Kinetic Study on New Generation Optical Fiber Coatings with Improved Processing Robustness

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Abstract

The cure speed of an optical fiber coating has always been considered a critical characteristic for assessing processing capability and robustness, especially under high-speed fiber drawing conditions. The evaluation methodology of cure speed for UV curable optical fiber coatings has expanded in recent years from the conventional double bond conversion rate to also including modulus buildup rate, which is more directly related to coating on-fiber properties and fiber performance. In this paper, a new kinetic parameter is introduced, i.e. modulus buildup rate constant/double bond conversion rate constant ratio (k_E/k_C). The new generation primary coatings as first introduced last year exhibit the unique characteristic of $k_E/k_C \geq 1$, corresponding to equal or faster modulus buildup vs. conversion and much less modulus increase at the last stage of conversion. This distinctive feature provides great benefits to optical fiber manufacturers in terms of imparting robust processibility with consistent primary coating mechanical properties to a wide window of different drawing conditions. The kinetic mechanism of this unconventional behavior was studied by analyzing kinetic data from coated wire fibers made by Draw Tower Simulator (DTS), Real-Time Dynamic Mechanical Analysis coupled with Real-Time Near Infrared Spectroscopy (RT-DMA/NIR), and film samples from a high intensity/high temperature (HIHT) curing system.

Keywords: optical fiber coating; optical fiber processing; coating cure speeds; kinetic modeling.

1. Introduction

Significant efforts have been made in recent years to further improve optical fiber coating cure speeds supporting ultra-high speed drawing processes. In the meantime, a wide window of processing conditions coexists in optical fiber manufacturing due to different draw tower designs having considerable variations on curing lamp setups, glass temperatures controlled by Helium cooling rate, and a wide spread of drawing speeds from 1000 to 3000 m/min to accommodate the needs for different fiber types.

While the primary coating cure degree represented by %RAU (% Reacted Acrylate Unsaturation) is typically >80%, the kinetic study previously conducted using a Draw Tower Simulator showed the general trend of modulus rising more sharply with increasing %RAU, where the last 20% of the %RAU could account for up to 80% of the modulus buildup [1]. This is a result from the kinetic behavior of crosslinking reactions, i.e. modulus buildup rate constant is typically slower than double bond conversion rate constant. Consequently, the primary In-situ Modulus (ISM) varies significantly among coated fibers even with the same coating. It has been well known that one of the most important roles of optical fiber coatings is to provide microbending protection to optical fibers, where the primary coating acts as a soft buffer isolating the glass from external stresses in cable environments. The microbending sensitivity of a dual layer coated fiber, according to the classic stress mechanics model [2], is proportional to k_s^2, the square of the spring constant of the coating buffer. As k_s is proportional to primary coating modulus, any variation of primary ISM could be amplified to the 2nd power change in fiber microbending sensitivity. This explains the need to broaden the cure speed concept to greater emphasize the modulus buildup rate besides the double bond conversion rate. More specifically, it is the relative comparison of modulus buildup versus conversion that controls how sharp the modulus increases at the last stage of the cure.

For kinetic study to best simulate coating reaction during fiber drawing, a method of making wire fibers by Draw Tower Simulator (DTS) and conducting the 1st order reaction kinetic curve fitting on primary %RAU and ISM data at a broad range of curing doses was introduced in the previous paper by Cao et.al. [1] and applied also in this study on the selected examples of new generation primary coatings. The new generation primary coatings as first introduced last year [3,4] can be characterized by the unique feature of $k_E/k_C \geq 1$, which means modulus buildup rate constant is equal to or higher than the conversion rate constant. This is in contrast with conventional coatings with $k_E/k_C<1$. Independent of absolute cure speeds, the relative comparison of modulus buildup rate constant versus conversion rate constant controls the degree of modulus increase at the last stage of cure and the higher this ratio, the smoother the ISM vs. %RAU at the last 20% of conversion.

For understanding this unique kinetic behavior of the example coatings, a customized setup coupling Real-Time Dynamic Mechanical Analysis (RT-DMA) and Real-Time Near Infrared (RT-NIR) Spectroscopy was used to monitor simultaneously both real-time shear modulus and real-time conversion versus exposure time. The results from RT-DMA/NIR confirmed the kinetic behavior from these conventional methods for UV curable coating cure kinetics are qualitatively different than the coating curing kinetics from fiber drawing process due to the lamps on these instruments being significantly weaker intensity (<100mW/cm^2) than lamps in actual fiber drawing. Curing of coating films under a conventional UV conveyor system is still much lower irradiance on coating (5-10 W/cm^2) than optical fiber drawing process due to the design of both primary and secondary elliptical reflectors, through which the light is highly focused onto the extremely small area of the optical fiber. The curing temperature of optical fiber drawing processes is also much higher due to the extremely fast reaction under high UV light intensity releasing intense heat from the reaction exotherm. To create film samples more closely simulating the fiber drawing conditions, a high intensity/high temperature (HIHT) curing system has been developed, with intensity reaching 20W/cm^2 and adjustable temperature up to 150°C. The comparison between these different curing systems demonstrated complex influences from light intensity and curing temperature on UV-

curable optical fiber coating cure kinetics and morphology of the crosslinking network structure which ultimately controls the mechanical properties of the coating on fiber.

