

TECHNICAL UNIVERSITY OF LIBEREC

FACULTY OF TEXTILE ENGINEERING



DIPLOMA THESIS

2012

ANUJ SHUKLA

TECHNICAL UNIVERSITY OF LIBEREC

FACULTY OF TEXTILE ENGINEERING

DEPARTMENT OF TEXTILE TECHNOLOGIES

CHARACTERIZATION OF OPTICAL FIBER

AFTER SURFACE MODIFICATION

ANUJ SHUKLA

Supervisor: Dr. Rajesh Mishra

Statement

I have been informed that the Law no. 121/2000 Coll., about copyright, especially section 60-academic work, is fully applicable on my thesis.

I, hereby grant permission to the Library of Technical University of Liberec to reproduce my thesis in whole or in part. Any reproduction will not be for commercial use or profit.

I acknowledge that I am obliged to inform TUL about this fact that, TUL has right to claim expenses incurred for this thesis up to amount of actual full expenses.

I have elaborated the thesis alone utilizing listed literature and on basis of consultations with the supervisor.

Date:

Signed

Anuj SHUKLA

Acknowledgements

This work would have not been possible without the input and guidance of many individuals.

My utmost gratitude to my supervisor, Dr. Rajesh Mishra, for his patience, guidance and encouragement. Thank you to those that gave me this opportunity and those that helped me along this path.

Lastly and most importantly, to my family and friends; for their endless love and support during this time. Without you'll, it would have not been possible.

“It always seems impossible, until it is done”.....Nelson R. Mandela

Abstract

Optical fibers have been used principally for data transmission, since it offers fast connectivity, low cost, and high resistance to damage. The purpose of this research was not to evaluate the data capabilities of plastic optical fibers (POF) which transmits axially, but rather to exploit the ability of the fiber emit light through the side of the fiber.

The uses of side emitting fibers in textile would prove to be beneficial in several ways, few of them being the flexibility of the fiber for integration into fabrics, and possibly to mask this fiber like all others, with the aid of classical textile dyeing methods. The POF, with trade name *Flexi* was used in this case, because of its flexibility, and variation in diameters available on the market.

Flexi cores were stripped from its cladding, and were dyed using a disperse dye, under various conditions including changing in dye concentration and dye time. Samples were then analysed for side emission of light with the use of *Prototype 1*, which was an instrument specifically designed for the measurement of this nature. The results showed that the dye penetration is dependent on the dye time, if dye concentration and temperature are kept constant. After 40 minutes of dyeing, the fiber core showed an increase in side emission, with lower loss due to attenuation. Also excessive time in the hot conditions degraded the fiber, such that the fiber became very stiff and brittle.

Fibers were also subjected to heat, in the form of boiling water bath, for selected periods of time, and it was found that the effect was similar to that of the prior experiments.

Surface treatment of *Flexi* fibers were carried out using ethyl acetate as an etching agent, to possibly accept more disperse dye on the fibers surface. The results after dyeing showed a more than significant improvement in both side emission and attenuation of light. The influence of the illuminating source of the fiber also proved to be important, such that the side emission is dependent on the temperature of light from the source.

Keywords: Optical fibers, polymethyl methacrylate, PMMA, side emission, surface treatment, dyeing.

Table of Contents

Chapter I	Introduction.....	11
Chapter II	Literature Review	13
II . I.	Optical Fibers	13
II . II.	Types of Optical Fibers	13
II . III.	Optical Fiber Construction	14
II . IV.	Total Internal Reflection[6]	15
II.IV.I	Reflection of light from optical surfaces	15
II.IV.II	The law of reflection on plane surfaces:	16
II.IV.III	Refraction of light from optical interfaces	17
II.IV.IV	Critical angle and total internal reflection.....	21
II.IV.V	Reflection from a curved surface:	22
II.IV.VI	Numerical Aperture.....	23
II . V.	Classification of dyes[9].....	25
II.V.I	Acid dyes	27
II.V.II	Reactive Dyes	27
II.V.III	Metal Complex Dyes	27
II.V.IV	Direct Dyes	27
II.V.V	Basic Dyes.....	27
II.V.VI	Mordant Dyes.....	27
II.V.VII	Disperse Dyes[11].....	28
II.V.VIII	Pigment Dyes	30
II.V.IX	Vat Dyes.....	30
II.V.X	Anionic dyes and ingrain dyes	30
II.V.XI	Sulphur dyes.....	30

II.V.XII	Solvent dyes	30
II.V.XIII	Fluorescent brighteners	31
II.V.XIV	Other dye classes	31
II . VI.	Colour Measurement[12].....	32
II.VI.I	Factors influencing colour perception	32
II.VI.II	Light sources and illuminants[12].....	33
II.VI.III	Reflection or transmission of light by an object	34
II . VII.	Chemical composition of optical fibers	36
II.VII.I	Polymethyl methacrylate.....	36
Chapter III	Materials and Methods	39
III . I.	Fiber composition.....	39
III . II.	Dyeing of Core	39
III . III.	Temperature effect on core and parental fiber.....	41
III . IV.	Side emission of fibers[18].....	41
III.IV.I	Principle	41
III.IV.II	Description of instrument.....	42
III . V.	Cross section analysis of plastic optical fibers	43
III . VI.	Surface treatment with Ethyl Acetate	45
III . VII.	Dyeing of surface modified optical fibers	45
Chapter IV	Results and Discussion	46
IV . I.	Identification of chemical composition for <i>Flexi</i>	46
IV . II.	Cross section analysis of dyed fibers.....	47
IV . III.	Dyeing of Core	54
IV . IV.	Effect of time for a constant temperature on core of <i>Flexi</i>	56
IV . V.	Effect of time at constant temperature on <i>Flexi</i> with cladding.....	57

IV . VI.	Surface treated fibers	58
IV . VII.	Comparison of light sources	61
Chapter V	Conclusions.....	65
Chapter VI	References.....	67
Chapter VII	Appendix	70

List of figures

Figure 1: Total internal reflection principle [6].....	11
Figure 2: Structure of a POF [5].....	15
Figure 3: Specular and diffuse reflection[6].....	16
Figure 4: Reflection on a plane surface[6]	16
Figure 5: Reflection and refraction at an interface[6]	17
Figure 6: Refraction at an interface between media of refractive indexes n_1 and n_2 [6].....	19
Figure 7: Snell's Law[6]	20
Figure 8: Total internal reflection.....	21
Figure 9: Reflection at a curved surface: Angle B equals angle A[6].....	22
Figure 10: Light gathering on surface[6].....	23
Figure 11: Common dye classes[10]	26
Figure 12: Typical disperse dye structures[11]	29
Figure 13: Common spectrophotometer geometries [12,p443].....	34
Figure 14: Radical formation of alkene addition.....	36
Figure 15: Formation of Poly(methyl methacrylate).....	37
Figure 16: Apparatus setup for dyeing of fibers.....	40
Figure 17: Schematic diagram of Prototype 1, for measurement of side emission.....	42
Figure 18: Cross section analysis of fibers.....	43
Figure 19: IR spectrum of cladding.....	46
Figure 20: IR spectrum of core.....	46
Figure 21: Macroscopic images of dyed optical cores	47
Figure 22: Macroscopic image of longitudinal view - dyed core and parent core	49
Figure 23: Optical fiber cross sections of 70um.....	50
Figure 24: Graphical interpretation of dye distribution in flexi core	53
Figure 25: Effect of time in dye bath.....	54
Figure 26: Illuminated dyed fiber with Light source one.....	55
Figure 27: Effect of time at constant temperature for PMMA Core	56
Figure 28: Effect of time at constant temperatures on flexi with cladding	57
Figure 29: Surface treated fibers after dyeing	58
Figure 30: 15g/L after 20min of dyeing, showing length of fiber illuminated.....	59

Figure 31: Effect of dying time on the side emission of fiber	60
Figure 32: Light source 2, high discharge LED	61
Figure 33: Comparison of light source on sample.....	63
Figure 34: Light source 2 vs. Light source 1, comparison of 20g/L after 20minutes of dyeing ..	64

List of tables

Table 1: Indices of refraction for common materials at 589nm[6].....	18
Table 2: Characteristic chemical structures forming chromophores and auxochromes.....	25
Table 3: MMA characteristics	36
Table 4: Characteristics of PMMA.....	37
Table 5: Flexi fiber characteristics	39
Table 6: Dyeing parameters of fiber core.....	40
Table 7: Parameters of heat treatment to fibers.....	41
Table 8: Calibration settings for light microscope	44
Table 9: Surface treatment parameters	45
Table 10: Dye parameters for <i>Flexi</i> fiber	45
Table 11: Objective measurements of fiber radius and diameter by image analysis	51
Table 12: Dye penetration measurements by image analysis.....	52
Table 13: Side emission of dyed fibers, with respective time intervals in dye bath- 65mm maximum measured	70
Table 14: Effect of time at a constant temperature - parent fiber - length 200mm	71
Table 15: Side emission of dyed fibers, with respective time intervals in dye bath- 200 mm maximum measured	73
Table 16: Side emission of dyed fiber cores	75
Table 17: Side emission of dyed parent fibers	77
Table 18: Side emission of dyed parent fibers with second light source	79

Chapter I Introduction

Polymer (Plastic) Optical Fibers, or better known as POF's, has many great features, which is making it more popular in applications. It offers high speed data transmission, reliability and quick installation[1] at an affordable price. In today's world, everything is about cost, if the items are cheaper; it makes a product more accessible and desirable to a larger market.

