Deformation of Cartridge Assembly

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Abstract

Epoxy is usually used in making cartridge assembly in inkjet printing. Adequate cross-linking or curing is necessary to bring stable cartridge assembly. Tri and tetra functional amines are used in curing epoxies. DSC, RHEOMETRY and fracture tests were done epoxies with and without blends with butyl rubber liquid. In rheometry, experiments were done in a parallel plate rheometer ARES to analyze cross-linking of epoxy using different levels of tri and tetrafunctional amines. Elastic and viscous modulus were measured as function of time at a fixed shearing frequency. Reaction kinetic equation was set up, equilibrium modulus and cross-link density was calculated. This parameter was correlated to breakage of the cartridge assembly

Introduction

In Thermal Inkjet Printer, assembling a printhead module for a printhead assembly consists of the steps of: mounting at least two printhead integrated circuits to an upper surface of at least one fluid distribution member,with each having nozzles formed therein for printing fluid onto the surface of print media; and fixedly attaching with an adhesive material a lower surface of the at least one fluid distribution member onto an upper surface of a support member having fluid delivery channels for the nozzles. Another step consists of adhering an electrical connector to a section of the upper surface of the fluid distribution member for connecting electrical signals to the printhead integrated circuits. The adhesive material used may be a curable resin such as epoxy, in which case, the attaching step includes the step of curing the curable resin so as to fix the fluid distribution member to the support member.. Anothere attaching step may include the step of depositing the curable resin about apertures on the upper surface of the support member which extend to the fluid delivery channels. Another attaching step may include the step of curing the curable resin so as to form sealing gaskets about the apertures of the support member and associated apertures of the fluid distribution member.

Epoxy resins are reactive intermediates usually composed of a mixture of oligomeric materials containing one or more epoxy groups per molecule. To convert epoxy resins into useful products they must be “cured” or crosslinked by chemical reaction into a three-dimensional network by the use of a curing agent. Crosslinking agents or curing agents, as they are also called, function by reacting with or causing the reaction of epoxide or the hydroxyl groups in the epoxy resin. Cross-linking proceeds by only two possible routes: the reaction of epoxy group with themselves (homopolymerization), or the reaction of the epoxy and/or hydroxyl functionality with a reactive intermediate or curing agent. There are three major chemical types of curing agents employed in structural applications of epoxy resins; amines, acid anhydrides, and Lewis acids and bases. The amines comprise well over half volume of the total curing agent market. The amines can be further divided into aliphatic, cycloaliphatic, aromatic, tertiary amines as well as heterocyclic nitrogen compounds (imidazoles). All amines, including the aliphatic, cycloaliphatic, and aromatic amines, react with the epoxide ring by addition reaction without formation of by-products [1]. The amine addition to an epoxide rings in shown in Figure 1.

Aromatic amine cured epoxy resins, where the diglycidyl ether of bisphenol-A (DGEBA) resin cured with meta-phenylene diamine (MPDA) is a representative member, are the most widely used matrix materials for preparing conventional composites. Resins of this class are brittle and their ability to absorb energy during failure is limited[2].

Epoxy resins are unique among all the thermosetting resins due to several factors viz. minimum pressure is needed for fabrication of products normally used for thermosetting resins, shrinkage is much lower and hence lower residual stress in the cured product than that encountered in the vinyl polymerization used to cure unsaturated polyester resins,

use of a wide range of temperature by judicious selection of curing agent with good control over the degree of crosslinking, availability of the resin ranging from low viscous liquid to tack free solid etc.

