

Calorimetric Quality Control of UV Cured Optical Fiber-Coatings

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Synopsis

The application of ultraviolet (UV)-curable polymeric coatings provides optical fibers with improved strength, microbending resistance, and long-term durability. To ensure constant optical properties of the glass fibers during their life, fully polymerized coatings are needed. Test methods capable of determining the degree of cure and the consistency of the polymeric materials used are therefore required by the fiber technology. This investigation deals with the description of a calorimetric test method for the direct determination of the prepolymer reactivity and its final degree of cure. The analytical technique uses a modified differential scanning calorimeter (DSC) capable of direct measurements of heat fluxes generated during the UV-activated polymerization of photoinitiated acrylic prepolymers. Finally, the degree of cure and the glass transition temperatures were determined for the polymerized coating also in presence of sorbed moisture.

INTRODUCTION

In recent years, there has been increasing interest in the use of photopolymerization for industrial coating processes, owing to their high cure and application speeds. Most of the current technologies use photoinduced radical polymerization. The application of radiation-curable coatings involves the optimization of a large number of process variables in order to achieve optimum material properties. In optical fiber technology two coatings are generally applied in line with the drawing of the glass fiber: an internal soft compliant, which acts as a stiffening enclosure, and an external hard shell which improves fiber handling characteristics. Their action is addressed to the protection of the silica core from abrasion and microbending. Forces capable of causing microscopic departure from straightness in the waveguide axis have, in fact, a detrimental effect on the optical attenuation. Proper fiber design parameters and the application of a thick shield primary coating, which increases the composite structure rigidity, are used to minimize microbending losses. Moisture sensitivity of the glass fibers is recognized in literature.¹ The presence of water molecules produces an undesired stress corrosion when associated to stress concentration at the silica surface flaws. However, optical fiber degradation due to water adsorption on the silica surfaces is partially inhibited when a polymeric coating is used, since water diffusion rate through the fiber is reduced by the organic barrier. Nevertheless, reduction of the performance of the optical fibers as a consequence of the exposure in humid environments also has been reported in literature.² After moisture saturation, the primary coating experiences a significant change of the elastic modulus and of the glass transition² as a consequence of hydrogen-bonding

formation between water molecules and polymer polar groups.³

Low viscosities, good fiber wettability, and fast cure characteristics, required for the prepolymer mixture to spread easily and adhere to the silica surfaces, are achieved by the addition of appropriate reactive diluents and photoinitiators. Generally, the free radical polymerization process is activated by a photoinitiator present in the prepolymer that forms free radicals when ultraviolet (UV) irradiated at fixed wavelengths. The polymer mechanical properties and hence their optical and strength-preserving functions are, therefore, determined by the degree of crosslinking produced in the thermosets by the radiation curing. The viscoelastic characteristics, which depend on the degree of crosslinking of the two coatings, are determinants either for the reduction of the stress concentration at the fiber interface and for the inhibition of optical losses due to microbending. In particular, UV-curable organic coatings play a critical role in determining the durability and physical properties of optical fibers in actual service conditions.

Incomplete cure of the reactive prepolymer may therefore induce differences in the viscoelastic and chemical characteristics of the resulting materials which may cause chemical and physical aging of the organic coating which negatively influence the performance of the optical fiber. The leaching out of unreacted prepolymer components and the presence of still reactive functional groups, in fact, modify the mechanical coating properties in use.

A number of tests such as solvent resistance, abrasion, or slide-angle tests^{4,5} have been proposed for the determination of the degree of cure of UV-curable coatings. However, they often represent only indirect relative evaluations of the potential cross-linking density that can be achieved for a complete prepolymer reaction. Absolute characterization techniques require the use of methods of investigation able to determine the presence in the cured coating of double bonds or of extractable residuals, whose concentrations in the swelling solvent should be chromatographically measured. A differential scanning calorimetry (DSC) technique has been investigated in the present work. This method of analysis uses a modified calorimeter capable either of the direct measurement of the cure kinetic under UV radiation and of the determination of the residual reactivity in the processed coatings. A quality control of the incoming materials based on the verification of their actual reactivity, and of the degree of cure of the processed parts based on the determination of the residual reactivity, is of great utility to ensure the product consistency and to predict the end-use performance.