In the case of this research, the integration of optical fibers into clothing will be beneficial to a large number of people, in particular for safety. Besides having good data transmission capabilities, optical fibers have the principle ability to transfer light from one point to another, by means of total internal reflection. So what is total internal reflection?

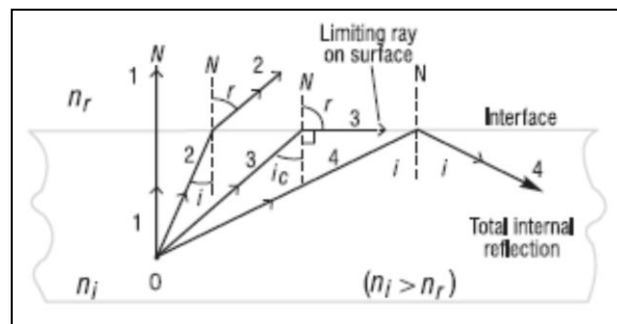


Figure 1: Total internal reflection principle [6]

In the figure above, light starts from a single point, the light will either pass through, as in ray 1, refract or bend in the case of ray 2, travel along the surface in ray 3, or finally reflect back into the medium with the light source, reflecting back into the system. Hence by this system, i.e. ray 4, optical fibers have the ability to keep the light within the fiber.

The fiber consists of two main elements which aid it to do this, a core and cladding. This system provides the method of light propagation in the fiber, rather than the light being emitted from the source only or dispersing through certain points in the fiber.

If light is propagated through the side of the fiber, it would provide illumination of the whole fiber length, and thus design and integration into clothing can take place, extending the use of POF's to not just data transmission but illumination. The POF's are flexible, and

hard wearing components, which cannot be easily damaged by daily use, thus it provides another advantage towards clothing integration.

Uses of side emitting optical fibers could be for:

- Night jackets for emergency personal (police, fireman, paramedics)
- Integration into clothing of cyclists and runners for night use
- Emergency illumination of stairways and emergency exits in buildings
- Illumination strip on car doors if they are open
- Fashion

In order for the fibers to be integrated into clothing, and to be unnoticed during the day, it would be an advantage to dye the fiber the same colour as the garment.

Chapter II Literature Review

II . I. Optical Fibers

Optical fibers have a very broad spectrum of use, ranging from transporting light from a source to some device, transmitting optically encoded data or even functioning as a sensor for temperature or strain [2].

Most fibers are used to guide light, and since optical fibers have the ability to keep the light inside the fiber, this is advantageous. The fiber does this by internally reflecting the light in the core of the fiber, along the fiber axis. These principles will be discussed in the subsequent sub-chapters.

II . II. Types of Optical Fibers

Principally there are three types of optical fibers used in telecommunications; the type off course is dependent on its use and the final application. The three types can be further split into two categories, namely single and multi-mode fibers[3].

- Step-index multi-mode fiber
- Graded-index multi-mode fiber
- Single-mode fiber

Single-mode, or also known as mono-mode fiber is approximately 8-10 μ m in diameter [4] and has only one mode of transmission, i.e. the signal or light wave will travel in only one direction, which is linear. Having a smaller diameter, the fiber requires a light source with a narrow spectral width. This fiber is used when the signal required has to transmit at a higher rate, and for longer distances. The reason for the ability to transmit over longer distances is because of the single light wave and the small core, which eliminates most distortion in the signal. The typical wavelengths transmitted using single-mode fibers are between 1310-1550nm.

In comparison to single-mode fibers, multi-mode fibers have a typical diameter range of 50-100µm. The functions are principally the same, for primarily for light transmission which is converted into a signal, but the multi-mode fibers are able to process more light, at high speeds. The light waves are dispersed into a number of paths, and due to this, long lengths of multi-mode fibers are not possible due to interference within the line. The other major factor is that multi-mode fibers do not require a light source of narrow spectral width and thus are able to transmit light of lower wavelengths (850nm) in comparison to the single-mode fibers.

II . III. **Optical Fiber Construction**

A single optical fiber is made up of several components and these include the

- Core
- Cladding
- Coating buffer
- Strength member
- Outer jacket

The core is the light carrying element, whereas the cladding assists in total internal reflection. This is achieved by using a cladding which has a lower refractive index as compared to the core, causing the light transmitted in the core to reflect off the cladding and remain within the core. The refractive index can be described as the ratio between the velocity of light in vacuum and the velocity of light in the material. Thus the higher the refractive index, the slower the speed of light through the material.

$$\text{Index of Refraction} = \frac{\text{Light velocity}_{\text{vacuum}}}{\text{Light velocity}_{\text{material}}}$$

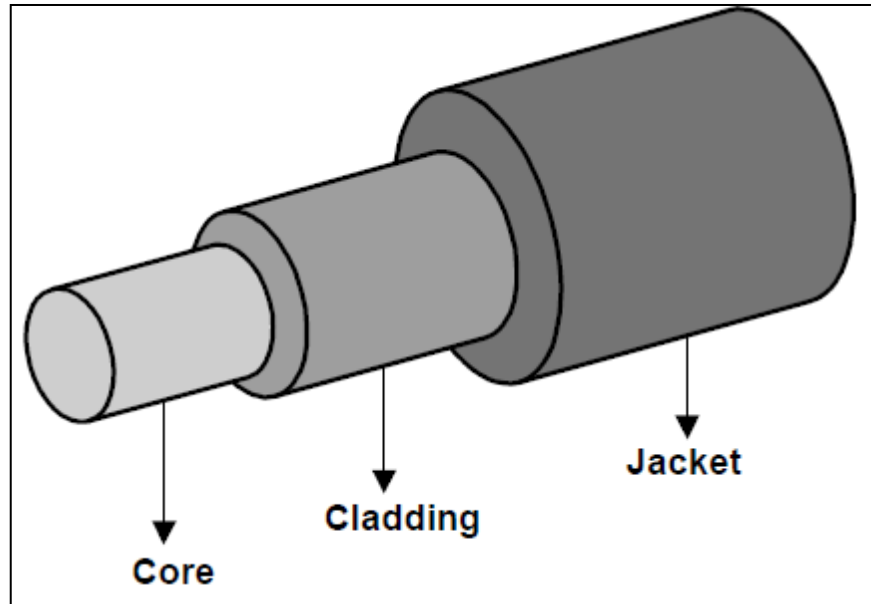


Figure 2: Structure of a POF [5]

II . IV. Total Internal Reflection[6]

Optical fibers function well because of its ability to keep the light within the fiber core. When light travels from one material to another of different density[7], the light's path will bend. At a particular point, or rather angle the light will not pass through the surface, but instead bounce off the surface. Optical fibers make use of this phenomenon to bend light at its boundary, which is the cladding, and trap the light within the core. Thus by selecting material differences i.e. different refractive indices between the core and cladding, it is possible to select the angle at which total internal reflection occurs.

II.IV.I Reflection of light from optical surfaces

When light is incident on an interface between two transparent optical media, such as between air and glass or between water and glass, four things can happen to the incident light.

- It can be partly or totally reflected at the interface.
- It can be scattered in random directions at the interface.
- It can be partly transmitted via refraction at the interface and enter the second medium.

- It can be partly absorbed in either medium.

In the case of Optical Fibers, the surfaces are smooth, and thus the rough surfaces can be ignored[5].

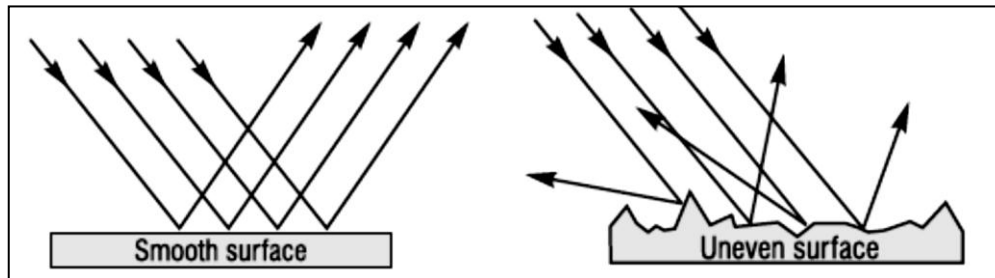


Figure 3: Specular and diffuse reflection[6]

II.IV.II The law of reflection on plane surfaces:

When light reflects from a plane surface (*Figure 4*), the angle that the reflected ray makes with the normal (line perpendicular to the surface) at the point of incidence is always equal to the angle the incident ray makes with the same normal. Important to note is that the incident ray, reflected ray, and normal lie in the same plane.

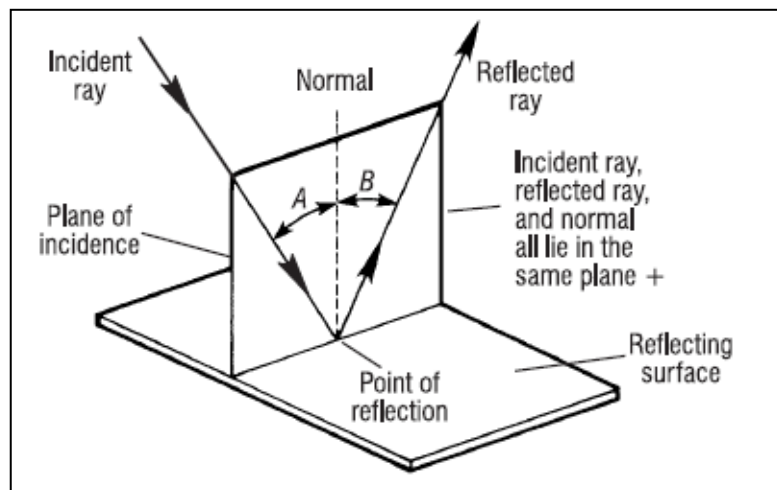


Figure 4: Reflection on a plane surface[6]

II.IV.III Refraction of light from optical interfaces

When light is incident at an interface, the geometrical plane that separates one optical medium from another, it will be partly reflected and partly transmitted. *Figure 5* shows a three-dimensional view of light incident on a partially reflecting surface (interface), being reflected there (according to the *law of reflection*) and refracted into the second medium. The bending of light rays at an interface between two optical media is called *refraction*.

