

Chapter 4

Optical Fiber Coatings

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4.1 INTRODUCTION

It could be said that the modern era of fiber optics began in 1966, with the publication of the paper, "Dielectric-fibre surface waveguides for optical frequencies" by Dr. C. K. Kao and G. A. Hockham of Standard Telecommunications Laboratories Ltd. (STL) [1]. This paper discussed the theory and potential use of optical fiber for communications. Dr. Kao believed that fiber loss could be reduced below 20 decibels per kilometer by eliminating metal impurities in the glass. Such attenuation would allow 1% of the light entering one kilometer of this type of fiber to successfully reach the other end.

During the same period of time, Corning Glass Works researchers, R. Mauer, D. Keck, and P. Schultz were experimenting with high purity fused silica [2]. They employed titanium as a dopant to produce a higher refractive index (1.466) fiber core, compared with the surrounding lower refractive index (1.4584) silica cladding. They were able to draw fibers, at 1900°C, to a diameter of 100 μm . In 1970, "Method of Producing Optical Waveguide Fibers", was filed with the US Patent Office and issued three years later as US 3,711,262.

Prior to 1966, fibers had losses of roughly 1000dB/km [2]. The Corning team effort reduced this loss to only 16dB/km, thus demonstrating the feasibility of optical fibers as a communication medium. Such fibers were said to be capable of carrying 65,000 times more information than copper wire [3].

This chapter will focus on the development, science and performance of protective coatings for optical fiber. The widespread deployment of high bandwidth optical fiber would not have been feasible without the immediate protection afforded by UV curable coatings. Applied on fiber draw towers, at speeds approaching 60 mph, these coatings enable fibers to survive the rigors of proof testing, cabling and installation. UV curable coatings have also proven to be durable in the field, with millions of kilometers of fiber already in operation for more than 20 years.

4.2 EARLY HISTORY OF COATINGS FOR OPTICAL FIBER

Although the inherent strength of pure silica [4] is known to be nearly 14,000 N/mm², it soon became apparent, during the development of optical fibers, that some type of protective coating was required to shield the fibers from abrasion to preserve their strength. The combination of moisture and stress causes microscopic flaws in the glass to propagate, resulting in fiber failure. Without protective coatings, optical fibers would never have been a practical alternative to copper for telecommunications.

According to Stevens and Keough [5], the prime requirements for optical fiber coatings were protection against microbending and static fatigue. This necessitated that cured coatings "be concentric about the fiber, be continuous over the length of application, be of constant

thickness, be abrasion resistant and moisture retardant.” Suitable liquid coatings, consequently, had to be of a workable and stable viscosity (minimally 6 months) [6], adhere to glass, have a relatively low surface tension, be free of particle contamination, have minimal hydrogen generation (10^{-2} - 10^{-4} $\mu\text{l/g}$) [6, 7] and fast cure speeds. In addition, it was expected that cured coatings would have stable modulus and adhesion properties over the 25-year operating life of the installed cable.

In the early 1970s, J.E. Ritter Jr. [8] explored the effectiveness of polymeric coatings in preventing the degradation of abraded soda-lime glass in the presence of moisture. His results indicated “acrylic, epoxy and silicone coatings all significantly increased the short-term strength of abraded glass.” He believed that the coatings functioned as a diffusion barrier and limited the availability of water at the glass surface.

Wang, et al [9] and Wei [10] issued additional reports on the contributions of polymeric coatings towards providing resistance to moisture, in the early and mid-1980s. Wang et al reported on the accelerating effects of water on the deterioration of fiber strength through fatigue and aging. Wei further described how the combination of moisture and stress initiates crack propagation and ultimately reduces fiber strength and provided examples how this was retarded by polymeric coatings [10].

Early coating materials used in the protection of optical fiber included two package systems, blocked urethanes, solvent-based lacquers, silicone rubbers and ultraviolet radiation curable epoxy acrylates [11, 12]. By the early 1980s, UV curable coatings proved to become the popular choice for protection of optical fibers, largely because of their rapid cure response and easily tailored properties [6, 13, 14, 15].

In 1974, H. N. Vazirani of Bell Telephone Laboratories developed one of the first UV curable coatings for optical fiber. US Patent 4,099,837 [13] describes that the “polymer coating comprises the polymerization product of a prepolymer mixture resulting from reacting acrylic acid with a 0.4 to 1.0 weight ratio mixture of aliphatic diglycidyl ether to aromatic diglycidyl ether, and further characterized in that polymerization product contains a UV sensitizer in order to cure said prepolymer mixture with ultraviolet light.” Additional claims cited 1,4-butanediol diglycidyl ether as the aliphatic ether and the diglycidyl ether of halogenated bisphenol A as the aromatic ether. The use of a silane or titanate coupling agent was also claimed.

The fiber coating, described above, was applied and cured as the fiber was drawn at a speed of 25m/min. Physical properties of the polymer coating were reported as a Young’s modulus of 6,000psi and an elongation at break of ~20%. The resulting coated fiber was evaluated by Schonhorn, et al [11, 16] and found to have tensile strengths > 500,000 psi, in 1 km gauge lengths, and long term strength retention properties, in moist environments [17, 18]. Schonhorn, et al [19] also demonstrated that the interaction between the coating and the glass interface determines the ability of the coating to prevent degradation of fiber strength, and that this is enhanced by the inclusion of silane coupling agents within the coating.

4.3 EVOLUTION OF OPTICAL FIBERS AND PROTECTIVE COATINGS

Attenuation losses associated with optical fibers continued to decline during the 1970s: 4dB/km (1975); 0.5dB/km (1976); and, 0.2dB/km (1979). The latter value corresponds to 63% of a light signal reaching the end of a 10km long fiber [20]. In 1982, Corning achieved an

attenuation of 0.16 dB/km, on singlemode fibers transmitting at 1550nm, representing a 100-fold improvement over the 1970 transmission of Mauer's first low-loss fiber [21]. It has been reported that if the ocean had the same transparency as the glass in such low-loss fibers, one could see to the bottom of the Mariana Trench in the Pacific Ocean, a little more than 6 miles below sea level [22].

4.3.1 Coating Contributions to Microbending Minimization

Concurrent with the above improvement in fiber transmission properties, fiber coatings evolved from single layer to dual layer systems. In the early 1980s, the outer diameter for dual layer systems was standardized to between 245 and 250 microns, while the outer diameter for the inner coating, contacting the glass, ranged from 190-210 microns. The dual layer coating system was designed to enhance protection for fibers against microbending-induced attenuation. This phenomenon is caused by microscopic departures from straightness in the waveguide axis [23]. Varying causes of microbending include longitudinal shrinkage of the fiber coating, poor drawing or cable manufacturing methods, or stresses imposed during cable installation [24].

