

Relating Tensile Properties of Improved UV-Cure, Heat-Resistant Coatings and Thermogravimetric Data

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Heat-resistant, UV-cure coatings for optical fibers and other applications are desirable for many uses, including monitoring well drilling, under-hood automotive cable applications and others.^{1,2} In prior papers and reports, the authors have shown the formulation of improved UV-cure, heat-resistant coatings and they have determined comparative sets of thermodegradation kinetic parameters by assorted thermogravimetric methods and analytical treatments of the data. These degradation kinetic parameters are important for both formulating chemists and design engineers. It was also shown that the degradation of solid-film crosslinked networks of these new coatings are a complex of numerous reactions whose rates may vary both as exposure temperatures rise and as exposure durations become longer as is consistent with the literature.^{3,4}

Another difficulty in gauging long-term durability of coatings in harsh environments is matching calculated degradation rate constants from particular accelerated testing methods with actual in-field performance at the intended service temperatures. In the present work, the authors studied the tensile properties of cured compositions by various methods to determine how they may relate

to thermal degradation weight loss. In these efforts, a method has been developed to study the important properties of tensile modulus and elongation at elevated service temperatures to better estimate the “real-life” performance and durability of these improved UV-cure coatings.

Materials and Equipment

For these studies with coatings of similar modulus, 75-micron flat film drawdowns were prepared according to the method of Szum.⁵ Drawdown specimens were cured under nitrogen on a Fusion Systems Model DRS-120N2Q unit with 600 Watt/inch, 13mm D-bulb, with a dose of 1 J/sqcm. Elevated temperature aging of cured films and specimens were conducted in a Lindberg/Blue M Box Furnace, Model BF51748C, at specified temperatures and times. Other thermal characterizations were conducted using TA Instruments Hi-Res TGA 2950 Thermogravimetric Analyzer in an air environment. The DMA instrument was a Rheometrics Solids analyzer RSA 3, with provision to run in either dry air or pure nitrogen environments. The UV-cure formulations (UV1 and UV2) were variations of a common mix of modified epoxy mono- and di-acrylate esters, with long-chain aliphatic acrylate monomers to adjust

viscosity and initial cured-film tensile properties. These coatings also contain a rather typical mix of photoinitiators and in-can stabilizers. Further details of composition and certain properties are presented in more detail in prior publications.^{6,7}

Presentation of Selected Data and Analysis

A principal tool to gauge progress in the development of new heat-resistant, UV-cure coatings for fiber-optic applications is the analysis of thermogravimetric weight loss.⁸ Specimen preparation is not critical and data gathering is straightforward, precise and repeatable. However, simple cured film weight loss at elevated temperatures may not convey suitable and necessary information about the integrity of the films, nor does it necessarily predict the durability of the fiber protection afforded by such coatings. It is, therefore, the object of this present work to correlate weight loss studies with measurements of key film physical properties such as tensile modulus (T_g) and elongation to better gauge the protective durability of the fiber coatings.

In the first instance, two versions of a UV-cure composition were prepared—UV1 and UV2 (which was identical with UV1 except for an addition of 1.5% of a commercial coating antioxidant additive). Cured-film drawdowns of 75 μ were prepared in the usual manner with a dose of 1 J/sqcm from a 600 W/in., D-lamp under nitrogen. Specimens were also prepared for concurrent weight loss determinations. Cured films and specimens were placed in the Lindberg box furnace at selected temperatures for 168 hours, with weight loss determinations and temperature sweep DMA analysis at 24, 48, 72, 96 and 168 hours. After 168 hours exposure, the tensile properties