2. Experimental

2.1 Wire Fibers by Draw Tower Simulator

The Draw Tower Simulator is capable of draw speeds up to 3500 m/min for both wet-on-wet (WOW) and wet-on-dry (WOD) coating applications using a stainless-steel wire as a substitute filament with OD of 130 µm. The WOW configuration with three 20W 395nm UV-LED lamps for curing of the dual layer primary/secondary coatings was used for the DTS draw trials of the selected new generation coatings in this study. The coating applicator and die temperature setting was at 50ºC, with N_2 flow rate at 20 L/min. A wide range of dose conditions were selected from draw speeds of 500 m/min to 2700 m/min with all three lamps, plus two more lowest dose conditions of 1 lamp and 2 lamps at 2700 m/min.

2.1.1 Primary In-situ %RAU Measurement. The wire fiber sample for primary in-situ %RAU was prepared by dissecting the coating layers and exposing the inner primary coating surface for FTIR-ATR measurement. The degree of cure was measured by Nicolet 8700 Fourier Transfer Infrared (FTIR) Spectrometer of Thermo Scientific using Attenuated Total Reflectance (ATR) technique. The acrylate double bond conversion, %RAU, was calculated from the FTIR spectra of the cured coating on fiber and the liquid resin using the conventional method characterizing the reduction of absorbance peak corresponding to acrylate unsaturation; in this study, 810 cm^{-1} acrylate double bond peak was used.

2.1.2 Primary In-situ Modulus Measurement. A detailed description of the test method and data processing methodology of primary coating in-situ modulus on glass fiber has been introduced in previous paper [5], converting the directly measured primary storage shear modulus G_p from DMA into tensile modulus E_p with contributions from the glass compliance corrected through mathematical equations based on mechanical analysis. The primary coating in-situ modulus (ISM) on wire fiber follows the same methodology, only adapting the geometry to 130 µm wire OD and compliance to the stainless-steel material. At least 3 wire fiber specimens were measured for each fiber sample and the average storage tensile modulus E_p was reported as the primary in-situ modulus.

2.2 Cured Films by UV Conveyor Unit

Each coating sample was drawn down at a nominal 75 µm film thickness on glass plate. The sample was then cured on Fusion Light Hammer10 conveyor system of Heraeus Noblelight with 10 inch 600 W/in D lamp, purged with 8 ft^3/min N_2. The peak irradiance measured by radiometer IL490T was ~8 W/cm^2. The standard curing dose was 1.0 J/cm^2 . The film samples were then conditioned in the temperature/humidity controlled room at 23°C/50%RH and measured within 16-24 hrs after curing. The film modulus in this study was reported from the storage modulus E' at 25°C measured by DMA.

2.3 RT-DMA/NIR Spectroscopy

Rapid real-time dynamic mechanical analysis (RT-DMA) and rapid real-time near infrared (RT-NIR) spectroscopy have been successfully coupled into one time resolved analytical instrument: RT-DMA/NIR. It allows simultaneous real-time monitoring of photo-polymerizations of acrylates in terms of both their chemical parameters (double bond conversion) and network formation (modulus buildup). A TA Instruments RSA-G2 was used for the RT-DMA setup. The UV-light source is coupled-in via a hollow geometry fitted with a quartz prism to guide the UV-light onto the reflecting sample plate holder in the rheometer. As UV-source an Excellitas Omnicure LX500 385nm LED lamp with an irradiance of ~50 mW/cm^2 at the sample plate was used. An EIT Power Puck II was used to determine the Intensity. Through the same geometry, perpendicular to the UV-light, the NIR light is coupled in via prisms and reflected back via the same sample plate holder and guided to the detector. For the NIR an AVALIGHT-HAL-S-MINI2 was used as irradiation source in combination with a broadband (200-2500nm) light guide and a UV/VIS AVASPEC-NIR256-1.7-EVO NIRLine Spectrometer (900-1750 nm).

2.4 Cured Films by High Intensity High Temperature Curing System

The HIHT curing system was custom made for high Intensity/ high temperature film curing. A 395nm LED lamp with reflector design reached maximum high intensity ~20W/cm^2. Standard HIHT cure setting was 100ms exposure time, with 100% lamp intensity giving output UV dose of ~ 1.5 J/cm^2. The hot stage for controlling of curing temperature had temperature range from RT to 150°C. The HIHT film modulus was reported from the storage modulus E' at 25°C measured by DMA.

