FLUORESCENT DEGREE OF CURE MONITORS

FIELD OF THE INVENTION

This invention relates to curable and cured compositions containing compounds useful in, and a method for, non-destructive determination of the extent of cure of a polymer. The method is particularly suitable for on-line manufacturing processes wherein polymer films or coatings are cured, for example, in adhesive tapes, release liners, protective coatings, and printed circuit boards.

BACKGROUND OF THE INVENTION

In an increasingly competitive environment, industry is looking for ways to improve product reliability and quality, maximize efficiency to reduce costs of their manufacturing processes, and reduce product inventory. Such objectives are critically dependent upon the accurate and rapid measurement of product properties, which in many applications depends upon uniform and reproducible curing of polymers. In particular, abrasion and solvent resistance of protective coatings is diminished when a coating is incompletely cured. Similarly, performance of pressure sensitive adhesives and release coatings is particularly sensitive to incomplete and non-uniform cure.

Traditional processes of measuring extent of cure generally rely upon off-line methods, including non-destructive methods such as infrared or UV-visible absorption spectroscopy, and destructive methods such as solvent extraction, thermal analysis (glass transition temperature), and surface tack (for example ASTM-D1640-83).

A non-destructive, on-line process for monitoring degree of cure, recently disclosed in U.S. Pat. No. 4,651,011, teaches a method wherein a fluorescent material such as a dye is dissolved in a monomer, oligomer, or polymer and can be used to monitor the degree of cure or polymerization via fluorescence anisotropy or polarization by means of an optical inspection system.

Other method of following degree of cure by means of fluorescence spectroscopy utilize probe molecules such as those described in (a) F. W. Wang, R. E. Lowry, W. H. Grant, *Polymer* (1984), 25, 690; (b) R. 0. Loutfy in "Photophysical and Photochemical Tools in Polymer Science: Conformation, Dynamics, Morphology", NATO ASI Series, Series C, Vol. 182, M. A. Winnik, Ed., Reidel: Boston (1986) pp. 429–448; and (c) Dickinson, C. S. P. Sung, *Polymer Preprints* (1988), 29, 530-531; W. C. Yu, X. Y. Huang, C. S. P. Sung, *Polymer Preprints* (1988), 29, 532–533.

The Wang, Loutfy and U.S. Pat. No. 4,651,011 (Ors and Scarlata) methods of monitoring extent of cure require use of soluble probe molecules which are not covalently bound to the resulting polymer, providing potential environmental and measurement problems with probe "bloom".

The Wang and Loutfy methods have been shown to be useful as cure monitors only at low viscosity (less than 300 cP, reference (b) above). The Sung method requires use of special fluorescent crosslinking agents.

As to the curatives themselves, many dibenzofulvene derivatives are known in the art, as in U.S. Pat. Nos. 3,091,651 and 3,091,652, *Helv. Chim. Acta* (1977), 60, 1073; *J. Org. Chem.* (1987), 52, 688; and *Ber.* (1906), 39, 3062. Furthermore, it is known that certain dibenzofulvenes are either non-fluorescent or weakly fluorescent (H. Stegemeyer, *Ber. Bunsenges. Phys. Chem.* (1968), 72, 335–340).

SUMMARY OF THE INVENTION

The present invention provides novel curable compositions and a method of measuring the degree of cure of compositions such as hydride curable silicones, ethylenically unsaturated compounds, and cationically polymerizable compounds, incorporating a latent uvaphore that is converted during cure to a uvaphore, which can be used on-line, and which can be polymer-bound, thereby obviating environmental and measurement problems of "bloom". In another aspect of the invention, the latent uvaphore can additionally function as an inhibitor for certain polymerization catalysts, preventing polymerization from occurring until desired.

Briefly, the present invention provides a curable composition, the cure of which can be monitored optically in the UV, comprising at least one of a hydride curable silicone, an ethylenically unsaturated compound, and a cationically polymerizable monomer, and as cure monitor dibenzofulvene or derivatives thereof. The cure monitor is a latent uvaphore which reacts under cure conditions to form a uvaphore which preferably is polymer-bound.

In another aspect, the invention provides a method for measuring degree of cure of a polymeric material comprising the steps of:

(a) polymerizing a mixture comprising a polymerizable composition comprising at least one of a hydride curable silicone, an ethylenically unsaturated monomer or oligomer, and a cationically polymerizable monomer or oligomer, optionally a polymerization promoter, optionally a solvent, and a spectroscopically detectable amount of a latent uvaphore comprising at least one of dibenzofulvene and dibenzofulvene derivatives, in the presence of added energy when required, to provide an at least partially polymerized composition comprising a uvaphore that absorbs radiant energy of a wavelength centered around λ_1 and emits radiant energy of a wavelength centered around λ_2, λ_1 and λ_2 each being a wavelength in the ultraviolet portion of the electromagnetic spectrum, and the mean of the range of λ_1 being below the mean of the range of λ_2, and all permutations of order of mixing of above materials, and

(b) exposing the resulting polymerized composition to radiant energy of a wavelength range centered around λ_1,

(c) measuring uvescence intensity at a wavelength range centered around λ_2 emitted by said composition during or after polymerization to provide an indication of degree of cure, using for example, a photomultiplier, a photodiode or a phototube.

There is also provided a method for measuring degree of cure of a coated article, comprising the steps of:

(a) applying the polymerizable mixture as described above to a substrate by methods known in the art, such as bar or knife coater, reverse roll, knurled roll, or spin coatings, or by dipping, spraying, brushing, and the like, with or without a coating solvent,

(b) optionally allowing the solvent to evaporate,

(c) allowing the mixture to polymerize or adding energy to the mixture to effect polymerization and provide a composition comprising a uvaphore that absorbs radiant energy of a wavelength centered around λ_1, and emits radiant energy of a wavelength centered around λ_2, λ_1 and λ_2 each being a wavelength in the ultraviolet