FIGURE 1

Combined weight loss data for UV1 and UV2

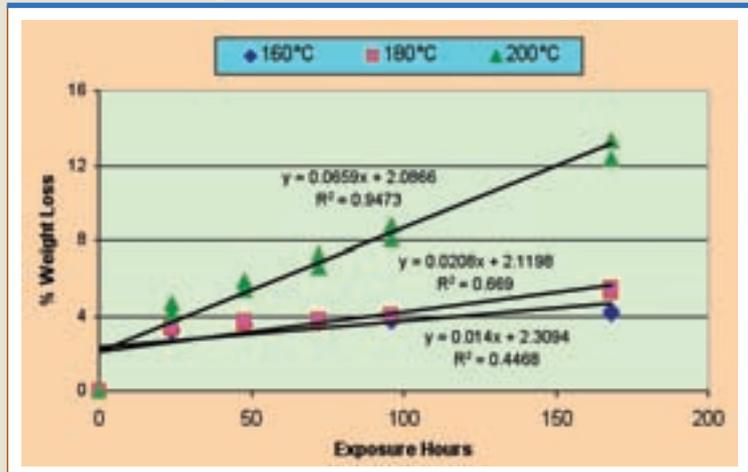
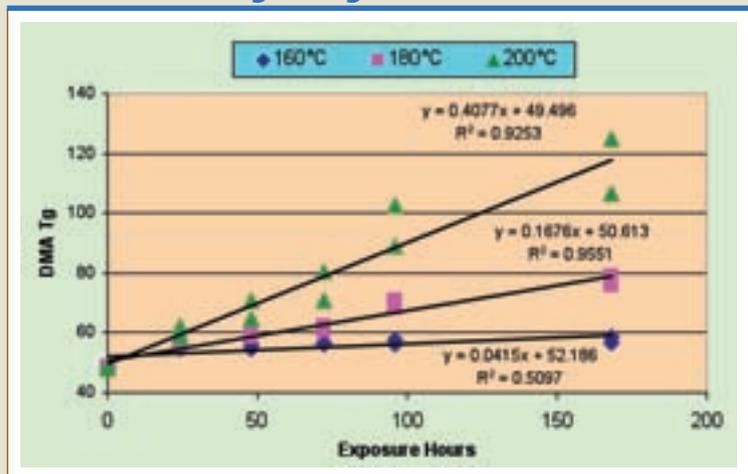


FIGURE 2

Combined DMA Tg change for UV1 and UV2



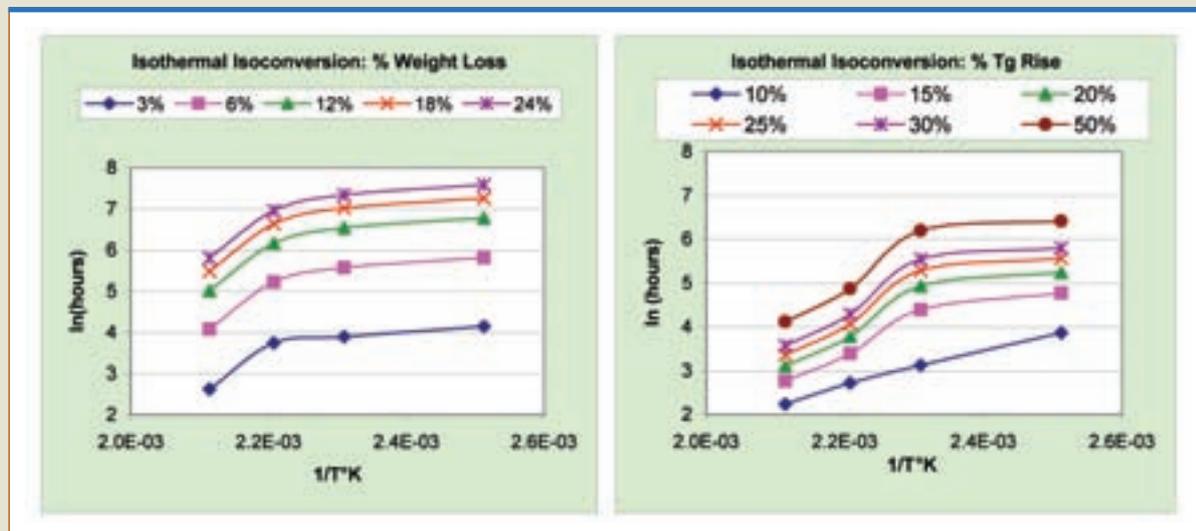
of the films were determined by the usual Instron methods.