D. Gloge [25] first reported that losses, due to microbending, could be reduced by shielding the fiber from outside forces by using a soft, inner coating, having a modulus of 14,000 psi (~100 MPa), and an outer shell of a material having a modulus of 140,000 psi (~1000MPa). The inner primary coating is designed to act as a shock absorber, under the tougher outer layer, to minimize attenuation due to microbending. It has a very low crosslink density and current primary coatings typically have a modulus between 0.5 – 3 MPa. It must adhere to the glass, yet strip cleanly from the glass, to facilitate splicing and connecting.

The outer primary coating, sometimes called the secondary coating, protects the primary coating against mechanical damage and acts as a barrier to lateral forces. It also serves as a barrier to moisture. It is a hard coating, having a high modulus and Tg, to facilitate good handling and durability. It is generally fast curing, for ease of processing, and has good chemical resistance to solvents, cable filling gels and moisture. The surface properties of the secondary coating must be carefully controlled, to allow good adhesion of the ink, used in color identification, while at the same time allowing for good winding onto take-up spools. A schematic diagram of an optical fiber is shown below.

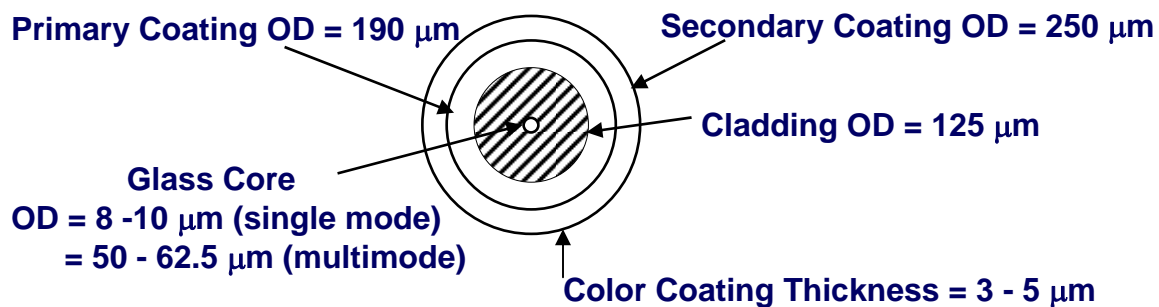


Figure 4.1 Schematic of coated fiber cross-section

During the development of dual layer coating systems, it was important to not only consider the modulus of the inner coating at room temperature, but also at colder temperatures to which fibers could reasonably be exposed [12]. Viscoelastic coating materials are known to increase in modulus, as temperature drops, i.e. they become stiffer. If these coatings also adhere tightly to glass, they can impose forces on the fiber that will produce microbending induced signal attenuation.

Kuzushita, et al [26] reported on the low temperature modulus properties of nine different coatings and correlated them with the added attenuation observed at -30°C , for fibers coated with four different resin types: polyesterpolyol type urethane acrylate, polyetherpolyol type urethane acrylate, polybutadiene acrylate and UV curable silicone.

The modulus of coating films at cold temperatures was initially determined by Instron® tensile strength testing of films in temperature controlled chambers. This process proved fairly time consuming, because of the time required for temperature equilibration between runs.

The development of dynamic mechanical analyzers gave rise to the exceedingly more efficient dynamic mechanical analysis of UV cured films. This non-destructive test, allows for temperature sweeps, at a chosen frequency, to define a material's modulus as a function of temperature. The slope of a coating's modulus curve, as it changes from the glassy phase to the rubbery phase, can, in part, determine the suitability of coatings for use at low temperatures. Sarkar, et al [27] share examples of DMA curves for soft, RTV silicone and UV cured urethane acrylate primary coatings and show how they compare with the attenuation properties of fibers on which they are applied. This reference also illustrates improved temperature induced attenuation at 1300nm, for the UV cured urethane acrylate coating, which exhibited a significantly lower modulus profile, at lower temperatures.

4.3.2 Glass Fiber Fracture Mechanics and Coating Contributions to Fiber Strength Retention

Fiber fatigue is an important mechanical property of optical fibers. Pristine silica fibers have strengths of $\sim 7\text{GPa}$ at ambient condition. However, fibers can show fatigue when subjected to lower stresses for long periods of time. Fiber fatigue is thought to occur by crack growth of existing flaws on the glass surface, due to interaction between the Si-O bond and the moisture in the environment, when the fiber is subjected to stress.

The coating is thought to contribute to fiber fatigue in that basic compounds, present in the composition, accelerate glass corrosion. Conversely, acidic components have been shown to improve fatigue resistance. Skutnik [28] found that coatings with strong adhesion facilitated a greater n-value fatigue parameter for coated fibers. Supporting this is the observation that both n-value and adhesion generally increase with time after draw.

When measuring fatigue, it is typical to measure either static fatigue or dynamic fatigue. In static fatigue a constant stress is applied to the fiber, and the time to failure is measured. In dynamic fatigue, the strength of the fiber is measured as a function of the applied stress rate.

There are two techniques for measuring dynamic fatigue: tension and two-point bending. In the tensile test, a fiber is gripped at each end and pulled, in tension, until it breaks. In the two-point bending test, fibers are bent between two faceplates that move towards each other, at a controlled rate, until the fibers break [29-32].

Gulati [33] published one of the earliest papers, which discussed the test methods for measuring the tensile and bending strengths of optical fibers. He also calculated the required proof stress level to insure fiber durability of at least 20 years, when subjected to a known value of service stress.

Michalske and Bunker [34-38] published a number of studies on the fracture mechanics of glass and glass fibers. Helfinstein published a very thorough review on delayed failure or sub-critical crack growth in glass [39].

Wang and Zupko [17] found fiber strength retention to be a function of fiber wetting and adhesion by protective polymeric coatings. Fiber strength decreased when application viscosity was increased and wetting of the fiber was consequently decreased.

Sakaguchi, et al [40] demonstrated that silane treatment stabilizes glass surfaces against water. The group evaluated the behavior of untreated, silicone treated and silane treated glass, in water, at different temperatures. Infrared spectroscopy was used to monitor the interaction of water molecules with glass silanol groups.

Schlef, et al [41] evaluated the performance of a number of UV curable primary and secondary coatings, via static fatigue, dynamic tensile and proof testing, and concluded that these coatings “retain the initial strength and fatigue resistance of optical fibers.”

Dunn and Smith [42] performed a variety of abrasion and static fatigue tests which demonstrated that the use of hard, UV cured secondary coatings yielded fibers with improved strength and handling characteristics, compared with silicone single coatings.

4.3.3 Durability of Fiber Optic Coatings

Long term durability of protective coatings was considered to be of considerable importance since fibers installed into Outside Plant networks were expected to have a minimum service lifetime of 25 years [43-45]. D. R. Young [46] provided “the first report on a long term, long length static fatigue test in an outdoor, in-ground trough environment.” He reported that UV-cured acrylate Composite Protective Coatings were shown to provide excellent protection against a variety of environments: 65°C air, high and low pH solutions and temperature/humidity cycling of 150 days 65°C/98% RH to 10°C/4% RH. Weibull plots, which describe the probability of failure at a given stress for a given length, were provided for fibers exposed to temperature/humidity cycling and immersed in petroleum jelly, similar to what is used as loose tube filling compound.

