I. INTRODUCTION

Among the various structural adhesives commercially available today, epoxies are the most widely accepted and used. A recent market study\(^1\) showed that epoxy structural adhesives account for approximately 41% of all structural adhesives sold, and it is expected that they will maintain this market share over at least the next several years. Numerous references exist, both in the patent and journal literature, describing every facet of these adhesives. It is not the intention to review all of the available information. Rather, this chapter will concentrate on three main areas: (1) A general description of epoxy adhesives; (2) A discussion of commercially available raw materials, formulations, properties, and uses of epoxy adhesives; (3) A review of developments in epoxy adhesives since 1979. Earlier work has been discussed in several reviews, and will not be covered in detail in this chapter.\(^2-12\)

Epoxy structural adhesives typically contain several components, the most important being the epoxy resin around which the adhesive is formulated. Epoxy resins run the gamut of properties, ranging from low-viscosity liquids to high-melting solids. They can be aromatic or aliphatic, cyclic or acyclic, monofunctional or polyfunctional. The one feature common to all of these resins is the three-membered, oxygen-containing epoxy (oxirane) group (1). To the base resins can be added a variety of materials; co-curing agents, cure catalysts, toughening and/or flexibilizing materials, and fillers. These additives contribute to the properties of the formulated adhesive. For
instance, they can improve the cured adhesive modulus, impart thixotropy, or provide electrical conductivity. Depending on the particular formulation, the adhesives can range from low-viscosity, free-flowing liquids, useful in potting applications, to solid films, useful in bonding large aircraft components. Cure temperatures can also be varied, ranging from subzero to 350°F.

Although their properties may vary considerably, there are a number of characteristics common to all epoxy adhesives. They are usually compositions containing 100% solids which emit essentially no volatiles upon curing. Bonding operations can, therefore, be performed at low pressures without expensive solvent- or water-removal equipment on impervious substrates, such as metals and plastics. Upon cure of epoxy adhesives, some shrinkage of the adhesive bondline takes place, a phenomenon common to most polymerizing systems. However, the amount of shrinkage is typically very small, especially in filled systems. As a consequence, there is relatively little residual stress developed in the bonded assembly. This results in high-strength bonds being obtained. Typical epoxy adhesives have very good cohesive strength and low creep under applied stress, due to the fact that they are crosslinked and can participate in hydrogen bonding interactions (arising from the resins themselves and the curatives). Because of the presence of both polar and nonpolar moieties in epoxy resins and adhesives, epoxy-based adhesives display good adhesion to a wide variety of substrates, such as metals, plastics, glasses, and woods. The combination of good adhesive and cohesive strength can frequently result in the substrates being the weak link in bonded assemblies. In service conditions involving exposure to a wide variety of environments, including water and solvents, epoxy adhesives can be formulated that have good resistance to these agents. However, as discussed in Chapter 8, structural adhesive joints can be adversely affected by severe environmental exposure, owing to attack at the adhesive/substrate interface.

Monofunctional epoxy resins, such as phenylglycidyl ether, can be used alone in adhesive formulations, but they are generally only used as reactive diluents or curable solvents. This is due to the fact that monofunctional epoxy resins give cured adhesives with low (if any) crosslink density, which results in poor heat, creep, and solvent resistance. Therefore, polyepoxy functional resins are most commonly used in adhesives. The most important class of polyfunctional epoxy resins are the aromatic resins, such as those based on bisphenol A–epichlorohydrin condensates (2). Depending on the molecular weight and molecular weight distribution of these condensates, they can either be viscous liquids or solids of varying melting