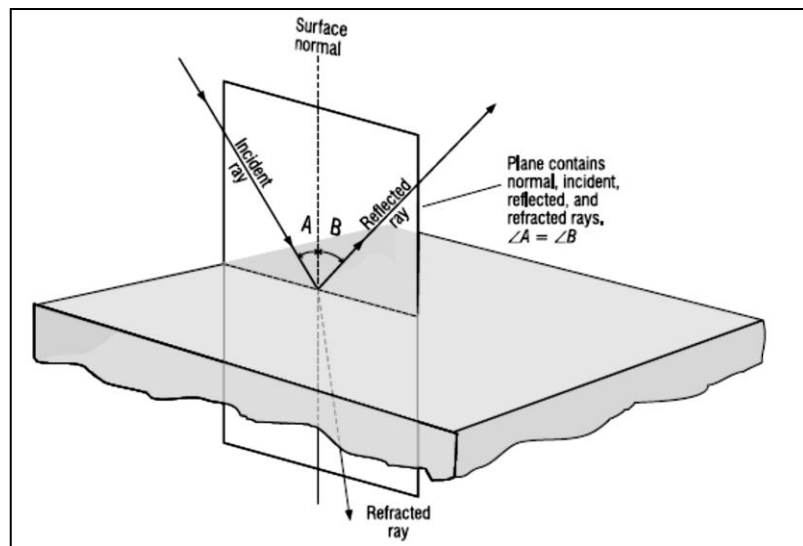


Figure 5: Reflection and refraction at an interface[6]

Index of refraction: The two transparent optical media that form an interface are distinguished from one another by a constant called the *index of refraction*, generally labelled with the symbol n . The index of refraction for any transparent optical medium is defined as the ratio of the speed of light in a vacuum to the speed of light in the medium, as given in

Equation

$$n = \frac{c}{v}$$

where

c = speed of light in free space (vacuum)

v = speed of light in the medium

n = index of refraction of the medium

The index of refraction for free space is exactly *one*. For air and most gases it is very nearly one, hence in most calculations it is taken to be 1.0. For other materials it has values greater than one.

Table 1: Indices of refraction for common materials at 589nm[6]

Substance	n	Substance	n
Air	1.0003	Quartz (fused)	1.46
Glass (flint)	1.66	Diamond	2.42
Benzene	1.50	Sodium Chloride	1.54
Glycerin	1.47	Ethyl Alcohol	1.36
Carbon Disulfide	1.63	Water	1.33
Polystyrene	1.49	Gallium Arsenide	3.40
Corn Syrup	2.21	Ice	1.31

The greater the index of refraction of a medium, the lower the speed of light in that medium and the more light is bent in going from air into the medium. *Figure 6* shows two general cases, one for light passing from a medium of lower index to higher index, the other from higher index to lower index. Note that in the first case (lower-to-higher) the light ray is bent toward the normal. In the second case (higher-to-lower) the light ray is bent away from the normal.

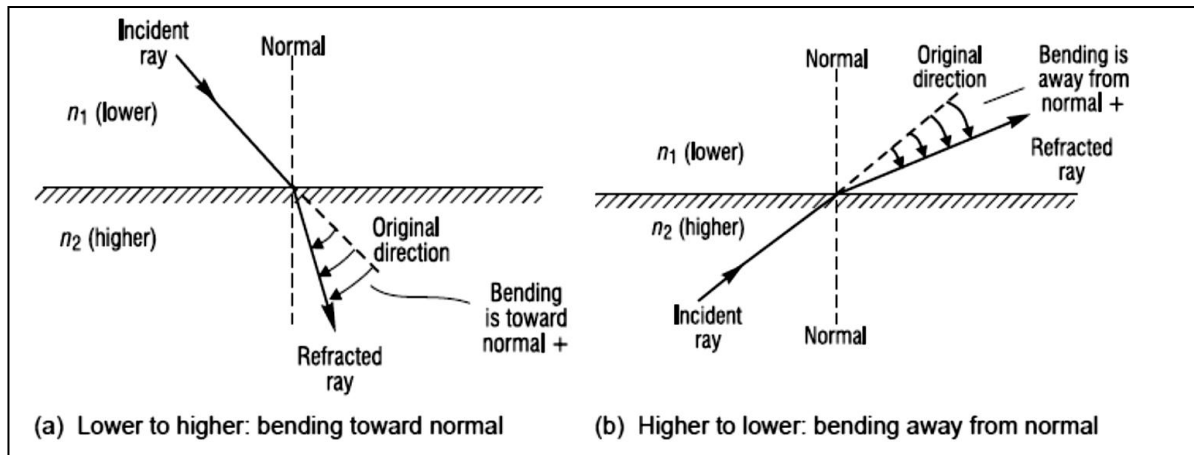


Figure 6: Refraction at an interface between media of refractive indexes n_1 and n_2 [6]

Snell's law

Snell's law of refraction relates the sines of the angles of incidence and refraction at an interface between two optical media to the indexes of refraction of the two media. The law is named after a Dutch astronomer, Willebrord Snell[8], who formulated the law in the 17th century. Snell's law enables us to calculate the direction of the refracted ray if we know the refractive indexes of the two media and the direction of the incident ray.

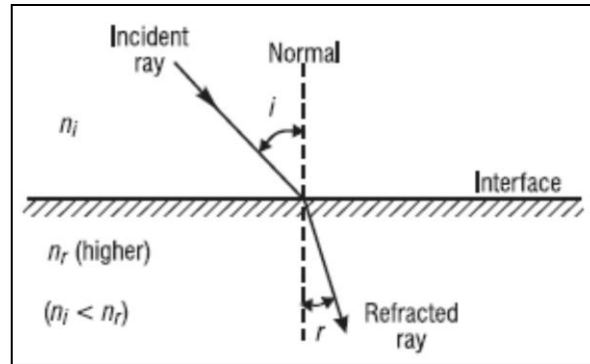


Figure 7: Snell's Law[6]

$$\frac{\sin i}{\sin r} = \frac{n_r}{n_i}$$

Where,

i is the angle of incidence

r is the angle of refraction

n_i is the index in the incident medium

n_r is the index in the refracting medium

Snell's law is often written simply as

$$n_i \sin i = n_r \sin r$$

II.IV.IV Critical angle and total internal reflection

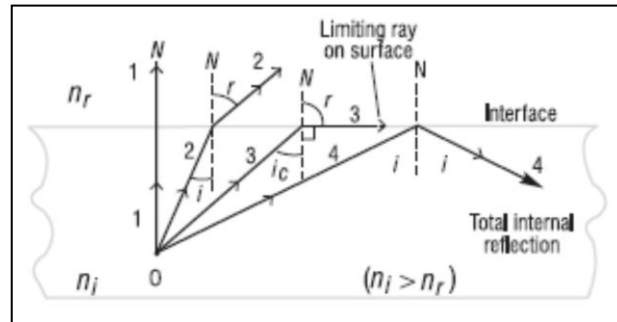


Figure 8: Total internal reflection

Figure 8, Shows four rays of light originating from point O in the higher-index medium, each incident on the interface at a different angle of incidence. Ray 1 is incident on the interface at 90° (normal incidence) so there is no bending. The light in this direction speeds up in the second medium but continues along the same direction. Ray 2 is incident at angle i and refracts (bends away from the normal) at angle r . Ray 3 is incident at the *critical angle* i_c , large enough to cause the refracted ray bending away from the normal (N) to bend by 90° , thereby traveling along the interface between the two media. (This ray is trapped in the interface.) Ray 4 is incident on the interface at an angle *greater than* the critical angle, and is *totally reflected* into the same medium from which it came. Ray 4 obeys the *law of reflection* so that its angle of reflection is exactly equal to its angle of incidence. The phenomenon of total internal reflection is exploited when designing light propagation in fibers[6] by trapping the light in the fiber through successive internal reflections along the fiber. In comparison to ordinary reflection from mirrors, the sharpness and brightness of totally internally reflected light beams is enhanced.

The calculation of the critical angle of incidence for any two optical media whenever light is incident from the medium of higher index is accomplished with *Snell's law*. Referring to Ray 3 in *Figure 8* and using Snell's law appropriately, we have

$$n_i \sin i_c = n_r \sin 90^\circ$$

where n_i is the index for the incident medium, i_c is the critical angle of incidence, n_r is the index for the medium of lower index, and $r = 90^\circ$ is the angle of refraction at the critical angle. Then, since $\sin 90^\circ = 1$, we obtain for the critical angle,

$$i_c = \sin^{-1}\left(\frac{n_r}{n_i}\right)$$

This phenomenon explains the principles of the functioning of optical fibers.

II.IV.V Reflection from a curved surface:

With spherical mirrors, reflection of light occurs at a curved surface, and this principle is similar to that in optical fibres. The Law of reflection holds, since at each point on the curved surface one can draw a tangent and erect a normal to a point P on the surface where the light is incident, as shown in *Figure 9*. One then applies the *law of reflection* at point P just as was illustrated in *Figure 4*, with the incident and reflected rays making the same angles (A and B) with the normal to the surface at P . Note that successive surface tangents along the curved surface in *Figure 9* are ordered (not random) sections of “plane mirrors” and serve, when smoothly connected, as a spherical surface mirror, capable of forming distinct images.

