

Influence of Phenoxy Addition on the Curing Kinetics for Uncatalyzed and Catalyzed Cyanate Ester Resin

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ABSTRACT: The curing behavior of the dicyanate ester of bisphenol-A (DCBA) modified with poly(hydroxy ether of bisphenol-A) (phenoxy) is studied by differential scanning calorimetry in dynamic and isothermal tests at temperatures between 120 and 240°C. The addition of phenoxy to DCBA produces an increase in the reaction rate and a decrease in the temperature of maximum reaction rate for the uncatalyzed resin, and also for the system catalyzed with copper (II) acetyl acetonate/nonylphenol. The exothermic heat of curing for the mixtures is also dependent on the phenoxy content. These facts evidence a catalytic effect of phenoxy on the curing of the cyanate ester resin, even though an autocatalytic behavior is observed

for all uncatalyzed DCBA/phenoxy mixtures. A simplified mechanistic kinetic model is used to calculate the kinetic parameters. For the uncatalyzed systems, a decrease in the kinetic constant for the initiation reactions, and an increase in the propagation constant are measured when the cyanate content increases. The thermal activation energy for the initiation reaction of the catalyzed systems is lower than that of the uncatalyzed ones, and it depends on the weight fraction of cyanate in the mixture. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 2869–2880, 2010

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INTRODUCTION

Polycyanurates, which result from the thermal cure of dicyanate esters, are a family of thermosetting resins which possess an excellent combination of thermal, electrical, and mechanical properties, making them an ideal matrix for electronic and aerospace composite applications. The characteristic properties of polycyanurates are a high thermal stability, low outgassing, high radiation resistance, dimensional stability at solder temperatures and low moisture absorption.^{1–4} In addition, they have epoxy-like processability, but their thermal stability is lower than that of other thermosetting resins such as bismaleimides, and they have some other drawbacks. For instance, like other thermosetting resins, they are too brittle to be used alone in certain structural applications.

The curing of dicyanate ester monomers occurs through thermal cyclotrimerization of cyanate ester groups to give polycyanurates. Cyanate esters can cure with or without the presence of catalyst. How-

ever, uncatalyzed homopolymerization will proceed slowly at temperatures around 170–200°C, but more useful polymerization and curing rates can be achieved by the addition of specific catalysts to develop attractive curing rates. Different catalyst systems may be used for the curing to be more efficient in terms of reducing the curing temperature and attaining high conversion degrees, while minimizing weight losses by volatility. Generally, these catalyst packages comprise metallo-organic compounds such as the carboxylates and chelates of copper, zinc, manganese, cobalt, tin and nickel, in the presence of a hydrogen donor, such as an alkyl phenol, known as co-catalyst, which is used to dissolve the former. In this way, the presence of phenolic initiators and metal catalysts in the cyanate system strongly influence the kinetic evolution of the resin.

To overcome their weaknesses and to improve their performance, polycyanurates have been blended with other thermosets. Among them, epoxies^{5–11} and specially, bismaleimides^{12–15} have evidenced great interest. Also, for improving their low fracture toughness, cyanate esters have been frequently modified by means of the addition of certain thermoplastics and elastomers. Usually, amorphous thermoplastic polymers of high glass transition temperature, T_g , such as polysulphone^{16–21} or polyetherimide^{20,21} among others, are preferred as a way of

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