CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1. Plastic Optical Fiber (POF)

2.1.1 Historical Evolution

The first optical fibers that were used as a communication channel were made of glass. In the past several decades, the successive of improvement in glass fibers, POF have become increasingly popular, owing to their growing utility. Although POF have been available for some time, they found application as a high-capacity transmission medium, because of the successive improvements in their transparency and bandwidth. At present, they are advantageously replacing copper cables in short-haul communications links. In addition, POF serves as a complement for glass fibers in short-haul communications links because they are easy to handle, flexible, and economical, although they are not used for very long distances because of their relatively high attenuation. These characteristics are suitable for the connection between a large net of glass optical fiber and a residential area, where distances to cover are generally less than 1 km. An example would be Internet access from home or from an office. For this purpose, POF has been manufactured. Nowadays, with the PMMA-core optical fibers, transmissions at 156 Mb/s over distances up to 100 m can be carried out, and transmission speeds of 500 Mb/s over 50 m can be reach. To achieve higher transmission speeds graded index POF can be used. In addition, a special type of POF made from an amorphous fluorinated polymer called CYTOP and developed by Koike and Asahi Glass will be soon available in the market. This new fiber presents a considerably lower attenuation than the common POF $\approx$ 30 dB/km., which allows the transmission distance to be increased up to 1 km for a transmission speed of 1.2 Gb/s/km. Table 1 shows the most significant landmarks of POF during the past 30 years.

Table 2.1 Historical Evolution of the Most Important Landmarks Related to POF during the Past 30 Years (Zubia, *et al.*, 2000)

Year	Organization	Landmark
1968	Dupont	First SI POF with PMMA core
1972	Toray	First SI POF with PS core
1981	NTT	Low attenuation PMMA SI POF (55 dB/km at 568 nm)
1982	Keio	University First GI POF (1070 dB/km at 670 nm)
	NTT	First SI POF with deuterated PMMA core (20 dB/km at 650 nm)
1983	Mitsubishi	Rayon PMMA"Eska" SI POF (110 dB/km at 570 nm)
1987	France	The French POF Club is established
1990	Keio University	First high speed transmission with a PMMA-core GI POF (300 MHz*Km at 670 nm)
1991	Hoechst	Celanese SI PMMA "Infolite" POF (130 dB/km at 650 nm)
1992	Keio	University GI deuterated PMMA POF (55 dB at 688 nm)
1993	Essex University	Transmission at 631 Mb/s over 100 m by means of a PMMA-core SI POF and an equalizer circuit
1994	USA/Japan	The high speed POF Network (HSPN) Consortium is created
	Keio University,	The POF Consortium of Japan is created
	IBM	Transmission at 1 Gb/s over 30 m by means of a GI
	Keio University,	POF and a VCSEL at 670 nm
	NEC	Transmission at 2.5 Gb/s over 100 m by means of a
	Asahi Chemical	GI POF at 650 nm; First multicore SI POF for high speed transmission
1995	Mitsubishi Rayon, NEC	Transmission at 156 Mb/s over 100 m by means of a low NA SI POF and a fast red LED

Year	Organization	Landmark
1996	Keio University,	First perfluorinated (PF) GI POF (50 dB/km at 1300 nm)
	KAST	Theoretical estimation of the losses in a PF POF (0.3 dB/km at 1300 nm)
		Theoretical estimation of the transmission speed in a GI POF optical link (PMMA: 4 Gb/s over 100 m; PF: 10 Gb/s over 1 km)
1997	POF Consortium of Japan	Standardization at ATM LAN (156 Mb/s over 50 m of SI POF) in the ATM Forum.
		Standardization of the norm IEEE 1394 (156 Mb/s over 50 m of SI POF.
	Keio University,	Transmission at 2.5 Gb/s over 200 m by means of a PF-core
	Fujitsu, Asahi	Glass GI POF at 1300 nm
1998	COBRA, Eindhoven University, Keio University, Asahi Glass, NEC	Transmission at 2.5 Gb/s over 300 m by means of a PF-core GI POF at 645 nm
	Matsushita	Transmission at 500 Mb/s over 50 m by means of a GI POF and a fast red-color LED (RC-LED; 650 nm)
1999	COBRA, Eindhoven University, Keio University, Asahi Glass	Transmission at 2.5 Gb/s over 500 m by means of a PF-core GI POF at 840 and 1310 nm
	University of Ulm, Asahi Glass	Transmission at 7 Gb/s over 80 m by means of a PF-core GI POF at 950 nm
	Bell Laboratories,	11 Gb/s data transmission through 100 m of perfluorinated
	Asahi Glass	GI POF at 830 nm and 1310 nm.