EXPERIMENTAL

Commercially available primary and secondary coating resins based on acrylate monomers containing reactive diluents and a photoinitiator were used. A spun silica glass of 125 μm in diameter passed through resin applicators producing constant thickness coatings concentric with the fiber (Fig. 1). The two coatings were cured independently. After application of the primary coating resin, in fact, the fiber passed through a first set of UV lamps before entering in a second combination of coating applicator and UV lamps. In order to minimize the cure inhibition caused by the presence of oxygen, the

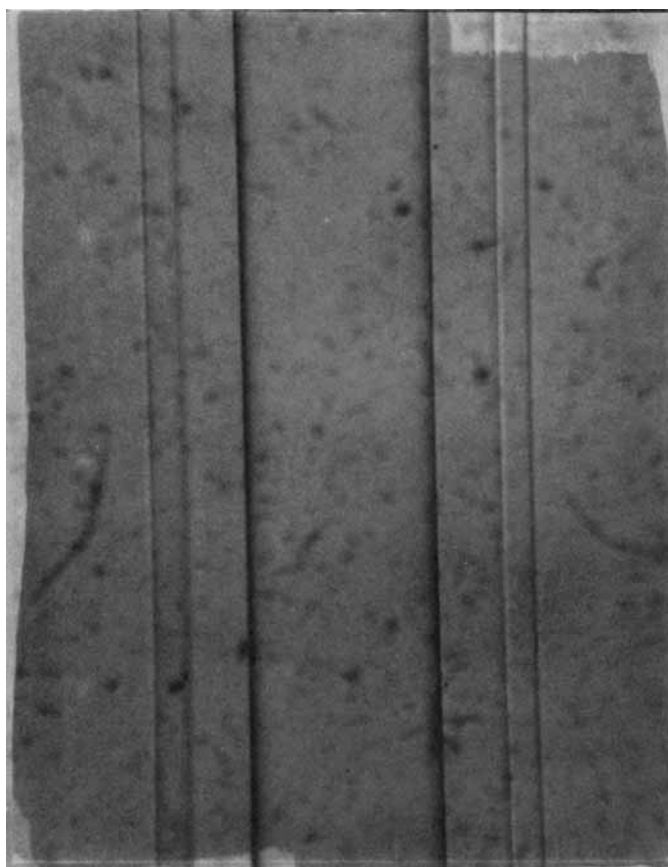


Fig. 1. Appearance of the optical fiber coated with the primary and secondary coating resins. The diameter of the glass fiber is 125 μm .

lamps used to produce the UV radiation (which intensities were controlled in low, medium, and high stages) worked in a nitrogen-purged environment.

A Mettler DSC 30 was used to calorimetrically characterize the cure kinetics of the prepolymer and the glass transitions of the cross-linked materials. UV-transparent quartz windows were used to permit irradiation from a UV source (Vilber-Lourmat) placed at constant distance from the sample (5 cm) and presenting a maximum emission at 365 nm. Isothermal cure was performed at 35°C while dynamic scans were performed from -100°C to 150°C at 10°C/min. Aluminum pans without covers were used in the isothermal cure under UV irradiation.

RESULTS AND DISCUSSION

Cure Kinetics

The unreacted acrylic prepolymer has been allowed to thermally equilibrate at 35°C in the DSC until a flat thermogram baseline was obtained (see Fig. 2).