In 1984, O. R. Cutler [47] reported on the results of his durability testing on UV curable coating films. In his study, Cutler exposed 3 mil thick films of a variety of commercial fiber coatings to temperatures of 38°C, 54°C, 88°C, 125°C and 175°C, for up to one year. He developed Arrhenius plots that showed, based on the time required to double the coating’s modulus, operating lifetimes of primary and secondary coatings could extend beyond 100 years, at room temperature. Several coatings had similar calculated service lifetime when aged continuously at 54°C (130°F).

Nevins and Taylor [43] issued their report on the effect of a variety of environmental conditions on the “three key characteristics of fiber optic waveguides which may be affected by

environmental conditions: strength, attenuation and resistance to losses caused by microbending.” In addition to the conditions reported earlier by Young [46], the research team of Nevin and Taylor mentioned exposure to seawater, fungi and abrasives. They also cited an experiment, Procustes, designed to correlate accelerated aging tests with actual long-term aging.

Simoff, et al [48] studied the aging of a polyether urethane acrylate primary coating, both in films and on fiber, and correlated the changes in physical properties of the films with the stripping force required to remove the coating from the fiber.

In 1993, Chawla, et al [49], reported on fiber optic coating durability, as was measured by weight changes and shifts in dynamic mechanical analysis (DMA) modulus profiles. Dynamic mechanical analysis provides insight into a material’s durability following exposure to a wide variety of environments such as hydrolytic, thermo-oxidative, and chemical exposure. Comparison of DMAs, before and after exposure to these conditions, allows one to monitor changes in the material’s glass transition temperature profile and also the material’s equilibrium modulus. The equilibrium modulus region of the DMA curve is observed at the modulus plateau reached in the rubbery phase. This modulus can be related to the crosslink density of a cured coating’s network through the equation

$$\rho_0 = E_0 / 6kT$$

where ρ_0 represents cross-link density, k is the Boltzman constant, and T is the temperature, in degrees Kelvin.

Decreases in equilibrium modulus indicate a reduction of a coating network’s crosslink density, through chain scission, and hence a weaker coating. Conversely, increases in the equilibrium modulus can signify embrittlement of the coating network through crosslinking. Chawla, et al, demonstrated excellent durability of several primary coatings after 1 year of aging at 125°C.

The results of additional durability studies [44, 45, 50-56] have been published and are available to give the reader a deeper understanding of this subject.

4.4 CABLING OF OPTICAL FIBERS

Early 250 μm outer diameter coated fibers were further protected from the potential hazards of the cabling process by placement in buffer tubes. The tubes had an inside diameter many times larger than the diameters of the enclosed fibers. Fiber length was designed to slightly exceed the length of the buffer tubes, in order to introduce fiber slack. This slack was necessary to prevent tensile loading, which could compromise the optical transmission of the fiber. The buffer tube also contained water blocking filling compound. The filling compound not only blocked water from reaching the fiber, but also provided a medium in which the fibers could freely move past each other during thermal expansions and contractions. Protective fiber coatings had to be resistant to changes in material properties induced by such filling compounds, which often comprised fumed silica dispersed in mineral oil.

An alternative to the above “loose tube” cable design was the “direct strand buffer” construction. An example consisted of a fiber that was coated with a silicone coating to

400 μm outer diameter and then over extruded with a nylon jacket to 900 μm outer diameter. Fibers of this type were wound about a strength member that had a lower expansion coefficient than that of the tight-buffer coating materials.

In tight-buffered or upjacketed fiber, 250 μm fiber is overcoated with a tough, thermoplastic extrusion, such as a Nylon 12, polyethylene or PVC. These thicker fibers provide improved handling, and mitigate the use of a cabling gel. Tight-buffered cables have been used in premise applications for over two decades. Although widely used, thermoplastic extrusions are limited by slow line speeds, 100-200 m/min, and high scrap rates.

UV materials have successfully been employed as a cushioning layer between flame retardant thermoplastic extrusion and the fiber. Construction of these types of fibers involves upjacketing a standard 250 μm fiber to 400-500 μm , with a UV coating, and then extruding with a colored thermoplastic to bring the final thickness to 900 μm .

Another approach to tight-buffering, using UV curable materials, involves upjacketing a colored 250 μm fiber, with a clear UV resin, directly to 500 or 900 μm . The development of flame-retardant UV cure coatings has been reported [57, 58]. Montgomery, et al [59] describe the use of a tight-buffer coating containing a pigmented flame retardant, thus giving performance typically observed by thermoplastics. These UV curable upjacketed fibers can be processed on a modified ink-coloring machine, giving much faster processing speeds, up to 600m/min, than thermoplastics [60].

During the early to mid-1980s, Japan began using UV curable matrix materials to bond fibers together in 4-fiber ribbon arrays. AT&T had earlier pioneered 12-fiber Adhesive Sandwich Layer Ribbons, in which fibers were packaged between two plastic tapes coated with pressure sensitive adhesive. UV curable matrix materials for ribbon application became more popular globally, with the growing demand for fiber, in the 1990s.

Prior to the cabling of fiber, in either loose tube or ribbon configuration, the vast majority is colored with a UV curable ink, in an off-line operation. UV curable inks are designed to provide high-quality color on fiber for good identification, and are typically applied at 3-5 μm thickness. The UV cured ink layer has a hard and slick surface finish to allow suitability in both loose tubes and ribbons. It is also designed to have excellent adhesion to the secondary coating, and to provide excellent resistance to cabling gel. Colors are designed to be bright and distinct, giving good color retention over time.

4.5 SPECIALTY COATINGS

Low refractive index coatings are used for cladding of plastic optical fiber or glass cores. They are by nature relatively low modulus materials and are therefore often protected by overlaying a standard secondary coating. The lower refractive index coating is preferred for fiber used in laser and amplifier applications. The low RI coating increases the numerical aperture (NA value) allowing for higher power inputs and thus higher-powered lasers. These coatings typically have a refractive index less than 1.41. For application as a single coat, a modulus of approximately 120-200 MPa is desirable, however when used as the primary layer in a dual coating system, a modulus of 15-50 MPa may be used.

4.6 BASICS OF OPTICAL FIBER CHEMISTRY

In the late 1970s and early 1980s, UV curable coatings designed for the protection of optical fiber transitioned from single coatings, based on epoxy acrylate chemistry, to dual layer coatings based on urethane acrylate chemistry. These coatings are comprised of one or more urethane acrylate oligomers [12, 61], diluent monomer(s), photoinitiator(s) and various additives.

4.6.1 Oligomers

Urethane acrylate oligomers are based on stoichiometric combinations of di-isocyanates (DIC), polyols and some type of hydroxy-functional terminating species containing a UV reactive terminus (A). Urethanes are known for their toughness and flexibility, combinations that add value to the performance and protective nature of the coatings in which they are contained.