Year	Organization	Landmark
2000	Asahi Glass	GI POF (Lucina) with an attenuation of 16 dB at 1300 nm and 569 MHz*km

Note: SI, step-index; GI, graded-index; PMMA, polymethyl methacrylate; PS, polystyrene; PF, perfluorinated fiber.

2.1.2 POF Structure

POF used for optical communications are highly flexible waveguides composed of nearly transparent dielectric materials. The cross-section of these fibers is circular and, generally, divisible into three layers, as shown in Fig.2.1.The three layers are called the core, cladding, and jacket or a protective cover. Within the core, the refractive-index profile can be uniform (step-index fibers, SI) or graded (graded-index fibers, GI), while the cladding index is typically uniform.
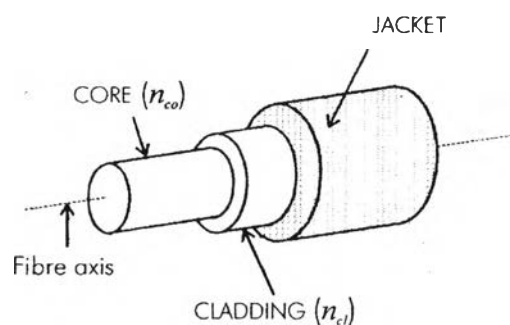

Figure 2.1 Structure of a POF.

2.1.3 POF classes

The POF developed so far has been divided into two classes of structure: one is of step-index (SI) and the other is of graded-index (GI). In the case of the SI POF which has a core region and a cladding as shown in Fig. 2(a), as light is transmitted by reflecting at the boundary of core and cladding, an impulse injected into the fiber is spread over a time interval that is equal to the difference of the arrival times of the slowest and fastest modes. After the pulses have traveled a

certain distance, this spreading causes them to overlap to such an extent that the information which they contain scrambled. Therefore, the SI POF is aimed at low data-rate transmission, image guide, and illumination. Fig.2.2 (a) shows the real data of input and spread output pulses for the SI POF with 15-m length.

The GI POF, a remedy for the pulse broadening problem in SI POF can be found by constructing a refractive index distribution which is a parabolic form in the fiber core. The reason why this type of the fiber exhibits less pulse broadening can be understood in the following way. As the shortest ray path of GI POF follows the fiber axis, while longer ray paths oscillate around the ray axis as shown in Fig.2.2 (b). However, along most of the oscillating ray path, the refractive index is smaller than that on the fiber axis. As the velocity of light is inversely proportional to the refractive-index n, the light that travels along the oscillating paths travels at a higher speed than the light that follows the axis. This greater speed partially compensates for the longer distance traveled. This result suggests that transit times for the oscillating ray paths are not very different from the transit time for the axial ray path. Since the pulse broadening is proportional to the maximum difference in transit times, small pulse broadening is expected of the GI POF.
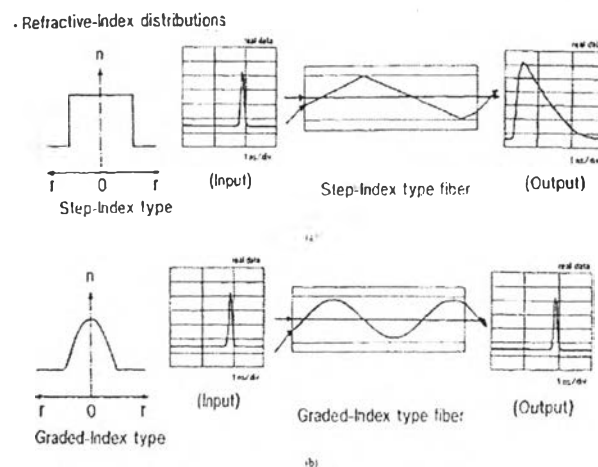

