and usually more brittle. This effect has also been observed with phenolic resins, in that cure times influenced both the degree of cure and the mechanical properties (Wolfrum and Ehrenstein 1999). This is important in considering the production of composites. For particleboard, strandboard, and fiberboard, the adhesive near the surface is at a higher temperature for longer times and at a lower moisture content compared to the adhesive toward the center of the board. The gradient in the heat and moisture causes less polymerization and cross-linking to occur in the center of the composite. The primary curing problem can be reduced by using a faster reacting resin or a higher molecular weight resin in the core than in the face. However, the gradient in the reaction rates can influence the properties of the board and makes studies on the curing process exceptionally difficult.

### 9.7.2 SELF-ADHESION

Under certain conditions wood can self-adhere, but generally adhesives are needed to give sufficient product strength. The forces working against good self-adhesion are the roughness of the surface and the lack of mobility of the wood components that inhibit wetting and interdiffusion. For good adhesion, the two surfaces have to be brought into contact at the molecular level. Obviously, this is difficult with the high surface roughness of a cellular material like wood. Contact becomes more likely if the surface cells are pressed together under high pressure and if the wood is more compliant, such as when one goes from wood laminates to chips to particles and finally to fibers. One product made with little or no added adhesive is high-density fiberboard. The adhesion of the hardboard is dependent upon hydrogen bonding and auto-cross-linking (Back 1987). Of the main wood components, the greatest likelihood for self-adhesion is with lignin and hemicellulose components. Both lignin and hemicellulose soften under high moisture and temperature conditions. Hemicellulose more readily forms hydrogen bonds to bond the adjoining fibers, while lignin more readily forms chemical bonds. The process works adequately for hardboard, but other wood products are not bonded under sufficient heat and pressure to obtain high intersurface bonding.

Another process of self-adhesion is wood welding. Vibrational welding was first demonstrated to cause bond formation (Gfeller et al. 2003). This process uses the heat and cellular distortion generated by friction to bond the wood together. The products show good adhesion under dry conditions, but so far have not been able to provide good wet strength. An even more interesting case is rotational

welding. This involves driving a wood dowel into a hole in another piece of wood. With the proper conditions, a strong bond can be formed (Segovia and Pizzi 2009).

Chemical modification of wood surfaces has been shown to give improved bond strengths. A base activation of wood was found to give significant improvement in the dry strength of wood bonds, but not the wet strength (Young et al. 1985). Iron salts with hydrogen peroxides will give more durable bonds with wood particles than with unactivated wood (Stofko 1974, Westermarck and Karlsson 2003), and surface activation with peracetic acid has also been used in making particle-board (Johns and Nguyen 1977).

The use of enzyme modification of wood has been shown to increase the strength of bonded wood (Felby et al. 2002, Widsten et al. 2003). Although most studies have been at the laboratory stage, at least one investigated has been done at the pilot plant stage (Kharazipour et al. 1997).

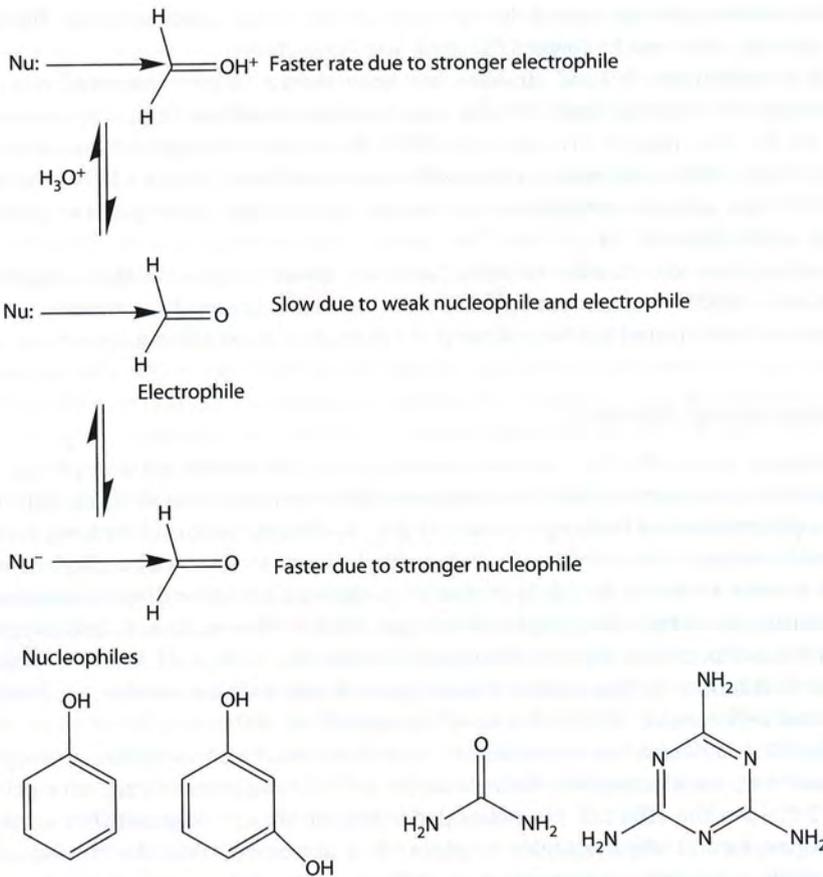
### 9.7.3 FORMALDEHYDE ADHESIVES

The most common wood adhesives are based on reactions of formaldehyde with phenol, resorcinol, urea, melamine, or mixtures thereof. The reactions can sometimes involve three steps of reaction with a nucleophilic center of the co-monomer with formaldehyde to form a hydroxymethyl derivative, then condensation of two of these hydroxymethyl groups to form a bismethylene ether group with loss of a water molecule or the hydroxymethyl derivative can be directly attacked by a co-monomer nucleophile to form the methylene-bridged product. The methylene bridge predominates and is preferred due its greater stability. The specific chemistry is very pH sensitive. The discussion of the chemical reactions in this section is quite general and does not involve the details because these have been well covered in other books (Pizzi and Mittal 2003).

The rates of the individual reactions depend very much on the co-monomer nucleophile that is copolymerized with the electrophilic formaldehyde. All of these reactions are very pH dependent (see Figure 9.17), but the effect of pH varies depending on the co-monomer. For example, under acidic conditions, formaldehyde addition to phenol is a slower step than the condensation step to form the methylene bridged product, while the relative rates of these two reactions are reversed under basic conditions. Thus, control of the pH is very important in controlling the polymerization reactions; thus, the pH and buffering capacity of the wood may alter the curing in the interphase region. In addition to the pH, these reactions are also controlled by adjusting the temperature and adding catalysts or retarders.

The formaldehyde adhesives are usually water-borne resins so that the curing process is not only polymerization, but also the loss of the water solvent. Because the polymerization process generates water, too much water remaining in the bondline retards the reaction. On the other hand, too little water prior to polymerization not only influences wetting but also can reduce the mobility of the resins and limit collisions needed for polymerization, in addition to limiting heat transfer. Control of both the open and closed assembly times are important for controlling both the penetration and water content of the bondline.

Most wood bonding applications need an adhesive that does not creep over time, leading to the use of cross-linked or thermoset adhesives. High glass transition temperature polymers could also exhibit low creep, but they have been too expensive and hard to use for wood bonding. The formaldehyde copolymers produce thermoset polymers by cross-linking in the later stages of curing. These reactions occur by formaldehyde bridging the reactive sites on different chains. The co-monomers used with the formaldehyde all have three or more reactive sites, leading to plentiful opportunities to cross-link. Having many available reactive sites is important due to the limited mobility of the polymer backbones, which allows close proximity between only a few locations. It is highly unlikely that every site that is converted to a hydroxymethyl group can find another group in close proximity with which to react. Longer cure times at higher temperatures will tend to push the product to a higher degree of cure. Thus, the ultimate performance of the adhesives is going to depend on the processing conditions.



**FIGURE 9.17** Reaction of formaldehyde with phenol, resorcinol, urea, and melamine. All of these compounds will copolymerize with formaldehyde, generally in an alternating fashion. The first step is the reaction of a nucleophile with an electrophilic formaldehyde that can be promoted under acidic or basic conditions.

Generally, the molar ratio of formaldehyde needs to be greater than that of the co-monomer to accommodate the need for extra formaldehyde to cross-link the chains, to compensate for formation of bismethylene ethers, and to allow for unpolymerized hydroxymethyl groups. Extra formaldehyde was therefore used to produce fast-setting adhesives with a high degree of curing. However, this caused the problem of significant formaldehyde emissions from the bonded products, mainly those made using urea as the co-monomer. The formulations needed to be adjusted to reduce the formaldehyde levels, but still give good final cures and fast set rates. This has been accomplished through a good understanding of the adhesive chemistry, but then there has been some sacrifice in operability of the bonding process and performance of the bonded assembly.

Formaldehyde copolymer adhesives are used for the production of most laminates, finger joints, and composite products, although the isocyanates are taking over some of the market share as the result of a lower sensitivity to wood moisture content and process temperatures. These formaldehyde-containing adhesives provide good wood adhesion and rigid bonds that do not creep because the formaldehyde not only forms the polymeric chain, but also provides the cross-linking group. However, the properties vary depending on the co-monomer used with the formaldehyde. OF adhesives are the least expensive of all wood adhesives, but they have poor durability under wet conditions. PF adhesives offer a good balance of cost and water resistance. Higher cost melamine-containing adhesives are used because they also provide good water resistance, and are light in color compared

to the phenol resins. RF resins are useful because they cure at room temperature, but are expensive. The co-monomer or combination of co-monomer used with formaldehyde is selected depending on the costs, production conditions, and expected performance of the product.

### 9.7.3.1 PF Adhesives

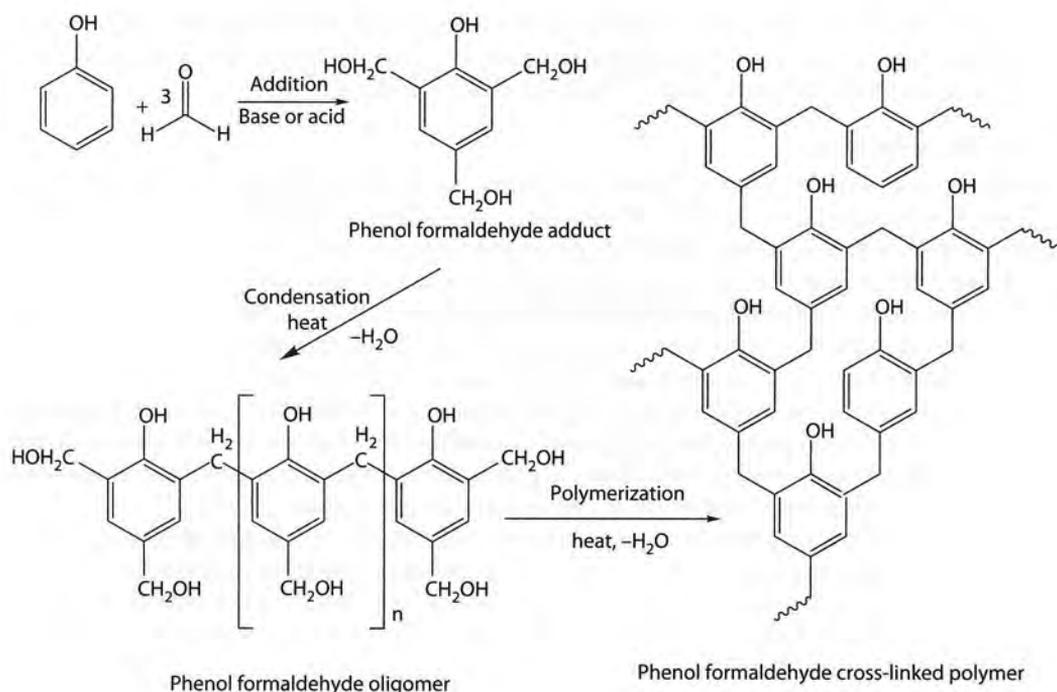
PF polymers are the oldest class of synthetic polymers, having been developed at the beginning of the twentieth century (Detlefsen 2002). These resins are widely used in both laminations and composites because of their outstanding durability, which derives from their good adhesion to wood, the high strength of the polymer, and the excellent stability of the adhesive. In most durability testing, PF adhesives exhibit high wood failure and resist delamination. There are a vast number of possible formulations, and selection of the wrong one can lead to poor bond strength. Among the factors that can lead to poor adhesion are incomplete polymerization due to too little time at temperature; a resin with too high a molecular weight, leading to poor wetting and penetration; not enough assembly time to allow good wood penetration; or too much assembly time or pressure leading to over penetration of the adhesive and a starved bondline. In general, PF adhesives can meet the bonding needs for most wood applications if cost and heat curing times are not an issue.

For all these adhesives, phenol is reacted with formaldehyde or a formaldehyde precursor under the proper conditions to produce an oligomer that can undergo further polymerization during the setting process. There are two basic types of oligomers, novolaks that have a formaldehyde/phenol (F/P) ratio of less than 1 and are generally made under acidic conditions, and resole resins made under basic conditions with F/P ratios of greater than 1. Although at first glance the acid and base processes may seem to be similar, the chemical reactions and the polymer structures are quite different. For most wood adhesive applications, the resole resins are used because they provide a soluble adhesive that has good wood wetting properties and the cure is delayed until activated by heat allowing product assembly time.

The formaldehyde addition reaction depends on an electron-donating hydroxyl group for activation of the aromatic ring, specifically at the positions *ortho* and *para* to the hydroxyl group; these positions are nucleophilic enough to attack the electrophilic formaldehyde. Although all three sites are activated, the reaction conditions control which sites are more reactive toward the initial and subsequent modifications. The availability of three positions for reaction leads to the ability to form a polymer chain that can be cross-linked to provide good strength and durability. The chemistry described here is general because more details have been published elsewhere (Detlefsen 2002, Pizzi 2003a, Robins 1986).

Novolak resins are made using acidic conditions with typical formaldehyde to phenol ratios of 0.5-0.8 at a pH of 1-4 (Detlefsen 2002). The chemistry involves, first, the addition of the acid-activated formaldehyde to the phenol via a nucleophilic attack by the activated *ortho* or *para* positions of the phenol. This molecule can then lose a water molecule under acidic conditions due to stabilization with the phenol group. The methylene group is then reactive with another phenol group to form the methylene-bridged dimer. Continuation of this process leads to a low molecular-weight linear novolac oligomer. Under acid conditions, the linking step is faster than the addition step, which leads to polymers if the formaldehyde content is not limited. Commercial products are normally oligomers that are converted to polymers by adding more paraformaldehyde, which is usually called the hardener, just prior to application. Novolak oligomers are generally not used for wood bonding due to their low water solubility and very low pH.

On the other hand, resole resins are generally made using alkali hydroxides with a formaldehyde to phenol ratio of 1.0-3.0 at a pH of 7-13 (Detlefsen 2002, Pizzi 2003a). The chemistry involves the reaction of the base-activated phenol attacking formaldehyde, as shown in Figure 9.18. In contrast to the reaction under acidic conditions, the addition of formaldehyde to phenol under basic conditions is the rapid step, while the conversion of the hydroxymethyl derivatives to oligomers is the slow step. Thus, higher formaldehyde levels can be used without forming the final polymer until sufficient heating is applied. Some of the hydroxymethylphenols may dimerize to form a bismethylene



**FIGURE 9.18** PF chemistry involves first formation of the hydroxymethyl group, followed by partial polymerization to the oligomer that makes up the adhesive. After applying adhesive to the substrate the polymerization is completed to form a cross-linked polymer network.

ether bridge and are then always converted to the methylene-bridged species. This process is used to generate oligomers with sufficient reactive groups to cure under the proper heating conditions without additional formaldehyde. The molecules in Figure 9.18 show the fully functionalized species, but the molar ratio of formaldehyde to phenol is usually less than 3, leading to enough groups to form the polymer backbone and some cross-linking in the cured product. Drawings often depict only one position of reaction, but it should be remembered that all the *ortho* and *para* positions are reactive, with position selectivity due to the reaction conditions. After being applied to the wood, these resins are then converted to the final adhesive by using heat and water removal conditions. The structure in Figure 9.18 shows the limited mobility of the polymer chain due to only methylene bridges between the aromatic rings and the cross-linking process. There are some hydroxymethyl groups that cannot find a reactive site.