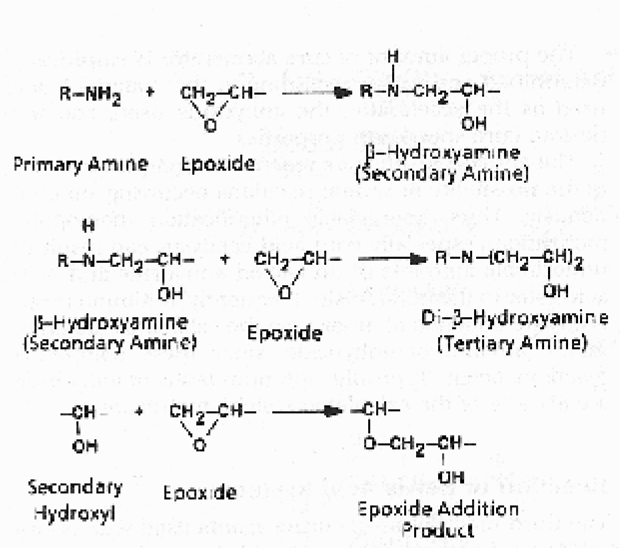

Figure 1. *Crosslinking reaction between epoxide ring and primary amine.*

Because of these unique characteristics and useful properties of network polymer like high strength, very low creep, excellent corrosion and weather resistance, elevated temperature service capability and adequate electrical properties, epoxy resins are widely used in structural adhesives, surface coatings, engineering composites, electrical laminates[3].

The major drawback of epoxy resins is that in the cured state they are brittle materials having fracture energies some two orders of magnitude lower than engineering thermoplastics and three orders lower than metal. This inherent brittleness causes the poor damage tolerance to impact of the composites made from epoxy resin and poor peeling and shear strength of epoxy based adhesive. Hence toughening of epoxy resins has been the subject of intense investigations throughout the world. The epoxy resins are most successfully toughened by incorporating a rubbery filler as a distinct phase of microscopic particles. This can be achieved in two ways : 1) blending with functionalized liquid rubber having restricted solubility which is miscible initially, with the epoxy hardener mixture and undergo phase separation at a certain stage of the curing reaction leading to two phase microstructure 2) by dispersing preformed rubbery particles directly in the epoxy matrix without undergoing phase separation[4].

The curing reaction of epoxy resin is highly exothermic. Therefore differential scanning calorimetry (DSC) which measures the heat flow from the reacting system is a very convenient tool to study the overall reaction between epoxy resin and crosslinking agent. Different models have been used to determine activation energy. Most direct being Ozawa model[5].

$$In\beta = A' - 0.4567.\frac{E}{RT} \tag{1}$$

Where β is the heating rate and for a given conversion degree, the activation energy, E, and the constant, A', can be obtained from linear regression according to equation (1). Following is an equation attributed to Awami that shows relation between curing rate, the rate of conversion $\frac{d\alpha}{dt}$ and activation energy E_a and extent of curing α , fractional conversion, where n is the reaction order for a given temperature T.

$$\alpha' = \frac{d\alpha}{dt} = A\exp\left(-\frac{E_a}{RT}\right)(1-\alpha)^n \tag{2}$$

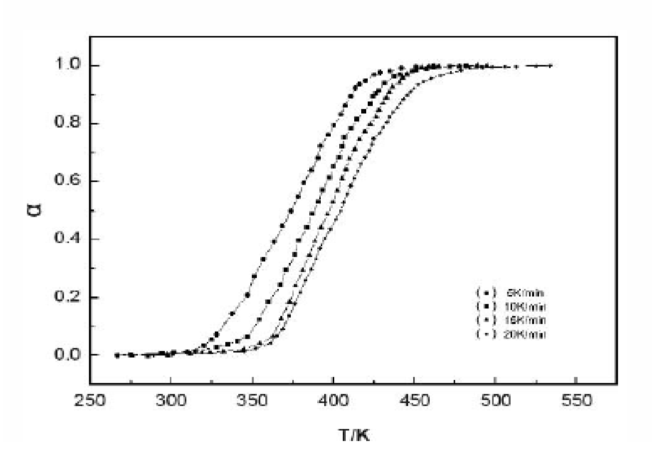

Figure 2 below gives extent of conversion α at temperature T for different heating rates

Activation energy of epoxy was determined to be 111.5 kJ/mole

Methods and Materials

EPON 828 and EPICURE 3234 were obtained from Resolution Performance Products Inc. EPON 828 is a difunctional bisphenol A epichlorohydrin is a liquid epoxy resin and used as general purpose epoxy pre-polymer.