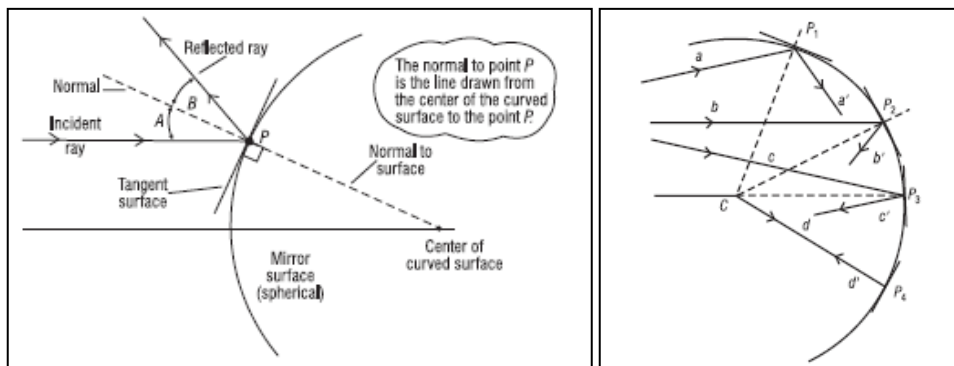


Figure 9: Reflection at a curved surface: Angle B equals angle A[6]

Since point P can be moved anywhere along the curved surface and a normal drawn there, we can always find the direction of the reflected ray by applying the *Law of reflection*.

II.IV.VI Numerical Aperture

Is an important design parameter for a lens, related directly to how much light the lens gathers. If the focal length of a design lens increases and its diameter decreases, the solid angle (cone) of useful light rays from object to image for such a lens decreases. An application of numerical aperture is in the design of the objective lens (the lens next to the specimen under observation) for a microscope, Light-gathering capability is crucial for microscopes.

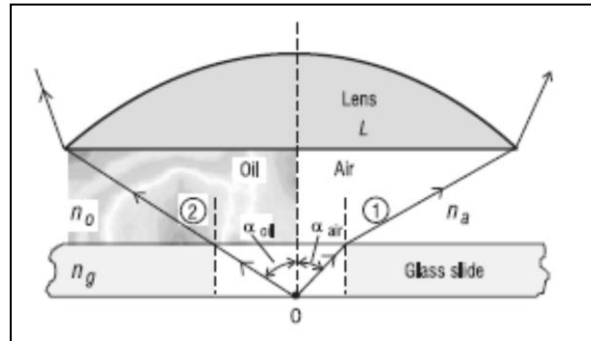


Figure 10 Light gathering on surface[6]

Figure 11, depicts the light-gathering power of a lens relative to a point O on a specimen covered by a glass slide. Lens L is the objective lens of a microscope focused on the specimen. On the right side of the symmetry axis of the lens, the light-gathering power of the lens, with air between the cover slide and the lens, is depicted in terms of half-angle α_{air} . On the left side, by contrast, the increased light-gathering power of the lens, with oil situated between the cover slide and the lens is shown in terms of the larger half-angle α_{oil} . The oil is chosen so as to have an index of refraction (n_o) very near that of the cover slide (n_g) so that little or no refraction occurs for limiting ray 2 at the glass-oil interface. Consequently the half-angle α_{oil} is greater than the half-angle α_{air} . As *Figure 10* shows, ray 1 suffers refraction at the glass-air interface, thereby restricting the cone of rays accepted by the lens to the smaller half-angle α_{air} . The *numerical aperture* of a lens is defined so as to exhibit the

difference in solid angles (cones) of light accepted, for example, by an “oil-immersion” arrangement versus an air-immersion setup.

The definition of numerical aperture (*N.A.*) is given as

$$N.A. = n \sin \alpha$$

where n is the index of refraction of the intervening medium between object and lens and α is the half-angle defined by the limiting ray (α_{air} or α_{oil}). The “light-gathering” power of the microscope’s objective lens is thus increased by increasing the refractive index of the intervening medium. Since the rays entering a fiber face are in air, the *numerical aperture* is

$$N.A. = \sin \alpha$$

II . V. Classification of dyes[9]

All aromatic compounds will absorb electromagnetic energy, but the compounds which can absorb in the visible range (350-700nm) will be coloured. Dyes contain chromophores, which are in essence double bonds in the structure and auxochromes, which are either electron donating or electron withdrawing, which in combination with chromophores will amplify the colour of the chromophore.

Table 2: Characteristic chemical structures forming chromophores and auxochromes

Chromophores
$-C = C -$
$-C = N -$
$-C = O -$
$-N = N -$
$-NO_2$
Quinone rings
Auxochromes
$-NH_3$
$-COOH$
$-SO_3H$
$-OH$

Some of the most common dye types are illustrated below

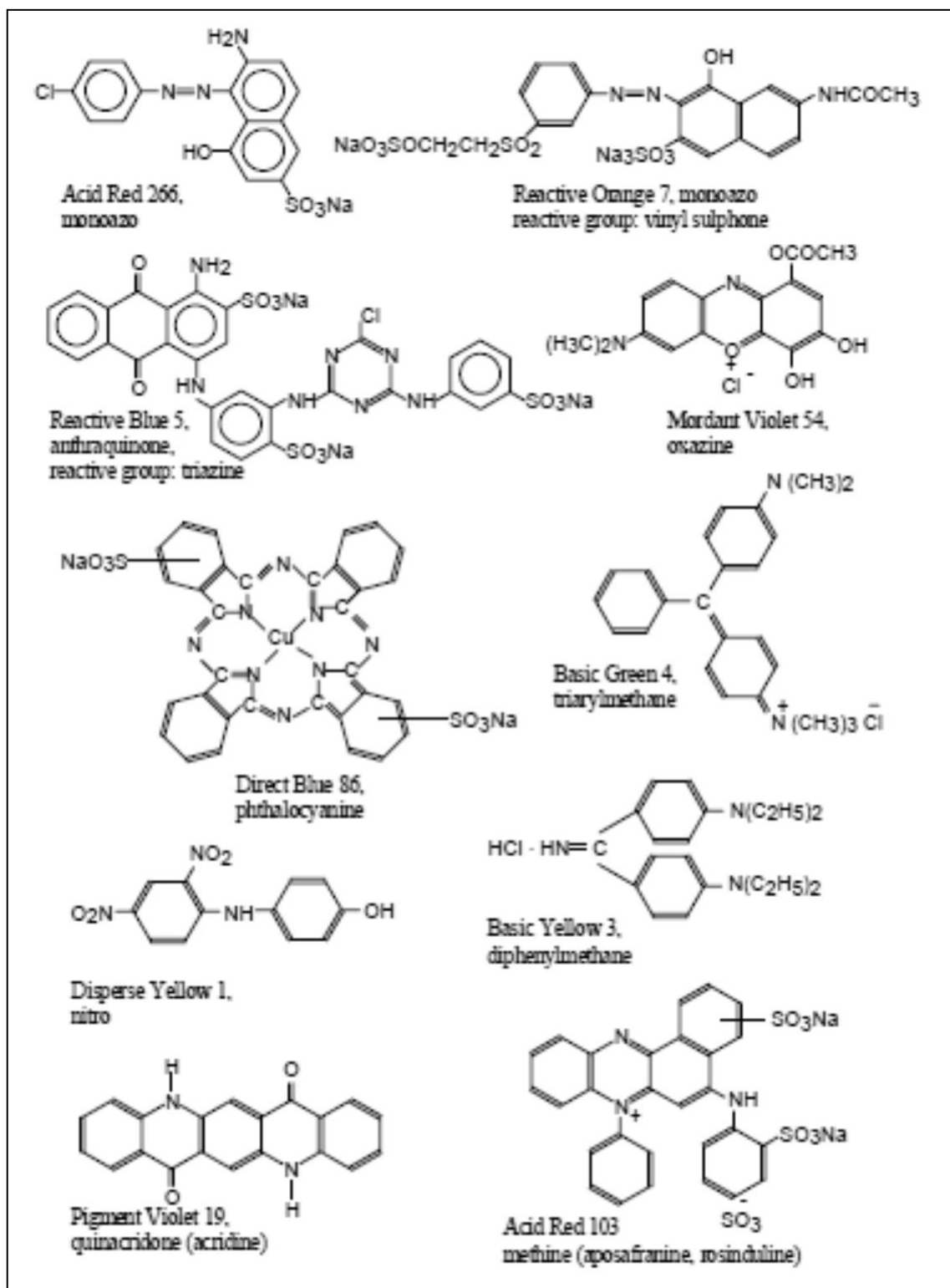


Figure 11: Common dye classes[10]

Since there are a wide variety of commercial colorants, the classification of dyes are done by colour, structure and application in the Colour Index (C.I.). The Colour Index has 15 different application classes:

II.V.I Acid dyes

Acid dyes constitute the largest class of dyes in the index (approximately 2300). Acid dyes are anionic compounds that are used to dye predominantly nitrogen containing fabrics and yarns such as wool, polyamide, silk and modified acryl. They bond with the cationic ammonium group (NH_4) of those fibres.

II.V.II Reactive Dyes

These dyes have reactive groups that form covalent bonds with $-\text{OH}$, $-\text{NH}$ or $-\text{SH}$ groups in fibres such as cotton, wool, silk and nylon. The reactive groups are usually a heterocyclic aromatic ring substituted with chloride or fluoride. This group forms the second largest group in the C.I.