Figure 2.2 Schematic representation of light transmission through SI and GI POFs (Koike, *et al.* (1995)).

The POF of SI type was developed at Du Pont for the first time by using PMMA as the core material and fluoropolymer as the cladding material.

Throughout the 1970's, Nippon Telegraph and Telephone (NTT) and Mitsubishi Rayon have worked on the improvement in the attenuation of the POF by adopting the extrusion method based on the Du Pont's method. In 1982, Kaino et *al.* reported that low-loss POF with 20 dB/km attenuation was achieved by using the all deuterated PMMA (PMMA-d8). All of them have been of the SI type. The first GI POF was reported from Keio University in 1982. Since the GI POF at that time was prepared by utilizing the monomer reactivity ratio, the excess scattering loss due to the phase separation of the copolymer increased the total attenuation up to 1000 dB/km, which was about ten times larger than that of the SI POF. Development of the interfacial-gel polymerization technique enabled the dramatic reduction in the total attenuation of the GI POF. Further, the high bandwidth of 2 GHz*km which was about 400 times larger than that of the conventional SI POF was experimentally recognized by using 55-m length GI POF.

2.1.4 Total Internal Reflection

As refractive index of core materials (n_{core}) is slightly higher than refractive index of cladding materials (n_{clad}), so light is kept in core by total internal reflection. Total Internal Reflection is the phenomenon when the light passes from a medium with one refractive index (n_1) to another medium with a lower refractive index (n_2) and the angle of incidence is increased beyond the critical angle (θ_C), light is totally reflected back, nothing is transmitted (Fig.2.3). It is the fundamental optical effect for light propagation through optical fibers. The critical angle (θ_C) is given by:

$$\theta_C = \sin^{-1}\left(\frac{n_2}{n_1}\right)$$
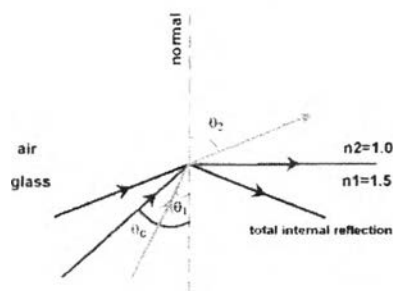
(1)

Figure 2.3 The reflection of light through the difference medium.

2.1.5 Numerical aperture

Numerical aperture (NA) determines the light gathering power of an optical fiber. A light ray (with an incidence angle θ) to be guided through the fiber is given by:

$$n \cdot \sin \theta_{max} = NA = \sqrt{\left(n_{core}^2 - n_{clad}^2\right)} \qquad (2)$$

where n is the refractive index of air and sin θ_{max} is the maximum incidence acceptance angle. It can be schematically represented as shown in Fig.2.4.
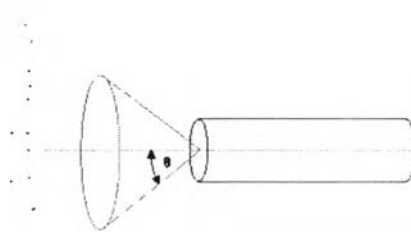

Figure 2.4 Numerical Aperture-acceptance.