3. Results and Discussion

3.1 Analysis of ISM vs. %RAU Kinetic Curves of Conventional Coatings

The simplified kinetic model of pseudo first-order free radical polymerization reaction kinetics has been fit very well to the double bond conversion and the modulus buildup (or relative modulus) versus exposure time from the measured DTS wire fibers [1]:

$$R_P = -\frac{d[M]}{dt} = k_C[M] \quad (1)$$

$$\%RAU = 1 - \frac{[M]}{[M_0]} = 1 - e^{-k_c(t-t_{0C})} \quad (2)$$

$$\frac{E}{E_{max}} = 1 - e^{-k_E(t-t_{0E})} \quad (3)$$

where the polymerization reaction rate R_p scales with the first order of reactant [M], which in this case refers to the acrylate double bond concentration; k_C is the reaction rate constant for acrylate double bond conversion; k_E is the reaction rate constant for modulus buildup; t_{0C} and t_{oE} are induction time for conversion and modulus buildup respectively. The reported negative t_{0C} from the DTS %RAU kinetic fit is considered artificial because the measured %RAU was not real-time monitoring of the reaction, but the result of final cure degree including dark cure stage. Even though the absolute values of t_{oC} and t_{oE} may not represent actual induction time, t_{oE} - t_{oC} may correlate with gel time, the time for the reaction to reach gel point when an infinite polymer crosslinking network is formed and the coating abruptly changes from liquid to solid with a measurable elastic modulus.

The kinetic fit parameters of the three conventional coating types with different cure speeds as reported in [1] are re-analyzed in Table 1. The new parameter modulus buildup rate constant/double bond conversion rate constant ratio (k_E/k_C) is listed, as well as t_{oE} - t_{oC}. While the cure speeds of both conversion and modulus buildup increase with the trend of Coating C > Coating B > Coating A, they all share the same feature of $k_E/k_C<1$, which is responsible for the ISM vs. %RAU curve having a shape of accelerated increase, i.e., the ISM increasing rate with %RAU accelerates at higher %RAU. This leads to sharper rising of ISM at the last stage of %RAU, as shown in Figure 1 top plot. Coating A shows the sharpest increase at the last 20% of conversion because it has the lowest k_E/k_C ratio

of 0.5, i.e. the modulus buildup rate constant is only half of conversion rate constant. Coating C, despite having slightly lower k_E/k_C ratio than Coating B, shows less modulus rise at the last 20% conversion. This is from the influence of having the lowest $t_{0E} - t_{0C}$, which means the gel time of this coating is extremely short, building modulus fast at early stage. Figure 1 bottom plot visualizes the level of k_C and k_E of each coating and the shared feature of the three conventional coatings all having $k_E/k_C<1$, which all position in the area below the line of $k_E/k_C=1$.

Table 1. Re-Analysis of Kinetic Fit DTS Data from [1]

Curve Fit Results	Coating A	Coating B	Coating C
k_C (ms^{-1})	0.048	0.065	0.137
t_{0C} (ms)	-9	-7.2	-1.7
k_E (ms^{-1})	0.024	0.051	0.094
t_{0E} (ms)	8	6.9	-1
k_E/k_C	0.5	0.8	0.7
t_{0E}-t_{0C} (ms)	17	14	1
ISM vs. %RAU curve shape	accelerated increase	accelerated increase	accelerated increase

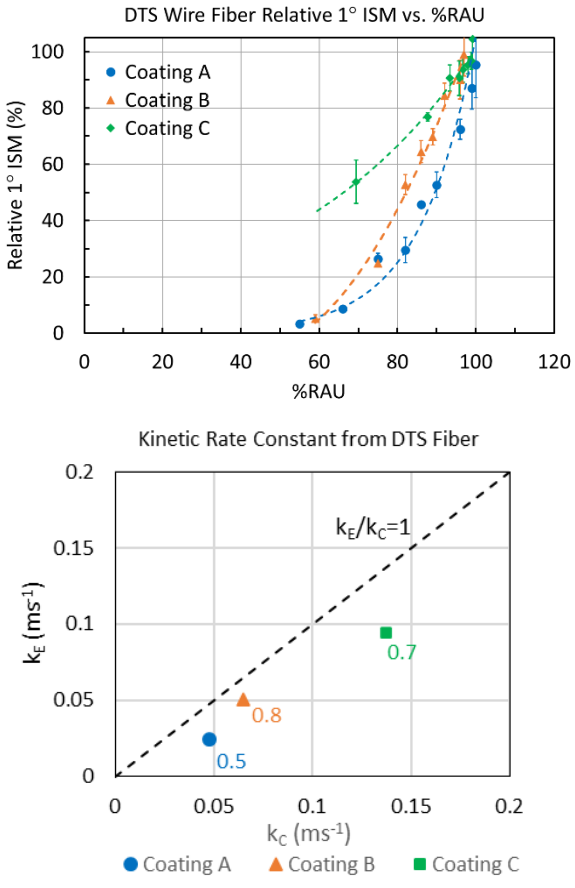

Figure 1. DTS wire fiber [1] (Top): Relative ISM vs. %RAU experimental and fit curves (Bottom): k_E vs. k_C with k_E/k_C labelled