II.V.III Metal Complex Dyes

This group falls within acid and reactive dyes. They are strong complexes of one metal atom which could be chromium, cobalt, copper or nickel, and also one or two dye molecules. Metal complex dyes are usually azo compounds.

II.V.IV Direct Dyes

These dyes consist of large molecules with high affinity to cellulose fibers. They bond to the fiber by weak Van der Waal forces. These dyes are mostly azo compounds (R-N=N-R) with more than one azo bond.

II.V.V Basic Dyes

This group of dyes are used to dye fibers which have acid containing groups such as modified polyacryl, since they are cationic compounds. Most contain anthraquinone or azo compounds.

II.V.VI Mordant Dyes

Mordant dyes are fixed to a fabric by the addition of a mordant. In simple terms a mordant is a chemical which combines the dye with the fiber. It's used to dye wool, leather and modified cellulose fibers. Mordant's usually contain dichromates or chromium complexes.

II.V.VII Disperse Dyes[11]

Unlike cotton, which can be dyed with anionic direct, sulphur, vat, reactive and azoic dyes, these dyes have little use for dyeing synthetic fibers. Disperse dyes are non-ionic, and use a direct dyeing technique to dye synthetic fibers such as acetate fibers. The only variance is the dyeing temperature from fiber to fiber.

A disperse dye is a non-ionic dye, which is relatively insoluble in water at room temperature, and have a limited solubility at higher temperatures. The dye is present in the dyebath as a fine aqueous suspension usually in the presence of a dispersing agent. The water dissolves a small amount of dye, such that the hydrophobic fibers can then absorb the dye from the solution. The dyes are non-ionic organic compounds of relatively low molecular weight.

The first disperse dyes were simple and relatively insoluble azo and anthraquinone compounds dispersed in water using a sodium salt. A fine dispersion is required for rapid dyeing and also avoids large dye particles on the material.

Disperse dyes have a slight water solubility due to the presence of polar substituents on their molecular structure, therefore a small quantity of dye becomes present in a true aqueous solution. This aqueous solution is able to penetrate into hydrophobic synthetic fibers. Because of this phenomena, dye is much more soluble in the fiber as compared to the water, therefore deep dye penetration is possible. The solubility equilibrium can be described by the following



Fastness of fibers or fabrics dyed using disperse dyes have moderate to good fastness to washing and light.

Dyeing of acrylic fibers can be achieved with disperse dyes, but the extent of dyeing is limited and the colour build up is poor. Dyeing at temperatures above 100°C to solve this problem is not possible because of the effect of high temperatures on the fiber. Due to many factors, dyeing of acrylic fibers using disperse dyes are limited to pale shades.

The dye usually contains small azo or nitro compounds (yellow to red), anthraquinones (blue and green) or metal complex azo compounds. Some typical disperse dye structures are as follows

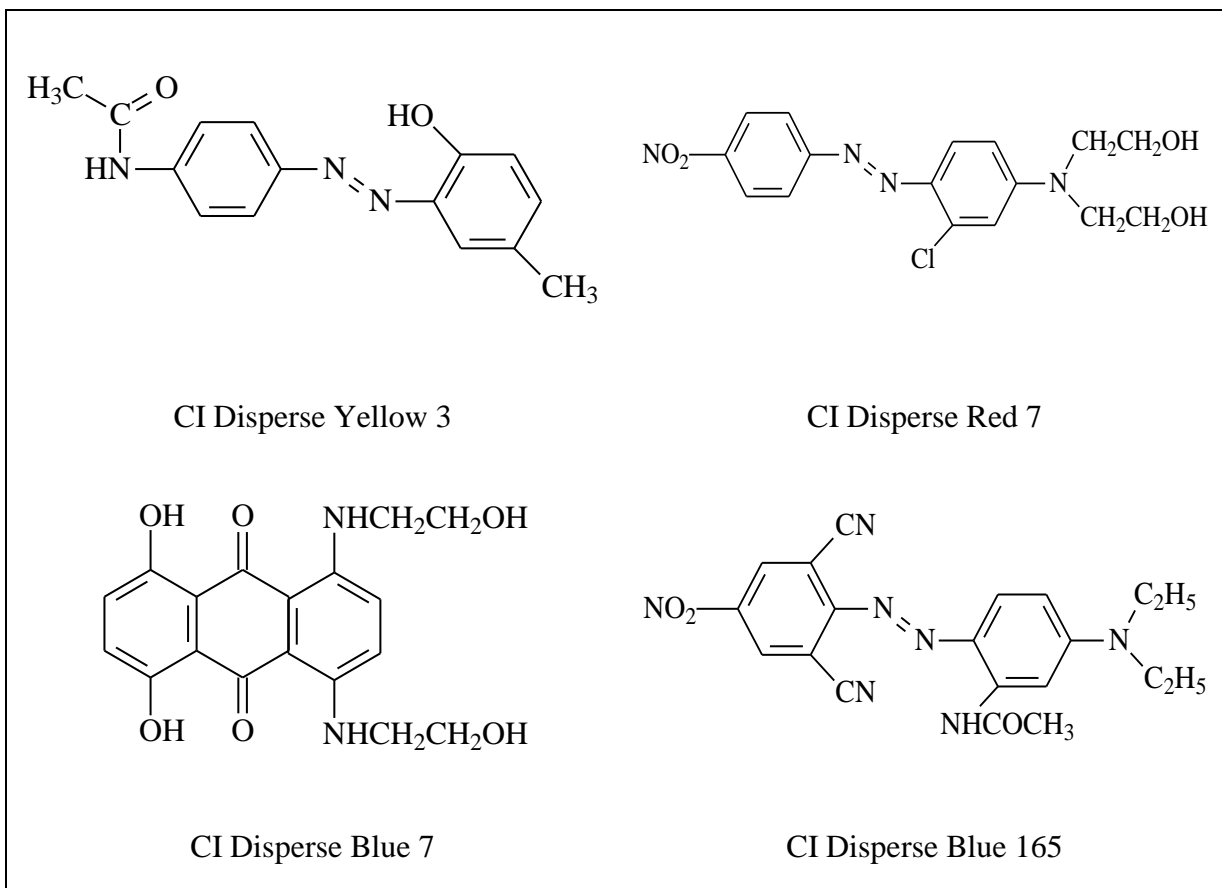


Figure 12: Typical disperse dye structures[11]

II.V.VIII Pigment Dyes

Pigment dyes are also known as organic pigments, which represent a small part of pigments applied in dyeing. The dye is insoluble, non-ionic compounds or salts, and retain their structure throughout the application. It is applied by dispersion in an aqueous solution, which requires off course a dispersing agent. Most pigment dyes are azo compounds (yellow to red) or metal complexes (Blue and green).

II.V.IX Vat Dyes

This group of dyes are water insoluble dyes which are used most commonly for cellulose fibers. The method of dyeing is based on the solubility of vat dyes in their reduced form (reduced with sodium dithionite), thereafter once impregnated on the fabric, oxidation is allowed, to bring back the dye to its original form. Almost all vat dyes are anthraquinones or indigoids. Indigo is one of the very old examples of vat dyeing.

II.V.X Anionic dyes and ingrain dyes

Azoic dyes and *Ingrain dyes* (naphthol dyes) are the insoluble products of a reaction between a coupling component (usually naphthols, phenols or acetoacetylammides; listed in the Colour Index as C.I. azoic coupling components) and a diazotised aromatic amine (listed in the Colour Index as C.I. azoic diazo components). This reaction is carried out on the fibre. All naphthol dyes are azo compounds.

II.V.XI Sulphur dyes

Dyeing with sulphur dyes involves reduction and oxidation, comparable to vat dyeing. They are mainly used for dyeing cellulose fibres.

II.V.XII Solvent dyes

Solvent dyes (lysochromes) are non-ionic dyes that are used for dyeing substrates in which they can dissolve, e.g. plastics, varnish, ink, waxes and fats. They are not often used for textile-processing but their use is increasing. Most solvent dyes are diazo compounds that underwent some molecular rearrangement. Also triarylmethane, anthraquinone and phthalocyanine solvent dyes are applied.

II.V.XIII Fluorescent brighteners

Fluorescent brighteners (or bluing agents) mask the yellowish tint of natural fibres by absorbing ultraviolet light and weakly emitting visible blue. They are not dyes in the usual sense because they lack intense colour. Based on chemical structure, several different classes of fluorescent brighteners are discerned: stilbene derivatives, coumarin derivatives, pyrazolines, 1,2-ethene derivatives, naphthalimides and aromatic or heterocyclic ring structures. Many fluorescent brighteners contain triazinyl units and water-solubilising groups.

II.V.XIV Other dye classes

Apart from the dye classes mentioned above, the Colour Index also lists *Food dyes* and *Natural dyes*. Food dyes are not used as textile dyes and the use of natural dyes (mainly anthraquinone, indigoid, flavenol, flavone or chroman compounds that can be used as mordant, vat, direct, acid or solvent dyes) in textile-processing operations is very limited.

II . VI. Colour Measurement[12]

Colour measurement is important in dyeing of textiles, specifically for matching samples, determining colour differences and for formulating dye baths. Fundamentals of colour measurements, or better known as colorimetry, are required for dyeing technology.

Colorimetry is the numerical description of colours by means of physical measurements. Two samples with the same numerical colour specification, in a specific viewing condition, will always have an identical perception of colour under those conditions. Colour differences should be measured, and acceptable values of difference be kept minimal. Many industries producing coloured garments or products, use colorimetry, thus making it a key technique in textile dyeing.