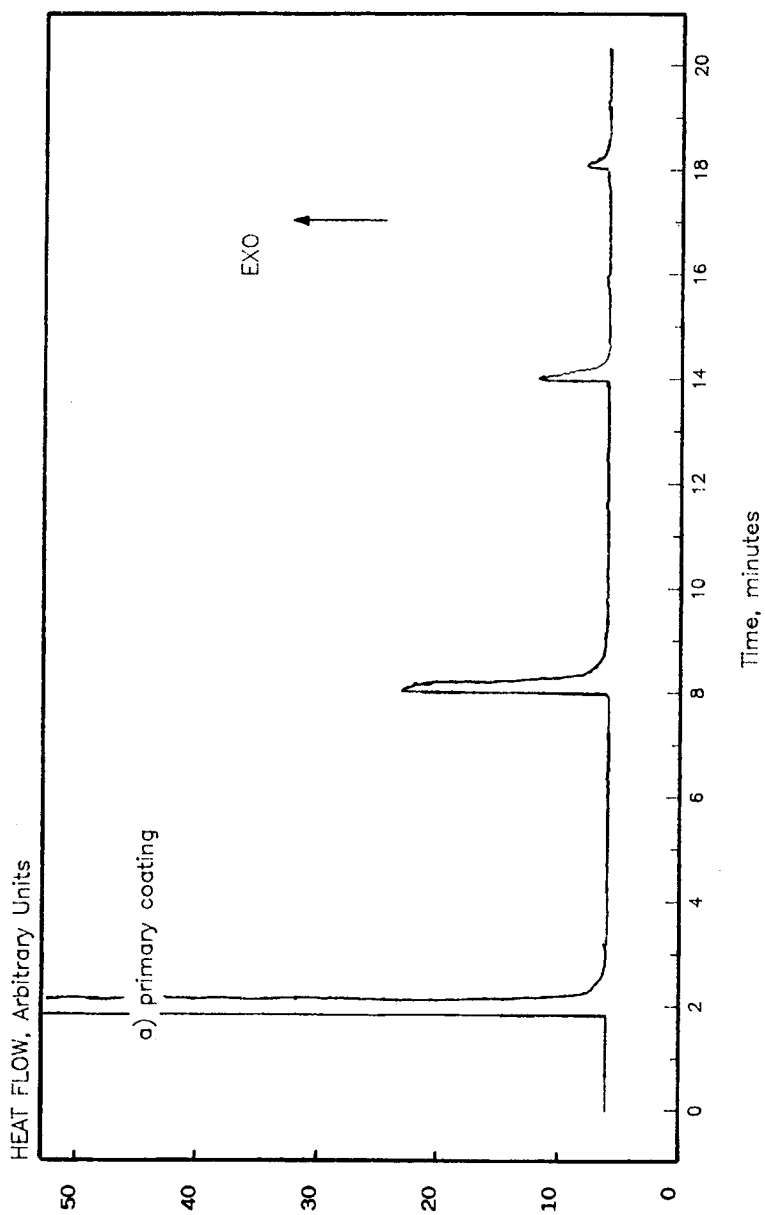


Fig. 2. Cure kinetics under UV irradiations of (a) primary and (b) secondary coatings.

