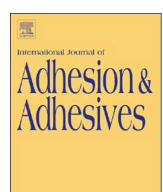
International Journal of Adhesion & Adhesives 74 (2017) 6–14

Contents lists available at ScienceDirect

International Journal of Adhesion and Adhesives

journal homepage: www.elsevier.com/locate/ijadhadh



Critique of dielectric cure monitoring in epoxy resins – Does the method work for commercial formulations?

Lisa Garden, Richard A. Pethrick*

WestCHEM, Department of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow G1 1XL, United Kingdom

ARTICLE INFO

Keywords:
Dielectric relaxation
Dipole relaxation
Epoxy resin
Differential scanning calorimetry
Curometer
Viscosity

ABSTRACT

Dielectric techniques can be used as an in situ monitor of resin cure. This study reports measurements on two commercial resin formulations and aims to establish the extent to which identifiable turning points in the dielectric behaviour are dependent of the formulation used. Complementary curometer and differential scanning calorimetry data are used to monitor the progress of cure and are compared with the dielectric data. System [A] is a simple epoxy amine system, whilst system [B] is a blend of both epoxy and amine resins. It is clear that without calibration of the dielectric data against other methods it is difficult to unambiguously derive absolute cure information on a system not previously studied. However, dielectric data does allow identification of the points at which gelation and vitrification occur and demonstrates its utility as an in situ monitoring method for the cure process.

1. Introduction

Optimisation of the state of cure in situ is very important in the fabrication of adhesive bonded structures, coatings and composite structures. The thermal mass of the substrate and the influence of fillers can significantly influence the magnitude of the temperature rise produced through the reaction exotherm and hence the degree of cure achieved. In autoclave fabrication of composite structures, it is important to know when pressure should be applied to consolidate a moulding or aid the creation of a uniform adhesive bonded structure. Application of pressure too early in the cure cycle, when the resin is in a low viscosity state, can lead to thinning of a joint or the creation of resin rich and resin depleted areas in a composite. If the pressure is applied too late, then compaction will not occur and voiding may result.

The use of dielectric spectroscopy in cure monitoring of epoxy resin systems has been explored by a number of researchers [1–15], and involves monitoring changes in the dielectric permittivity ε'(ω) and dielectric loss ε"(ω) as cure proceeds. In previous studies, the cure of epoxy resins with various aliphatic diamines [7–10], triethylenetetramine [11], aromatic diamines [12] and mixtures containing a toughening agent [13,14], have been reported. Cessation of ionic conduction is an indication of gelation and dipole relaxation can be used to follow the growth of the epoxy network. In many cases the dipole relaxation processes retain their original shape but shift in frequency as the matrix changes from a gel to a glass [15–17].

Viscosity is the primary physical property which changes during cure and reflects the topography of the growing matrix and influences both ionic mobility and dipole relaxation rates [18]. In general, it is only once the molecular weight of the polymer entities are greater than 10k that there is a significant change in the ion mobility and ionic conduction is observed to cease. Ion conduction is sensitive to the local viscosity in the resin and reflects the growth in topography as cure proceeds. Further reductions in the dielectric loss and permittivity allow vitrification to be identified and are sensitive to the local chain mobility and hence degree of cure of the resin.

This study explores the cure characteristics of two commercial adhesive systems. Unlike the cure systems studied previously, these formulations contain components with a variety of different functionalities, designed to enhance the rate of cure and improve the final mechanical properties of the resin matrix. The different reaction rates will influence the cure process and the topography created as a function of time and this is reflected in the path by which gelation and vitrification are achieved.

Comparison of the data from these two very different systems and correlation of results obtained from other techniques allows a better understanding of the dielectric method as an in situ monitor of the cure process.

* Corresponding author.
E-mail address: r.a.pethrick@strath.ac.uk (R.A. Pethrick).

http://dx.doi.org/10.1016/j.ijadhadh.2016.12.005
Accepted 12 December 2016
Available online 16 December 2016
0143-7496/ © 2016 Elsevier Ltd. All rights reserved.

Table 1
Epoxy resin and amine hardeners used in the formulations studied.

Component	Structure
bisphenol A-(epichorohydrin); epoxy resin (no. av. molecular wt<700) DEGBA	
1,4-bis(2,3-epoxypropoxy) butane BDGE	
diglycidylether of polypropyleneglycol PPGDGE	
diglicidylether of bisphenol F DGEBF	
C12/C14 alkylglycidylether	n = 10, 12
3-aminomethyl-3,5,5-trimethylcyclohexylamine Isophoronediamine	
2-piperazin-1-ylethylamine	
polypropylene glycol bis (2-aminopropyl ether) Jeffamine D	
m-phenylenebis (methylamine)	
2,2,4(2,4,4)-trimethyl-1,6-hexanediamine -TMHDA	R = H, R' = CH_3 or R = CH_3, R' = H

2. Experimental

2.1. Materials and cure characteristics

The chemical structures of the components used are summarised in Table 1. The formulations contained various amounts of epoxy and hardener components, adjusted to achieve different initial viscosities, pot life, cure rates and mechanical properties in the cured resin. In both cases, cure was carried out at the stoichiometric ratios of epoxy and hardener. Small amounts, typically < 0.5 w/w% of additives; 4-tert-butyl phenol, benzyl alcohol and petroleum solvent were present to adjust the viscosity or catalyse the reaction [19]. The two formulations studied are summarised in Table 2.

Both systems are based on bisphenol A-(epichlorohydrin) which has an ‘n’ value of ~1.3 and are formulated to be close to stoichiometric ratios of epoxy and hardener. System (1) has a pot life of *ca.* 60 minutes at 20 °C and was studied at 25 °C, 30 °C, 35 °C, 40 °C and 45 °C. System (2) is designed to be used between 15 and 25 °C with a pot life

Download English Version:

https://daneshyari.com/en/article/5014727

Download Persian Version:

https://daneshyari.com/article/5014727

Daneshyari.com