II.VI.I Factors influencing colour perception

Colour and how we see it is a difficult question to answer. Colour perception is a complicated theory, linked to the absorption of light in the eye and processing in the brain. In textiles the material will selectively absorb some of illuminated light, and transmit or reflect the remainder of the light to the eye of the observer. The light received by the eye is what gives the viewer (person) the feeling of colour.

Perception of light may vary according to three factors:

1. The wavelength distribution, or colour of the light source illuminating the object;
2. The degree of reflection or transmission of each wavelength of the incident light by the object;
3. Or the visual response of the observer's eye to the wavelengths of light entering from the object.

The numerical specification of a colour requires these numerical description of each of the above influencing factors.

II.VI.II Light sources and illuminants[12]

White light as opposed to specific colour light, such as red light, consists of all wavelengths of visible light, approximately in equal proportions, which makes white light the best provider of colour rendering properties.

Visible light sources include those with:

1. discontinuous line spectra from a source only emitting certain discrete wavelengths of light, such as a low pressure mercury lamp. These are often coloured lights of low colour rendering ability;
2. continuous emission spectra from sources emitting at all wavelengths, such as an incandescent tungsten lamp or the sun. These are usually white lights;
3. both line and continuous emissions, as in the light from a fluorescent tube. These often give good quality white light.

The spectral power distribution (SPD) of a light source gives the required numerical description of it. SPD gives the emitted power ($\text{W m}^2 \text{nm}^{-1}$) as a function of the wavelength.

Daylight, which has an irregular, continuous SPD, is a white light composed of all wavelengths in the visible region. An incandescent light source (eg. Tungsten lamp) is more yellow than daylight, and thus has a more regular SPD. Fluorescent light generates an irregular SPD.

Light sources are usually categorised according by the colour temperature, given by the absolute temperature scale in Kelvin ($273+^{\circ}\text{C}$). The higher the temperature of the emitting source, the greater the total power of the emitted radiation, and lower wavelength of the maximum emission.

The Commission Internationale de l'Eclairage (CIE) proposed SPD's for light sources used in colorimetric purposes, called CIE standard illuminants. Example of a CIE Illuminant D_{65} , has a specified SPD for a number of illuminants corresponding to daylight. D represents daylight and the number gives the colour temperature in hundreds ($65=6500\text{K}$).

II.VI.III Reflection or transmission of light by an object

II.VI.III.I Reflection spectrophotometry[12]

Spectrophotometry provides the numerical description of the reflection or transmission of light by an object. The spectrum provides the fraction of incident light that an object reflects or transmits as a function of wavelength.

In most reflection spectrophotometers, the reflection of light by the sample is measured at each wavelength relative to that of a white standard such as a plate coated with MgO or BaSO₄. The standards diffuse approximately 100% of reflection between the range of 380-750nm. Some spectrophotometers may have continuous or pulsed light sources, different angles for the beams of incident and reflected light, double or single beam optics, different systems for dispersion into its component wavelengths, and different wavelength ranges and measurement frequency.

The three most common instrument geometries are:

1. illumination of the sample at an angle of 45° to its surface and detection of the reflected light at close to right angles;
2. the reverse of the above;
3. diffuse illumination of the sample from all directions, using an integrating sphere, and detection of reflected light at close to perpendicular to the sample.

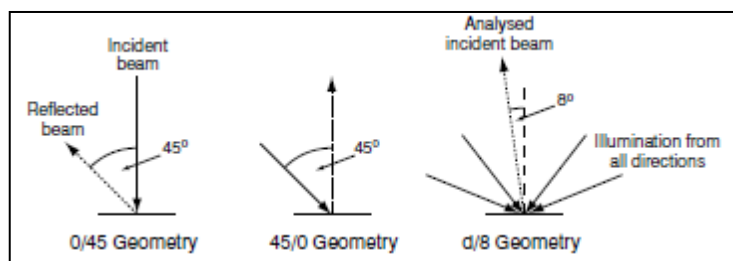


Figure 13: Common spectrophotometer geometries [12,p443]

Some spectrophotometers are able to continuously scan through the entire visible spectrum, whilst other instruments, only measure at selected wavelengths. Because of variation in instrument technologies, results are not exactly the same for identical samples.

II.VI.III.II Reflectance measurements in textiles

Textile fabrics have variations in texture and colour, which are due to production processes. Due to these conditions, samples are taken from various parts of a batch during production and the reflection spectrum of each sample is measured several times. From this analysis, the average reflectance spectrum can be obtained.

For reflectance measurements, the sample should be opaque, meaning that no light should pass through the material. This will result in light reflecting back from the sample holder, which is not desired, thus the fabric maybe layered to avoid this.

Almost all textiles have a characteristic texture that will influence the diffusion of the incident light, thus affecting the appearance from different angles. In order to minimize this effect, the fabric should be rotated in orientation by 90° between analysis, and an average taken, minimizing the effects of direction caused by texture.

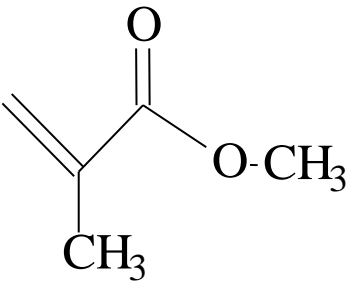
For reproducibility of results, conditions should be kept controlled. Reflectance changes may occur with the effect of temperature, humidity on the sample. Light sources also play an important role in reflectance measurements, for example when there is a small portion of ultra-violet light (below 400nm), excitation of fluorescent dyes are possible.

II . VII. Chemical composition of optical fibers

Plastic optical fibers have been manufactured from a number of transparent polymers such as Polymethyl methacrylate(PMMA), polystyrene(PS), polycarbonate(PC), CYTOP (amorphous fluorinated polymer), hard core silica(HCS), and plastic clad silica(PCVS)[13]

II.VII.I Polymethyl methacrylate

Table 3: MMA characteristics

	Methyl methacrylate[14]	
	Chemical Formula	C ₅ H ₈ O ₂
	Molar mass	100.12g.mol ⁻¹
	Density	0.94 g/cm ³
	Melting point	-48°C, 225K
	Boiling point	101°C, 374K

Methyl acrylate is the monomer of Poly(methyl methacrylate), and the polymer is formed by the simple addition of alkenes, the reaction was adapted from Clayden, Organic chemistry[15]

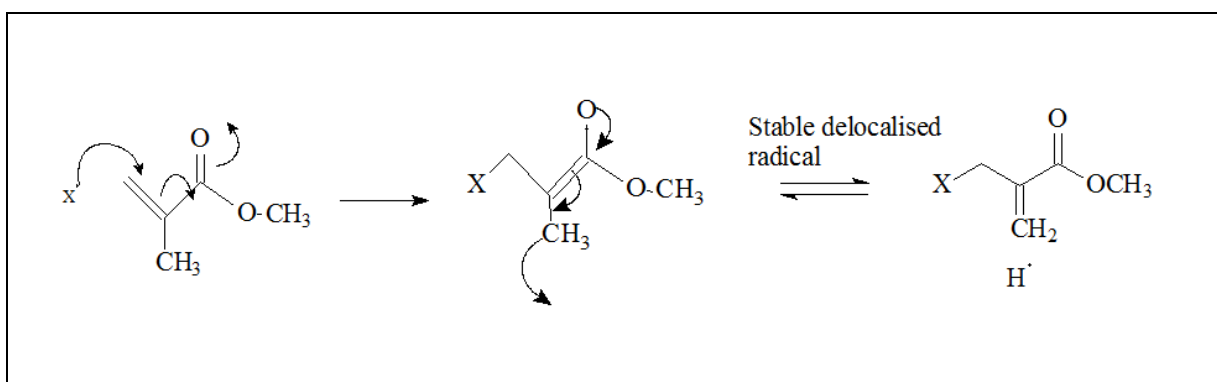


Figure 14: Radical formation of alkene addition

After the radical formation, the polymer can be easily formed by the following

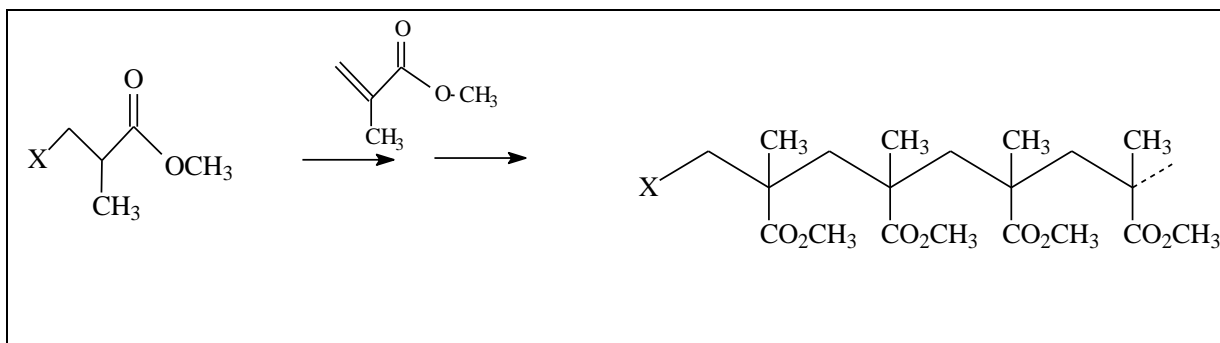
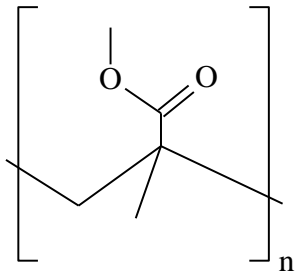


Figure 15: Formation of Poly(methyl methacrylate)

Table 4: Characteristics of PMMA

	Poly(methyl methacrylate)[16]	
	Molecular Formula	$(C_5H_8O_2)_n$
Density	1.18 g/cm ³	
Melting point	160°C, 433K	
Boiling point	200°C, 473K	
Refractive index	1.4914 at 587.6nm	

Poly(methyl methacrylate) is known as PMMA. It is a strong and light weight material, with a density half of that of glass (density of glass is between 2.4 -2.8 g/cm³)[17]. It also has good impact strength when compared to glass and polystyrene.