Figure 4.2 Typical Urethane Acrylate Structure

Depending on the properties desired, different types of polyols are chosen. Typically oligomers are made using the following types of polyols:

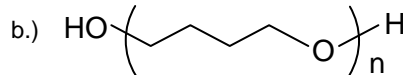
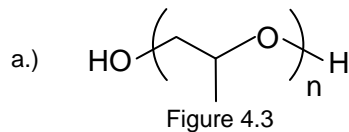


Figure 4.3 (a) Polyether- Polypropylene glycol (PPG) (b) Polyether- Polytetramethylene glycol (PTMG)

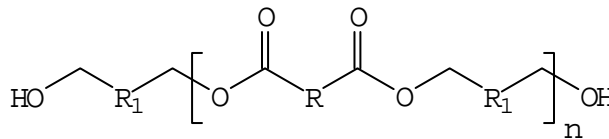


Figure 4.4 Polyester

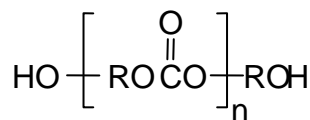


Figure 4.5 Polycarbonate

Urethane acrylate oligomers employed in UV curable optical fiber coatings generally range between 1,000-10,000 number average molecular weight. Higher molecular weights tend to be exceedingly viscous. The viscosity can be reduced either by heat and/or addition of diluent monomer. Typical viscosities of coatings supplied to producers of optical fiber are less than 10,000 mPa.s. The viscosity of coatings, as they are applied to fiber, is typically 2,000 mPa.s

or less. In general, high molecular weight urethane acrylate oligomers are used in soft, low modulus coatings, while low molecular weight oligomers are employed to produce hard, high modulus coatings.

Acrylated epoxies are another type of oligomer commonly used in optical fiber coatings. Epoxy acrylates are tough, fast curing materials that have good chemical resistance. They tend to be used in secondary coatings.

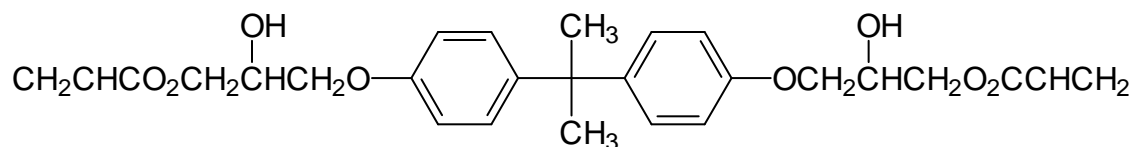


Figure 4.6 Bisphenol-A diglycidylether diacrylate

4.6.2 Monomers

Diluent monomers can be mono- or multi-functional with respect to UV reactive terminal groups. Mono-functional diluent monomers are generally more efficient in their diluency; however they are only capable of reacting linearly and will not add to the crosslinking of polymer networks. Mono-functional monomers can be aliphatic, e.g. isodecyl acrylate (IDA), aromatic, e.g., phenoxyethyl acrylate (PEA), or alicyclic, e.g. isobornyl acrylate (IBOA). In general, mono-functional monomers find their greatest utility in soft primary coatings, which are designed to have very low modulus. Mono-functional monomers generally give good flexibility and low shrinkage.

Multifunctional monomers are most often employed in secondary coatings, which have higher modulus and crosslink density relative to primary coatings. Multifunctional monomers are added for fast cure speed, increased crosslinking and tensile strength [61].

Monomers possess a variety of useful properties beyond their acrylate functionality. These property differences provide skilled formulators the latitude to design coatings with optimized performance with regards to viscosity, cure speed, tensile properties, glass transition temperature profile, oleophobic/hydrophobic balance, adhesion, and long-term durability in various environments.

4.6.3 Photoinitiators

Photoinitiators, as their name implies, initiate the photopolymerization process by absorbing light. In UV curable acrylate systems they form radicals by cleavage (Norrish type I) or hydrogen abstraction (Norrish type II). The effectiveness and efficiency of photoinitiators is largely governed by their absorption spectra and extinction coefficients. It is important to appropriately match the absorption spectrum of a photoinitiator with the emission spectra of the lamps employed for coating cure.

4.6.4 Adhesion promoters

Primary coatings based exclusively on oligomers, monomers and photoinitiators generally do not provide adequate adhesion to the glass fiber. This is especially true in humid

environments. It is therefore necessary to incorporate an adhesion promoter or glass-coupling agent. Typically adhesion promoters have an organic functional group, which bonds with, or associates with, the coating. The adhesion promoter bonds to the glass surface through hydrolysis and condensation reactions.

Alkoxy silanes are commonly employed as adhesion promoters in fiber optic coatings.

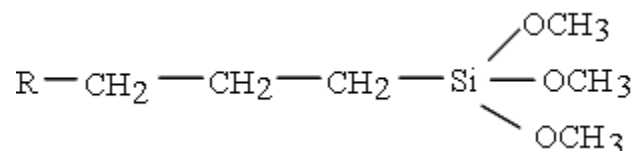


Figure 4.7 Organopropyl trimethoxysilane

The organofunctional end of the adhesion promoter covalently links with the oligomer or other radiation curable moieties. The glass-coupling moiety is generally inorganic in nature and bonds with the glass surface. Types of organic functionality include amino, epoxy, vinyl, methacryloxy, isocyanato, mercapto, polysulfide, and ureido. The inorganic end of the coupling agent must have hydrolyzable groups, which leave silanol groups that can condense with the surface silanol groups of the glass fiber surface. Methoxy and ethoxy groups are typically employed as hydrolyzable groups of silane coupling agents.

Several types of non-silane adhesion promoters include chromium, orthosilicate, inorganic ester, titanium, and zirconium systems.

4.6.5 Other Additives

Other additives in fiber optic coatings include anti-oxidants and stabilizers and slip additives. Anti-oxidants and stabilizers are added to coatings to maintain the desired viscosity of the liquid composition, and impart resistance to cured films against degradation by light and oxidation. Hindered phenols are widely used anti-oxidants in fiber optic coatings, whereas hindered amines provide stability against light. Additives such as silicones are added to the coatings to modify the surface properties.

The standard components of a fiber optic coating are shown in the table below, together with typical levels at which they are present, and their contribution to the coating

Table 4.1
Typical fiber coating composition

Component	Contribution	% concentration
Oligomer acrylate	Controls final cured film properties, flexibility, chemical resistance	30 – 60
Reactive diluent or monomer	Reduces coating viscosity and contributes to coating cure speed	20 – 40
Photoinitiator	Absorbs UV light and initiates polymerization	<5
Additives (inhibitors, adhesion promoters, slip additives)	Stabilizes liquid coating, enhance cured film adhesion to glass, and reduce surface friction	<2

As mentioned above, acrylate systems cure by free radical photopolymerization. Photopolymerization occurs in several stages as shown in the following subsections.