The PF adhesives could serve in almost all wood bonding applications, as long as the adhesive in the assembly can be heated; however, in many cases, high environmental resistance is not needed so a lower cost and more readily cured OF adhesive is used. Like most adhesives, the commercial products contain more than just the resin. The most common additive is urea to provide improved flow properties, to scavenge free formaldehyde, and to reduce cost. It is generally assumed that most of the urea does not become part of the polymer backbone due to its low polymerizability under basic conditions. For plywood, fillers and extenders are added to provide holdout on the surface and control rheology, including tack, for the specific application method.

### 9.7.3.2 Resorcinol and Phenol-RF Adhesives

RF resins have the advantage over PF resins of being curable at room temperature due the resorcinol to being 10 faster in reaction than phenol. Resorcinol is 1,3-dihydroxybenzene, and is very reactive because of the combined effect of the two hydroxyl groups on the aromatic ring in activating the

*ortho* and *para* positions toward reaction with formaldehyde for the addition reaction, and with hydroxymethylresorcinol in the condensation step (Pizzi 2003b). Because phenol and resorcinol have three reactive sites, they are able to cross-link to form a thermosetting adhesive. The chemistry of modification and polymerization is illustrated in Figure 9.19. The resorcinol copolymerizes well with formaldehyde at room temperature. Thus, it is important to have a formaldehyde—resorcinol ratio low enough to make a noncross-linked novolac polymer, but it also requires the addition of a formaldehyde hardener just prior to applying the adhesive to wood for completing the cure.

Like the PF resins, these adhesives form very durable bonds. They are resistant to both bond failure and to degradation. The main drawback to resorcinol adhesives has been the cost of the resorcinol. To lower the cost, but to maintain the room temperature curing properties, phenol-resorcinol—formaldehyde (PRF) adhesives were developed. PRF adhesives are widely used in wood lamination and finger jointing. PRFs are covered in this section because they behave more like RFs than PFs in their cure.

Three different PRF polymers can be prepared, but all depend on the ability of the resorcinol to react at room temperature.

- A PF resole is reacted with resorcinol at the hydroxymethyl sites to form a resorcinol-terminated adhesive that is then mixed with a formaldehyde hardener just prior to bonding (most common).
- A PF resole is mixed with a resorcinol—formaldehyde hardener just prior to bonding.
- A PF resole is reacted with resorcinol at the hydroxymethyl sites to form a resorcinol-terminated adhesive that is mixed with a PF resole just prior to bonding.

The three methods give different polymer structures, and each has its own advantages and disadvantages depending on the specific application. The PRFs generally have a lengthy assembly time because of the room temperature cure. If the cure were rapid at room temperature, then there would not be enough time to mix the components, spread them on the wood, and press the wood pieces together prior to adhesive curing. The slow cure results in a longer clamping time before the adhesive has sufficient strength to allow handling of the wood pieces. Thus, a room temperature cure is desirable, to avoid heating large laminated pieces, but suffers from the long clamping times.

An interesting use of a RF resin is for making a low solids primer, called hydroxymethylated resorcinol (HMR). This primer has been found to be very useful in improving the delamination resistance of PRF adhesive to CCA treated wood (Vick 1995), epoxy bonds to Douglas-fir (Vick et al. 1998), polyurethane and epoxy to yellow birch and Douglas-fir (Vick and Okkonen 1998, Vick 1997), yellow cedar with PRF adhesive (Okkonen and Vick 1998), and epoxy to Sitka spruce (Vick et al. 1996). The original primer had to be manufactured shortly before use and had a short use time, but an improved process has solved these issues (Christiansen and Okkonen 2003).

Another type of PRF is the honeymoon adhesive, developed for finger jointing and laminating; this process circumvents the long clamping times associated with room temperature cures. In this application, the adhesive is placed on one wood surface and the activator or copolymer material is placed on the other, with the mating of these two pieces leading to the faster cures (Pizzi 2003b). One system for fast curing used an amine cure-promoter on one wood piece and a formaldehyde-based adhesive on the other, and showed that this produced rapid curing with good bonds even to green wood (Parker et al. 1997). The use of hydrolyzed soybean flour and a PRF adhesive as the two components has been shown to produce very good finger joints even with green wood (Kreibich et al. 1998).

### 9.7.3.3 UF and Mixed Urea Formaldehyde Adhesives

UF adhesives have several strong positive aspects: very low cost, nonflammable, very rapid cure rate, and a light color. On the negative side, the bonds are not water resistant and formaldehyde

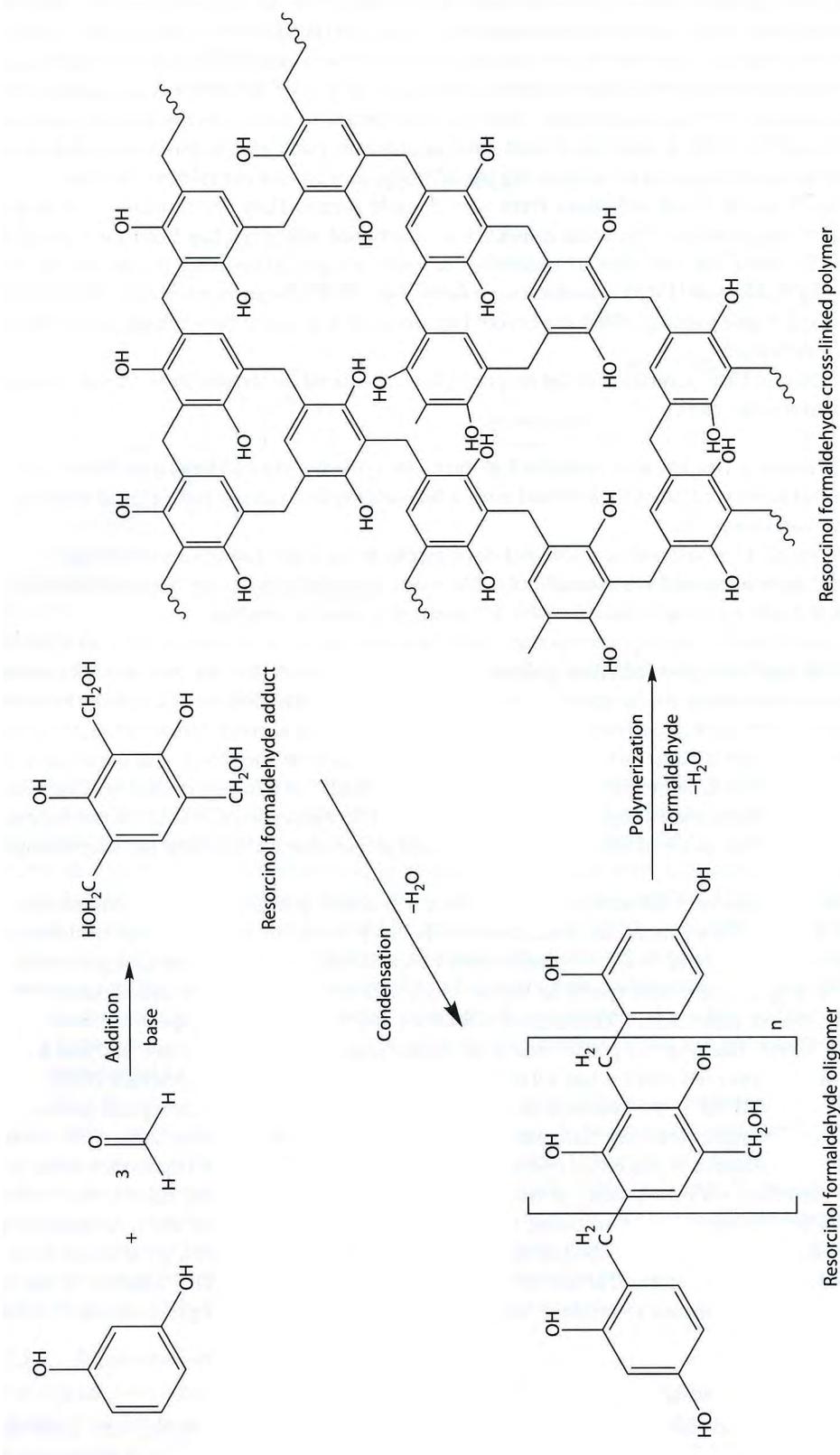


FIGURE 9.19 RF chemistry is similar to the PF in Figure 9.18, but the reaction rates are fast enough that heat does not need to be applied.

continues to evolve from the adhesive. UF adhesives are the largest class of amino resins, and are the predominate adhesives for fiberboard, particleboard some interior plywood.

The chemistry of the UF adhesives involves several steps, with the first being the addition of the formaldehyde to the urea under neutral or basic conditions (Pizzi 2003e, Updegauff 1990). Although there are only two nitrogen atoms on which the formaldehyde can add, the literature shows that the N,N,N'-tris(hydroxymethyl)urea, along with the bis- and mono-hydroxymethyl ureas are the primary products. These hydroxymethyl compounds then react under slightly acidic conditions and heat to generate oligomers, in which the urea molecules are linked by bismethylene ether or methylene bridges, see Figure 9.20. After reaching the desired molecular weight for the specific application, the polymerization is slowed by raising the pH and cooling. An additional charge of urea is added to reduce formaldehyde emissions from the resin. The UF resins are mixed with a latent acid catalyst that produces an acid catalyst during the heat cure. Latent catalysts can be salts, such as

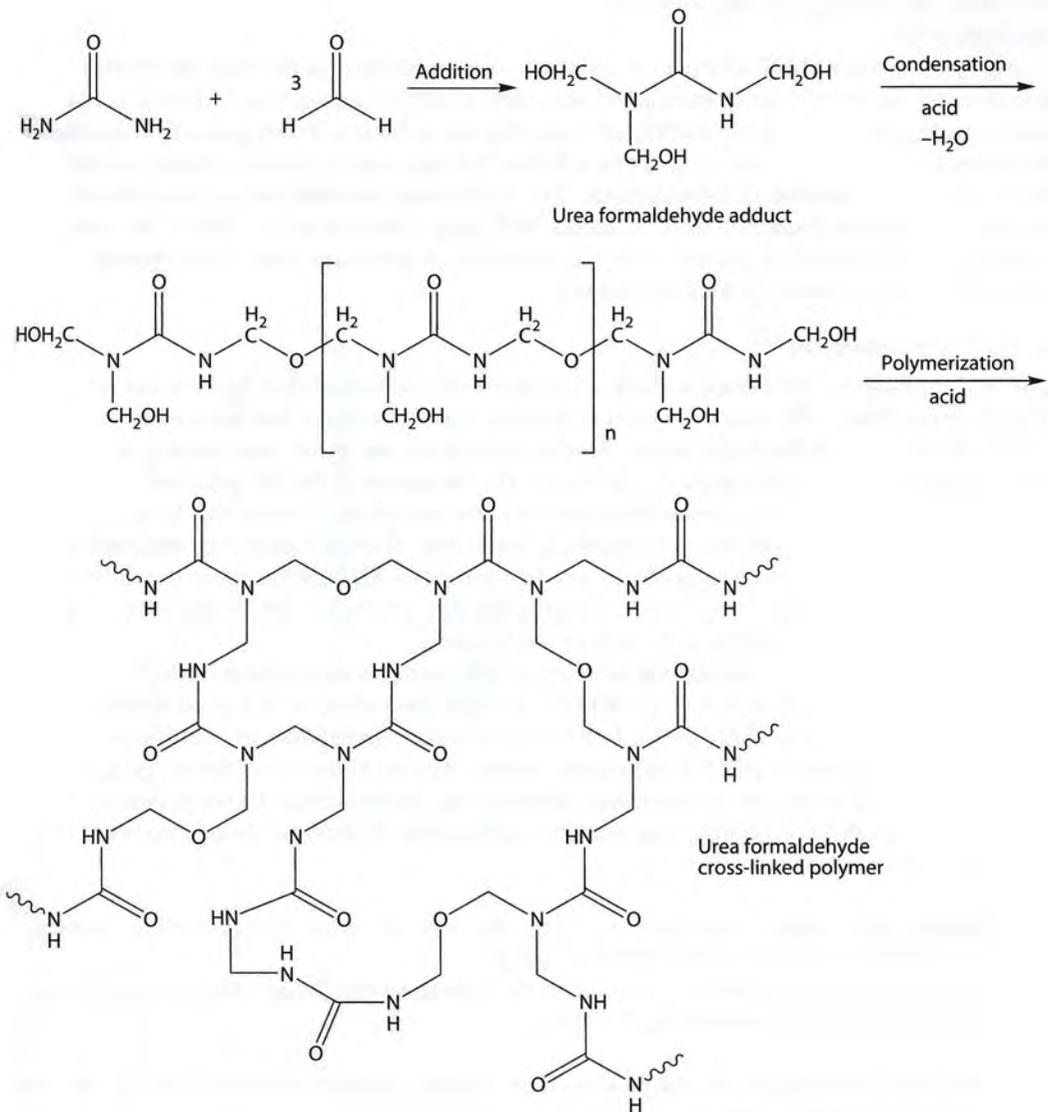


FIGURE 9.20 UF polymerization goes through an addition reaction and then condensation to give an oligomer that is applied to the wood. After application, the polymerization is completed to give a cross-linked network.

ammonium sulfate or chloride, which generate ammonia and sulfuric or hydrochloric acid, respectively. These acids and heat cause the UF to cure rapidly, giving the UF adhesive its desirable rapid setting properties. The rapid strength development leads to shorter press times than with other adhesives. The chemistry and formulation are much more complicated than there is space here to describe and understanding the chemistry has led to efficient products that are used commercially (Pizzi 2003e, Updegaff 1990).

Concern about formaldehyde emissions during production and indoor applications has led to lower formaldehyde/urea ratios, addition of melamine to the formulations, and use of scavengers in current products. However, this has not come about without some sacrifice in ultimate strength and robustness of commercial production, but was needed to meet current environmental standards. The specific UF formulation and bonding conditions are adjusted to meet acceptable formaldehyde emissions for the end product. The classes of products are more rigidly defined in Europe and the United States (Dunky 2003). The formaldehyde emissions are high initially, and decrease with time, but do not go to zero even over a long time. For further discussions and current status, see Section 9.8.

A major drawback of UF adhesives is their poor water resistance; in that they have high bondline failure under accelerated aging tests, restricting them to indoor applications. Another area of concern is the long-term hydrolytic stability of these adhesive polymers, which generally show the least durability of any formaldehyde—copolymer adhesive. UF resins are believed to depolymerize resulting in continuing emission of formaldehyde. The use of some modified ureas can reduce the poor resistance to the mechanical effects of accelerated aging (Ebewele et al. 1993). The poor water resistance of UF adhesives has led to the development of melamine—urea—formaldehyde (MUF) adhesives that are covered in the next section.

#### 9.7.3.4 MF Adhesives

Unlike UF adhesives, MF adhesives have acceptable water resistance, but they are much lighter in color than the others. MF resins are most commonly used for exterior and semi-exterior plywood and particleboard, and for finger joints. Another significant use is for impregnating paper sheets used as the backing in making plastic laminates. The limitation of the MF adhesives is their high cost due to the cost of the melamine. This has led to the use of MUF resins that have much of the water resistance of MF resins, but at substantially lower cost. The MUF adhesives, depending on the melamine-to-urea ratio, can be considered as a less expensive MF that has lower durability or as a more expensive UF that has better water resistance (Dunky 2003). The MUF adhesives can replace other adhesives that are used for some exterior applications.