Epicure 3234 curing agent is an aliphatic amine with the chemical name of triethylene tetra amine (TETA). Differential Scanning Calorimetry and rheometry was used to study curing

kinetics and cured materials were tested for fracture toughness.

kinetics of curing. Additionally, curing of epoxy was undertaken by first blending epoxy with the elastomer carboxyl terminated butadiene acrylonitrile (CTBN) copolymer and then crosslinking with EPICURE 3234.at 150C.

Results and Discussion.

The isoconversional methods are based on dynamic analysis by DSC. On curing samples at different heating rates extent of cure can be plotted as function of temperature

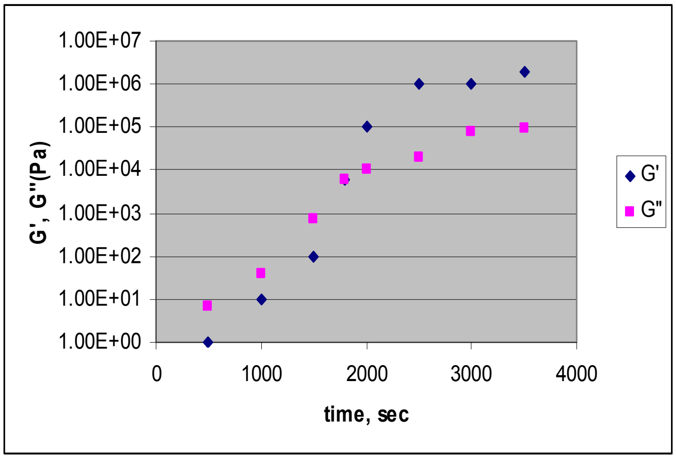

***Figure 3** - Storage modulus (G') and loss modulus (G'') as a function of cure time at 150 0C for the cured epoxy.*

On plotting the storage (G') and loss moduli (G'') as a function of time at 150 C for the cured epoxy as shown in Fig. 3. The G'/G'' crossover is taken as the gel points for epoxy systems.

Cosslink density is calculated from plateau in storage modulus by using theory of rubber elasticity. The values of crosslinking density may be calculated by using equation (3) as given by Kaji et al [5]

$$\rho = \frac{E'}{3RT} \tag{3}$$

where E′ is the storage modulus at Tg + 50°C, R the gas constant and T the absolute temperature at Tg + 50°C. The storage modulus decreased with increase in temperature of curing indicating lower crosslink density. At lower temperature, the cured material was hard and as the temperature increased the cured material became less hard.

The loss modulus (E″) and the loss tangent (tan δ) values, however, showed an increasing trend with rise of temperature up to a maximum (peak) followed by a gradual fall in both cases.

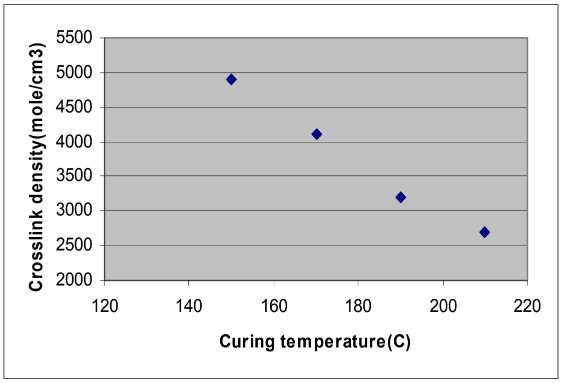

Figure 4 shows the dependence of crosslink density on curing temperature

It has been shown by Verchere et al [6] that gradual drop of storage modulus with addition of CTBN revealed increased flexibility of the blended epoxy terminated butadiene/acrylonitrile rubber in an aliphatic amine cured DGEBA epoxy.