2.1.6 Attenuation

Attenuation or power loss of an optical fiber is the loss of optical power as light rays travel along its length. It is defined as the ratio of the optical power input (P_I) to the optical power out put (P_o). The following equation characterizes the attenuation as a unit of length

$$attenuation(\alpha) = \frac{10}{L-x} \cdot \log\left(\frac{P_o}{P_i}\right) \qquad (3)$$

where L is the fiber length in kilometers and α ☐is expressed in dB/km.

2.2 Materials

2.2.1 Polycarbonate

Polycarbonate (PC) is a versatile, tough plastic used for a variety of applications. The main advantage of PC over other types of plastic is unbeatable

strength combined with light weight. Polycarbonate of bisphenol A (Fig.2.5) is transparent because its amorphous nature and having high glass transition temperature ($T_g \approx 150$ °C) so high mechanical properties—Young's modulus (E): 2-2.4 GPa, Tensile strength (σ_t): 55-75 MPa, Elongation (ε) at break: 80-150%). Refractive index of PC is 1.584-6. PC core POF is developed specially for high temperature applications. However, the optical loss of these polymers is quite high, especially for PC and PS based POF.
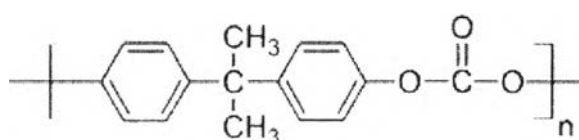

Figure 2.5 Chemical stucture of polycarbonate made from bisphenol A.

For applications with working temperatures less than 80 °C, PMMA and PS cores are usually employed in POF fibers. In applications with temperatures up to 125 °C, such as automobile data systems and sensors, PC appears to be a more adequate core material. Along this line, several PC optical fibers have been developed: Optipol by Bayer AG, FH by Mitsubishi Rayon, PC-Core by Fujitsu, and HMC by Asahi. In addition to their wider temperature range, PC optical fibers show lower infrared absorptions at the bands centered at 780 and 820 nm than PMMA and PS fibers. Therefore PC core fibers are more suitable for applications involving solid-state emitters and detectors, which are more efficient at these wave lengths than the devices which operate at 660 nm, where the transmission window for PMMA and PS optical fibers lies.

Nichiguchi, *et al.* (1997) produced POF having polycarbonate AF as a core. An aromatic polycarbonate is excellent in optical properties, transparency, heat resistance and good molding properties.

Guerrero, *et al.* (1998) investigated the mechanical and optomechanical properties under different environmental conditions on PC. They

found that fiber properties are not sensitive to moisture cycles or low temperatures (-40 °C), but they are significantly affected by temperatures over 85 °C.

2.2.2 Poly (methyl methacrylate)

Poly (methyl methacrylate) (PMMA) (Fig.2.6) is a clear plastic, colorless polymer used extensively for optical applications. PMMA is a member of a family of polymers which chemists call acrylates or acrylics. The glass transition temperature of PMMA ranges from 85 to 165 °C. It has good impact strength, higher than that of glass or polystyrene, but significantly lower than that of polycarbonate or engineering polymers.
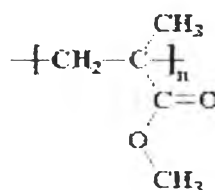

Figure 2.6 Poly (methyl methacrylate) (PMMA).

2.2.3 Fluorinated polymer

Fluorine containing polymers are of great interest for use in optical and electronic applications because of their unique properties and high temperature performance. They have excellent thermal and chemical stability, low dielectric constant and low refractive index. Due to these properties, many fluorinated polymers have been studied in last decades. Especially, polymers containing perfluorinated aromatic units have been studied extensively in the last decade because perfluorinated aromatic units increase thermal stability and Tg.

Kim, *et al*. (2003) synthesized and characterized a highly fluorinated poly (arylene ether sulfone) (FPAESO) designed from low loss optical waveguide materials containing ethynyl end group as thermal cross-linkable groups. To obtain high molecular weight ethynyl terminated fluorinated poly(arylene ether sulfone) (EFPAESO), EFPAESO was synthesized via nucleophilic aromatic substitution of 4,4'-(hexafluoroisopropylidene) diphenol (6F-BPA) with pentafluorophenyl sulfone.