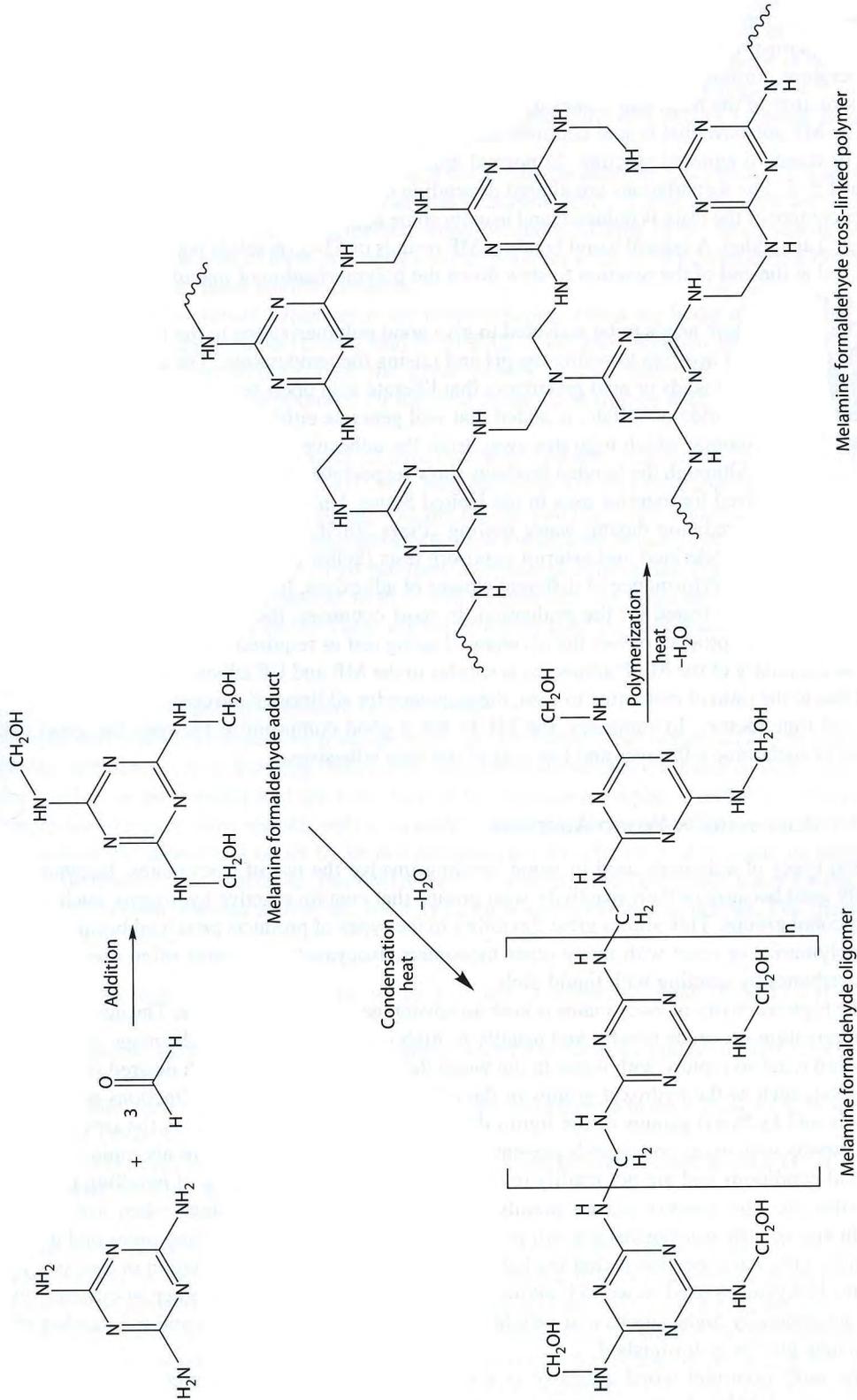
Like most formaldehyde curing, the first step in MF curing is the addition of the formaldehyde to the melamine, see Figure 9.21 (Pizzi 2003f). Because the melamine is a good nucleophile, the addition reaction with the electrophilic formaldehyde occurs under most pH conditions, although the rate is slower at neutral pH. The melamine can react with up to six formaldehyde groups to form up to two methylol groups on each exocyclic amine group, but the formaldehyde is usually limited. These hydroxymethyl compounds then react by condensation to form the resin. Two types of condensation reactions can occur:

- Bismethylene ether formation by the reaction of two hydroxymethyl groups,  

$$\text{RCH}_2\text{OH} + \text{R}'\text{CH}_2\text{OH} \Rightarrow \text{RCH}_2\text{OCH}_2\text{R}' + \text{H}_2\text{O}$$
- Methylene bridge formation by reaction of the hydroxymethyl group with an amine group,  

$$\text{RNH}_2 + \text{R}'\text{CH}_2\text{OH} \Rightarrow \text{RHNCH}_2\text{R}' + \text{H}_2\text{O}$$

The chemistry for the addition and condensation reactions is illustrated in Figure 9.21. The addition reaction is reversible, though generally the equilibrium is far to the right side. On the other hand, the condensation reaction to form oligomers and polymers is not very reversible, which is important for the water resistance of the product and makes it different from UF. It is evident from



**FIGURE 9.21 MF** chemistry goes through similar steps as the OF in Figure 9.20.

the dimers illustrated that many isomers can be produced. With the large number sites and reaction possibilities, the chemistry rapidly becomes very complex (Pizzi 2003f). Sato and Naito have studied the chemistry of some of these reactions (Sato and Naito 1973). The reaction conditions of time, temperature, formaldehyde/melamine (F/M) ratio, pH, and catalyst will influence the composition and structure of the resin that makes up the adhesive.

The MF adhesive that is sold commercially is a mixture of oligomers made by heat polymerization in standard agitated reactors. In normal applications, the formaldehyde to melamine ratio is about 1.5-2. The formulations are altered depending on the specific application. In some cases, the water content of the resin is reduced, and usually some additives (theology modifiers, fillers, extenders, etc.) are added. A typical wood bonding MF resin is of 53-55% solids with a pH of 9.9-10.3 (pH is raised at the end of the reaction to slow down the polymerization of manufacturing for stabilization of the resin).

The MF adhesive needs to be activated to give good polymerization to the final product. Similar to UF, this usually involves lowering the pH and raising the temperature. The catalysts added to the MF resin are either acids or acid precursors that liberate acid upon heating. Often a hardener, such as ammonium chloride or sulfate, is added that will generate either hydrogen chloride or hydrogen sulfate plus ammonia, which migrates away from the adhesive. In most applications, the products are heat-cured. Although the bonded products show respectable water resistance, phenol-containing resins are preferred for exterior uses in the United States. Unlike the UF adhesives, the MF resins do not show degradation during water boiling (Pizzi 2003f). They do show some loss of bond strength during accelerated and exterior exposure tests (Selbo 1965). Care often needs to be taken in comparing the performance of different classes of adhesives, for usually only one of many commercial products is tested for the evaluation. In most countries, the adhesive manufacturer has to show data that its product passes the accelerated aging test as required by specific standards.

The chemistry of the MUF adhesives is similar to the MF and UF adhesives, but more variations exist due to the ratio of melamine to urea, the sequence for addition of the components, temperature, pH, and time factors. In summary, the MUFs are a good compromise between the good performance of melamine adhesives and low cost of the urea adhesives.

#### 9.7.4 ISOCYANATES IN WOOD ADHESIVES

Several types of adhesives used in wood bonding involve the use of isocyanates. Isocyanates are widely used because of their reactivity with groups that contain reactive hydrogens, such as amine and alcohol groups. This allows great flexibility in the types of products produced because they can self-polymerize or react with many other monomers. Isocyanates are most often used to produce polyurethanes by reacting with liquid diols.

The high reactivity of isocyanates is both an advantage and a disadvantage. The advantage is that polymerization proceeds rapidly and usually to high conversion. One disadvantage is that isocyanates can react so rapidly with water in the wood that this can compete with desired reactions with the wood, such as the hydroxyl groups in the cellulose and hemicellulose fractions as well as the phenols and hydroxyl groups in the lignin domains. Another disadvantage is the isocyanates can react rapidly with many compounds present in human bodies. These reactions are rapid under physiological conditions and are not readily reversible which means that safety of handling isocyanates is a concern. The concern occurs mainly during the manufacturing stage when low molecular weight and volatile isocyanates are still present; once these react, the resulting ureas and urethanes are quite safe. An exception is that the heat of combustion causes the formation of free isocyanate groups. Isocyanates used in wood bonding are not as hazardous as some other isocyanates in that they are generally higher molecular weight so their volatility is decreased and the number of free isocyanate groups is diminished.

The most common wood adhesive is a self-curing isocyanate, polymeric diphenylmethane diisocyanate (pMDI). It reacts with water in the wood for curing and is used in both the production

of composites and in the gluing of laminated wood products. The PMDI is used mainly for production of the core of oriented strandboard and is the only known adhesive that works well for the bonding of strawboard. pMDI can be used in the face of OSB, but mold release is needed to reduce sticking to the platens. Although the per pound cost of the pMDI is higher, it is taking market share away from the PF adhesives due to its rapid cure and ability to work at lower application rates.

Another common wood isocyanate adhesive is the emulsion-polymer isocyanate (EPI or API), which is a two-component adhesive (Grøstad and Pedersen 2010). These adhesives are used in bonding of oriented strandboard in engineered wood products. Mixing of the diisocyanate with a diol starts the curing process to form primarily a linear polymer with, usually, a moderate degree of cross-linking to provide more flexible products.

Another class of isocyanate adhesives is the polyurethanes, which are being used in more specialty wood-bonding applications (Dunky and Pizzi 2002, Vick and Okkonen 1998). Their advantage is wide formulation ability, given the great variety of raw materials that can be used. Polyurethanes have shown good potential for bonding green wood (Lange et al. 2001), and are more widely used in Europe.

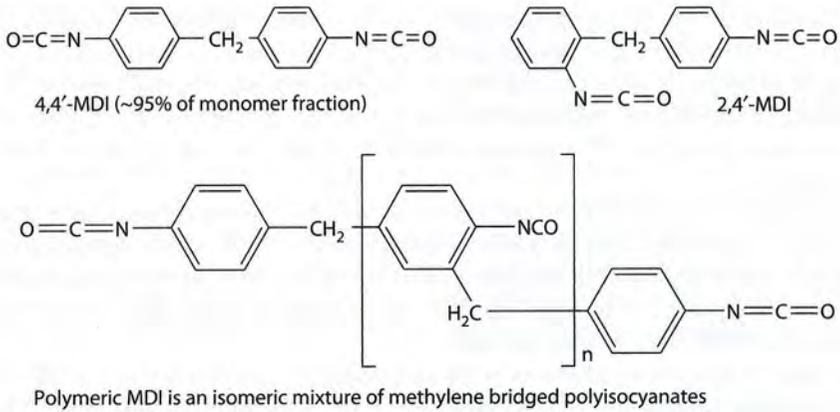
The most common reactive adhesives contain isocyanate groups, attached to the polymer backbone (Frisch 2002, Lay and Cranley 2003). Hot-melt adhesives are very desirable in product assembly because they develop their bond strength as the molten polymer cools and transforms from the melt to a solid. Unfortunately, the bond generally has poor resistance to heat, long-term stresses, and in some cases, moisture. Moisture-cured hot-melt isocyanates behave like typical hot-melts with good initial strength, but also cross-link to yield a thermoset that can resist the effect of heat, long-term loads, and moisture (Paul 2002). These are being widely used in product assembly areas, many of which involve wood.

#### 9.7.4.1 Polymeric Diphenylmethane Diisocyanate

Isocyanate adhesives have shown increasing use at the expense of other adhesives due to their high reactivity and efficiency in bonding. Polymeric diphenylmethane diisocyanates (pMDI) are commonly used in wood bonding and are a mixture of the monomeric diphenylmethane diisocyanate and methylene-bridged polyaromatic polyisocyanates, illustrated in Figure 9.22 (Frazier 2003). The higher cost of the adhesive is offset by its fast reaction rate, its efficiency of use, and its ability to adhere to difficult-to-bond surfaces. The pMDI forms a homopolymer, but needs water for the activation, which is not a problem with wood, but may be for bonding to other substrates. The chemistry involves several steps:

- The isocyanate first reacts with water to form a carbamic acid:  $R-NCO + H_2O = R-NHCOOH$ .
- The unstable carbamic acid gives off carbon dioxide to form an amine:  $R-NHCOOH \Rightarrow R-NH_2 + CO_2$ .
- The amine then reacts with another isocyanate group to form a urea:  $R-NH_2 + OCN-R \Rightarrow R-NHCONH-R$ .
- Some of the urea molecules react further with isocyanate to form a biuret:  $R-NHCONH-R + R-NHCON(CON-R)-R$ .

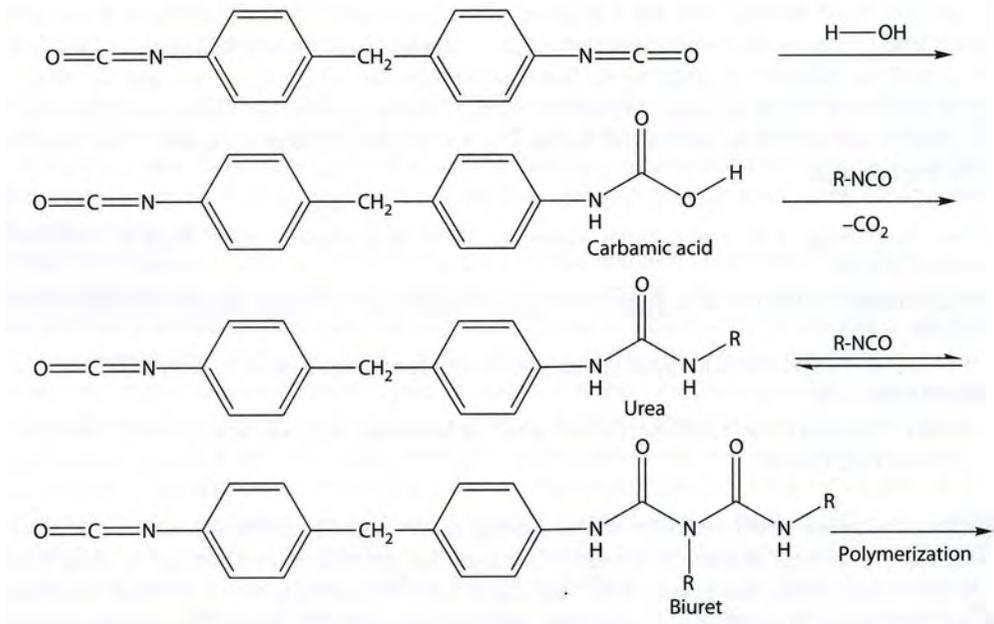
As shown by these reactions, once the isocyanate reacts with the water the rest of the process proceeds rapidly as long as there is enough isocyanate for reaction in comparison to groups with other reactive hydrogens, see Figure 9.23. Sufficient water is generally not a problem with wood given its high water content, but some other substrates need to be wetted for proper bonding. However, high water levels could potentially inhibit polymer formation by producing too many amine groups, but this has not been found to be the case in wood bonding. The carbon dioxide off gas can be a problem since it creates voids in the adhesive that can reduce the strength. Generally,



**FIGURE 9.22** The polymeric diphenylmethane diisocyanates is a mixture of the monomeric and polyfunctional isocyanates.

these reactions are not reversible under normal conditions, leading to good bond integrity of the isocyanate-bonded wood.

The interaction of pMDI with the composite surface is quite different from other wood adhesives, such as PR pMDI's low polarity and low viscosity compared to other wood adhesives leads to very rapid penetration into the wood (Frazier 2003). Normally this might lead to a starved bondline and poor strength, but this does not happen with the pMDI-bonded wood. It may be that the strength derives from the strong bridge created at the point where the wood is brought into close contact with the isocyanate adhesive. Some consider the isocyanate to be the most likely of all wood adhesives to form covalent bonds to wood due to the ease of isocyanate reacting with the hydroxyl groups of the wood to form urethane bonds (Frazier 2003). On the other hand, others believe that the fast reaction of the isocyanate with water and the large number of water groups present, especially  $\text{OH}=\text{C}=\text{N}$



**FIGURE 9.23** The isocyanate needs water to start the polymerization process. This reaction ends up forming carbon dioxide that can cause bubbles in the adhesive, but once the amine forms, self-polymerization takes place rapidly.

wood surface makes the urethane formation unlikely (Pizzi 1994a, Frazier 2003). Yelle and coworkers have proven definitely that there is no detectable reaction between the PMDI and wood polymers (Yelle et al. 2011a,b).

The unique properties of pMDI adhesives give it advantages in several markets. Its rapid polymerization and ability to form bonds in the presence of high water levels has led to its use as a core resin for OSB (Dunky and Pizzi 2002). The higher water content and lower temperatures of the OSB core section can make sufficient cure of a PF resin in the core more difficult, leading to increased use of pMDI. This ability to form bonds with high-moisture-content wood has also led to pMDI being used in bonding green or wet lumber. Low polarity allows pMDI to find cracks in the waxy coating of straw, leading to its use in strawboard, for which PF resins are unsatisfactory.