PMMA transmits up to 92% of visible light, and gives a reflection of about 4% due to its refractive index. The maximum water absorption ratio is 0.3 to 0.4% by weight, thus the polymer is highly hydrophobic.

The uses include:

- Transparent glass substitute
- Daylight redirection (in skylights, to spread light in a room)
- Medical technologies and implants
 - Has a good compatibility with human tissue
 - Orthopedic surgery (used as bone cement to fix implants)
 - Dentures
 - Dental fillings
- Aesthetic uses
 - Acrylic paints (hydrophobic nature)
 - Furniture
 - Signs (in advertising industry)
- Plastic optical fibers
 - For short distance communication – high flexibility and low cost are major advantages

Chapter III Materials and Methods

This chapter describes the materials involved in this research e.g. different types of optical fibers, dyes, reagents for surface modification and also the methods of dyeing and chemical treatment. Also the evaluation techniques for optical and dye penetration are described in detail.

III . I. Fiber composition

Fiber composition was determined by Infra-red spectroscopy (IR Spectroscopy)

Table 5: *Flexi* fiber characteristics

Properties of fiber	
Fiber description	Flexi 1.5mm
Core composition	PMMA
Cladding composition	Poly(tetrafluoro ethylene)

III . II. Dyeing of Core

The fiber consists of two principle parts:

- Core
- Cladding

The core of the fiber had to be mechanically stripped, by first cutting the desired length (60cm). Thereafter, minor cuts were made on each end, to free the core from the cladding, thus releasing any vacuum which may have been created in the fiber whilst cutting. The core was then removed by holding the cladding fixed on one end, and pulling on the core on the opposite end.

5g of Terasil Red GFF, was accurately weighed on a watch glass, and put into a dye bath (30cm x 25cm ,stainless steel) containing exactly 1 Liter of water at boiling temperature. After the addition of Dye, the temperature was recorded. Thereafter the fibers were added to

the dye bath, for their respective dye times (10, 20, 30, 40, 60, 90, 120, 150, 180 minutes). It is necessary to keep the water level constant in the boiling dyebath, to avoid change in the dye concentration. After the fibers were removed from the dye bath, it was necessary to wash with water thoroughly.



Figure 16: Apparatus setup for dyeing of fibers

Table 6: Dyeing parameters of fiber core

Dye Classification	
Trade name	Huntsman Terasil Red GFF
Dye concentration	5g/L
Temperature	98°C
Time	10, 20, 30, 40, 60, 90, 120, 150, 180 minutes

III . III. Temperature effect on core and parental fiber

60cm samples were prepared for this analysis. A set of core samples were prepared as described in the previous section. The parental fiber was cut to size, and was not modified in any way. Six samples respectively (with and without cladding) were placed in a boiling water bath and a single fiber of each type was removed at times 10, 20, 30, 40, 60 and 90 minutes.

Table 7: Parameters of heat treatment to fibers

Solvent	Water
Temperature	98-100°C
Time	10, 20, 30, 40, 60, 90 minutes
Samples	Core PMMA and Parental Flexi

III . IV. Side emission of fibers[18]

III.IV.I Principle

The device is intended for guiding laterally emitting optical fiber or a textile structure which contains optical fibers and to measure the light output that these structures emit. The optical fiber or textile structure is located between the feed rollers, which guide them to the measuring tunnel, where there is a single measurement of light output. The tow rollers are driven by step motor. After guiding the thread through the device, the thread is illuminated. The actual measurement is performed with the use of a light sensor, which reads the light output in pre-defined step lengths. Step lengths are processed by a step motor that drives the tow rollers. The actual device is controlled by a computer program created in MATLAB.

III.IV.II Description of instrument

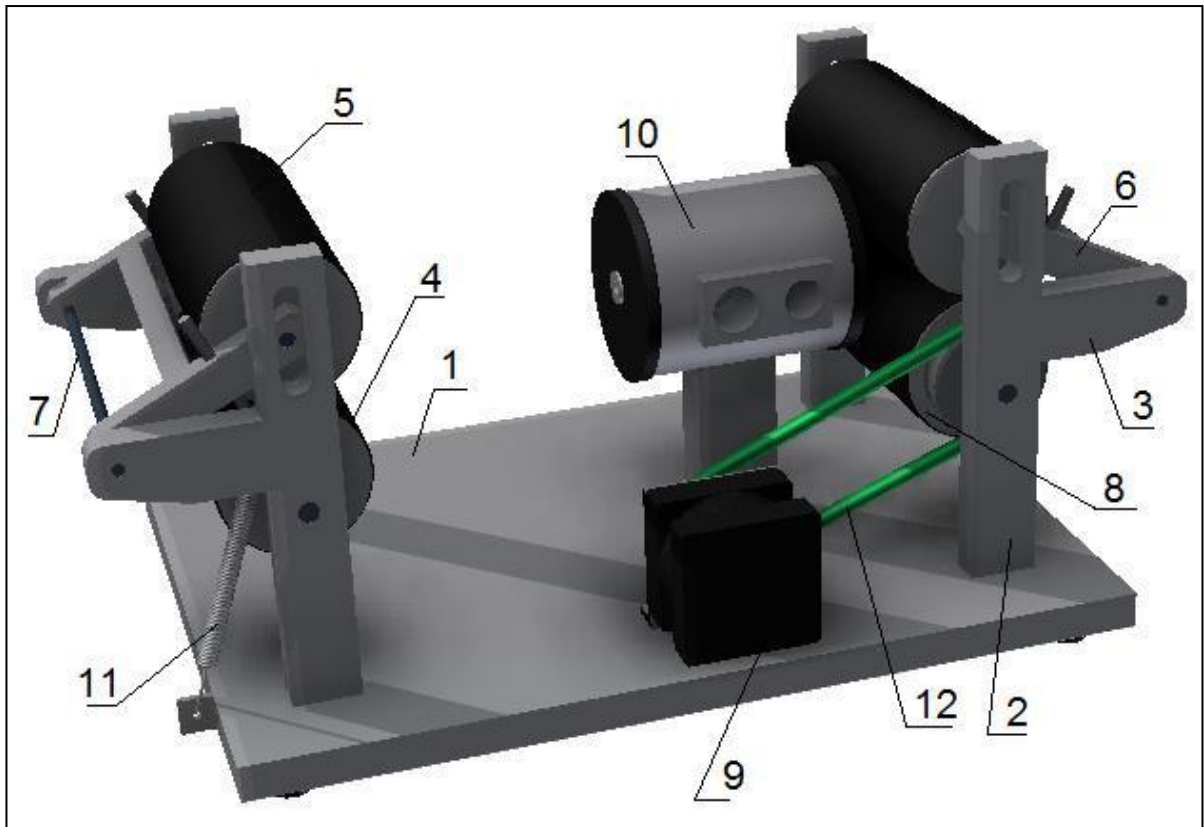


Figure 17: Schematic diagram of Prototype 1, for measurement of side emission

Referring to the above diagram, the device consists of a base plate (1). This plate is fastened on the edges of four columns (2), among which are fixed free (4) and pressure (5) rollers for feeding and extraction of fibers. The poles are brackets (3), which are mounted with the pressure roller which works as a shaft lever (7). It allows manipulation of the rollers. The actual pressure roller is placed on the push lever (6), the intensity of pressure that develops through two tension springs (11). Alongside the bottom roller (driving roller) (8) is a fixed drive belt (12) which is powered by a step motor (9). The middle measuring tunnel is mounted onto the base plate (10). It is equipped with two lids in order to avoid measurement bias. In addition, the measurement tunnel contains two holes to fix a spectrometer and a light sensor.

III . V. Cross section analysis of plastic optical fibers

After dyeing of samples, it was necessary to analyse cross –sectional images to investigate dye distribution into the fiber. This was done by first cutting the fiber to the size of the wax mould exactly, to ensure that the fiber remains straight. The fiber was then wrapped with cotton roving, therefore the cotton fibers are in parallel orientation. After wrapping the PMMA core, it was necessary to add a little twist to the cotton roving, such that the cotton will completely cover the PMMA sample. The sample was then place into the wax mould, and the sides of the mould were sealed using scotch tape. Paraffin wax was then heated to melting temperature, and allowed to stand and cool, thereafter it was transferred into a small beaker (50ml) to aid in easy pouring of the warm wax into the mould. After the wax was poured into the mould to the brim, it was left overnight in temperature below -5°C .

After overnight freezing, the wax was removed from the mould. The sample now encased in the wax was then cut into $70\mu\text{m}$ cross sections using the *Microtome* instrument. Samples were cut at a slow rate, and the cross section cleaned of all wax, and then carefully moved and placed onto a glass slide containa a thin layer of glycerin, for analysis.