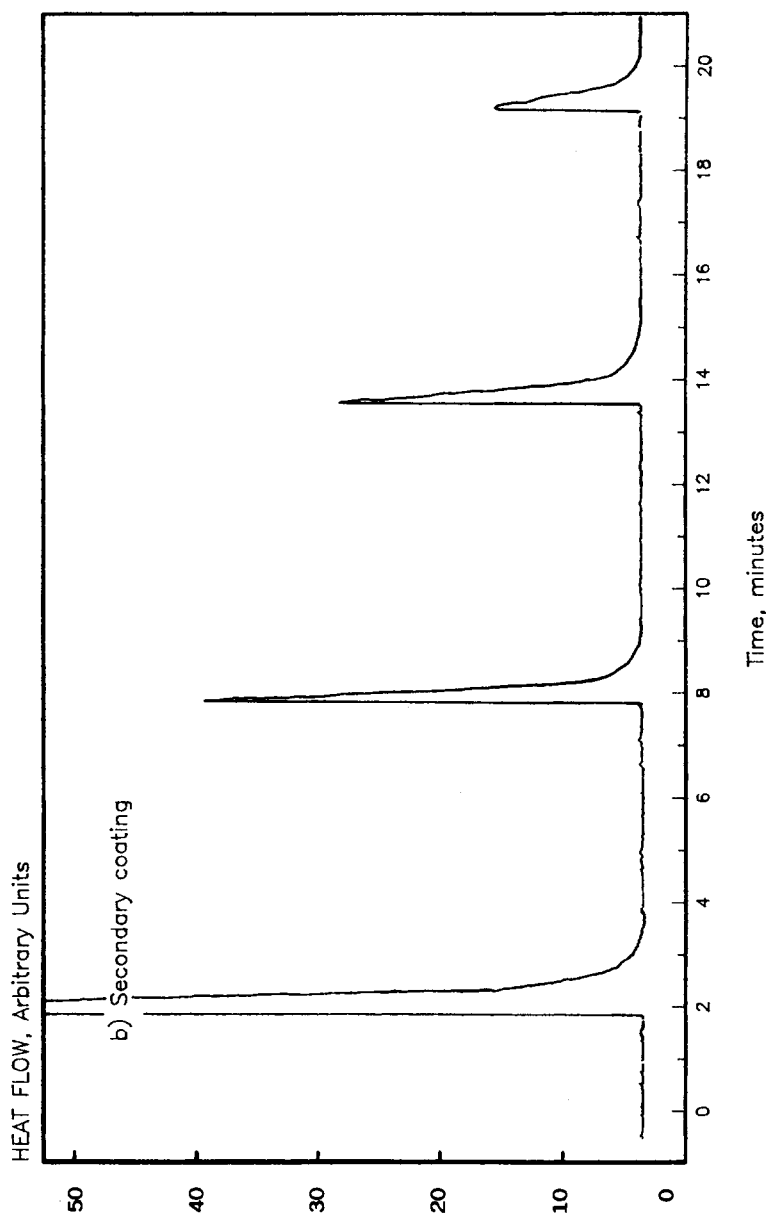


Fig. 2. (Continued from the previous page.)

TABLE I
Calorimetrically Determined Partial Heat of Reaction
in Subsequent Irradiations of UV Photoinitiated Acrylics

	$H_1, \text{J/g}$	$H_2, \text{J/g}$	$H_3, \text{J/g}$	$H_4, \text{J/g}$	$H_5, \text{J/g}$	$H_{\text{Tot}}, \text{J/g}$
Primary coating	133	26	9	4	0	172
Secondary coating	107	50	38	22	7	224

When the UV source irradiated the material for 10 s, an exothermic response associated with the cure reactions was monitored by the calorimeter. Additional irradiations were performed when the baseline reached the zero heat flux once the UV-activated cure reactions ended. The residual reactivity was, in fact, reactivated by the new irradiations. The intensities of the exotherms were progressively reduced by the previous cure steps. Complete cure of the prepolymer was defined when the irradiation did not produce any exothermic response. The potential overall heat of reaction of the resin was determined by the summation of the partial contributions detected in the single steps. The thermograms relative to the primary and secondary coatings are compared in Figure 2(a) and (b). The partial heats of reaction measured in the irradiation steps relative to the primary and secondary coatings are compared in Table I. As indicated by the partial heats of reactions measured in the two scans, the primary coating resin rapidly exhausted its reactivity (172 J/g) while the secondary coating resin, characterized by a higher overall heat of reaction (224 J/g), reacted slower.

An isothermal kinetic analysis was applied to the cure thermograms. A reaction order ranging from 0.30 to 0.60 and a kinetic constant of $0.10 + 0.02$ (1/min) were observed for the primary coating resin in the first and subsequent irradiations.

Determination of the Residual Reactivity of the Coatings

In order to obtain coatings presenting different degrees of cure, the primary and secondary resins were irradiated by the UV lamps of the spinning/coating/curing combination set to 9 and 27 W/cm² irradiation powers. The resulting coatings were stripped from the fibers, placed in uncovered DSC pans, equilibrated at the test temperature, and finally irradiated with the UV source. The residual reactivities of the partially cured acrylics were determined by the intensity of the exothermic peaks observed in the DSC thermograms.

Figure 3 compares the thermograms relative to the layers composite coatings irradiated at the two different powers. More than one additional irradiation was imposed to the samples in order to completely exhaust the cure reactions. Residual reactivity exothermic peaks were observed for the two materials. As expected, the coating irradiated to the lower lamp intensity showed significantly higher residual reactivity evident in more intense exothermic peaks [Fig. 3(B)]. A measure of the degree of cure has been defined as,