There are several disadvantages to pMDI besides cost. Unlike many wood adhesives that are poor bonders to substrates other than wood, pMDI bonds very well to other materials, including metal caul plates or press platens. Thus, this adhesive is less likely to readily displace PF from the face layer of OSB. Isocyanate's hazards have limited the use of pMDI due to the extra cost of maintaining safe operations in the plants. However, the safety issues can be addressed and no hazard exists in the bonded product due to the reaction of the isocyanate groups. PMDI is promoted as a formaldehyde-free adhesive.

#### **9.7.4.2 Emulsion Polymer Isocyanates**

Emulsion polymer isocyanates are generally two-part adhesives that are mixed prior to use and have been used for panel bonding, bonding of plastics to wood surfaces, and for bonding OSB web into the flange to make I-joists (Grøstad and Pedersen 2010). The components are a water-emulsifiable isocyanate and an emulsion latex containing polyhydroxyl functionalized molecules. The emulsion allows higher molecular weight polymers to be used while keeping a low solution viscosity for ease of application. Because the isocyanate readily disperses when mixed with the latex, it comes into contact with the hydroxyl groups as the water moves into the wood. Like all two-component systems, adequate mixing is important. As the adhesive cures, polyurethane groups are formed between by reaction of the isocyanate and hydroxyl groups. The hydroxyl functionalized pre-polymer can be varied in both its backbone structure and the number of hydroxyl groups to control the cross-linking. The variations in the latex portion allow products to be made with a wide range of stress—strain behaviors for different applications.

These adhesives can form fairly durable bonds depending on the formulation; some are known to give good water resistance. The ability to bond plastics and other non wood substrates is an advantage of these resins over many other wood adhesives. The higher cost and the need to mix the two components prior to use are disadvantages.

#### **9.7.4.3 Polyurethane Adhesives**

Polyurethanes are widely used in coatings and adhesives, but less common in wood bonding. Polyurethanes can be either one- or two-component systems, with the selection depending on the specific application. To obtain good wetting, the components need to be low molecular weight or a solvent needs to be added to reduce the viscosity for good wetting. Low molecular weight of the isocyanate components is not desirable because it leads to excessive volatility and health problems. The one-component system is an isocyanate-functionalized polymer that has remaining isocyanate groups. These groups will react with moisture causing the generation of amines that react with other isocyanate groups to form the backbone and cross-linking connections. The two-component adhesive has an isocyanate portion and an isocyanate-reactive portion. Good mixing of these two components just prior to bonding is critical.

The market for these products has been somewhat limited in structural markets because of their marginal levels of wood failure. They are widely used in many other bonding markets due to their good strength, flexibility, impact resistance, and ability to bond many substrates. The acceptance of these products has been greater in Europe than in the United States.

### 9.7.5 EPDXY ADHESIVES

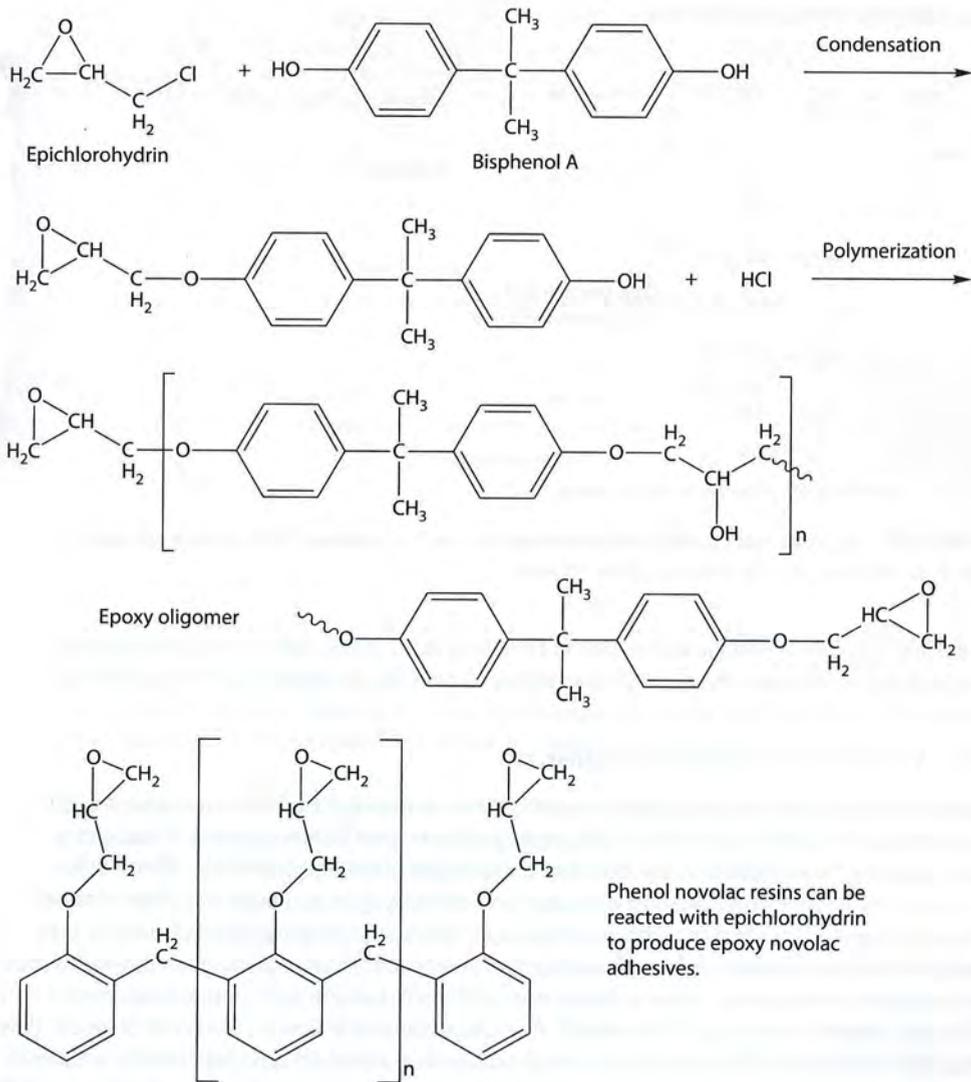
Epoxy adhesives and coatings are widely used because of their good environmental resistance and the ability to bond to a wide variety of surfaces, including wood, metals, plastics, ceramics, and concrete. They are less commonly used in wood bonding because they cost more than most wood adhesives, and in some cases, their durability is limited. On the other hand, they are structural adhesives that cure at ambient temperatures, have good gap filling ability, and do bond to many other surfaces, while most wood adhesives require heat cure, are not gap filling and do not bond well to other substrates. Thus, epoxies continue to be examined for their use in bonding wood to other materials and for in-place repair of damaged wood structural members. Besides cost, a main limitation of epoxies is their lack of acceptance for applications that require durable bonds (American Institute of Timber Construction 1990).

Although there are some cases of self-polymerization under the influence of acid or tertiary amine catalysts, most epoxies have an alternating ABABAB backbone of epoxy and hardener that is highly cross-linked, usually using a multifunctional hardener. The standard terminology is for the epoxy to be called the resin and the other component that polymerizes and cross-links the epoxy to be called the hardener. The formulation is expressed as parts per hundred resin (phr) with the weight of the epoxy as 100 and the rest of the components given relative to the epoxy weight. The hardener is anything that will react with the epoxy groups, including amines, thiols, hydroxides, and acid groups, but amines are the most common hardeners.

The most common epoxy resin is the diglycidyl ether of a bisphenol A (DGEBA), although other multifunctional epoxies can be used. The DGEBA synthesis begins by the condensation of phenol with acetone to give the bisphenol A (bisA) as illustrated in Figure 9.24. This then reacts with epichlorohydrin under basic conditions to yield the DGEBA molecule and sodium chloride. The removal of the salt is especially important in electronic applications to minimize metal corrosion by the chloride. The DGEBA epoxies vary in molecular weight due to oligomerization through the epoxy group. Another important class of the epoxies is made from the Novalak resins via the condensation of phenol with formaldehyde, as discussed in Section 9.7.3.1. Bis-F resins have also been used to impart some flexibility; these are similar to the bis-A resins except that formaldehyde is used in place of acetone for the condensation. Even more flexible resins can be made using epoxidized fatty oils and other nonaromatic epoxides. Brominated epoxies are often used for fire resistance.

The hardeners or curatives have an even wider variety of chemical structures than do the epoxies. The hardeners have an active hydrogen attached to a nucleophile and essentially add across the epoxy group. The process involves the nucleophile attacking the terminal carbon of the epoxy as illustrated in Figure 9.25, with the hydrogen then migrating to the hydroxyl anion. For less nucleophilic groups, use of a tertiary amine that interacts with the oxygen atom in the epoxy makes the epoxy ring easier to open. This continues until all the active hydrogens are reacted with epoxide or the epoxide is used up. Thus, for amine with two reactive hydrogens on a nitrogen, two epoxy groups can react, but the second addition is much slower. For formulating the ratio of hardener, the equivalent weight of the hardener is calculated by dividing its molecular weight by the number of active hydrogens and compared to a similar equivalent weight for the epoxies.

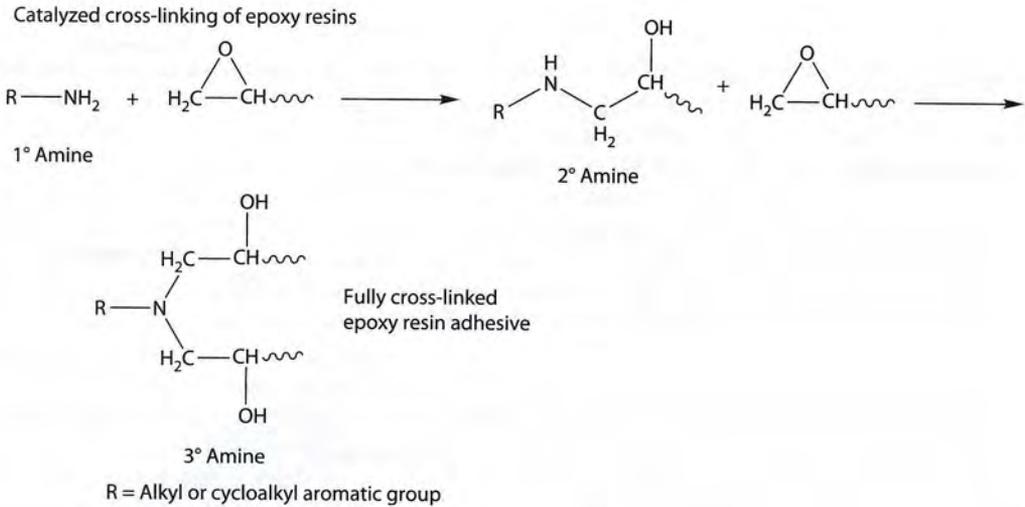
The amine hardeners are the most common for room-temperature curable epoxies; they can be divided into three different classes. The main class comprises polyamines, such as those made from the reaction of ethylene oxide and ammonia, to give products such as diethylene triamine, triethylene tetraamine, and tetraethylene pentaamine. These low molecular amines are hazardous due to their corrosivity and their ability to chelate metals. Their reasonable cost and high reactivity make them the most common curatives and are used in wood bonding and repair. Other amines used to make cured products more flexible are the amine-capped polypropylene oxide polymers and branched six carbon diamines. The other amine-containing curatives contain fatty acids that make the epoxies somewhat more flexible and hydrophobic. Polyethylene polyamines can be reacted with



**FIGURE 9.24** The epoxies are made by reaction of epichlorohydrin with phenols to produce glycidyl ethers. The bis-A epoxy is much more common than the novolak epoxies, but the latter can provide better heat resistance.

fatty acids to make amidoamines. Polyethylene polyamines can also be reacted with dimer acid, made via the dimerization of unsaturated fatty acids, producing polyamide curing agents. While the standard epoxies in home stores involve amine hardeners, those that exhibit a 5-min cure time use mercaptans hardeners. Epoxies can also be cured using anhydride hardeners or tertiary amine catalysts, but the high cure temperatures limit their use in wood products.

Although epoxies give strong and durable bonds to many substrates, they do not result in highly durable bonds to wood. There is some disagreement on the durability of epoxy bonds under wet conditions, but most standards limit epoxies for load bearing applications (American Institute of Timber Construction 1990). Considerable work has been done on supporting the use of epoxies for restoration work, but examination under severe testing shows that commercial epoxies do not pass the test requirements (Pizzo et al. 2003). Examination of the failure indicates that most of the failure is in the epoxy interphase region (Frihart 2003). Higher wood failure under wet conditions has been



**FIGURE 9.25** Epoxies react readily with nucleophiles, such as amines. Most amines are primary allowing multiple additions to provide a cross-linked network.

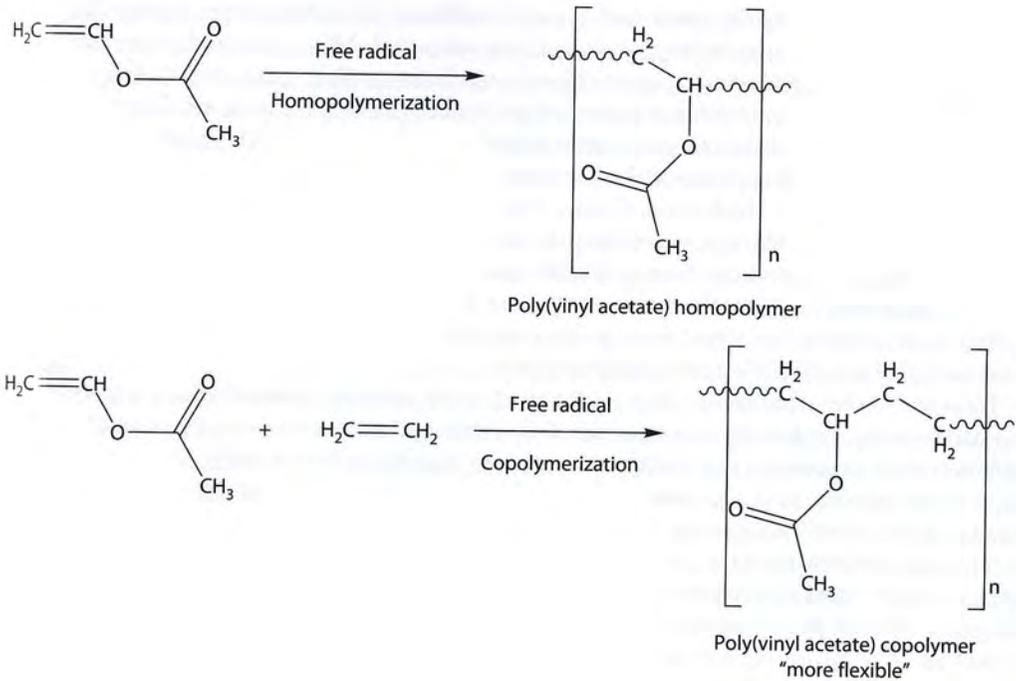
found using epoxies to bond acetylated wood (Frihart et al. 2004), while using a hydroxymethylated resorcinol primer allowed the bonded assemblies to pass the durability tests (Vick 1997).

### 9.7.6 VINYL ACETATE DISPERSION ADHESIVES

The water-borne adhesives poly(vinyl acetate), PVAc, and poly(ethylene-vinyl acetate), EVAc, find wide utility in the bonding of wood and paper products into finished goods. Common white glue (PVAc) has long been used in wood bonding including furniture construction. These adhesives easily set at room temperature, are cost effective and are easy to use. These waterborne adhesives set by the water being absorbed into the wood or paper product (and eventually released into the atmosphere), leading to wide use in manufacturing and construction operations involving wood. Because these products are not cured, they will lose much of their strength at high moisture levels.

The processes for making PVAc and EVAc dispersions are similar in many respects (Geddes 2003, Jaffe et al. 1990). The monomers (vinyl acetate and ethylene) are dispersed in water containing poly(vinyl alcohol), making an emulsion; the monomers in the droplets of the emulsion are polymerized to form a dispersion of an organic polymer in water. Making a stable product requires having an emulsion with small droplet sizes. Addition of the monomers is controlled to prevent overheating caused by the exothermic polymerization. The important part is to prevent the phases from separating to form the necessary fine dispersion. If there is too much surfactant, the product can have poor adhesion due to a weak boundary layer. After application, the water migrates away and the beads of adhesive coalesce to form a film, but the coalescence needs to take place on the wood surface. The polarity of the adhesive can be reduced by incorporation of ethylene in the polymerization to produce ethylene-vinyl acetate copolymers for bonding to less polar surfaces.