A rather surprising aspect of all the studies related to new heat-resistant coatings in this present work, and in prior efforts cited above, has been the lack of any stabilizing effect seen from the addition of antioxidants. For these UV-cured compositions at the temperatures of interest, there simply has been no improved

durability and this is both for weight loss and DMA performance as will be shown. Therefore, in the charts of Figures 1 and 2, the data for both UV1 and UV2 coatings are combined. There were two notable items from these figures—first, there seems to be a good correlation between weight loss and the rise of DMA T_g (max. $\tan \delta$) and, second, there is clearly a significant change in the behavior

FIGURE 3

Isothermal isoconversion curves for % Wt. Loss and % rise in DMA Tan δ



from 160-180°C to 200°C. The transitional behavior can also be seen in Figure 3 which shows isothermal isoconversion curves for % weight loss and % change in DMA Tg as functions of ln(hours) vs. 1/T°C. This change in degradation rate may reflect the transition from thermooxidative to primarily thermolytic mechanisms, and it may also be the temperature region for the breakdown of the carbon

chains formed from polymerization of the acrylates. This transitional behavior has been noted in numerous TGA studies, both internal and in the published literature.⁹

When the tensile data were examined, however, a rather different picture is seen. Table 1 shows the results of the tensile properties of films aged 168 hours at selected temperatures.

The data presented in Table 1 and shown in Figure 4 are surprising in comparison with weight loss and DMA studies. First, for both TGA and DMA, both coatings UV1 and UV2 seemed to be very stable with little change at 160°C; but the TEM data show a very significant rise in modulus and loss of elongation. Secondly, there does not seem to be evidence for a sharp transition of behavior

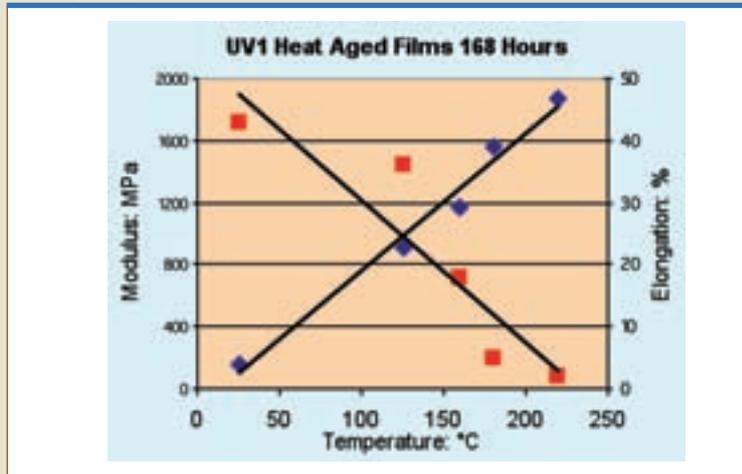
TABLE 1

Tensile properties for UV1 films after 168 hours exposure

	Initial	125°C	160°C	180°C	220°C
Tensile Strength: MPa	17 (2)	29 (3)	32 (2)	55 (2)	24 (6)
Elongation: %	43 (3)	36 (12)	18 (11)	5 (1)	1.5 (1)
Secant Modulus: MPa @ 2.5%	159 (19)	674 (28)	894 (48)	1,450 (55)	—
Elastic Modulus: MPa	161 (19)	906 (34)	1,164 (64)	1,557 (63)	1,869 (53)
Note: All data above determined with Instron crosshead speed of 1 inch/min.					
Regression for elastic modulus: Modulus = (8.78 x temp) – 115 R ² = 0.98					
Regression for elongation: Elongation = -(0.23 x temp) + 53 R ² = 0.85					
	Tensile	Elongation	Modulus		
UV1, 168 hrs. 160°C, Crosshead speed 1.0 in/min.	32 MPa	18%	1,164 MPa		
UV2, 168 hrs. 160°C, Crosshead speed 0.1 in/min.	30 MPa	40%	905 MPa		

FIGURE 4

TEM properties



between 160°-180°C and 180°-200°C. The regression analysis for both elastic modulus and elongation show continuous linear behavior with very good correlation coefficients. Some rationale for the TEM changes may be seen in the advance of DMA Tan δ . The glass transition region for these

coatings is rather steep as can be seen in the DMA Figure 5; so small advances in DMA Tg may be reflected as much larger changes in TEM properties when measured at room temperature. For instance, at temperatures of 25-35°C there are quite significant differences in E' storage modulus between the

initial and 180°C heat-aged specimens of UV1. It is also noted that TEM properties, especially elongation, are not inherent properties of the coatings but are dependent on the test parameters (such as crosshead speed as seen in the table). TEM properties are also dependent on the integrity and possible defects in the film strips cut for Instron testing, especially in the case of heat-aged specimens. All the accumulated data so far would seem to indicate that the urethane-free type formulas UV1 and UV2 can retain film integrity and durability at 160°-180°C for an indefinite period, and may perform well at 180°-200°C for shorter durations. However, the data also indicates that there is still room for improvement and better grasp of the heat-aged tensile properties.

