

NON-DESTRUCTIVE METHOD FOR DETERMINING THE EXTENT OF CURE OF A POLYMER

FIELD OF THE INVENTION

This invention relates to a non-destructive method for determining the extent of cure of a polymer. The method is particularly suitable for in-line manufacturing processes wherein polymer films or coatings are cured, for example, in the manufacture of multilayer printed circuit boards.

BACKGROUND OF THE INVENTION

In many manufacturing processes, the ability to repeatedly and uniformly cure a polymer system is highly important, if not critical, to the resultant product. Heretofore, methods for determining the degree of cure were not only time consuming, but were also destructive and could not be applied as an "in-line" process. Examples of such prior art methods are solvent extraction of the polymerized film wherein the quantity of uncured material which is dissolved in the solvent is measured and compared with the total weight of cured and uncured polymer to calculate the % Sol; and glass transition temperature (T_g) determinations of the polymer wherein the T_g is directly related to the extent of polymerization.

A major concern in the manufacture of high density multilayer printed wiring boards employing a thin photodefinable polymeric dielectric film to separate conductive layers is the ability to inspect the board prior to operations such as lamination, circuit formation and solder mask application to insure uniformity from board to board and to insure the proper degree of cure has been attained. Conductive paths in the various layers are selectively interconnected by photodefined microvias in the dielectric. The degree of cure achieved in these photodefinable dielectric layers is critical to the proper operation of the multilayer printed circuit board. Also, the ability to successfully inspect the degree of cure of the photodefinable polymer layers used in such boards allows for processing and/or repair schemes which can result in increased product yields.

We have now discovered a non-destructive, optical means, for determining the extent of cure of a polymer which can be operated as an on-line, real-time test during a manufacturing process and can be used to control the process.

SUMMARY OF THE INVENTION

A small amount of a compatible, non-reactive fluorescent material (fluorophore) is included in the polymer system to be cured. The fluorophore in the polymer is excited with linearly or plane polarized actinic radiation having a wavelength that causes the material to fluoresce. The fluorescent emission from the fluorophore is determined both at two predetermined angles with respect to the exciting radiation. The free space of rotation of the fluorescent material in the polymer matrix is determined from these measurements. This determination serves as an accurate non-destructive measure of the degree of cure of the polymer since the ability of the fluorophore to rotate will be reduced as curing and crosslinking of the polymer proceeds. The measured quantities can either be compared with a previously determined standard to obtain an absolute value for the degree of cure, or, can be utilized merely to compare or

maintain a uniform degree of cure throughout a manufacturing process.

In addition, the method can be used to control the degree of cure of a polymer by employing an output from the measuring apparatus to a mechanism, such as a comparator, which is coupled to the means is for controlling the degree of cure of the polymer to a predetermined level. For example, the output of the comparator can be coupled with and activate, deactivate or control the curing apparatus so as to control curing parameters such as radiation exposure or power in the case of a photopolymer cured by means of actinic radiation, or thermal cycling in the case of a polymer cured by heat.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic of an apparatus that may be employed for determining the extent of polymerization;

FIG. 2 is a graph indicating the measure of cure by polarization values as a function of photopolymer cure time for a photopolymer cured at both high and low intensity radiations;

FIG. 3 is a graph showing the measure of cure of a photopolymer as a function of cure time for the same polymers as shown in FIG. 1, but determined as a function of percent of solubility (destructive solvent extraction test);

FIG. 4 is a replot of FIG. 2 correcting the polarization value for film thickness;

FIG. 5 is a graph indicating the degree of cure from polarization measurements as a function of the weight percent TMPTA added to a base polymer system; and

FIG. 6 is a graph indicating the degree of cure of a polymer as a function of cure time as determined by polarization measurements.

DETAILED DESCRIPTION

Generally, we have demonstrated that a fluorescent material such as a fluorescent dye dissolved in a monomer, oligomer or polymer can be used to monitor, non-destructively, the degree of cure or polymerization via the fluorescence anisotropy (A) or polarization (p) of the fluorophore by means of an optical inspection system. Further, the system can be used to control the means for and hence, degree of polymerization. Such a scheme is particularly useful for monitoring the cure of a polymer film on a printed circuit board. It should be understood, however, that its use is not so limited and it is, in fact, applicable to determine and/or control the degree of polymerization for any polymer in any environment. It is, however, especially suitable for polymer films. The method is based upon the relationship of the measure of the relative restriction of the fluorophore's rotational motion caused by the changes in the surrounding polymer matrix as curing of the polymer proceeds. As the polymeric material cures, the crosslink density increases resulting in a tighter matrix which restricts the motions of the fluorophore. Loss of rotational freedom will cause an increase in the fluorescence polarization value of the excited fluorophore that will approach its limiting value (p_0) as its motion becomes more restricted during the lifetime (τ) of its fluorescent state. When coupled with automatic comparators in a feedback system, as shown in FIG. 1, an on-line evaluation and control of the surface of organic polymeric coatings can be obtained regardless of the substrate used.