PVAc is a linear polymer with an aliphatic backbone; thus, it is very flexible adhesives as opposed to the rigid nature of formaldehyde copolymers normally used as wood adhesives. These PVAc adhesives being water-borne generally exhibit good flow into the exposed cell lumens, but, given their high molecular weight, they most likely do not penetrate cell walls. PVAc, with its high content of acetate groups and flexible backbone, can form many hydrogen bonds with the various fractions of the wood for good interfacial adhesion. These adhesives maintain much of their bond strength as the wood expands and contracts due to dissipation of the energy into flexing of the polymer backbone. With this dissipation of the stress into the polymer chains, there is limited stress concentration



**FIGURE 9.26** Polyvinyl acetate is made by the self-polymerization of vinyl acetate usually under free radical conditions. The chains can be altered by adding ethylene to form a copolymer.

at the interface. However, PVA adhesives do not work well at high moisture levels due to loss of strength or high constant stress levels because of a lack of creep resistance. A solution to these problems is to convert the thermoplastic PVA into a thermoset. This is accomplished by cross-linking the linear thermoplastic, using covalent bond formation, such as reaction with glyoxal, formaldehyde resins, or isocyanates, or using ionic bond formation, such as reaction with organic titanates, chromium nitrates, aluminum chloride, or aluminum nitrates. Other ways for making cross-linkable PVAc are to make a copolymer adding N-methylolacrylamide or to add phenolic resins. Cross-linked PVAc (PVAcX) has improved resistance at high moisture levels, higher temperatures, and under load but is not as convenient because the cross-linker needs to be added just prior to application. However, these adhesives can be used in other applications, such as windows and door construction, for which regular PVA cannot be used.

Poly(vinyl acetate) is converted to poly(vinyl alcohol) (PVOH) by hydrolysis (Jaffe and Rosenblum 1990). PVOH products vary in degree of hydrolysis and molecular weight depending on the specific application, the main uses being textile and paper sizing, adhesives, and emulsion polymerization of vinyl acetate. Given the water solubility, these adhesives need to be either cross-linked or gelled to give some permanence under moist conditions. This conversion is done by cross-linking using a covalent bond formation, such as reactions with glyoxal, UF, and MF or using ionic bonds formations with metal salts, such as cupric ammonium complexes, organic titanates, and dichromates. The gelation is usually accomplished using boric acid or borax.

### 9.7.7 BIO-BASED ADHESIVES

The most common bio-based adhesives for wood bonding are protein based. In contrast to the other wood adhesives, protein glues have been used for thousands of years. Many of the early civilizations learned how to make adhesives from plants and animals (River et al. 1991, Keimel 2003). Although the original bonded wood products were made using natural protein adhesives, these bonds were

durable only at low moisture levels and generally softened at high moisture levels. This led to delamination, in addition to biological degradation when wet. Many sources have been used for protein-based adhesives, including animal bones and hides, milk (casein), blood, fish skins, and soybeans. The bonded wood industry expanded greatly due to the use of these adhesives in the early 1900s, as processes were developed to make more effective adhesives. The biggest advancement was the development of soybean flour adhesives that allowed interior plywood to become a cost effective replacement of solid wood. Today, most of the original bio-based adhesives have been replaced by synthetic adhesives due to cost, durability, and availability factors. Research has been done on incorporating soybean flour or protein into PF resins, but more success has been obtained by using the phenol and formaldehyde to cross-link the denatured soy flour protein (Wescott et al. 2006a). A resurgence has taken place in the use of soybean adhesives due to new cross-linking chemistry (Frihart 2010, Wescott and Frihart 2011).

Trees and bushes, themselves, provide many adhesive materials, some of which have been used in wood bonding. Pitch from trees was one of the earliest adhesives because of its availability, usefulness without processing and ability to bond many materials (Regert 2004). From this grew the naval stores industry, with the name indicating its importance to ship construction for sealing and bonding applications. Naval stores research led to the development of rosin resins that are important additives in both ethylene-vinyl acetate hot-melt and pressure sensitive adhesives, and to the development of fatty acid derivatives that are converted to epoxy hardeners and polyamide hot-melt adhesives. Tannins have been used as phenol replacement in some formaldehyde copolymers. Due to their phenolic nature, lignins have been examined extensively as phenol replacement in PF resins. Both tannins and lignin adhesives tend to have good moisture resistance and are not readily attacked by microorganisms.

Carbohydrates have been used as adhesives, but have not found much utility in wood bonding (Conner and Baumann 2003). Starch is widely used in paper bonding, especially in the construction of corrugated board used in many packaging applications, but generally lacks the strength and water resistance needed for use in wood bonding. The cellulosic adhesives not only lose strength under wet conditions, but also support the growth of microorganisms.

#### 9.7.7.1 Protein Glues

Once the dominant wood bonding adhesive, proteins had mainly disappeared from the market but are now seeing a resurgence (Frihart 2010, Wescott and Frihart 2011). Like most biomass materials, proteins are not uniform in composition as the source varies; thus, the processes for using these proteins and the properties of the adhesives vary as the protein source changes. To make the most effect adhesive, the native protein structure should be denatured to expose more polar groups for solubilization and bonding. The primary structure involves a polyamidoamine backbone made from the condensation of amino acids, while the secondary and tertiary structures are based on intra-chain and interchain interactions, respectively, which involve hydrogen bonds, disulfide linkages, or salt bonds. The main denaturation involves breaking the hydrogen bonds, while breaking other secondary and tertiary bonds depends on the denaturation conditions. Once the protein has been denatured, then it has the ability to come in intimate contact, and to form hydrogen bonds with the wood surface. The setting step involves reformation of the hydrogen bonds between the protein chains to establish bond strength. For prior protein adhesives, the main method of denaturation for adhesive applications was hot aqueous conditions (Lambuth 2003). The aqueous process is often done under caustic conditions and may also involve adding other chemicals to either stabilize the denatured glue or add strength to the final bonds.

Of the protein-based adhesives, soybean flour continues to be used in the largest volume; the flour is ground from the residue after the soybeans had the traditionally more valuable oil removed by extraction (Sun 2005). Traditionally, the flour was dispersed in aqueous caustic to obtain low solids dispersions that had to be used within eight hours before the adhesive starts to degrade (Lambuth 2003). These soybean protein adhesives allowed the development of the interior plywood

industry in the early 1900s. The adhesives were improved to give better water resistance (Lambuth 2003), but never achieved sufficient moisture resistance to make exterior grade plywood. PF resins were slow to displace soybean adhesives due to cost and marginal performance. The need for more durable plywood adhesives during World War II led to improved and lower cost PF resins and the ultimate demise of the soybean adhesives. The upsurge in soybean use during the 1950s shows the potential for soybean adhesives on a cost basis if the water resistance, short storage stability, and inconsistency of properties can be overcome.

With the rising cost of petroleum based adhesives, soy flour based adhesives have been of interest as a partial replacement of phenol in PF adhesives. The highest replacement has been about 50% when used the resin in the face of oriented strandboard (Wescott et al. 2006a). These alkaline resins behave very similarly to the standard PF resin. However, the soy flour can provide an unusual type of phenol resin; the alkaline soy-PF can be acidified to make a stable dispersion (Wescott et al. Frihart 2006b). This dispersion is light colored and does not give caustic burns.

Another approach to more durable soybean flour adhesives is the use a poly(amidoamine)-epichlorohydrin (PAE) resin as a curing agent (Li et al. 2004) These protein adhesives do not need the highly alkaline conditions previously used with soybean adhesives and have good stability (Allen et al. 2010). These adhesives with no added formaldehyde provide products with very low formaldehyde emissions not only under standard test conditions (Birkeland et al. 2010) but also at elevated temperature and humidity (Frihart et al. 2010). These adhesives have replaced OF in interior plywood, engineered wood flooring, and particleboard (Allen et al. 2010) to meet the new formaldehyde emission standards discussed in Section 9.8.

None of the other protein sources are available with sufficiently low cost, large supply, and consistent composition as soybean flour, but they still have advantages because of their special properties. Blood protein from beef and hogs has the best water resistance of any of the commercial protein adhesives but has great inconsistency (Lambuth 2003). To retard spoilage, the blood is spray dried. It has been mixed with PF adhesives for plywood bonding. Animal bone and hide glues are used in fine furniture manufacturing because they provide flexible bonds for good durability with indoor humidity changes (Pearson 2003). They have many other uses but are being replaced by synthetics, such as ethylene vinyl acetate polymers, which have lower cost and greater ability to be formulated for specific applications. Casein, like many of the protein adhesives, provides good fire resistance and is therefore used in fire doors. Each of these adhesives has its own process for denaturation and use (Lambuth 2003).

### 9.7.7.2 Tannin Adhesives

Tannins are polyhydroxypolyphenolics that occur in many plant species, but only a few species have a high enough concentration to make it worthwhile to isolate them. The commercial supplies of tannins are limited to a few countries. Tannins are used because they are more reactive than phenol, but they are also more expensive than phenol. Extraction of the plant material and subsequent purification of the isolates, followed by spray drying, yield powdered tannins (Pizzi 2003c). The purified isolates behave in many ways like a natural form of resorcinol, with their high reactivity and water-resistant bonds when polymerized with formaldehyde. Although tannin's reaction rate with formaldehyde is quite similar to that of resorcinol, the polymer structure is quite different. Instead of multiple additions of formaldehyde to a single aromatic ring, formaldehyde adds mainly as single additions and some double additions to the connected rings of the resorcinol, pyrogallol, phloroglucinol and catacheol structures in tannins. Thus, the final polymer structure is very different and will have different properties than the resorcinol product due to its lower cross-link density, despite the similarity in the chemical reactions.

Three limitations of tannins compared to synthetic adhesives are their high viscosity, limited availability, and inconsistent source and therefore reactivity. Their polycyclic structure that leads to fast cure speed also makes solutions of tannins high in viscosity; using more dilute solutions to reduce viscosity leads to additional steam in the hot pressing of the composite. Tannins exist in high

enough concentrations to be commercially viable in a few species, but are not available in the large quantities to compete with synthetic adhesives. Like many natural products, the composition of tannins varies depending on growing conditions; thus, making consistently performing adhesives difficult.

Tannins have been used as adhesives in South Africa, Australia, Zimbabwe, Chile, Argentina, Brazil, and New Zealand (Dunky and Pizzi 2002). The use is in composite (particleboard and medium density fiberboard) production, laminate and finger joint bonding, and for damp-resistant corrugated cardboard (Pizzi 2003c). The tannin market will always be of limited volume due to supply limitations.

### 9.7.7.3 Lignin Adhesives

Although lignins are aromatic compounds, they are very different from tannins—they are available in large quantities at lower cost, **but** they are much slower in their reaction with formaldehyde. The supply of lignin is large, being the by-product of pulping processes for papermaking; they constitute 24–33% of the woody substance in softwoods and 16–24% in hardwoods. Native lignin is a complex polymer, and this polymeric structure needs to be partially degraded to allow them to be separated from the celluloses. For adhesive purposes, these degraded lignins need to be further polymerized to obtain useful adhesive properties. Despite being almost completely aromatic,

have only a few phenolic rings and no polyhydroxy phenyl rings, leading to low reactivity with formaldehyde.

The low value of lignins has led to much research in finding ways to convert the lignin into useful thermoset adhesives. Lignin from the predominant Kraft pulping process does not lead to a useful product because of the cost of separating the lignin from the pulping chemicals and the inconsistency of the lignin product. However, lignosulfonates contained in the spent sulfate liquor (SSL) from sulfite pulping of wood have been found to be a more useful feed for the production of reactive lignins (Pizzi 2003d). Because of lignin's low reactivity with formaldehyde, other curing mechanisms have been investigated, including thermal cure with acids and oxidative coupling using hydrogen peroxide and catalysts. Three methods of using SSL as the main adhesive with particleboard are to use long press times with a postheating step, to heat with sulfuric acid during bonding, and to heat with hydrogen peroxide (Pizzi 2003d). SSL has also been used as PF and OF extenders. The poor reactivity of lignin can be altered by pre-methylation with formaldehyde, and this pre-methylated lignin has been used with PF resins in plywood bonding.

## 9.7.8 MISCELLANEOUS COMPOSITE ADHESIVES

Understanding adhesion to wood is as important for composites where wood is the minor component as it is for composites where wood is the main component. Three product areas for wood as a minor component are wood–fiber cement board, wood–plastic composites, and wood filler for plastics. In all three cases, the nonwood component is the main phase holding the material together, but the better the adhesion of the main phase to the wood fiber, the stronger and more durable the product.

Wood-fiber-reinforced cement board competes with traditional cement board that uses other reinforcing materials such as fiberglass cloths. The reinforcement serves to reduce the fracture of these preformed panels. Making improved products involves knowing the interaction of wood with the inorganic cement. Plant fiber reinforcement is still being studied, but the market is dominated by fiberglass reinforcement.

Developing good interaction of wood with low polarity plastics is of growing importance. PPE and PP being the most significant for wood–plastic composites with a main market being a wood replacement for exterior decking. The limited interaction between wood and PE or PP is not surprising, given the large difference in polarity and the difficulty in obtaining good molecular contact between a solid and high molecular weight polymer. The most common method of

addressing the polarity difference and the rheological issue is to use medium molecular weight, maleic anhydride-modified polyethylene or polypropylene that can serve as a coupling agent (Clemons et al. 2012). These agents have the polar maleic anhydride that can either react with hydroxyl groups to form esters or react with water to form organic acid groups that will form polar bonds with the hydroxyl groups in wood; thus, making the plastic more compatible with the wood. Better interaction between the hydrocarbon polymer network and the wood fiber will lead to stronger and more durable products. These products are mainly aimed at replacement of wood in decking (Morton et al. 2003), while retaining the appearance of wood.

Other areas for understanding wood—plastic interactions involve plastics filled with wood for applications such as automotive (Suddell and Evans 2003). These products are made to look like normal plastics, but wood filler is used as a partial replacement of the inorganic filler to reduce the weight of the product. The main polymer network is selected from a wide variety of polymers and more of the main fibers are agricultural (nonwood) than is the case in the previous paragraph. However, the fiber—polymer interactions are still very important, and worthy of further investigation. Poor interaction between the fiber and polymer network can cause early failure due to stress concentration. Although the plastic slows the migration of water to the fiber, under wet conditions, the fiber will eventually become saturated with water and begin to swell, putting additional stress on the interface.

### **9.7.9 CONSTRUCTION ADHESIVES**

Construction adhesives are used for attachment of floor and wall coverings, and in assembly of buildings (Miller 1990). Most building construction still uses nails or screws for attachment of wood pieces to each other. However, the use of an adhesive can give extra rigidity to the structure if the panel products are also bonded to the frame. Because the nail or screw holds the wood together, the adhesive does not need to set rapidly. Construction adhesives are normally made to be flexible to provide lateral "give" as the various house components expand and contract with changes in moisture and temperature (Blomquist and Vick 1977). A typical application uses an adhesive that is noncuring, high in molecular weight and with a small amount of solvent to provide some flow. The adhesive is applied at room temperature from a gun to one surface as a bead. Then, the nailing or screwing provides the force necessary for transfer, spreading, and penetration of the adhesive to both surfaces. Because the surfaces are not uniformly brought into close contact, the adhesive has to have gap-filling capabilities. Most standard wood adhesives are not able to be gap-filling due to void formation as the water escapes or gas bubbles form during the setting process (River et al. 1991). However, Vick made a gap-filling phenol—resorcinol resin (Vick 1973), but it would not have the flexibility needed for a construction adhesive.

Construction adhesives are usually elastomers, which provide the deformability needed for short-range movement to prevent fracture of the bondline as the wood expands and contracts. However, the adhesive is high in molecular weight to prevent long-range movement that would lead to separation of the bondline. These adhesives provide good strength for many years, but it is unlikely that many will last the lifetime of the building because most elastomers will react with oxygen and ozone, leading to embrittlement and fracture over such a long time.

### **9.7.10 HOT MELTS**

Hot-melt adhesives are used mainly in specialty wood applications. The main applications in wood bonding are related to furniture and cabinetry assembly, although they have also been used in window construction and edge banding of decorative laminates due to their ability to form bonds quickly. Rapid bond formation is valuable for manufacturing operations because minimal clamping time is needed for assembly (Dunky 2003). Hot melts generally set by cooling that turns the molten polymer into a solid, although some hot melts can acquire additional strength by cross-linking.