3.2 Theoretical Curves with Different Arbitrarily Set Kinetic Parameters

For better understanding the behavior of modulus buildup vs. conversion, a set of theoretical curves are plotted in Figure 2. The top plot shows relative ISM vs. %RAU curves with 4 different sets of kinetic parameters. All 4 curves were set with the same conversion kinetics, and k_E was set to be $0.5\times k_C$ for Curve 1, $1\times k_C$ for Curve 2, $2\times k_C$ for Curve 3 and 4. Curve 4 was set with t_{0E} much shorter than the other three curves.

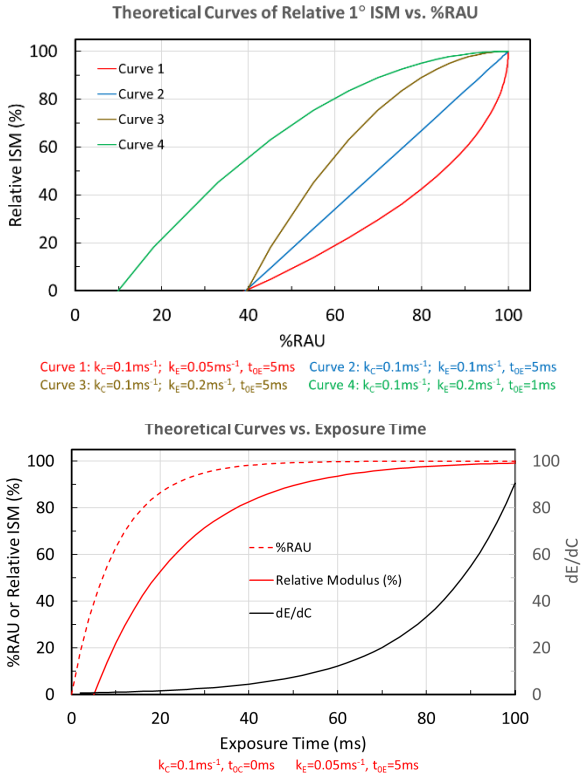

Figure 2. Theoretical curves (Top): Relative ISM vs. %RAU with the set kinetic parameters as listed (Bottom) %RAU, Relative ISM and dE/dC vs. Exposure Time

These theoretical curves clearly demonstrate the effect of k_E/k_C on determining the shape of relative ISM vs. %RAU: accelerated increase shape when $k_E/k_C<1$; linear increase shape when $k_E/k_C=1$; and decelerated increase shape when $k_E/k_C<1$. t_{0E}-t_{0C} does not affect the type of the shape, but lower t_{0E}-t_{0C} value representing faster gel time can effectively shift the modulus buildup earlier and smooth out the rising of the modulus at the last stage of the conversion.

To better understand the controlling role of k_E/k_C on the shape of modulus buildup vs. conversion curve, Figure 2 bottom plot shows the separate kinetic curves of %RAU and relative ISM vs. exposure time, with the given kinetic parameters from Curve 1 where $k_E/k_C = 0.5$, $t_{0E} = 5$ms. Both curves follow the same mathematical type of exponential increase to maximum shape (Eq. 2, 3), however, with k_E much lower than k_C, relative modulus rises slower than conversion in early stage; and as approaching later stage of curing, relative modulus is still significantly rising when conversion already approached final plateau stage, which explains the sharp rising of modulus at the last stage of the conversion. The derivative curve of dE/dC further demonstrates, mathematically while both growth rates of modulus and conversion versus time (the slopes of the two red curves) all decrease with time due to the reaction rate

R_p decreases as [M] consumed [Eq.1], the growth rate ratio of dE/dC is increasing with acceleration as the reaction proceeds. This is an intrinsic consequence as both relative modulus and conversion reach 100% when the reaction is completed. If modulus buildup rate is slower than conversion rate in the early stage of the reaction, its growth rate will intrinsically pick up more and more vs. the growth rate of conversion, and as a result the relative modulus rises sharply vs. conversion when approaching to the last stage of the reaction. It should be noted that this does not mean modulus sharply increases at the later stage of cure, as it is shown in the curve of relative ISM vs. exposure time that it is reaching plateau with exposure time. This is all about the relative comparison between growth rate of relative ISM and growth rate of conversion. Vice versa, when $k_E/k_C=1$, relative ISM linearly increases with %RAU with the same growth rate as shown in Curve 2; when $k_E/k_C>1$, the growth rate of relative ISM increase with conversion decelerates as the reaction proceeds, i.e. modulus buildup rate is faster than conversion rate in the early stage of the reaction and it intrinsically slows down when approaching to the last stage of the reaction reaching plateau region at the last 20% of conversion as in Curve 3 and 4.