4.6.5.1 Initiation

Initiation involves the absorption of light, which, via several intra-molecular energy transfers, yields primary radicals. This is followed by the addition of the resulting primary radicals in a Michael type reaction to a suitable double bond, thereby resulting in propagating radicals [63].

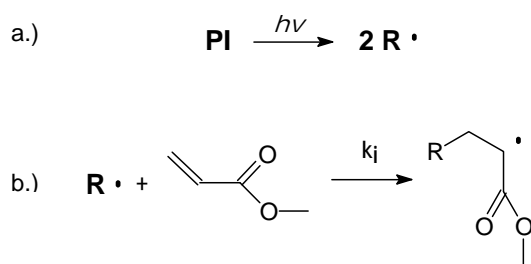


Figure 4.8 (a) Photoinitiation fragmentation (b) Free radical initiation

4.6.5.2 Propagation

As propagation reactions, all additions after the primary addition are counted and treated in a similar manner (Fig.4.9).

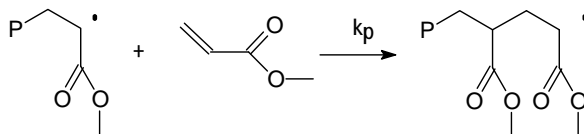


Figure 4.9 Chain Propagation

4.6.5.3 Termination

Bimolecular termination: The standard that is employed in all classical descriptions of radical polymerization.

Primary Radical termination: The propagating radicals are terminated by initiator radicals (Fig. 4.10).

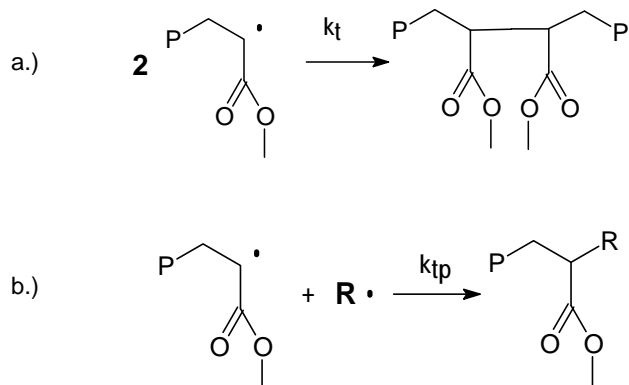


Figure 4.10 (a) Bimolecular termination (b) Primary radical termination

In addition to acrylate systems, free radical polymerization may also employ thiol-ene chemistry. An alternate curing mechanism to free radical polymerization is cationic polymerization

In thiol-ene chemistry [64], a thiol (mercaptan) radical reacts with an olefin in the presence of UV light. While thiol-ene systems have been evaluated for their potential use in optical fibers, they have never been used commercially, to the knowledge of the authors.

Cationic polymerization involves the acid polymerization of an epoxy or vinyl ether group. Typically diaryliodonium or triarylsulfonium salts are used as photoinitiators. Epoxies are fairly slow curing; however vinyl ethers cure extremely fast. Advantages of cationic cure include an absence of oxygen inhibition, and good through-cure. However, cationic cure suffers from moisture inhibition, limited raw material selection and higher cost. With cationic polymerization, curing continues after irradiation.

Some hybrid systems such as acrylate free radical and cationic cure have also been employed in fiber optic coatings, however these are very rare [65].

4.7 APPLICATION OF COATINGS ON THE DRAW TOWER

Optical fibers are drawn from glass preforms at temperatures approximating 2000^oC. The majority of tower systems employ the wet-on-dry application method, wherein fibers pass through a primary coating applicator, followed by one or more UV radiation emitting lamps, and then through a secondary coating applicator, again followed by one or more UV radiation emitting lamps. In an alternative wet-on-wet application protocol [66, 67], fibers are passed through both the primary and secondary coatings prior to UV exposure.

It is imperative to apply concentric coating layers, to prevent damage to the fiber during the drawing operation, and to maximize fiber strength and microbending resistance. Non-concentric coating application puts differential stress on the fiber when cured. An unevenly coated fiber will experience non-uniform forces during periods of coating expansion and contraction and is susceptible to greater attenuation of light signals passing through the fiber.

The earliest applicators used were of open cup geometry with either rigid or flexible tips [68]. Some of these comprised a temperature-controlled cylinder, which contained fitted split conical dies [23, 69] that produced “constant coating thickness over a wide range of coating viscosities and drawing speeds.” Tapered dies aided concentric application of each of the coatings to the fiber [42, 70].

At drawing speeds >1.5 m/sec, open cup applicators tended to have problems with coating meniscus collapse and bubble entrainment. Paek [71] studied a number of factors that were critical to increasing operating speed. These factors included fiber cooling rate, applicator efficiency and available UV energy. He noted that shear force in the coating die needed to be minimized to avoid beading on the fiber due to non-Newtonian flow effects of the coating. The conical shaped dies, used in open-cup applicators, were calculated to produce a shear rate of 10,000 sec⁻¹, at a speed of 1m/sec.

Paek and Schroeder [72] were among the first to publish results on the behavior of forced cooling of bare glass fibers, during draw, to prevent deterioration of the coating. This doubled the allowable drawing speed from 1-2 m/sec. Paek increased the height and diameter of the coating cup to increase the “wetting time and minimize the air trapping effect in the interface

between the coating and the fiber.” These modifications facilitated a coating speed of ~5m/sec.

Kimura, et al [73] reported on the effect of fiber temperature, forced convection of liquid resin and viscosity of coating. They found that the fiber temperature had to be maintained below 50°C when applying a viscous coating, with a standard open cup die. A fiber temperature of up to 120°C could be tolerated when a forced convection of liquid was brought about by the use of a rotating rotor within the die. Draw speeds could be increased when the viscosity of coating was decreased from 2500 to 1200 mPa.s.

Geyling, et al [74] reported on their development of a pressurized applicator, wherein the coating was injected radially from a cylindrical plenum and filled a thin bore at the applicator. The thinner coating channel stabilized the coating application and facilitated application speed of ~2.5-3m/sec. Pressurized die construction evolved during the early 1980s and became the standard coating application tool, because of the improvement it offered in coating circulation and meniscus stability.

Kassahun and Viriyayuthakorn [75] described the improvements offered by pressurized coating application, 40-80N/cm², towards bubble-free coatings on fiber.

Paek and Schroeder [76] reported substantial improvement in high speed drawing up to 12 m/sec. Fibers were determined to have uniform 50 micron coating thickness and concentricity along a 50 km length. The fibers survived a proof test stress level of 0.7 GN/m² (100,000 psi), and most survived stress levels of twice that level. Draw speed rates of 0.7 and 10 m/sec were found to produce singlemode fibers with identical optical properties.

Draw tower coating speeds ranged from 1-2 m/sec in the 1979-81 timeframe [71]. Improvements in optical glass technology began to yield larger performs which significantly improved production efficiency. As a result, fiber prices became more competitive; fiber consumption jumped and the demand for faster drawing technology was created.