Hot-melt adhesives are fully formed polymers that are molten for application, but they have such high viscosities that their ability to wet wood surfaces is limited. Upon cooling they recover their strength as the molten polymer solidifies.

The hot-melt version of ethylene vinyl acetate (EVA) copolymer sets by cooling to room temperature and is used more with paper products and nonwovens (Paul 2002) than with wood products, although there is some use in wood furniture assembly. These EVAs are made by gas phase polymerization to yield nonsolvated polymers that have a range of properties. Variation in the ethylene to vinyl acetate ratio and molecular weight of the final polymer creates the various properties needed for individual applications. These products are formulated with tackifiers and waxes (Eastman and Fullhart 1990). Although EVAs are relatively inexpensive, they often have problems with creep as the temperature increases because they contain large amounts of lower molecular weight compounds (tackifiers and waxes) in the adhesive formulations and there is limited attraction between the polymer chains.

Polyamide hot-melt adhesives are also used in wood bonding because of their stronger interactions between chains, leading to better creep resistance. These polyamides are made by the reaction of various diamines with "dimer acid," a diacid that is made from the coupling of unsaturated fatty acids at their olefinic sites (Rossitto 1990). These polyamides offer good creep and heat resistance for a thermoplastic polymer due to the strong hydrogen bonds between the chains. These interchain hydrogen bonds resist flow until enough heat is applied to break these bonds, rapidly turning the solid into a fluid. After application to the substrate, cooling then converts the melt into a strong solid, with good adhesive strength. These properties have made the "dimer acid" polyamides useful for edge banding of laminates, cabinet construction, and window assembly. The higher cost of these adhesives limits their use to high-value products that need more durable bonds.

The moisture-cured isocyanates that were discussed in Section 9.7.4 and polyesters are other hot melts that are also used in wood products. The polyesters are made by reacting aromatic diacids with aliphatic diols, where the aromatic rings provide rigidity to the polymers (Rossitto 1990).

### 9.7.11 PRESSURE SENSITIVE ADHESIVES

Pressure sensitive adhesives (PSAs) have been a high growth area not only for tapes and labels, but also for application of decorative laminates. PSAs are different from other adhesives in that there is no setting step in their end use. PSAs readily deform to match the topography of the surface to which they are being bonded. Because PSAs are high molecular weight polymers, and in some cases cross-linked polymers, they have limited ability to flow, though their low modulus allows enough deformation to wet the surface. Although these adhesives may not have high interfacial adhesion, most of the applied force is not concentrated at the interface, because the force is mainly expended in deformation of the elastomeric adhesive (Rohn 1999). Because rheological properties are time and temperature dependent, the development of PSAs has been strongly dependent upon dynamic mechanical analysis (DMA) measurements. DMA provides useful information about a formulation's effect on the glass transition temperature and modulus (inverse of compliance) with the small dimensional changes that occur during bonding (Satas 1999a). However, the debonding process occurs over large dimensional changes and is more dependent upon the stress—strain properties of the adhesive. PSAs offer a wide range of properties from easily removed tape or Post-It™ notes to high peel and shear strength tapes, by alterations of both the bonding ability and the energy dissipation ability in debonding.

Given that bonding involves deformation of the adhesive to conform to the substrate surface, PSAs give satisfactory bonds to most surfaces because almost all surfaces are rough on the sub-micrometer scale. Elastomeric polymers provide the strength for the PSA, but the formulations usually contain low molecular weight materials that are used to tackify and plasticize the polymer. Many types of homopolymers and copolymers (random and blocked) are used in PSAs; Satas' book is an excellent reference source for PSAs (Satas 1999b).

Pressure-sensitive adhesives are often used for bonding plastics (usually having information or decorations printed on them) to wood products for informational or decorative purposes. Applications for this technology range from indoor office furniture to outdoor signs.

### 9.7.12 OTHER ADHESIVES

Contact adhesives have been used for bonding of plastic laminates to wood. A contact adhesive is a polymer dissolved in a solvent that is applied to both surfaces that are brought into contact after most of the solvent has evaporated. Thus, a countertop is produced by first coating both the particleboard base and the plastic laminate with a contact adhesive, usually neoprene dissolved in a solvent or emulsified in water; then, after the volatiles evaporate, the coated surfaces are pressed together. It is interesting to note that plastic laminates are primarily paper that has been impregnated with resin and then surface coated. Contact adhesives are mainly used in bonding plastic laminates to particleboard for countertops and furniture.

Polymerizable acrylic and acrylate adhesives are not used often for wood because of their high cost. The most common products of this type are structural acrylic (Righettini 2002) and cyanoacrylate instant adhesives (Klemarczyk 2002) that can bond to wood, but these generally require smooth surfaces. These adhesives are more often used in electronics assembly with radiation (light) curing rather than in wood bonding. They do provide rapid cure rates and high strength bonds. Light curing of adhesives does not work with an opaque substrate like wood, but the acrylates can be used for a tough finish over the paper decorative layer on paneling.

Film adhesives involve either partially cured adhesives or adhesives applied onto a carrier such as a fiberglass mat or tissue paper. They are used where applying a liquid adhesive may be difficult, such as in bonding of very thin wood veneers.

### 9.7.13 FORMULATION OF ADHESIVES

Adhesives are composed of several different components in addition to the base polymer. Although the other components are added for a specific purpose, they often will alter several properties of the adhesive, as applied or after setting.

*Base* is the polymer, either synthetic, biobased, or a combination, that provides the adhesive the strength to hold the two substrates together. This is the material from which the adhesive usually takes its name, such as PF, epoxy or casein. The base material provides the "backbone" of the adhesive, controlling its application, setting, and curing.

*Solvents* are liquids often used to dissolve or disperse the base material and additives in order to provide a liquid system for application to the adherends, but are removed from the adhesive in the setting step. The most common solvent for wood adhesives is water. Water is not used in many other adhesive applications due to poor wetting, low volatility, and corrosion of surfaces, but for wood it is an ideal and low-cost solvent. In some cases, the base material of the adhesive is a liquid itself and can be applied in this form without the need for solvents; for example, epoxies or pMDI. These are often referred to as "100-percent solid" adhesives. Such systems shrink less on hardening, thus reducing internal stresses in the film.

*Diluents* or *thinners* are liquids added to reduce the viscosity of the adhesive systems, and make them suitable for spraying or other special methods of application. However, unlike solvents, they have low volatility. A reactive diluent not only reduces the viscosity of the adhesive for application purposes, but also becomes part of the final polymeric chain.

*Catalysts* or *accelerators* are chemicals added in small amounts to increase the rate of chemical reaction in the curing or hardening process. True catalysts are not consumed in the reaction, while accelerators may be consumed in the reaction. An example of a catalyst is the acid catalyst generated from ammonium salts for curing OF resins (Pizzi 2003e), while an example of an accelerator is an *ortho* ester used to speed up the cure of PF resins (Conner et al. 2002).

*Curing agents or hardeners* are chemicals that actually undergo chemical reaction in stoichiometric proportions with the base resin and are combined in the final cured polymer structure. A good example is the amine component that reacts with an epoxy resin to form the final adhesive.

*Fillers* are solids that are added primarily to lower the cost and to give body to liquid adhesives, reducing undesired flow or over-penetration into wood. Fillers usually increase the rigidity of the cured adhesive. They may also modify the thermal expansion coefficient of the film to more nearly approximate that of the adjacent adherends, thus reducing thermal stresses in the joint formed during the cooling, following heat-curing conditions or when thermally cycled in service. Two examples of such fillers include walnut shell flour, incorporated in urea or phenolic adhesives to improve spreading or reduce penetration into open wood pores, and china clay that is sometimes added to epoxy resin systems primarily for thickening or to modify thermal expansion coefficients.

*Extenders* primary purpose is reducing the adhesive costs while also improving some adhesive properties. At times they can also alter other properties, such as increasing the tack of the adhesive. A good example of an extender is wheat gluten added to UF resins in making hardwood plywood for interior applications.

*Stabilizers or preservatives* are chemicals added to an adhesive to protect one or more of the components and/or the final adhesive against some type of deterioration. Preservatives are usually used for preventing biological deterioration, while a stabilizer can protect against either biological or chemical degradation. Prevention of biological deterioration can involve the use of fungicides or biocides, while chemical degradation prevention may involve the use of antioxidants or antiozonates. In some cases stabilizers are used to avoid the premature curing of an adhesive.

*Fortifiers* are generally other base materials added to modify or improve the durability of the adhesive system under some specific type of service. A good example is the addition of more durable melamine resins to UF resins in wood bonding to provide greater resistance to deterioration under hot and moist conditions (Dunky and Pizzi 2002).

*Carriers* are sometimes used to produce film-type adhesives. The carrier is usually a very thin, rather porous fabric or paper on which the liquid adhesive is applied and then dried. Examples include the use of thin tissue paper as a carrier for phenolic film adhesives in making thin hardwood plywood, where spreading the liquid adhesive on a conventional roller spreader might tear or break the thin veneers.

Adhesive formulating is an important skill, often requiring a mixture of empirical and scientific knowledge. Because there is no universal adhesive, systems must be formulated for the specific applications, for example, for a given type of joint or even for a given type of commercial bonding operation. While billions of pounds of phenolic adhesives are used each year in wood bonding, the actual adhesive formulation used in one plant may be quite different from that used in another. Additionally the adhesive formulation used within the same plant may vary with the season due to changes in temperature and humidity. The moisture content or surface roughness of the veneers or the time sequence between one operation and the next influences the actual types and proportions of additives, solvents, and resins used to make a cost effective adhesive.

## 9.8 ENVIRONMENTAL ASPECTS

Although wood is a natural material, some bonded wood products have caused environmental concerns. There are a number of problem areas, but the foremost area of concern has been formaldehyde emissions from the bonded products, mainly using UF resins. Formaldehyde can react with biological systems in reactions similar to those that are used for curing of adhesives. The problem can arise from both unreacted and generated formaldehyde. Unreacted formaldehyde is also a problem during the manufacturing operation and in freshly produced composites, but has been handled through formulation and engineering solutions. Formaldehyde emissions from composites decrease with time after production (Birkeland et al. 2010). The rate is high initially, but slowly decreases due to diffusion limitations. On the other hand, formaldehyde can be generated by the

decomposition of some formaldehyde containing adhesives, in particular the OF adhesives (Myers 1984a,b). These adhesive bonds are more prone to hydrolysis, generating free formaldehyde. The biggest concern is with particleboard, due to the large volume of indoor usage and the high level of adhesive in the product. The formulations of formaldehyde adhesives have been altered over the years to reduce the amount of formaldehyde used and formaldehyde scavengers have been used. The reduction in formaldehyde altered the curing rate and the strength of the product; thus, the process required much research. Many of the formaldehyde concerns were addressed through adhesive reformulation (Dunky and Pizzi 2002, Dunky 2003) with the science of formaldehyde in wood products has been extensively reviewed (Marutzky 1989). The formaldehyde issue continues to be an issue as the acceptable emission levels decrease. The level in the United States was lowered by the California Air Resources Board (Williams 2010), which were used for the United States federal law.

The main concern, emissions, has focused on formaldehyde, but this is not the only compound emitted by bonded wood products. Other volatile compounds in the adhesive formulation have also been detected. In addition, a number of other volatiles are present in wood and additional ones can be generated by the heat and moisture in the production of the composite (Wang et al. 2003). Careful analysis has revealed the presence of formaldehyde, other aldehydes, methanol, and pinenes, many of which come from the wood itself rather than from the adhesive (Baumann et al. 2000).

During the use of the adhesives, volatiles from the monomers that are used to produce the polymers generate additional health concerns. Thus, free formaldehyde, phenol, methanediophenyl diisocyanate, polyethylene polyamines, and so on, are all of concern depending on the type of adhesive used. Heating certainly increases the problem because it raises the vapor pressure of these reactive chemicals. In addition, many hot pressing methods cause other chemicals to be entrained in the steam from the presses (Wang et al. 2003).

## 9.9 SUMMARY

Although wood bonding is one of the oldest adhesive applications, it is less understood than the most bonding applications. Many modes are possible for both bond formation and failure. Wood structure has so many variables in the different species, cell structures within a tree, and complex morphology at all spatial scales that it is hard to model the process. Despite these problems, many adhesives have been developed that are stronger and some are even more durable than the wood itself. In addition, many functional adhesives have been developed that allow a wide variety of woods and wood pieces to be glued together in a useful and cost-effective manner.

The area that is best understood is the chemistry of the adhesives, even though there are aspects, such as the effects of the composite processing dynamics that need to be more thoroughly researched. The development of the physical properties during the setting process and the interaction of the adhesive with the wood need to be better understood to allow for a more cost effective development of new adhesives.

## REFERENCES

- Allen, A. J., B. K. Spraul, and J. M. Wescott. 2010. Improved CARB II-compliant soy adhesives for laminates. In: *Wood Adhesives 2009*, eds. C. R. Frihart, C. G. Hunt, and R. J. Moon, 176-184. Madison, WI: Forest Products Society.
- American Institute of Timber Construction. 1990. Use of epoxies in repair of structural glued laminated timber. AITC Technical Note 14. Englewood, CO AITC.
- ASTM International. 2011a. D 907-11. *Standard Terminology of Adhesives*. West Conshohocken, PA: ASTM International, Vol. 15.06.
- ASTM International. 2011b. D 2559-10a. Standard Specification for Adhesives for Structural Laminated Wood Products for Use Under Exterior Exposure Conditions. West Conshohocken, PA: ASTM International, Vol. 15.06.