Jiang, *et al*. (2006) synthesized novel low-loss optical polymers based on tetrafluorostyrene containing fluorinated poly(arylene ether)s as waveguide

materials for passive devices. These polymeric materials have high thermal stability and easy processability, but unfortunately suffer from relatively high birefringence values. However the co-polymerization of these polymers with monomers containing fluorinated aliphatic chains can decrease. Fluorinated styrene monomers containing aliphatic chains have been mixed and co-polymerized with the fluorinated poly(arylene ether) ketone (FSt-FPAEK) or sulfone (FSt-FPASO) during the thin film processing. Optimization of birefringence, while controlling refractive index for waveguide core and cladding layers, and maintaining other desirable optical waveguide properties is reported birefringence.

Qi *et al.*, (2005) synthesized fluorinated poly(arylene ether ketone)s (FPAEK) which have excellent thermal, mechanical, and environmental stabilities. The preparation of FPAEK is the reaction of 6F-BPA, and 1,1-Bis(4-hydroxyphenyl) ethyl-1-phenyl 2,3,5,6-tetrafluorostyrol Ether (BHPFS). The cross-linkable bisphenol (BHPFS) is synthesized from 1,1,1-Tris(4-hydroxyphenyl)ethane; 2,3,4,5,6-pentafluorostyrene; and *N,N*-dimethylacetamide (DMAc) in present of calcium hydride and cesium fluoride. Figure 2.7 show the synthesis of HPAEK and HPAES.
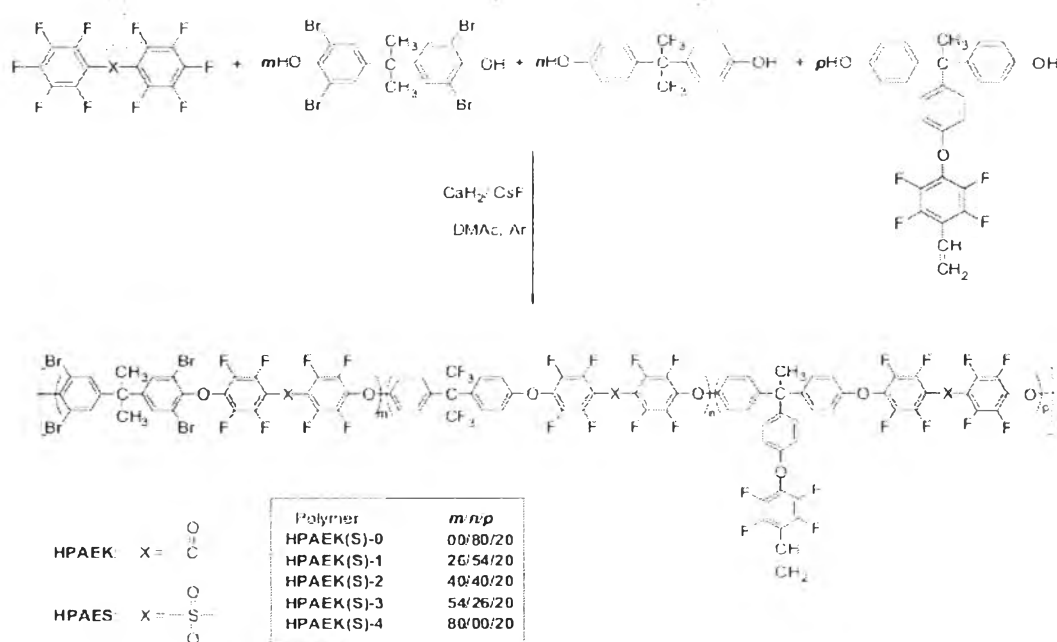

Figure 2.7 show the synthesis of HPAEK and HPAES.