In 1985, Sakaguchi and Kimura [77] published one of the first reports on pressurized coatings being applied to fiber at speeds up to 20 m/sec.

Paek and Schroeder [71] found that for an open cup applicator, the coating thickness remains constant, as the draw speed increases. They found however, that with a pressurized applicator, thickness depends heavily on the draw speed and decreases as the speed increases [78].

The two primary controls for fiber coating application consist of temperature and pressure. UV curable coatings have a non-linear decrease in viscosity with increasing temperature. Viscosities drop precipitously during a temperature increase from room temperature to 45°C. Increasing temperature further to 55°C and 65°C produces diminishing decreases in viscosity.

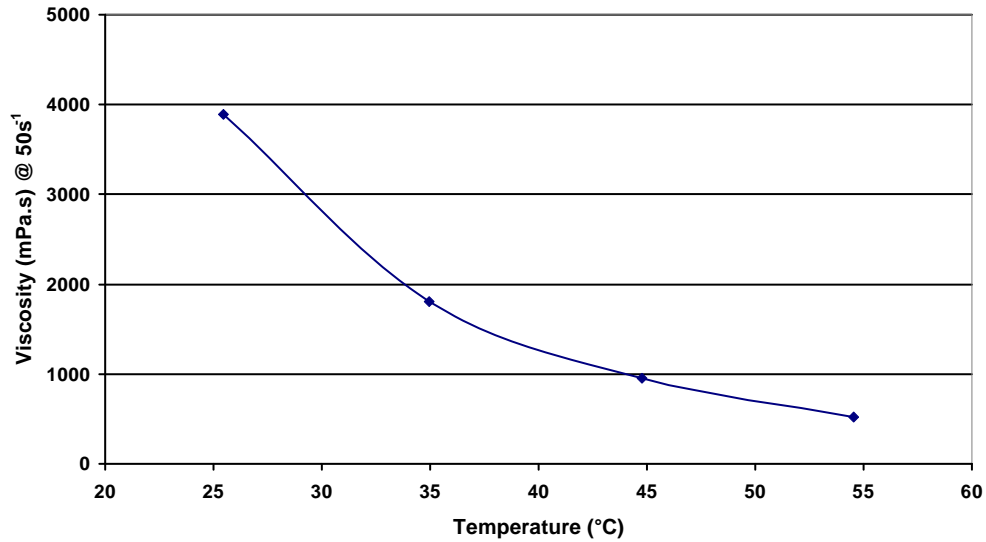


Figure 4.11 Typical viscosity vs. temperature curve for a fiber optic coating

It is important to have knowledge of the rheological properties of optical fiber coating resins at high shear rates. Steeman, et al [79] describe using the well-known Time-Temperature-Superposition technique, to avoid limitations of traditional direct measurement steady state methods, such as viscous heating in capillary viscometers and torque limitations in rotational viscometers.

A typical viscosity vs. shear rate plot of a fiber optic coating is shown in the Figure 12. Fiber coatings exhibit shear thinning behavior, whereby the viscosity is Newtonian at low shear, and decreases with increasing shear rate. The shear thinning behavior is generally controlled by the oligomer in the coating. Fiber optic coatings exhibit viscoelastic behavior.

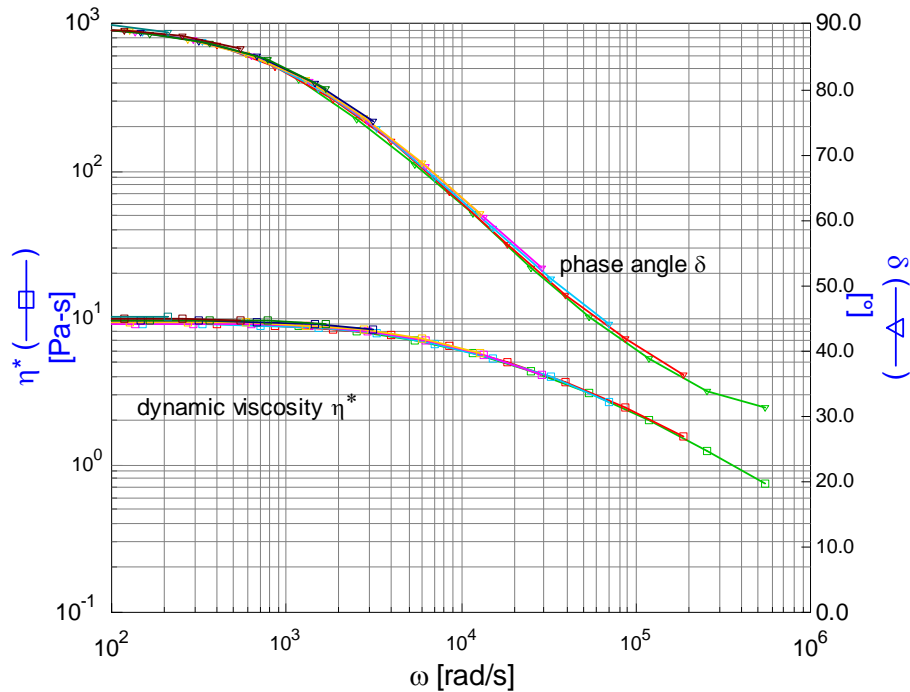


Figure 4.12 Typical viscosity vs. shear rate plot for a fiber optic coating

4.7.1 Coating Cure Speed Measurement Techniques

During the mid- to late 1980s, coating cure speeds were increased through design improvements. Many of these improvements came from the availability of new coating raw materials. As cure speeds improved, so did the test methods employed for their measurement.

An early method monitored the development of modulus in free coating films, as a function of UV dose, or more appropriately termed, UV energy density. Typical curves showed a rapid rise in modulus at low UV energy density and then a slow rise after further exposure. Some coatings did not reach their ultimate modulus until exposed to an energy density of 2 J/cm², or greater. An exposure of 3.5 J/cm² was chosen as the standard energy density for determination of a cured film's physical properties: tensile strength, elongation at break and modulus at 2.5% elongation. It is typical to measure the cure speed in terms of the dosage required to cure the coating to 95% of its ultimate modulus as shown in Figure 13 below.