- ASTM International. 2011c. D 4300-01. *Standard Test Methods for Ability of Adhesive Films to Support or Resist the Growth of Fungi*. West Conshohocken, PA: ASTM International, Vol. 15.06.
- Autumn, K., M. Sitti, Y. A. Liang, A. Peattie, W. Hansen, S. Sponberg, T. Kenny, R. Fearing, J. Israelachvili, and R.J. Full. 2002. Evidence for van der Waals adhesion in gecko setae. *Proc. Natl. Acad. Sci.* 99:12252-12256.
- Back, E. L. 1987. The bonding mechanism in hardboard manufacture. *Holzforschung* 41:247-258.
- Barton A. F. M. 1991. *CRC Handbook of Solubility Parameters and Other Cohesion Parameters* (2nd ed.). Boca Raton: CRC Press.
- Baumann, M. G. D., L. F. Lorenz, S. A. Batterman, and G-Z. Zhang. 2000. Aldehyde emissions from particleboard and medium density fiberboard products. *Forest Products J.* 50(9):75-82.
- Berg, J. C. 2002. Semi-empirical strategies for predicting adhesion. In: *Adhesive Science and Engineering-2: Surfaces, Chemistry and Applications*, eds. M. Chaudhury and A. V. Pocius, 1-73. Amsterdam: Elsevier.
- Bikerman, J. J. 1968. *The Science of Adhesive Joints* (2nd ed.). New York: Academic Press.
- Birkeland, M. J., L. Lorenz, J. M. Wescott, and C. R. Frihart. 2010. Significance of native formaldehyde in particleboards generated during wood composite panel production. *Holzforschung* 64:429-433.
- Blomquist, R. F. and C. B. Vick. 1977. Adhesives for building construction. In: *Handbook of Adhesives*, ed. I. Skeist (2nd ed.), Chapter 49. New York: Van Nostrand Reinhold.
- Bolton, A.J., J. M. Dinwoodie, and P. M. Beele. 1985. The microdistribution of UF resins in particleboard. In: *Proceedings of IUFRO Symposium, Forest Products Research International: Achievements and the Future*. Vol. 6.17.12-1-17.12-19. South Africa: Pretoria.
- Bolton, A.J., J. M. Dinwoodie, and D. A. Davies. 1988. The validity of the use of SEM/EDAX as a tool for the detection of the UF resin penetration into wood cell walls in particleboard. *Wood Sci. Technol.* 22:345-356.
- Brief, A. 1990. The role of adhesives in the economy. In: *Handbook of Adhesives*, ed. I. Skeist (3rd ed.), 641-663. New York: Van Nostrand Reinhold.
- Browne, F. L. and D. Brouse. 1929. Nature of adhesion between glue and wood. *Ind. Chem. Eng.* 21(1):80-84.
- Christiansen, A. W. 1990. How overdrying wood reduces its bonding to phenol-formaldehyde adhesives: A critical review of the literature, Part I: Physical responses. *Wood and Fiber Sci.* 22(4):441-459.
- Christiansen, A. W. 1991. How overdrying wood reduces its bonding to phenol-formaldehyde adhesives: A critical review of the literature, Part II: Chemical reactions. *Wood and Fiber Sci.* 23(1):69-84.
- Christiansen, A. W. 1994. Effect of overdrying of yellow-poplar veneer on physical properties and bonding. *Holz als Roh and Werkstoff* 52:139-149.
- Christiansen, A. W. and E. A. Okkonen. 2003. Improvements to hydroxymethylated resorcinol coupling agent for durable wood bonding. *For. Prod. J.* 53(4):81-84.
- Clemons, C., R. M. Rowell, and D. Plackett, 2012. *Wood-Thermoplastic Composites* (2nd ed.). Chapter 13. Boca Raton: Taylor & Francis.
- Conner, A. H. and M. G. D. Baumann. 2003. Carbohydrate polymers as adhesives. In: *Handbook of Adhesive Technology*, eds. A. Pizzi and K. L. Mittal (2nd ed.), 495-510. New York: Marcel Dekker.
- Conner, A. H., L. F. Lorenz, and K. C. Hirth 2002. Accelerated cure of phenol-formaldehyde resins: Studies with model compounds. *J. Appl. Polym. Sci.* 86:3256-3263.
- Dawson, B., S. Gallager, and A. Singh. 2003. *Microscopic View of Wood and Coating Interaction, and Coating Performance on Wood*. Forest Research Bulletin 228. Rotorua, NZ: Forest Research.
- De Fleuriot, L. 2004. Radio frequency glue bonding. [http://www/highfrequency.co.nz/webfiles/Radio\\_Frequency\\_Glue\\_Bonding.pdf](http://www/highfrequency.co.nz/webfiles/Radio_Frequency_Glue_Bonding.pdf). (accessed August 20, 2012).
- Detlefsen, W. D. 2002. Phenolic resins: Some chemistry, technology and history. In: *Adhesive Science and Engineering-2: Surfaces, Chemistry and Applications*, eds. M. Chadhury and A.V. Pocius, 869-945. Amsterdam: Elsevier.
- Dillard, D. A. 2002. Fundamentals of stress transfer in bonded systems. In: *Adhesive Science and Engineering-1: The Mechanics of Adhesion*, eds. D. A. Dillard and A. V. Pocius, 1-44. Amsterdam: Elsevier.
- Dunky, M. 2003. Adhesives in the wood industry. In: *Handbook of Adhesive Technology*, eds. A. Pizzi and K. L. Mittal (2nd ed.), 887-956. New York: Marcel Dekker.
- Dunky, M. and A. Pizzi. 2002. Wood adhesives. In: *Adhesive Science and Engineering-2: Surfaces, Chemistry and Applications*. eds. M. Chadhury and A. V. Pocius, 1039-1103. Amsterdam: Elsevier.
- Eastman, E. F. and L. Fullhart, Jr. 1990. Polyolefin and ethylene copolymer-based adhesives. In: *Handbook of Adhesives*, ed. I. Skeist (3rd ed.), Chapter 23. New York: Van Nostrand Reinhold.
- Ebewele, R. O., B. H. River, and G. E. Myers. 1993. Polyamine-modified urea-formaldehyde-bonded wood joints, III: Fracture toughness and cyclic stress and hydrolysis resistance. *J. Appl. Polymer Sci.* 49:229-245.

- Ebewele, R. O., B. H. River, G. E. Myers, and J. A. Koutsky, 1991. Polyamine-modified urea-formaldehyde resins, II: Resistance to stress induced by moisture cycling of solid wood joints and particleboard. *J. Appl. Polymer Sci.* 43:1483-1490.
- Felby, C., J. Hassingboe, and M. Lund. 2002. Pilot-scale production of fiberboards made by laccase oxidized wood fibers: Board properties and evidence for cross-linking of lignin. *Enzyme Microb. Technol.* 31:736-741.
- Fengel, D. and G. Wegener. 1984. *Wood: Chemistry, Ultrastructure, Reactions*. Berlin: Walter de Gruyter.
- Fowkes, F. M. 1983. Acid-base interactions in polymer adhesion. In: *Physicochemical Aspects of Polymer Surfaces*. ed. K. L. Mittal, Vol. 2,583-603. New York: Plenum Press.
- Frazier, C. E. 2002. The interphase in bio-based composites: What is it, what should it be? In: *Proc. 6th Pacific Rim Bio-Based Composites Symposium & Workshop on the Chemical Modification of Cellulosics*. 1:206-212. Corvallis: Oregon State University.
- Frazier, C. E. 2003. Isocyanate wood binders. In: *Handbook of Adhesive Technology*, eds. A. Pizzi, and K. L. Mittal (2nd ed.), 681-694. New York: Marcel Dekker.
- Frihart, C. R. 2003. Durable wood bonding with epoxy adhesives. In: *Proceedings, 26th Annual Meeting, Adhesion Society, Inc.* 476-478. Myrtle Beach, SC, Feb. 23-26.
- Frihart, C. R. 2004. Adhesive interactions with wood. In: *Fundamentals of Composite Processing: Proceedings of a Workshop*, eds. J. E. Winandy and F. A. Kamke. General Technical Report FPL-GTR-149, 29-38. Madison, WI: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory.
- Frihart, C. R. 2006. Wood structure and adhesive bond strength. In: *Characterization of the Cellulosic Cell Wall*, eds. D. D. Stokke and L. H. Groom, 241-253. Oxford: Blackwell Publishing.
- Frihart, C. R. 2010. Soy protein adhesives. In: *McGraw Hill Yearbook of Science and Technology 2010*. 354-356. New York: McGraw Hill.
- Frihart, C. R. 2011. Wood adhesives vital for producing most wood products. *Forest Prod. J.*, 61(1):5-11.
- Frihart, C. R., R. Brandon, and R. E. Ibach. 2004. Selectivity of bonding for modified wood. In: *Proceedings, 27th Annual Meeting of The Adhesion Society, Inc.* pp. 329-33, Wilmington, NC, February 15-18.
- Frihart, C. R. and C. G. Hunt. 2010. Adhesives with wood materials: bond formation and performance. In: *Wood Handbook: Wood as an Engineering Material*, Chapter 10. Madison, WI: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory.
- Frihart, C. R., J. M. Wescott, M. J. Birkeland and K. M. Gonner 2010. Formaldehyde emissions from ULEF- and NAF-bonded commercial hardwood plywood as influenced by temperature and relative humidity. In: *Proceedings of the International Convention of Society of Wood Science and Technology and United Nations Economic Commission for Europe - Timber Committee*. WS-20, Madison, WI: Society of Wood Science Technology.
- Frisch, Jr., K.C. 2002. Chemistry and technology of polyurethane adhesives. In: *Adhesive Science and Engineering-2: Surfaces, Chemistry and Applications*, eds. M. Chadhury, and A.V. Pocius, 759-812. Amsterdam: Elsevier.
- Furuno, T. and T. Goto. 1975. Structure of the interface between wood and synthetic polymer, VII: Fluorescence microscopic observation of glue line of wood glued with epoxy resin adhesive. *Mokuzai Gakkaishi* 21(5):289-296.
- Furuno, T. and H. Saiki. 1988. Comparative observations with fluorescence and scanning microscopy of cell walls adhering to the glue on fractured surfaces of wood-glue joints. *Mokuzai Gakkaishi* 34(5):409-416.
- Geddes, K. 2003. Polyvinyl and ethylene-vinyl acetates. In: *Handbook of Adhesive Technology*, eds. A. Pizzi, and K. L. Mittal (2nd ed.), 719-729. New York: Marcel Dekker.
- Gfeller, B., M. Properzi, M. Zanetti, A. Pizzi, F. Pichelin, M. Lehmann, and L. Delmotte 2003. Wood bonding by mechanically induced *in situ* welding of polymeric structural wood constituents. *J. Appl. Polymer Sci.* 92(1):243-251.
- Gindl, W., E. Dessipri, and R. Wimmer. 2002. Using UV-microscopy to study the diffusion of melamine urea-formaldehyde resin in cell walls of spruce wood. *Holzforschung* 56:103-107.
- Gindl, W. and H. S. Gupta. 2002. Cell wall hardness and Young's modulus of melamine-modified spruce wood by nano-indentation. *Composites: Part A* 33:1141-1145.
- Good, R. J. 1967. Intermolecular and interatomic forces. In: *Treatise on Adhesion and Adhesives, Volume 1: Theory*, ed. R. L. Patrick, 9-68. New York: Marcel Dekker.
- GrOstad, K. and A. Pedersen. 2010. Emulsion polymer isocyanates as wood adhesive: a review. *J. Adhes. Sci. Tech.* 24:1357-1381.
- Hansen, C. M. and A. Björkman 1998. The ultrastructure of wood from a solubility parameter point of view. *Holz forskning* 52(4):335-344.

- Horvath, A. L. 2006. Solubility of structurally complicated materials: I. wood. *J. Phys. Chem. Ref Data* 35(1):77-92.
- Jaffe, H. L. and F. M. Rosenblum 1990. Poly(vinyl alcohol) for adhesives. In: *Handbook of Adhesives*, ed. I. Skeist (3rd ed.), Chapter 22. New York: Van Nostrand Reinhold.
- Jaffe, H. L., F. M. Rosenblum, and W. Daniels. 1990. Poly(vinyl acetate) emulsions for adhesives. In: *Handbook of Adhesives*, ed. I. Skeist (3rd ed.), 381-400. New York: Van Nostrand Reinhold.
- Johns, W. E. and T. Nguyen. 1977. Peroxyacetic acid bonding of wood. *Forest Products J.* 27(1):17-23.
- Johnson, S. E. and F. A. Kamke. 1992. Quantitative analysis of gross adhesive penetration in wood using fluorescence microscopy. *J. Adhesion* 40:47-61.
- Keckes, J., I. Burgert, K. Frühmann, M. Müller, K. Kölln, M. Hamilton, M. Burghammer, S. V. Roth, S. Stanzl-Tschegg, and P. Fratzl. 2003. Cell-wall recovery after irreversible deformation of wood. *Nat. Mater* 2:810-814.
- Keimel, F. A. 2003. Historical development of adhesives and adhesive bonding. In: *Handbook of Adhesive Technology*, eds. A. Pizzi, and K. L. Mittal (2nd ed.), 1-12. New York: Marcel Dekker.
- Kharazipour, A., A. Hüttermann, and H. D. Lüdemann 1997. Enzymatic activation of wood fibres as a means for the production of wood composites. *J. Adhesion Sci. Technol.* 11(3):419-427.
- Kinloch, A. J. 1987. *Adhesion and Adhesives Science and Technology*. London: Chapman & Hall.
- Klemarczyk, P. 2002. Cyanoacrylic instant adhesives. In: *Adhesive Science and Engineering-2: Surfaces, Chemistry and Applications*, eds. M. Chadhury, and A. V. Pocius, 847-867. Amsterdam: Elsevier.
- Kreibich, R. E., P. J. Steynberg, and R. W. Hemingway. 1998. End jointing green lumber with SoyBond. In: *Wood Residues into Revenue: Residual Wood Conference Proceedings*. November 4-5, 1997, 28-36. Richmond, British Columbia: MCTI Communications Inc.
- Kretschmann, D. 2003. Velcro mechanics in wood. *Nat. Mater* 2:775-776.
- Kretschmann, D. E. 2010. Mechanical properties of wood. In: *Wood Handbook: Wood as an Engineering Material*, Chapter 5. Madison, WI: U.S. Department of Agriculture Forest Service, Forest Products Laboratory.
- Laborie M. P. G., L. Salina, and C. E. Frazier. 2006. A morphological study of the wood/phenol-formaldehyde adhesive interphase. *J. Adhesion Sci. Technol.* 20(8):729-741.
- Lambuth, A. L. 2003. Protein adhesives for wood. In: *Handbook of Adhesive Technology*, eds. A. Pizzi, and K. L. Mittal (2nd ed.), 457-477. New York: Marcel Dekker.
- Lange, D. A., J. T. Fields, and S. A. Stirn. 2001. Finger joint application potentials for one-part polyurethanes. In: *Wood Adhesives 2000*, pp. 81-90. Madison, WI: Forest Products Society.
- Lay, D. G. and P. Cranley. 2003. Polyurethane adhesives. In: *Handbook of Adhesive Technology*, eds. A. Pizzi, and K. L. Mittal (2nd ed.) 695-718. New York: Marcel Dekker.
- Li, K., S. Peshkova, and X. Gen. 2004. *J. Am. Oil Chemists Soc.* 81:487.
- Liechti, K. M. 2002. Fracture mechanics and singularities in bonded systems. In: *Adhesive Science and Engineering-1: The Mechanics of Adhesion*, eds. D. A. Dillard and A. V. Pocius, 45-75. Amsterdam: Elsevier.
- Marcinko, J. J., S. Devathala, P. L. Rinaldi, and S. Bao. 1998. Investigating the molecular and bulk dynamics of pMDI/wood and UF/wood composites. *Forest Products J.* 48(6):81-84.
- Marcinko, J., C. Phanopoulos, and P. Teachey. 2001. Why does chewing gum stick to hair and what does this have to do with lignocellulosic structural composite adhesion. In: *Wood Adhesives 2000*, 2000, pp. 111-121. Madison, WI: Forest Products Society.
- Marra, A. A. 1980. Applications in wood bonding. In: *Adhesive Bonding of Wood and Other Structural Materials*, eds. R. F. Blomquist, A. W. Christiansen, R. H. Gillespie, and G. E. Myers. University Park, PA: Pennsylvania State University. Chapter 9.
- Marra, A. A. 1992. *Technology of Wood Bonding: Principles in Practice*. New York: Van Nostrand Reinhold.
- Marutzky, R. 1989. Release of formaldehyde by wood products. In: *Wood Adhesives Chemistry and Technology*. Vol. 2. ed. A. Pizzi, Chapter 10. New York: Marcel Dekker.
- McBain, J. W. and D. G. Hopkins. 1925. On adhesives and adhesive action. *J. Phys. Chem.* 29:188-204.
- Miller, R. S. 1990. Adhesives for building construction. In: *Handbook of Adhesives*, ed. I. Skeist (3rd ed.), Chapter 41. New York: Van Nostrand Reinhold.
- Morton, J., J. Quarmley, and L. Rossi. 2003. Current and emerging applications for natural and woodfiberplastic composites. *Seventh International Conference on Woodfiber-Plastic Composites*, 3-6. Madison, WI: Forest Products Society.
- Myers, G. E. 1984a. How mole ratio of OF resin affects formaldehyde emission and other properties: A literature critique. *Forest Prod. J.* 34(5):35-41.