2.2.4 Polysiloxane

2.2.4.1 Chemistry of silane

The polymers with silicon in the main chain have attracted the attention as high performance materials. These polymers have further attractive characteristics such as good transparency, oxygen permeability, flexibility, and so on.

Since chlorosilanes are readily produced by various means and commercially available, the efficient conversion of their reactive Si-Cl bonds to more hydrolytically stable bonds is of interest in order to produce a useful material. Nucleophilic substitution has long been shown to be a flexible route of modifying the properties of reactive silanes. Highly reactive Si-Cl bonds are readily attacked by a variety of nucleophiles, facilitating mild reaction conditions. Furthermore, these products are used as biomedical materials, elastomers, coatings, and fibers.

Alcoholysis reactions have long been used in the functionalization of chlorosilanes. Even though alcohols are considered to be mild nucleophiles, they still readily substitute Si-Cl bonds. Due to the acidic by-products of the reaction, it is common to use a soluble base, such as hindered amine or pyridine, as a proton acceptor.

Liaw, et al. (1997) synthesized a poly(silyl ether)s having chloromethyl and sulfonyl groups in their main chain. The poly(silyl ether) with a sulfonyl group and reactive pendant chloromethyl groups was successfully synthesized by the addition reaction of CPS with the diglycidyl ether of bisphenol-S (BPSE). The polyaddition of CPS with BPSE proceeded very smoothly in toluene catalysed by quaternary ammonium or phosphonium salts. Number-average molecular weights (M_n) of the poly(silyl ether)s prepared $M_n = 12,200$

Minegishi, *et al.* (1996) synthesized copolymers containing both silicon and phosphorus atoms in the polymer main chain by the polyaddition of dichlorosilanes and dichlorophosphates with bisepoxides using quaternary onium salts (tetrabutylammonium bromide (TBAB)) as catalysts. The addition reaction of phenyl glycidyl ether (PGE) with dichlorodiphenylsilane (CPS) proceed very smoothly using TBAB as a catalyst in toluene at room temperature for 48 h, and silyl ether was obtained in 97% yield and the addition reaction of PGE with CPS proceed

without any side reaction. Furthermore, the competitive reaction between PGE with CPS and phenyldichlorophosphate (PDCP) was examined 60°C for 30 min. This result suggested that the addition reaction PGE with CPS occurred selectively to give silyl ether in 95% yield, although the any addition reaction of PGE with PDCP was not confirmed. The copolymers were obtained in good yields, when reactions were carried out at 60°C and 90°C for 48 h. Particularly, when the polyaddition was performed using TBAB in toluene at 60°C for 48 h, the copolymer with high molecular weight (M_n = 3900) was obtained in good yield (92%). However, both the yield and the molecular weight decreased at 72 h. It seems that the produced silyl ether linkage in the copolymer decomposed gradually due to stirring or heating for a longer time. The reaction of their work shows in Figure 2.8 and 2.9.
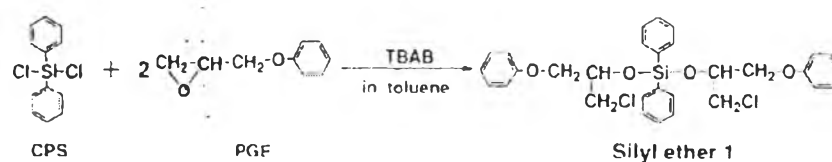
Figure 2.8 The reaction of CPS and PGE to produced silyl ether.
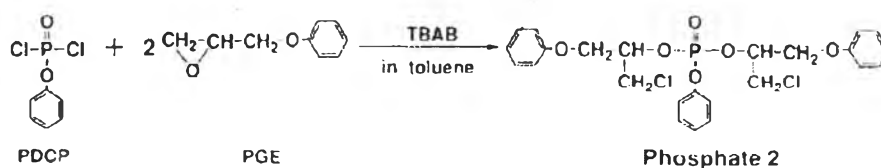
Figure 2.9 The reaction of PDCP and PGE to produced silyl ether.