Further understanding of the performance and durability of improved high-temperature resistant coatings is gained by examining the physical properties and changes at actual service temperatures; e.g., at 160°C for automotive under-hood cables and sensors. For these studies, the RSA3 DMA was used in constant tensile force mode with the oven of the instrument providing a convenient means to vary the specimen temperature for testing. Also, for convenience and better reliability of testing, cylindrical-rod, UV-cured specimens were prepared and mounted in the RSA3 as shown in Figure 6. The coating UV1 was injected into heat-resistant and UV-transparent silicone rubber tubing with nominal I.D. of 0.76mm and O.D. of 1.65mm and cured in the usual manner with a Fusion D-lamp.¹⁰ Specimens of about 3cm were then cut and a middle 1cm of cured coating was exposed. The silicone rubber tubing provided cushioning protection for the specimens in the DMA mounting fixture, as they were

FIGURE 5

Initial and heat-aged DMA

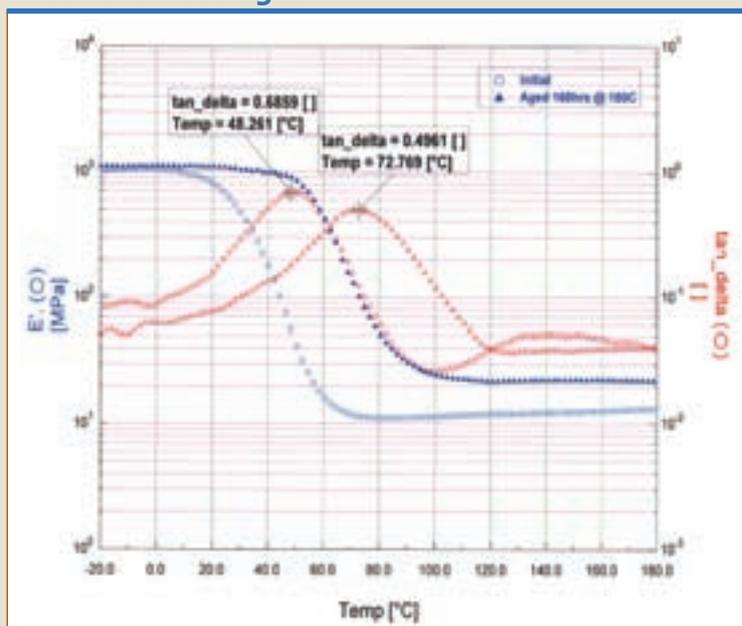
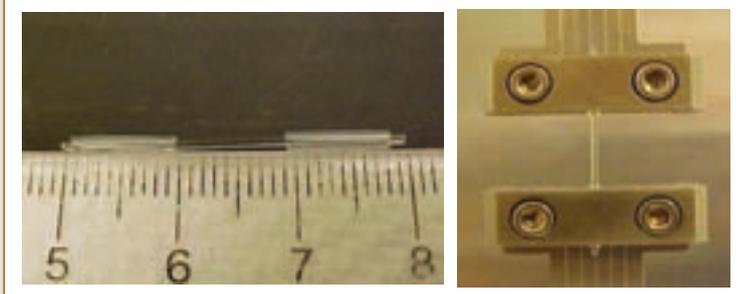


FIGURE 6

Specimen and mounting for tensile mode DMA at 160°



otherwise damaged at elevated test temperatures. Stress-strain curves could then be easily run on initial and heat-aged specimens. Collected data are shown in the table below.

The tensile properties of Table 2 are quite instructive relative to the differences in weight loss and DMA Tg data shown in Figures 1 and 2. The mechanical spectra and temperature dependencies derived from DMA and

weight loss measures do not provide immediate insight to their molecular origins. But the DMA Tg (max. $\tan \delta$) derived from storage and loss moduli are inherent of qualities linked to the energy-elastic deformations of bonds and viscous movements of molecular segments. While tensile properties may be useful in tracking changes to coatings, the measurement results are highly dependent on the test circumstances.¹¹

That there is thermal degradation of specimens is not to be argued, the changes are evident in weight loss, and both elongation and modulus for both Instron and DMA measurements. What may be argued is that Instron tensile data taken at ambient temperature after heat aging of specimens may not reflect the true ability of the improved heat-resistant, UV-cure compositions to continue to provide fiber protection at service temperatures such as 160°C. It can be seen in the elongation measures at 160°C that film integrity and pliability are still intact after 168 hours aging even up to 200°C.