The three types of scenarios with k_E/k_C <, =, > 1 as discussed above are simply mathematical models with arbitrarily set parameters. In actual situation of free radical polymerization kinetics building crosslinking network structure as in UV-curable acrylate coatings for optical fibers, the scenario of $k_E/k_C<1$ is considered conventional behavior and should apply in general. For soft primary coatings with a glass transition temperature far below room temperature, coating material is in the rubbery state and the modulus level is directly controlled by crosslink density of the network. Many different modeling work has been reported in the literature, for example the Durand and Bruneau model [6,7], a statistical model developed for modeling the free radical cure and network formation. The prediction from our past research work based on this model, using simple model coatings with typical compositions containing monofunctional monomer(s) and difunctional oligomer(s) similar to basic primary coating formulations, confirmed the modulus buildup vs. conversion is in fact in the shape of Curve 1, i.e. accelerated increasing trend. The statistical model does not use the simplified semi-empirical 1st order kinetic equations with k_E and k_C, but dives into the detailed calculations of probabilities of propagation and termination of free radicals from each type of reactive double bonds. But the fundamental scheme of network building is based on universal understanding, i.e. monofunctional monomers build linear backbones; only the difunctional oligomers build crosslinks when double bonds from both ends are converted and attached to the backbones. This makes the prediction straightforward that the modulus buildup should be slower than the conversion. But the growth rate of the relative modulus will intrinsically pick up more vs. the growth rate of conversion as both reach 100%, leading to this accelerated increasing shape of relative ISM vs. %RAU.

3.3 Kinetic Curves of the New Generation Coatings

An example of the new generation primary coating was introduced last year [3,4] demonstrating its excellent overall properties, more importantly superior fast cure feature and surprisingly the unconventional plateau shape of relative ISM vs. %RAU at the last 20% of the conversion. This feature not only offered more robust processing window and consistency of coating properties at fiber manufacture process, but also demonstrated post cure stability of the primary in-situ modulus improved over the conventional coatings, which is a valuable benefit to maintain superior microbending performance of optical fibers after cabling process with post cure procedures such as inking, ribboning and ring marking [4].

The new generation coatings have been designed not only with faster conversion cure speed but also with much faster modulus buildup cure speed. Table 2 compares the kinetic parameters from fitting DTS wire fiber %RAU and ISM data at different dose settings (see Figure 3), on a conventional coating P1 (same as Coating A in [1]) and three new generation primary coatings P2, P3, P4.

Table 2. Summary of Kinetic Fit DTS Data

Curve Fit Results	P1	P2	P3	P4
k_C (ms^{-1})	0.048	0.089	0.097	0.090
t_{0C} (ms)	-9	-12	-5.1	-16
k_E (ms^{-1})	0.024	0.088	0.117	1.14
t_{0E} (ms)	8	-1.6	1.0	3.7
k_E/k_C	0.5	1.0	1.2	12.7
t_{0E}-t_{0C} (ms)	17	10	6	20
ISM vs. %RAU curve shape	accelerated increase	linear increase	decelerated increase	decelerated increase

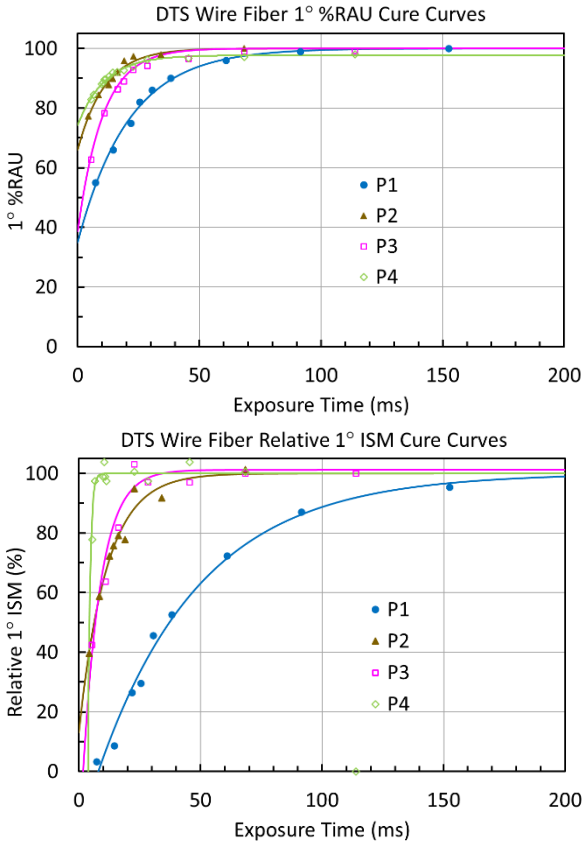

Figure 3. DTS wire fiber primary coating cure curves: (Top) %RAU vs. Exposure Time (Bottom) Relative ISM vs. Exposure Time