The damping characteristics also changed with the successive concentration of CTBN in the epoxy matrix as apparent in loss modulus and tanδ graphs. At higher rubber content, however, the matrix might be less restrained by the presence of rubber globules with sizes increased by rubber particles coalescence, cavitations and homogeneity of the system[7].

The pattern of morphology observed for the unblended epoxy was the characteristics of brittle systems having smooth, glassy fractured surfaces with cracks in different planes. In contrast SEM of CTBN-modified systems showed the presence of precipitated, discrete rubber particles that were dispersed throughout the epoxy matrix revealing the presence of two-phase morphological feature.

The size of the precipitated rubber particles increased with increasing rubber content in the formulation. This increase in size of the dispersed rubber phase might be associated with the coalescence of the dispersed rubber particles

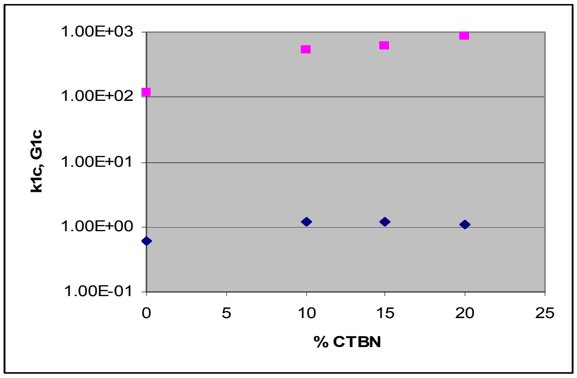

Figure 5 shows comparison of fracture toughness, K1c and fracture energy. G1c with CTBN in epoxy matrix.

Fracture toughness was compared for cured epoxy with epoxy containing butyl rubber and it was found that composite had significantly higher fracture toughness.

Pearson and Yee [8] have studied the effect of particle size on the fracture properties of rubber toughened epoxy network having particle size ranging from 0.2-200 mm. They found that large, 100 mm diameter particles are not as effective in providing a toughening effect whereas small, 0.1 mm diameter particles appear to be the most efficientand provides over a ten fold increase in fracture energy.

Conclusion

Models on curing of epoxy used in cartridge assembly used in thermal inkjet are analyzed. Amine cured epoxy is brittle but brittleness can be reduced by increasing the curing temperature at the expense of reduction in hardness. Optimization of cured material is to increase its toughness by blending with carboxyl terminated copolymer of acrylonitrile and butadiene CTBN which would significantly improve fracture properties.

References

[1] Bouer, R. S., *Epoxy Resin Chemistry*, Advances in Chemistry Series, 114, American Chemical Society, Washington, DC, 1979.
[2] Um M.K., calorimetry, *Compos. Sci. Technol.*, **62**, 29-40(2002).
[3] Kim, J.; Zhao, M.; Zhang, R. Z. , *Chin J Funct Polym*. 13 , 207. 2000.
[4] Hwang, J. F. . Manson, J. A, Hertzberg, R. W. Miller, G. A.and Sperling, H. L. *Polym. Eng. Sci.*, **29**, 1466 (1989).
[5] Kaji M, Nakahara K and Endo T J. Appl. Polym. Sci. 74, 690(1999)
[6] Verchere D, Sautereau H, Pascault J P and Mosechain S MJ. Appl. Polym. Sci. 42, 717 (1991)
[7] Tripathi G and Srivastava D 2007 Mater. Sci. Engg. A443 262 (2007)
[8] Pearson R. A.and Yee, A. F. *J. Mater. Sci.*, **26**, 3828 (1991)

Author Biography

Suresh Ahuja received his BS in physics and chemistry from the Punjab University (1959), his MS in Soil Physics from Indian Research Institute (1961) and his PhD in Polymer Physics from Polytechnic Institute of Brooklyn (1967). After working over 37 years at Xerox with several years as Principal Scientist he retired. He has over twenty(20) patents.. He has published over 60 publications and presentations at international conferences. He is a member of APS, ASME, SOR and IST.