$$DC = 1 - H_r/H_o$$

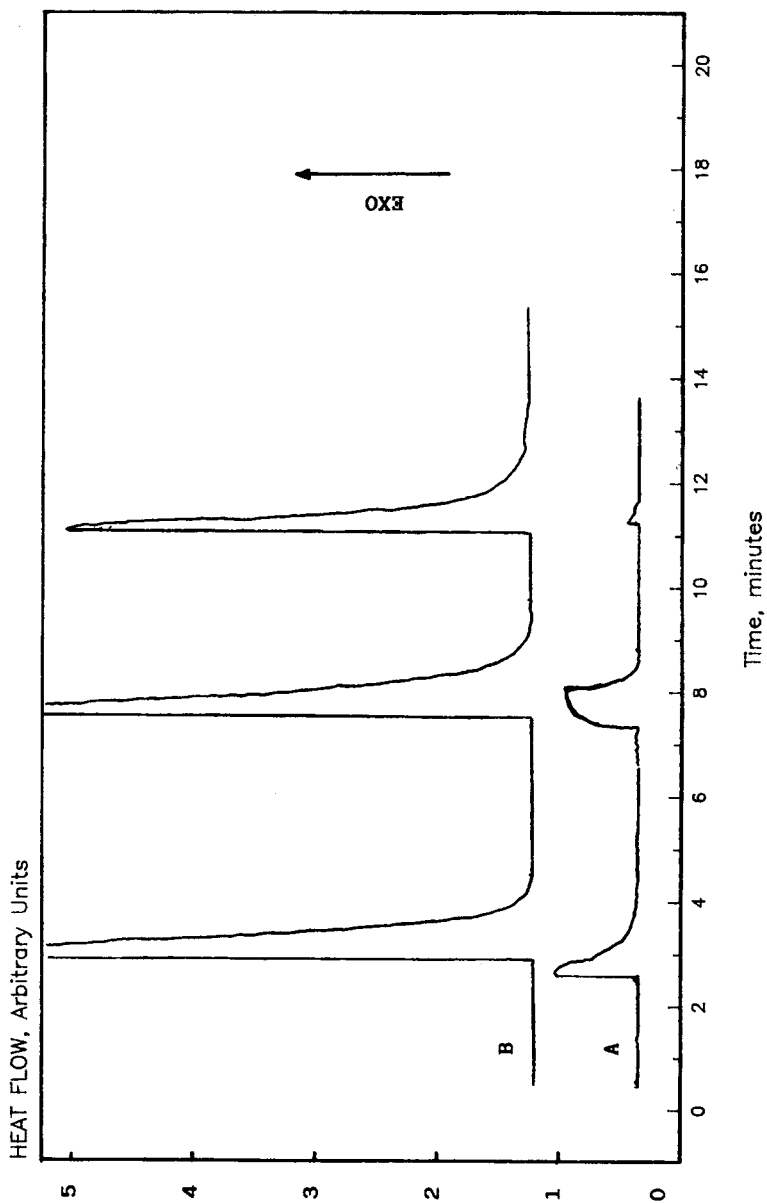


Fig. 3. Residual reactivity of UV processable coatings irradiated to the (a) maximum and (b) minimum lamp powers.