It is clear that both conversion rate constant k_C and relative modulus rate constant k_E of P2/P3/P4 are significantly higher than P1, which corresponds to the much faster rising of %RAU and relative ISM vs. exposure time as shown in Figure 3. Even more remarkable is the ratio of k_E/k_C reached 1 for P2 and >1 for P3 and P4. This is reflected in Figure 4 top plot where P2 shows relative ISM linearly increases with %RAU; P3 and P4 show decelerated increase shape, with ISM plateau in the last stage of %RAU. P4 has undoubtedly the highest k_E/k_C but the absolute value may not be reliable due to the early rising part of the ISM only had one data point as a result of its extremely fast modulus buildup speed. k_E vs. k_C in Figure 4 bottom plot illustrates the distinct difference between the conventional and the new generation coatings. Regardless the slow or fast cure coatings (lower or higher k_C or k_E), the conventional coatings all stay in the lower area of $k_E/k_C<1$, while the new generation coatings can reach the line of $k_E/k_C=1$ or even approach the upper area of $k_E/k_C>1$. $k_E/k_C\geq1$ is the key feature directly resulting in less modulus rise at the last stage of conversion, making coating on-fiber mechanical properties more robust in a wide window of processing conditions and more consistent towards fiber manufacture process variations.

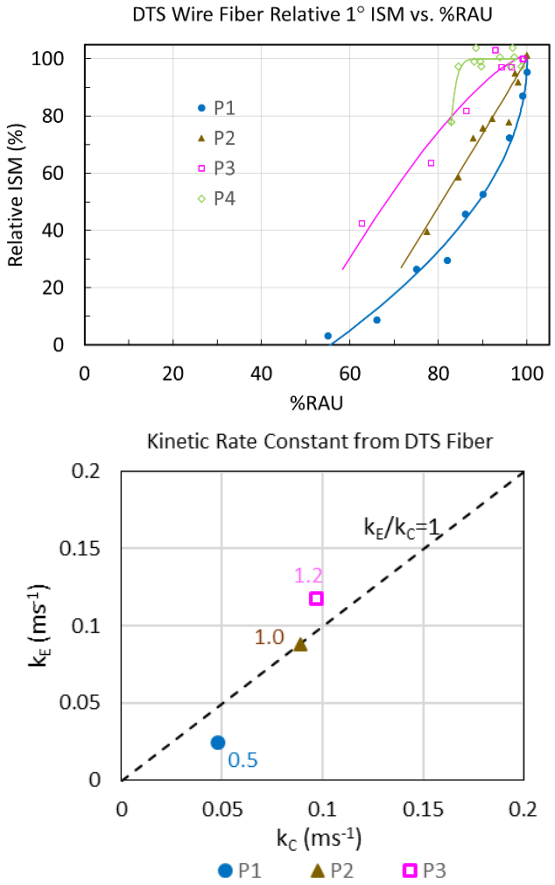

Figure 4. DTS wire fiber (Top): Relative ISM vs. %RAU experimental and fit curves (Bottom): k_E vs. k_C with k_E/k_C labelled

3.4 Study of Reaction Kinetics by RT-DMA/NIR

As discussed in section 3.2, $k_E/k_C<1$ is considered conventional behavior and should apply in general for chain growth free radical polymerizations building crosslinking networks. To understand the unconventional kinetic behavior, $k_E/k_C\geq1$, of the new generation coatings, an experimental study using real-time reaction kinetic monitoring instruments was conducted. Typical commercially available instruments include Real-Time FTIR or NIR for tracking double bond conversion, and Real-Time DMA for monitoring shear modulus buildup. A customized setup coupling Real-Time DMA and Real-Time NIR Spectroscopy was used in this study to simultaneously track the double bond conversion and shear-modulus G' with exposure time. All four coatings have been tested by RT-DMA/NIR method under two curing temperatures, 50°C and 100°C. 50°C represents typical coating die temperature and 100°C is to simulate actual coating temperature during fast curing with extensive exotherm at fiber drawing conditions. The results from RT-DMA/NIR of P1 and P4, selected to represent conventional coating and new generation coating, are plotted in Figure 5 for the two curing temperatures.