2.2.4.2 Development of POF with polysiloxane

Various POF comprising PC as the core material have proposed but they are not put into practical use, since the light transmission loss through PC is large. The transmitting characteristics of an optical fiber using PC as the core material, reported by Tanaka et al in Japanese Electronic Correspondence Society, Collective, Wh Country Grand Meeting, 1985 is shown that at wavelengths of 775 nm, 820 nm and 948 nm, the loss is minimum (5,100 dB/km), whereas within a wavelength region of blue color to green color, light of 500 nm is not transmitted at

all. Disclosed in Japanese patent application laid-open No. 57-46204/1982, light transmission has been observed only within an infrared ray region of 950 nm wavelength.

To overcome the drawback of conventional optical fibers having PC the core material, and as a result have found an optical fiber having a little vibration in the light transmitting characteristics within a visible light region. In addition, in order to improve the heat resistance and heat shrinkable characteristics of the optical fibers, a plastic having silane-crosslink structure may be chosen and used. In 1988, Yamamoto T. and coworkers produce plastic optical fiber having a silane-crosslink structure as a cladding material. The silane-grafted-polyolefins are obtained by react an alkoxy silane grafted onto or copolymerized with polyethylene or polypropylene chain, with water or the like, to from Si-O-Si bond through condensation to thereby affect crosslinking. As commercial available silane-graft-crosslinked polyethylene or silane-graft-crosslinked polyolefin, "Linklon", "Linklon-X", etc. (tradename of products manufactured by Mitsubishi Petrochemical Company) are exemplified.

In Japan patent application Laid-Open No. 18606/83, to enhance the heat resistance by forming a three or more layer structure wherein a protective layer or the like having the same composition as that of the core material is provided additionally around the cladding.

Yamamoto T., et al. (1988) provided a POF capable of exhibit good light transmitting characteristic even at high temperatures, which comprise a core layer, a cladding layer, and a protective layer as basic constitutional unit, wherein the protective layer has a heat distortion temperature (HDT) of at least 120 °c. As the base material for the protective layer laid inside the plastic coating layer having a silanecross-linked structure, it is desirable to use an organic polymer which is insoluble in the alcohols that will be produced by the water-crosslinking reaction and which is impermeable to alcohol and water and which does not undergo any chemical charge to cause decomposition or deformation.

There is a problem reported with a waveguide made with polydimethyl silxane cladding and a quartz glass core that is polydimethyl siloxane has a refractive index of approximately 1.40, while the quartz core has a refractive

index of about 1.46. The haft angle of the "acceptance cone" or "numerical aperture" (NA) is a function of the core/cladding indices of refraction as follows: NA=sine θ_c= $(n_1{}^2-n_2{}^2)^{1/2}$. Therefore, it is advantageous for efficient transmission to use a waveguide with a high numerical aperture. The higher numerical aperture of a waveguide, the greater the percentage of light provide by a light emitter that enters the core of the waveguide. There are other problems with use of polydimethyl siloxane as a cladding. For example, it has limited use at low temperatures. Polydimethyl siloxane can crystallize at about -50°c, which can give rise to an increase in optical attenuation. Thus, silicon cladding generally is not use for very low temperature application. In 1982, Clarke R. studied an optical fiber core and a cross-linked polyfluorosiloxane cladding having fluorine content of from 1 to 52% by weight. The use of polyfluorosiloxane cladding produces a waveguide having a high numerical aperture. The polyfluorosiloxane can have a refractive index substantially lower than 1.40, the waveguide have a higher numerical aperture than achievable with a polydimethyl siloxane cladding on the same core material. The cured polyfluorosiloxane has and elastic modulus of less than 10^7 Newton per square meter (N/m^2), which is desirable because at the higher elastic modulus, excessive microbending light loss are incurred along the waveguide.