- Myers, G. E. 1984b. Effect of ventilation rate and board loading on formaldehyde concentration: A critical review of the literature. *Forest Prod. J.* 34(10):59-68.
- Muszynski, L., F. Wang, and S. M. Shaler. 2002. Short-term creep tests on phenol-resorcinol-formaldehyde (PRF) resin undergoing moisture content changes. *Wood Fiber Sci.* 34(4):612-624.
- Nearn, W. T. 1965. Wood-adhesive interface relations. *Off. Dig., Fed. Soc. Paint Technol.* 37(June): 720-733.
- Nussbaum, R. 2001. Surface interactions of wood with adhesives and coatings. Doctoral thesis, KTH-Royal Institute of Technology, Stockholm, Sweden.
- Okkonen, E. A. and B. H. River. 1996. Outdoor aging of wood-based panels and correlation with laboratory aging: Part 2. *Forest Products J.* 46(3):68-74.
- Okkonen, E. A. and C. B. Vick. 1998. Bondability of salvaged yellow-cedar with phenol-resorcinol adhesive and hydroxymethylated resorcinol coupling agent. *Forest Prod. J.* 48(11/12):81-85.
- Packham, D. E. 2003. The mechanical theory of adhesion. In: *Handbook of Adhesive Technology*, eds. A. Pizzi and K. L. Mittal (2nd ed.), 69-93. New York: Marcel Dekker.
- Parbhoo, B., L.-A. O'Hare, and S. R. Leadley. 2002. Fundamental aspects of adhesion technology in silicones. In: *Adhesive Science and Engineering-2: Surfaces, Chemistry and Applications*, eds. M. Chadhury and A.V. Pocius, 677-709. Amsterdam: Elsevier.
- Parker, J. R., J. B. M. Taylor, D. V. Plackett, and T. D. Lomax. 1997. Method of joining wood, U.S. Patent 5,674,338.
- Paul, C. W. 2002. Hot melt adhesives. In: *Adhesive Science and Engineering - 2: Surfaces, Chemistry and Applications*, eds. M. Chadhury, and A.V. Pocius, 712-757. Amsterdam: Elsevier.
- Pauling, L. 1960. *The Nature of the Chemical Bond*. Ithaca, NY: Cornell University Press.
- Pearson, C. L. 2003. Animal glues and adhesives. In: *Handbook of Adhesive Technology*, eds. A. Pizzi, and K. L. Mittal (2nd ed.), 479-494. New York: Marcel Dekker.
- Petrie, E. M. 2000. *Handbook of Adhesives and Sealants*, Chapter 8. New York: McGraw-Hill.
- Pizzi, A. 1994a. *Advanced Wood Adhesives Technology*, 275-276. New York: Marcel Dekker.
- Pizzi, A. 1994b. *Advanced Wood Adhesives Technology*, 31-39 and 92-98. New York: Marcel Dekker.
- Pizzi, A. 1994c. *Advanced Wood Adhesives Technology*, 119-126. New York: Marcel Dekker.
- Pizzi, A. 2003a. Phenolic resin adhesives. In: *Handbook of Adhesive Technology*, eds. A. Pizzi, and K. L. Mittal (2nd ed.), 541-571. New York: Marcel Dekker.
- Pizzi, A. 2003b. Resorcinol adhesives. In: *Handbook of Adhesive Technology*, eds. A. Pizzi, and K. L. Mittal (2nd ed.), 599-613. New York: Marcel Dekker.
- Pizzi, A. 2003c. Natural phenolic adhesives I: Tannin, In: *Handbook of Adhesive Technology*, eds. A. Pizzi, and K. L. Mittal (2nd ed.), 573-587. New York: Marcel Dekker.
- Pizzi, A. 2003d. Natural phenolic adhesives H: Lignin. In: *Handbook of Adhesive Technology*, eds. A. Pizzi, and K. L. Mittal (2nd ed.), 589-598. New York: Marcel Dekker.
- Pizzi, A. 2003e. Urea-formaldehyde adhesives. In: *Handbook of Adhesive Technology*, eds. A. Pizzi, and K. L. Mittal (2nd ed.), 635-652. New York: Marcel Dekker.
- Pizzi, A. 2003f. Melamine-formaldehyde resins. In *Handbook of Adhesive Technology*, eds. A. Pizzi, and K. L. Mittal (2nd ed.), 653-680. New York: Marcel Dekker.
- Pizzo, B., P. Lavisci, C. Misani, and P. Triboulot 2003. The compatibility of structural adhesives with wood. *Holz als Roh- und Werkstoff* 61:288-290.
- Pizzo, B., G. Rizzo, P. Lavisci, B. Megna, and S. Berti, 2002. Comparison of thermal expansion of wood and epoxy adhesives. *Holz als Roh- und Werkstoff* 60:285-290.
- Pocius, A. V. 2002. *Adhesion and Adhesives Technology: An Introduction* (2nd ed.). Munich: Hansen
- Regert, M. 2004. Investigating the history of prehistoric glues by gas chromatography-mass spectroscopy. *J. Sep. Sci.* 27:244-254.
- Rice, J. T. 1990. Adhesive selection and screening testing. In: *Handbook of Adhesives*, ed. I. Skeist (3rd ed.), Chapter 5. New York: Van Nostrand Reinhold.
- Righettini, R. F. 2002. Structural acrylics. In: *Adhesive Science and Engineering-2: Surfaces, Chemistry and Applications*, eds. M. Chadhury, and A.V. Pocius, 823-845. Amsterdam: Elsevier.
- River, B. H. 1994a. Fracture of adhesively-bonded wood joints. *Handbook of Adhesive Technology*, eds. A. Pizzi, and K. L. Mittal (2nd ed.), 325-350. New York: Marcel Dekker.
- River, B. H. 1994b. Outdoor aging of wood-based panels and correlation with laboratory aging. *Forest Products J.* 44(11/12):55-65.
- River, B. H., R. O., Ebewe, and G. E. Myers. 1994c. Failure mechanisms in wood joints bonded with urea-formaldehyde adhesives. *Holz als Roh- und Werkstoff* 52:179-184.
- River, B. H. and V. P. Miniutti. 1975. Surface damage before gluing-weak joints. *Wood Wood Prod.* 80(7):35-36.

- River, B. H., C. B. Vick, and R. H. Gillespie. 1991. Wood as an adherend. In: *Treatise on Adhesion and Adhesives*, ed. J. D. Minford, Vol. 7.1-230. New York: Marcel Dekker.
- Robins, J. 1986. Phenolic resins. In: *Structural Adhesives, Chemistry and Technology*, ed. S. R. Hartshorn, 69-112. New York: Plenum Press.
- Rohn, C. L. 1999. Rheology of pressure sensitive adhesives. In: *Handbook of Pressure Sensitive Adhesive Technology*, ed. D. Satas (3rd ed.), Chapter 9. Warwick, RI: Satas & Associates.
- Rossitto, C. 1990. Polyester and polyamide high performance hot melt adhesives. In: *Handbook of Adhesives*, ed. I. Skeist (3rd ed.), 478-498. New York: Van Nostrand Reinhold.
- Saiki, H. 1984. The effect of the penetration of adhesives into cell walls on the failure of wood bonding. *Mokuzai Gakkaishi* 30(1):88-92.
- Sakata, I., M. Morita, N. Tsurata, and K. Morita. 1993. Activation of wood surface by corona treatment to improve adhesive bonding. *J. Appl. Polymer Sci.* 49:1251-1258.
- Salehuddin, A. 1970. A unifying physico-chemical theory for cellulose and wood and its application in gluing. PhD thesis, North Carolina State University at Raleigh.
- Satas, D. 1999a. Dynamic mechanical analysis and adhesive performance. In: *Handbook of Pressure Sensitive Adhesive Technology*, ed. D. Satas (3rd ed.), Chapter 10. Warwick, RI: Satas & Associates.
- Satas, D. 1999b. *Handbook of Pressure Sensitive Adhesive Technology* (3rd ed.). Warwick, RI: Satas & Associates.
- Sato, K. and T. Naito. 1973. Studies on melamine resin 7. Kinetics of acid catalyzed condensation of dimethylolmelamine and trimethylolmelamine. *Polymer J.* 5(2):144-157.
- Schultz, J. and M. Nardin. 2003. Theories and mechanisms of adhesion. In: *Handbook of Adhesive Technology*, eds. A. Pizzi, and K. L. Mittal (2nd ed.), 53-67. New York: Marcel Dekker.
- Selbo, M. L. 1965. Performance of melamine resin adhesives in various exposures. *Forest Products J.* 15(12):475-483.
- Segovia, C. and A. Pizzi 2009. Performance of Dowel-welded wood furniture linear joints. *J. Adhes. Sci. Tech.* 23:1293-1301.
- Skaar, C. 1984. Wood-water relationships. In: *The Chemistry of Solid Wood*, ed. R. Rowell, Chapter 3. Washington, DC: American Chemical Society.
- Skeist, I. and J. Mixon. 1990. Introduction to adhesives. In: *Handbook of Adhesives*, ed. I. Skeist (3rd ed.), Chapter 1. New York: Van Nostrand Reinhold.
- Smith, L. A. 1971. Resin penetration of wood cell walls-Implications for adhesion of polymers to wood. PhD thesis, Syracuse University, Syracuse, NY.
- Smith, L. A. and W. A. Cote. 1971. Studies on the penetration of phenol-formaldehyde resin into wood cell walls with SEM and energy-dispersive x-ray analyzer. *Wood Fiber J.* 56-57.
- Smith, M. J., H. Dai, and K. Ramani. 2002. Wood-thermoplastic adhesive interface-Method of characterization and results. *Int. J. Adhesion Adhesives* 22:197-204.
- Stamm, A. J. and R. M. Seborg. 1936. Minimizing wood shrinkage and swelling Treating with synthetic resin-forming materials. *Ind. Eng. Chem.* 28 (10): 1164-1169.
- Stark, N. M., Z. Cai, and C. Carll. 2010. Wood-based composite materials panel products, glued-laminated timber, structural composite lumber, and wood-nonwood composite materials. In: *Wood Handbook: Wood as an Engineering Material*, Chapter 11. Madison, WI: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory.
- Stehr, M. and I. Johansson. 2000. Weak boundary layers on wood surfaces. *J. Adhesion Sci. Technol.* 14:1211-1224.
- Stofko, J. 1974. The autoadhesion of wood. PhD thesis, University of California, Berkeley.
- Suddell, B. C. and W. J. Evans. 2003. The increasing use and application of natural fiber composite materials within the automotive industry. *Seventh International Conference on Woodfiber-Plastic Composites*, pp. 7-14. Madison, WI: Forest Products Society.
- Sun, X. S. 2005. Isolation and processing of plant materials. In: *Bio-Based Polymers and Composites*, eds. R. P. Wool and X. S. Sun, 33-55. Burlington, MA: Elsevier-Academic Press.
- Tarkow, H. 1979. Wood and moisture. In: *Wood: Its Structure and Properties*, ed., F. F. Wangaard, 155-185. University Park, PA: Pennsylvania State University.
- Tarkow, H., W. C. Feist, and C. F. Southerland, 1965. Interpenetration of wood and polymeric materials, II: Penetration versus molecular size. *Forest Products J.* 16(10):61-65.
- Tsoumis, G. 1991. *Science and Technology of Wood: Structure, Properties and Utilization*. New York: Van Nostrand Reinhold.
- Updegaff, I. V. 1990. Amino resin adhesives. In: *Handbook of Adhesives*, ed. I. Skeist (3rd ed.), Chapter 18. New York: Van Nostrand Reinhold.
- Vick, C. B. 1973. Gap-filling phenol-resorcinol resin adhesives for construction. *Forest Products J.* 23(11):33-41.

- Vick, C. B. 1995. Coupling agent improves durability of PRF bonds to CCA-treated southern pine. *Forest Products J.* 45(3):78-84.
- Vick, C. B. 1997. More durable epoxy bonds to wood with hydroxymethylated resorcinol coupling agent. *Adhesives Age* 40(8):24-29.
- Vick, C. B., A. W. Christiansen, and E. A. Okkonen, 1998. Reactivity of hydroxymethylated resorcinol coupling agent as it affects durability of epoxy bonds to Douglas-fir. *Wood Fiber Sci.* 30(3):312-322.
- Vick, C. B. and E. A. Okkonen. 1998. Strength and durability of one-part polyurethane adhesive bonds to wood. *Forest Products J.* 48(11/12):71-76.
- Vick, C. B., K. H. Richter, and B. H. River. 1996. Hydroxymethylated resorcinol coupling agent and method for bonding wood. U.S. Patent 5,543,487.
- Wang, W., D. J. Gardner, and M. G. D. Baumann. 2003. Factors affecting volatile organic compound emissions during hot-pressing of southern pine particleboard. *Forest Products J.* 53(3):65-72.
- Winandy, J. E. and F. A. Kamke. 2004. *Fundamentals of Composite Processing: Proceedings of a Workshop*, General Technical Report FPL-GTR-149. Madison, WI: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory.
- Wellons, J. D. 1983. The adherends and their preparation for bonding. In: *Adhesive Bonding of Wood and Other Structural Materials*, eds. R. F. Blomquist, A. W. Christiansen, R. H. Gillespie, and G. E. Myers, Chapter 3. University Park, PA: Pennsylvania State University.
- Westermarck, U. and O. Karlsson. 2003. Auto-adhesive bonding by oxidative treatment of wood. In: *Proceedings, 12th Intl. Symp. Wood and Pulping Chem.* Vol. 1. 365-368. Madison, WI, June 9-12.
- Wescott, J. M., C. R. Frihart, and A. E. Traska. 2006a. High-soy-containing water-durable adhesives. *J. Adhes. Sci. Technol.* 20(8):859-873.
- Wescott, J. M., C. R. Frihart, A. E. Traska, and L. Lorenz. 2006b. in: *Wood Adhesives 2005*, 263-269. Madison, WI: Forest Products Society.
- Wescott, J. and C. Frihart. 2011. Sticking power from soya beans. *Chemistry & Industry*. February 7, 21-23.
- Widsten, P., J. E. Laine, S. Tuominen, and P. Qvintus-Leino. 2003. Effect of high defibration temperature on the properties of medium-density fiberboard (MDF) made from laccase-treated hardwood fibers. *J. Adhesion Sci. Technol.* 17(11):67-78.
- Williams, J. R. 2010. The CARB rule: Driving technology to improve public health. In: *Proceedings of the International Conference on Wood Adhesives 2009*, eds. C. R. Frihart, C. G. Hunt, and R. J. Moon, pp. 12- 16. Madison, WI: Forest Products Society.
- Wolfrum, J. and G. W. Ehrenstein. 1999. Interdependence between the curing, structure, and the mechanical properties of phenolic resins. *J. Appl. Polymer Sci.* 74:3173-3185.
- Wool, R. P. 2002. Diffusion and autoadhesion. In: *Adhesive Science and Engineering-2: Surfaces, Chemistry and Applications*, eds. M. Chadhury and A. V. Pocius, 351-401. Amsterdam: Elsevier.
- Wool, R. P. 2005. Fundamentals of fracture in bio-based materials. In: *Bio-Based Polymers and Composites*, eds. R. P. Wool and X. S. Sun, 149-201. Burlington, MA: Elsevier-Academic Press.
- Wu, S. 1982a. *Polymer Interface and Adhesion*. 29-65. New York: Marcel Dekker.
- Wu, S. 1982b. *Polymer Interface and Adhesion*. 449-463. New York: Marcel Dekker.
- Yelle, D. J., J. Ralph, and C. R. Frihart 2011a. Delineating pMDI model reactions with loblolly pine via solution-state NMR spectroscopy. Part 1. Catalyzed reactions with wood models and wood polymers. *Holzforchung* 65:131-143.
- Yelle, D. J., J. Ralph, and C. R. Frihart. 2011b. Delineating pMDI model reactions with loblolly pine via solution-state NMR spectroscopy. Part 2. Non-catalyzed reactions with the wood cell wall. *Holzforchung* 65:144-154.
- Young, R. A., M. Fujita, and B. H. River. 1985. New approaches to wood bonding: A base-activated lignin system. *Wood Sci. Technol.* 19:363-381.

# Handbook of Wood Chemistry and Wood Composites

---

SECOND EDITION

---

Edited by **Roger M. Rowell**



**CRC Press**

Taylor & Francis Group

Boca Raton London New York

---

CRC Press is an imprint of the  
Taylor & Francis Group, an informa business

CRC Press  
Taylor & Francis Group  
6000 Broken Sound Parkway NW, Suite 300  
Boca Raton, FL 33487-2742

© 2013 by Taylor & Francis Group, LLC  
CRC Press is an imprint of Taylor & Francis Group, an Informa business

No claim to original U.S. Government works

Printed in the United States of America on acid-free paper  
Version Date: 20120725

International Standard Book Number: 978-1-4398-5380-1 (Hardback)

This book contains information obtained from authentic and highly regarded sources. Reasonable efforts have been made to publish reliable data and information, but the author and publisher cannot assume responsibility for the validity of all materials or the consequences of their use. The authors and publishers have attempted to trace the copyright holders of all material reproduced in this publication and apologize to copyright holders if permission to publish in this form has not been obtained. If any copyright material has not been acknowledged please write and let us know so we may rectify in any future reprint.

Except as permitted under U.S. Copyright Law, no part of this book may be reprinted, reproduced, transmitted, or utilized in any form by any electronic, mechanical, or other means, now known or hereafter invented, including photocopying, microfilming, and recording, or in any information storage or retrieval system, without written permission from the publishers.

For permission to photocopy or use material electronically from this work, please access [www.copyright.com](http://www.copyright.com) (<http://www.copyright.com/>) or contact the Copyright Clearance Center, Inc. (CCC), 222 Rosewood Drive, Danvers, MA 01923, 978-750-8400. CCC is a not-for-profit organization that provides licenses and registration for a variety of users. For organizations that have been granted a photocopy license by the CCC, a separate system of payment has been arranged.

Trademark Notice: Product or corporate names may be trademarks or registered trademarks, and are used only for identification and explanation without intent to infringe.

Visit the Taylor & Francis Web site at  
<http://www.taylorandfrancis.com>

and the CRC Press Web site at  
<http://www.crcpress.com>