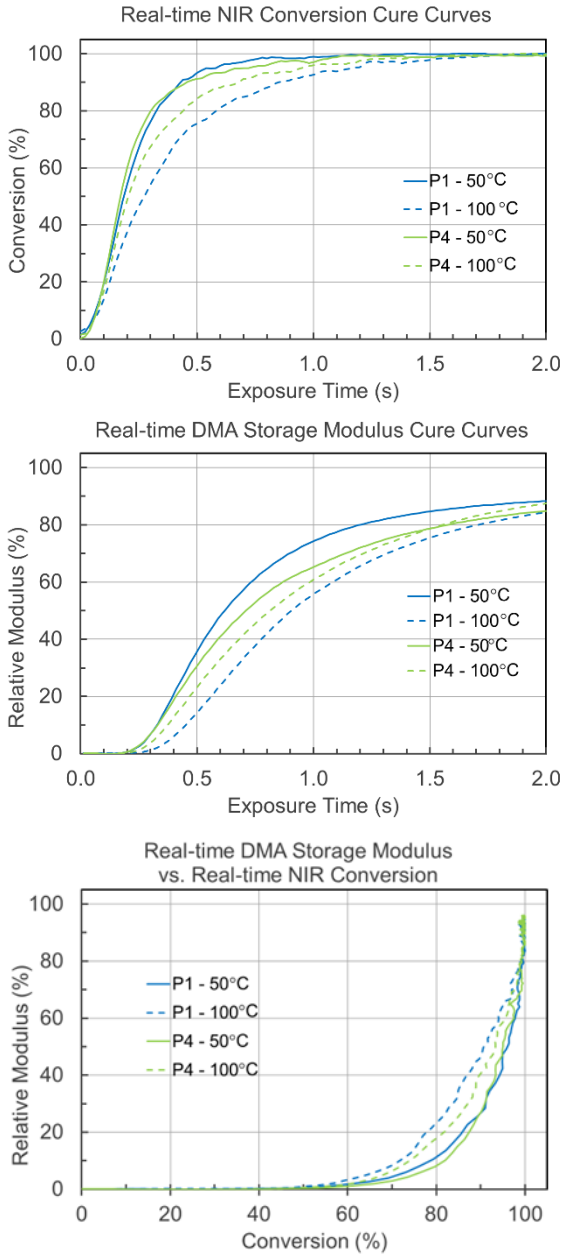

Figure 5. Real-time DMA/NIR cure curves: (Top) Real-time NIR Conversion vs. Exposure Time (Middle) Real-time DMA Relative Modulus vs. Exposure Time (Bottom) Real-time DMA Relative Modulus vs. Real-time NIR Conversion

As expected, cure speeds of both conversion and relative modulus are lower at higher temperature. High temperature favors side reactions (e.g. back-biting, chain scission, branching). With increasing temperature, the relative increase in side reaction rates is higher than free radical propagation reaction rate, resulting in lower cure speed as well as lower modulus due to more network defect formation from the side reactions. Different coating designs could influence temperature sensitivity of the cure speeds. P4 consistently shows less temperature sensitivity than P1: at 50°C, P4 conversion speed is similar to P1 and the relative modulus is even slower than P1, but both are faster than P1 at 100°C. This feature of cure speed insensitivity to temperature is expected to have contributed to the observed faster cure speed of P4 than P1 at fiber drawing conditions where with extensive exotherm the coating temperature could very well reach 100°C.

On the other hand, the trend of relative ISM vs. %RAU remains to be the conventional shape of accelerated increase for all coatings with $k_E/k_C<1$, as shown in Figure 5 bottom plot and Figure 6. This is consistent with the prediction from the classic modeling of the chain growth free polymerization and crosslinking network building kinetics. This means the new generation coatings are supposed to also follow the conventional kinetics of $k_E<k_C$. The discrepancy between the drastically different kinetic behaviors from DTS or glass fiber drawing process vs. RT-DMA/NIR seems to point to the fact that fast speed fiber drawing process is a very unique fast reaction process under much higher light intensity coupled with much higher temperature than any other normal UV-curable coating processing conditions. It is understandable RT-DMA/NIR with extremely low intensity <100mW/cm^2 UV light cannot accurately simulate the same kinetic behavior as from fiber drawing. It is however interesting to notice the high temperature effect from this RT-DMA/NIR study already drove k_E/k_C higher as shown in Figure 6. This was achieved by k_E decreasing less than k_C from 50°C to 100°C leading to higher k_E/k_C at 100°C, which corresponds to smoother rise of relative modulus vs. conversion at the last stage of conversion (see Figure 5 bottom plot).

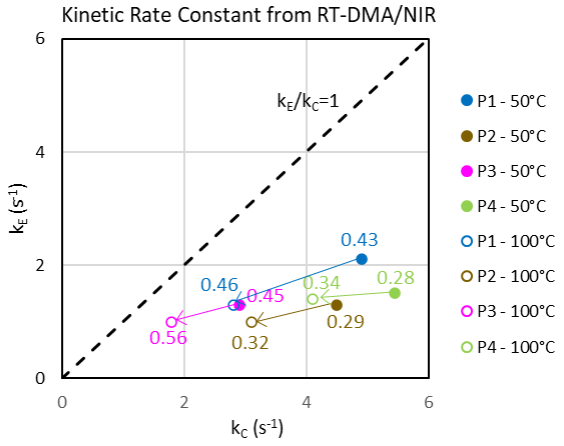

Figure 6. Real-time DMA/NIR k_E vs. k_C with k_E/k_C labelled

Before having experimental evidence confirming the effects from high intensity on k_E/k_C, it is safe to predict two major effects:

1) Cure speed per exposure time increases with higher light intensity. Based on the well-known model of steady state propagation [8],

$$\frac{R_P}{[M]} = k_p\sqrt{\frac{R_i}{2k_t}} \qquad (4)$$

where R_p is rate of polymerization; R_i is rate of initiation; k_p and k_t are rate constants of propagation and termination. As R_i is directly proportional to light intensity I, the entire form of this pseudo first order reaction rate constant k is proportional to $\sqrt{I}$. Depending on how different coatings respond to the higher intensity, the degree of modulus buildup rate constant increase vs. the degree of conversion rate constant increase, the new generation coatings may have been benefited more significantly on increase of k_E/k_C from the fiber drawing process.

