Chapter 5

EFFECT OF CHEMORHEOLOGY ON EPOXY RESIN PROPERTIES

A. APICELLA

Polymer Engineering Laboratory, Department of Material and Production Engineering, University of Naples, Italy

SUMMARY

Chemoviscosity is the term which denotes the variations in viscosity induced by chemical reactions, and chemorheology is the science which studies the viscoelastic behaviour of reacting systems. This chapter briefly reviews some of the theoretical and experimental aspects of the chemorheology of epoxy resin systems.

5.1. INTRODUCTION

The synthesis and the processing of thermoplastics are two distinct operations. These polymeric materials soften and flow on heating but return to the solid state when cooled. Thermosets, on the other hand, are polymerised and processed in a single irreversible operation which transforms a low molecular weight liquid into a cross-linked polymer. Although thermosets, as solid materials, should potentially have superior engineering properties they often do not possess good reproducibility in their characteristics, in contrast to thermoplastic polymers, because of the less controlled and more complex formation process. The cure of a reactive prepolymer involves the transformation of low molecular weight monomers or oligomers from liquid to rubber and solid state, as a result of the formation of a polymeric network by the chemical reaction of the reactive groups in the system. Gelation
and vitrification, which are two macroscopic phenomena encountered during this process, strongly alter the viscoelastic behaviour of the material.

Gelation, associated with a dramatic increase in viscosity, occurs at a degree of reaction calculable for each reacting system according to the theory first proposed by Flory.\(^1\) On a molecular level, the increase in viscosity corresponds to the increase in molecular weight, and to the incipient formation of infinite branched molecules. The growth and branching of the polymer chains occur in the liquid state, while the system is still soluble and fusible, whereas the infinite network is developed after the gel point, by intramolecular reactions of the branched molecules, finally leading to an insoluble cross-linked solid.

Vitrification is the formation of a glassy solid, which usually follows gelation, occurring as a consequence of the network becoming denser through further cross-linking. Vitrification may prevent further reaction by reducing the mobility of the unreacted functional groups. Although chemical control is the basic assumption of all statistical treatments of curing, in some cases, cure may also be controlled by physical factors, such as diffusion constraints in the glass transition region, leading to the formation of nonhomogeneous structures, which indirectly alter the physical properties and durability of cured epoxy resins.\(^2\) Knowledge of the structural parameters of the cured systems, as a function of the reactivity of the functional groups and their stoichiometric ratios, is important for the elucidation of the curing reaction, the control of processing, and application properties.

The chemical characterisation and reproducibility of thermosetting epoxies, which are the dominant form of polymeric matrices for carbon fibre composites, is therefore an important area of concern.

Completed studies of graphite epoxy composites for aerospace applications have revealed two dominant classes of hygrothermal degradation mechanisms: microscopic defects in the molecular network structure of the matrix phase, and macroscopic defects such as voids, bubbles, debonded and broken fibres produced during the processing of the composite.

The influence of the matrix nodular structure on the durability in aggressive environments, the mode of failure and mechanical properties of TGDDM–DDS* based composites has been reported in the

* Tetraglycidyl diamino diphenyl methane cured with diphenyl dimethyl sulphone.