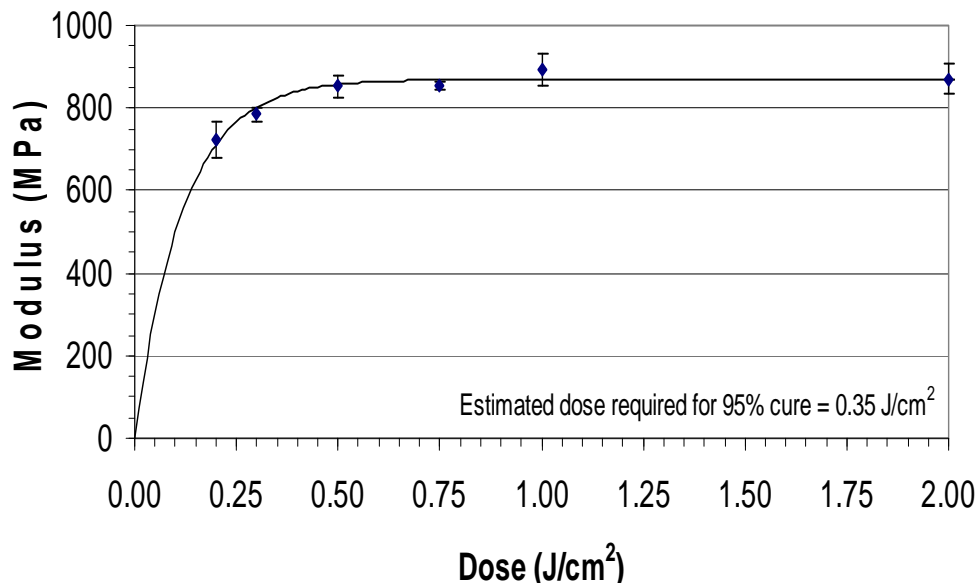


Figure 4.13 Typical modulus vs. dose curve for a fiber secondary coating

As demand for faster curing coatings grew, and with the advent of faster curing monomers and more efficient photoinitiators, UV energy densities of $1\text{J}/\text{cm}^2$, or less were required to achieve fully developed physical properties. Around this time another analytical method became popular for the characterization of cure speed. FTIR spectroscopy had long been used to identify chemical species and to follow chemical reactions. In the 1970s and 1980s, a number of papers were published [80-90] which described how this technique could be used to follow the disappearance of absorbance peaks corresponding to acrylate unsaturation.

Julian and Millon [91] reported on how FTIR could be used as a quality control test for monitoring UV curable coating cure speed. However, they cautioned that doses required for property development were different from those required to cause disappearance of acrylate unsaturation, suggesting that “loss of acrylate unsaturation is only one of a number of mechanisms which lead to the development of a properly cured coating film.”

While the FTIR cure speed measurement method related more to the inherent chemical crosslinking taking place on UV exposure, the development of Real Time Dynamic Mechanical Analysis gave rise to a more time efficient means to evaluate the property development of a coating.

Coating cure is dependent on the peak intensity, emission spectrum, temperature and geometry of the lamps to which it is exposed. It is also dependent on the coating’s absorption of incident UV radiation. It has not been possible to exactly measure the environment encountered by the coating as it is exposed to UV energy on the draw tower. However, it is possible to measure both the reacted acrylate unsaturation on cured fiber coatings, as well as the in-situ modulus of coatings cured on fiber. Therefore, some approximations can be made for the conditions that produced these types of properties.

Other cure measurement analytical tools include monitoring of glass transition temperature development, dielectric relaxation, and differential scanning photocalorimetry.

4.7.2 Cured Properties of Coatings on Fiber

Hussain [23] employed a torsional pendulum technique comprising small, coated optical fiber specimens to determine the suitability of coatings and their processing parameters. Using this technique, he was able to compare the shear modulus properties of different primary coatings as cured on fiber.

Frantz, et al [92], evaluated a number of techniques for determining the extent of cure on optical fibers. These techniques included infrared spectroscopy (FTIR), differential photochemistry (DPC), solvent evaporation rate analysis (ERA), solvent extraction, water/solvent soak, dielectric measurement, hydrogen generation, weight loss, oxidation onset, abrasion resistance, coating strip force, and coating pullout. FTIR, DPC, ERA and solvent extraction were found to have the greatest sensitivity and reproducibility for measuring the degree of cure of a given coating on fiber.

In-situ modulus is a useful test for measuring the modulus of the coating on the fiber. It has been observed that the in-situ modulus could be substantially lower than the flat film modulus even at high cure degree. Small variation of the in-situ RAU can result in large differences in in-situ modulus. Even with the same degree of cure large variations of polymer networks may be formed, largely due to variations in the intensity of UV light and the resultant heat from the drawing process [93].

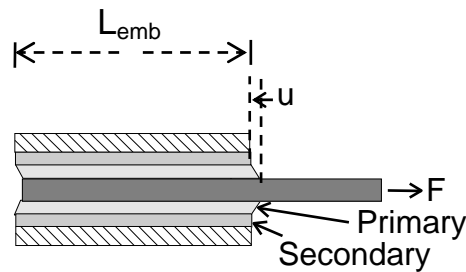


Figure 4.14 Illustration of pull-out testing for determination of shear modulus

The shear modulus of primary coatings can be measured in-situ, by pull-out test using TEM or DMA [93-95].

Traditional techniques involved the use of an adhesive to immobilize the fiber on a substrate cylinder. A new method using mechanical clamping [93] has the advantage of easy sample preparation and very small data scattering. Steeman, et al measured the primary modulus on a DMA by applying an oscillating shearing stress to the coating.

The secondary in-situ secondary modulus can be measured by applying an oscillating tensile stress to a stripped coating tube, on a DMA. The coating tube is prepared by separating the glass fiber from the coating, in liquid N_2 . Since the modulus of the primary coating is several orders of magnitude lower than that of the secondary coating, it can be assumed that its effects are negligible, thus the measured Young's modulus of the coating tube can be assumed to come from the secondary coating.

Strip force provides an indication of the ease of stripping the coating from the glass. The coating must have adequate adhesion to the glass, while at the same time be mechanically

strippable for splicing and connectorization. There is little or no correlation between strip force and primary coating adhesion. The modulus, deformation and failure mode of the secondary coating are the dominating factors that influence strip force [96].

Pull-out force measures the force required to pull a glass fiber out from the coating layers. It gives a measure of the adhesion of the primary coating to the glass. The sample is glued to a support, prepared by gluing the fiber onto a support tab. The application area, the uniformity of the glue and drying time can significantly affect the results. A mechanical clamping method has been tested; however, the measured force inevitably is a complex result of adhesion force and friction force.

The FTIR/ATR technique can be used to measure cure of both the primary and secondary coating on fiber. The cure, in terms of % RAU, i.e. reacted acrylate unsaturation, of the inner surface of primary coating is measured by cutting through the coating layers to the glass, removing the glass fiber, and laying the coating flat on a diamond ATR crystal, thus exposing the primary. The degree of cure of the secondary coating can be measured by directly measuring the %RAU on the fiber surface.

4.7.3 Test Methods for UV Curable Liquids and UV Cured Films

Julian [97] reviewed many techniques used to characterize the quality of radiation curable coatings. For UV curable coatings, it is also important to characterize the quality of the raw materials that are used to formulate the coating.

For coatings to be of commercial utility, they need to have sufficient liquid stability in a variety of containers (plastic bottles and lined steel drums) and also in heated application dies and coating reservoirs. Pasternack, et al [98] mentioned that changes in properties could be “evaluated by accelerated aging of the liquid coating at temperatures high enough to cause changes within reasonable times but still below thermal degradation levels.” A typical temperature for such testing is 54°C (130°F).