2) Plateau modulus decreases with higher light intensity. Direct consequence of high intensity is the generation of a high concentration of radicals, which results in enhanced termination, and consequently results in more dangling chain ends and chain branches reducing effective crosslinking network density. While the overall number of chemical crosslink junctions may remain the same, defects such as dangling ends and chain branches compromise the capability of those crosslinks forming an elastically effective network that contributes to the material's load bearing capability, i.e. coating modulus. The reduction of E_{max} in fiber drawing compared to the plateau modulus from normal curing processes, such as conventional conveyor film curing, has been well known as the fact that primary coating in-situ modulus always lower than film modulus even when both attain full cure. As the modulus buildup refers to relative modulus to plateau modulus E_{max}, the reduction of E_{max} could contribute to a larger apparent k_E of relative modulus rate constant as it is faster to reach a suppressed plateau modulus. Even though all primary coatings have lower on-fiber in-situ modulus compared to the film modulus, conventional coatings were still proven to have $k_E/k_C<1$ in general. It is the advanced design with optimization of complex factors, such as faster modulus buildup speed vs. conversion speed, better control of temperature and intensity sensitivities of the reaction kinetics, boosted k_E/k_C from the conventional <1 region to the new window of ≥1 for the new generation coatings at fiber drawing conditions.

3.5 Cured Films by High Intensity High Temperature Curing System

To quantify the effects of high temperature and high intensity on coating modulus, the film modulus of selected primary coatings cured by a regular conveyor curing unit with intensity ~8W/cm^2 and by HIHT curing system with high intensity ~20W/cm^2 under 25°C cure and 100°C hot stage cure respectively are compared to the plateau in-situ modulus from DTS wire fibers in Figure 7. All four conditions were under sufficient doses ensuring %RAU reached ~100%. The modulus values were all reported from the storage modulus E' at 25°C measured by DMA.

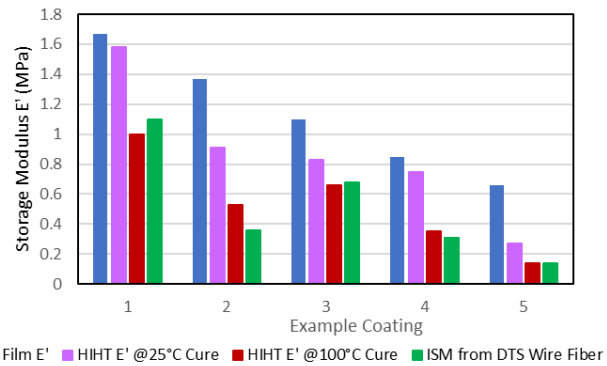

Figure 7. Examples of intensity and temperature effects on modulus of primary coating

Despite differences in the degrees of drop from regular film modulus to HIHT film modulus, the trend is universal that film moduli from HIHT are all lower than regular film moduli from conveyor curing unit, with the 100°C drop even lower than that at 25°C cure. The combination of this high intensity condition ~20W/cm^2 coupled together with high temperature condition at 100°C appears to match well with the in-situ modulus measured from DTS wire fibers. These comparisons provide strong evidence that the primary coating in-situ modulus on fiber even at full cure always being lower than film modulus is essentially the result from the combined high intensity and high temperature effects at fiber drawing.

4. Conclusions

A new kinetic parameter is introduced, i.e. modulus buildup rate constant/double bond conversion rate constant ratio (k_E/k_C). The new generation coatings demonstrated breakthrough behavior of $k_E/k_C \geq 1$ in contrast to the conventional coatings with typical behavior of $k_E/k_C < 1$. This key feature directly results in less modulus rise at the last stage of conversion, making coating on-fiber mechanical properties more robust in a wide window of processing conditions and more consistent towards fiber manufacture process variations. It has been manifested in this study that this unconventional kinetic behavior is closely related to the unique high intensity high temperature curing condition of optical fiber drawings. The optimized design of the new generation coatings with improvements in multiple attributes, such as faster modulus buildup speed vs. conversion speed, better control of temperature and intensity sensitivities of the reaction kinetics, all contributed to k_E/k_C level being fundamentally elevated to the new window of ≥1 at fiber drawing conditions, which has been proven to be a key advantage to optical fiber processing robustness.

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