Another curious characteristic behavior of these UV-cured compositions, both urethanes and the improved non-urethane formulas, is that a substantial portion of weight loss or DMA Tg change occurs in the first 24 hours of elevated temperature aging. This is especially so for weight loss at 160° and 180°C, as reflected in the somewhat low R² values.

TABLE 2

Tensile properties of by Instron at 23°C and by DMA at 160°C

Specimen and Test Conditions	Tensile: MPa	Elongation: %	Modulus: MPa
1. UV1, 75 μ film, Instron, 23°C, Initial unaged	17	43	159 / 161
2. UV1, 75 μ film, Instron, 23°C, aged 125°C	29	36	674 / 906
3. UV1, 75 μ film, Instron, 23°C, aged 160°C	32	18	894 / 1,164
4. UV1, 75 μ film, Instron, 23°C, aged 180°C	55	5	1,450 / 1,557
5. UV1, 75 μ film, Instron, 23°C, aged 200°C	—	6	1,625
6. UV1, 75 μ film, Instron, 23°C, aged 220°C	24	2	— / 1,869
7. UV2, as per #3, crosshead speed 0.1 in/min	30	40	905
8. UV1, DMA @ 160°C, Initial unaged	6.8	46	16 (E ₀)
9. UV1, DMA @ 160°C, aged 168 hrs @ 160°C	4.3	32	15
10. UV1, DMA @ 160°C, aged 168 hrs @ 180°C	4.6	19	25
11. UV1, DMA @ 160°C, aged 168 hrs @ 200°C	6.9	12	46

Notes: For 1-6 Instron crosshead speed is 1.0 in/min., and test strips are cut from heat-aged films. Modulus is first reported for secant modulus at 2.5% strain, then for elastic modulus approximation of Young's. For #5, elongation and modulus are approximated from regression parameters. For 8-11 cylindrical specimens of nominal diameter 0.76 mm are prepared and run as described in text. Modulus at #8 is DMA E₀ equilibrium modulus.

TABLE 3

Relative % of heat aging changes in first 24 hours

Box Furnace Heat-Aged Weight Loss				
Hours	% of Hours	160°C	180°C	200°C
24	14.3	-3.26%	-3.42%	-4.40%
168	100.0	-4.20%	-5.39%	-12.85%
% Wt. Loss first 24 hrs.		77.6%	63.5%	34.2%
% DMA Tg Change after Box Furnace Heat Aging				
Hours	% of Hours	160°C	180°C	200°C
24	14.3	14.8%	16.8%	24.1%
168	100.0	19.0%	59.9%	139.2%
% Tg Change first 24 hrs.		77.6%	28.0%	18.0%

Note: Weight loss for 0.5 gm cured specimen. DMA Tg change for cut strip from cured 75 μ film.

Table 3 does not show all the data, but shows the percent changes from initial specimen for 24 hours, then 168 hours. The table also shows the relative percent of the total change that occurred in the first 24 hours. These data may offer a significant clue to substantial improvement of future coatings. These losses and changes in the first 24 hours are most probably from absorbed water, low molecular weight, photoinitiator residue and stabilizing additives, and small amounts of residual unreacted acrylate esters. If these residual volatile components could be eliminated from the initial formulations, commensurate improvements in heat-aged performance may be possible.

Conclusions

From all the results of these present studies, the authors offer the following conclusions. There is a good correlation between weight loss after elevated temperature aging and the coating's inherent property of Tg, as determined by DMA maximum tan δ —although it would appear that DMA Tg is a more sensitive indicator of thermal aging change. From weight loss and

DMA Tg data, and from DMA tensile properties at elevated temperature, the durability and film integrity of new and improved heat-resistant, UV-cure coatings is indefinite in the range of 160-180°C, and may perform quite well in the range of 180-200°C for shorter durations. This relative thermal behavior and thermolytic transitions can also be clearly seen in the isothermal isoconversion plots. It has also been seen that much of heat aging change occurs in the first 24 hours of elevated temperature exposure. If low-molecular weight, volatile “contaminants” could be removed or replaced, commensurate improvements in heat resistance may be possible.

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