Chawla, et al [99] published a very thorough study on the factors that impact measurement of the mechanical properties (tensile strength, elongation and modulus) used to characterize UV cured films of optical fiber coatings. The study led to a number of improvements in equipment (more sensitive load cells and more accurate gauges for specimen measurement) and environmental controls (temperature, relative humidity and cured film preparation parameters). These improvements were important to both characterizing the properties of new coatings, as well as providing accurate and precise measurements of batch-to-batch variation in commercial coating production.

The modulus of primary coatings is typically calculated by taking the slope of the stress-strain curve from the origin to 2.5% strain, i.e. the segment modulus technique. For secondary coatings, secant modulus is typically measured and calculated from a tangent to the single point of the stress-strain curve at 2.5% strain. Chawla, et al found that there was no difference in which approach was used to measure the modulus of secondary coatings, however the segment modulus was found to give greater accuracy for primary coatings.

For optical fiber coatings, it is customary to characterize the mechanical properties of a coating by running a temperature sweep on a dynamic mechanical analyzer. A coating film is subjected to a controlled oscillating strain at a fixed amplitude and frequency, whereby the

elastic modulus E' , the viscous modulus, E'' , and $\tan \delta$ are measured. Information regarding crosslink density and glass transition can be obtained from the plot. There are a variety of methods for measuring the T_g of a coating. The peak $\tan \delta$ is often referred to as the glass transition point, however since the glass transition is a region rather than a single point, it is customary to quote the temperatures at which $E' = 1000$ MPa, and $E' = 100$ MPa. Typically polymers exhibit glassy behavior at low temperatures and rubbery behavior at high temperatures. The equilibrium modulus, measured at the minimum of the E' curve, is proportional to a coating's crosslink density. An example of DMA curves for a fiber optic primary coating is shown in Figure 15 below.

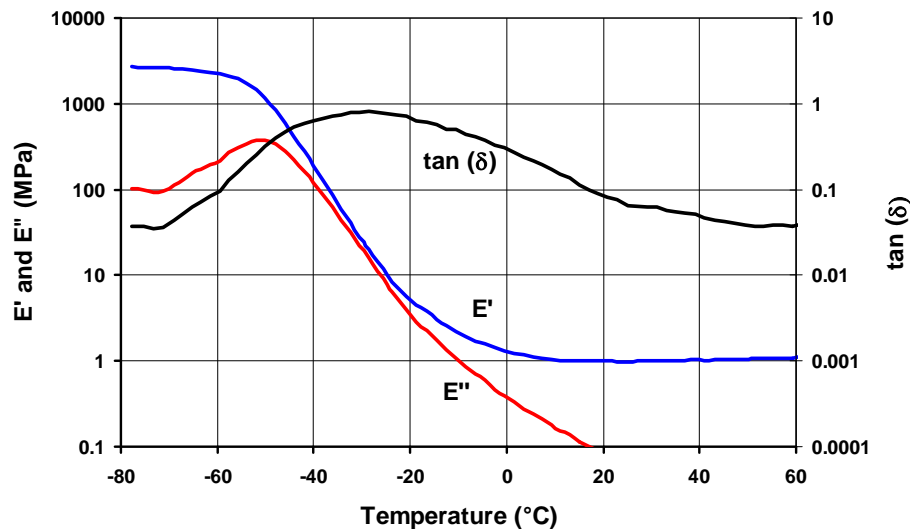


Figure 4.15 Typical DMA curves for a fiber optic primary coating

As mentioned earlier in the chapter, DMA curves are useful to characterize the aging behavior of a film by inspecting the changes between spectra taken before and after environmental exposures.

Szum [100] observed that coatings with glass transition temperatures above room temperature, notably secondary coatings, exhibited changes in physical properties over time. DMA analysis changes showed that these changes in properties were due to relaxation of the polymer network, rather than chemical changes. In general, it was observed that a high T_g crosslinked polymer's properties were dependent on heat history. If a UV cured film was quenched, i.e. quickly cooled after cure, it was found that the modulus of the film tended to increase over time, through densification, as the cured coating relaxed.

Julian [97] reviewed a number of characterization methods for UV curable liquids and cured films. These included viscosity measurement, cleanliness (freedom for particulate contamination, molecular weight determination, cure speed, mechanical property measurement (tensile properties and DMA properties), and thermal stability.

Julian cited three goals for equipment utilization as mentioned in the paper: to provide a thorough characterization of materials, both raw materials and finished coating formulation; to perform analyses at reasonable cost; and, to improve product consistency.

4.7.4 Coating Adhesion

Coating adhesion was thought to be a pre-requisite for retention of fiber strength. This is why many optical fiber coatings in direct contact with glass have contained some type of adhesion promoting agent, since the time of Vazarani's patent [13]. Silane coupling agents have typically filled this role. Many of these silane molecules contain three alkoxy silane groups on one end of the molecule and an organo-functional terminus, of some type, at the opposite end. The organo-functional group is selected to react with the coating network and thus be tied to the glass through the alkoxy silane groups. Silane coupling agents improve the adhesion of coatings in wet and dry environments. In 1982, Plueddemann [101] produced an excellent reference on the chemistry of silane coupling agents.

Overton and Taylor [102] stated that reliable adhesion of the primary to glass is necessary to protect against coating delamination. This can decrease the fiber's robustness and degrade its performance. They reported that adhesion is achieved through intermolecular forces, achieved by intimate contact between coating and glass, and chemical bonding afforded by silane coupling agents.

The adhesion to glass for some early fiber primary coatings was very high and made coating removal for splicing and terminations difficult. Chemical removal was often the preferred method to avoid damaging fibers in the field. As cable fiber counts began to increase, outside craft personnel spent more and more time making fiber connections. Amos, et al [103] reported on a primary coating with improved lower stripping force and its suitability for mechanical removal without damage to the underlying fiber.

Overton and Taylor [102] described a coating removal test that resolved the problem of measuring the adhesive strength between the primary coating and the glass. The pullout test revealed that the temperature dependence of the pullout force is similar to that of the primary coating's modulus. Continued decline in pullout strength at temperatures much greater than the coating Tg was attributed to the relaxation of hoop stress in the secondary coating.

4.8 SUMMARY

There are many aspects of the protective coatings that impact the final optical fiber performance as shown below.

<u>Primary Coating Feature</u>	<u>Performance Impact</u>
Composition	Fiber strength/fatigue, Long-term durability
Reactivity	Drawing speed
Refractive index	Concentricity monitoring
Viscosity	Ease of processing
Tg	Low temperature microbending loss
Modulus	Buffering (protection against microbending), Strippability (Residue left on fiber)
Adhesion	Delamination resistance, Strippability
<u>Secondary Coating</u>	<u>Performance Impact</u>
Composition	Long-term durability
Modulus	Shielding (protection against lateral load), Strippability, Abrasion resistance, Handling ability
Surface properties	Ink adhesion, Fiber friction
Crosslink density	Chemical resistance

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