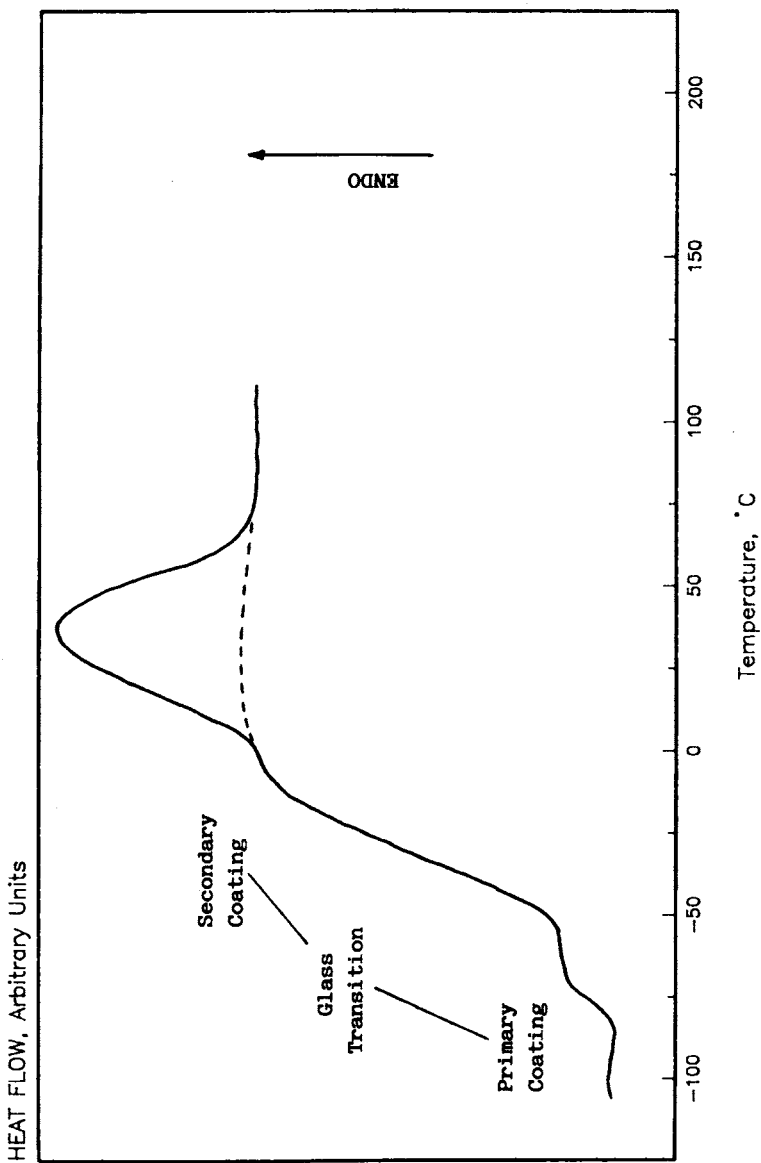


Fig. 4. DSC thermogram of a processed coating.

where H_o is the overall heat of reaction determined in the previous DSC characterization and H_r the residual heat of reaction determined for each partially cured coating from Figure 2. The sample cured to the higher lamp intensity was almost completely cured, $DC = 0.99$, while the coating irradiated to lower intensity presented a $DC = 0.91$.

Determination of the Glass Transition Temperatures of the Processed Coatings

The DSC thermograms of the processed coatings are reported in Figure 4. The thermogram of the two-layer coating shows in the range of temperature from -80 to -60°C a first endothermic step gradient of the heat fluxes associated to the glass transition of the internal soft primary resin, and a broader second step, relative to the glass transition of the harder external shell, in the range of temperature from -40 to 0°C . At temperatures higher than 20°C a relatively intense endothermic peak is observed. This thermal event is probably associated with the desorption process of the moisture sorbed by the acrylic resin equilibrated in the external humid environment. A second scan carried out on the same sample showed a thermogram characterized by the same glass transitions observed in the first scan but presenting a significantly less intense endothermic peak. The previous thermal treatment performed in the dry nitrogen atmosphere of the DSC cell was, in fact, sufficient to eliminate part of the water molecules sorbed by the polymeric material. However, when the sample was exposed again to the humid environment of the laboratory, it rapidly regained its equilibrium level of sorbed moisture. A new DSC thermal scan was, in fact, characterized by an endothermic peak as intense as that observed in the first scan.

The influence of the sorbed moisture on the viscoelastic properties of the polymeric coatings depends on the actual mechanisms of sorption of the water molecules. These can be adsorbed on hydrophilic sites, such as polar or hydrogen bonding groups, or molecularly dispersed in the available polymer-free volume⁶. The intensity of the glass transition depression, which is usually associated with the presence of sorbed low molecular species, and the detrimental effect on the mechanical properties is determined by the actual mechanism of water sorption. Additional investigations are therefore needed in order to evaluate correctly the influence of the moisture sorption on these materials.

CONCLUSIONS

The use of a calorimetric characterization of the resins employed as polymeric coatings for the glass optical fibers is of great utility in the quality assurance of these high technology materials. A quality control of the reactivity of the incoming UV-curable resins may be easily achieved using a modified form of a differential scanning calorimeter by measurements of the kinetic and thermal parameters (kinetic constant, reaction order, and overall heat of reaction) carried out under controlled temperature and UV-irradiation conditions. Moreover, the same calorimetric technique is useful for the identifica-

tion of an incomplete cure of polymeric coatings undergoing the factory glass fiber spinning, resin application, and irradiation processes.

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Received March 3, 1986

Accepted July 1, 1986