The samples were then analysed using **NIS Elements and Nikon microscope**, under 5.00x magnification, specific calibration settings stated below in *Table 8*



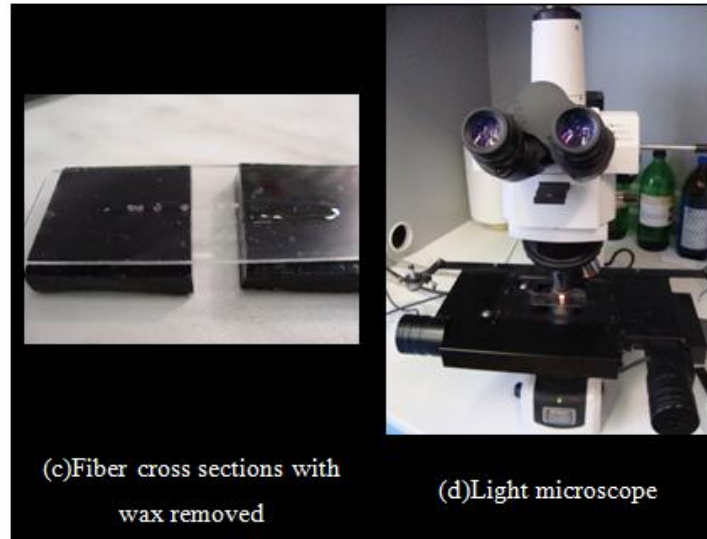


Figure 18: Cross section analysis of fibers

Table 8: Calibration settings for light microscope

Instrument	DS-5M-US
Format	640 x 480
Magnification	5.00x
Exposure	ME 10ms
Gain	1.70x
Noise Reduction	On
White Balance	1.02, 1.00, 3
Saturation	0.19
Hue	0.19
Offset	0.00
Contrast	Dynamic
Sharpness	Smoothest

III . VI. Surface treatment with Ethyl Acetate

Ethyl acetate was used as an etching solvent, to create a surface modification to the parent fiber. 90% concentration was used to treat 1meter samples of fibers for one and a half hours in a sealed container. It is important to note that the solvent is highly flammable and care should be taken accordingly. After solvent treatment, the fibers were then washed thoroughly using water, and left to dry at room temperature.

Table 9: Surface treatment parameters

Solvent	
Ethyl Acetate	900g/1000ml
Molecular Formula	C ₄ H ₈ O ₂
Molecular weight	88.11 g/mol
Sample	
Flexi	PMMA core and Poly(tetrafluoro ethylene) cladd

III . VII. Dyeing of surface modified optical fibers

Dyebath's were prepared using 10g/L and 15g/L concentrations respectively. The bath was left to reach boiling temperature (98°C), and thereafter the treated fibers were added to their respective dyebath's. Dyeing was done for a period of 20 minutes, thereafter the fibers were removed and washed with water.

Table 10: Dye parameters for *Flexi* fiber

Dye Classification	
Trade name	Huntsman Terasil Red GFF
Dye concentration	5g/L, 10g/L
Time	20 minutes
Temperature	98°C

Chapter IV Results and Discussion

IV . I. Identification of chemical composition for *Flexi*

The optical fibres were evaluated with IR spectra to determine their composition.

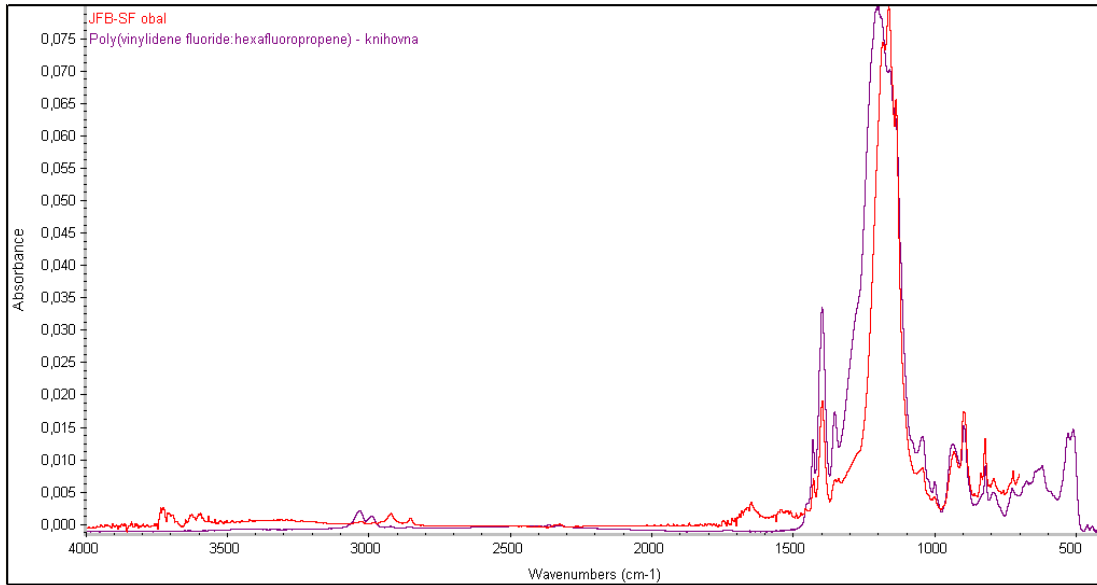


Figure 19: IR spectrum of cladding

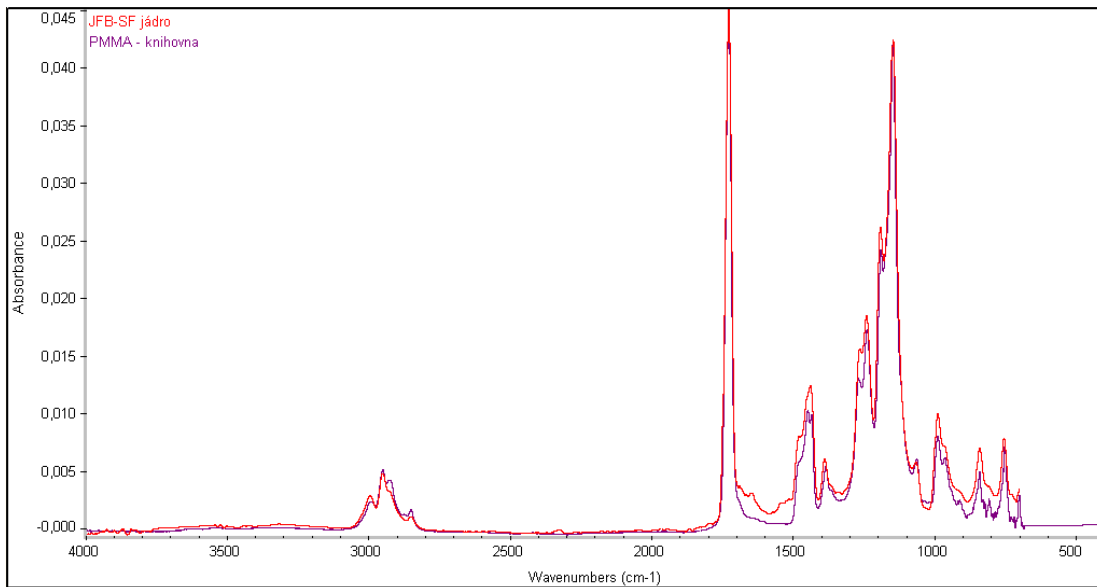
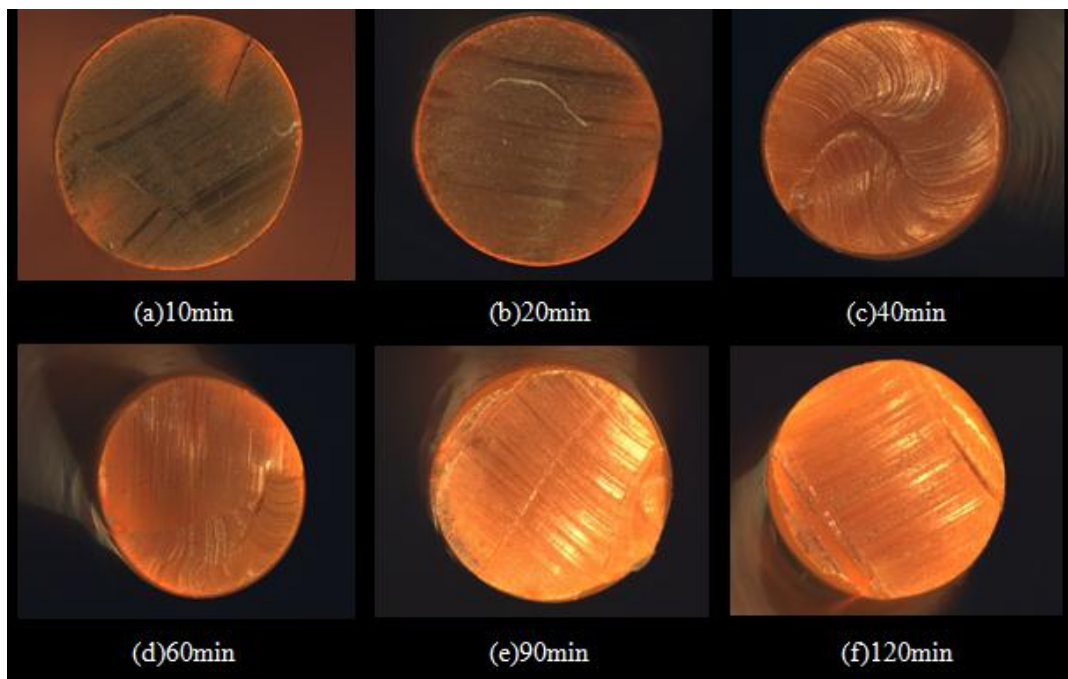


Figure 20: IR spectrum of core

From the above spectrums, *Flexi* optical fiber was found to have the composition comprising of a (poly) tetrafluoroethylene cladding and a PMMA core. These results were important in finding various treatment methods of the fiber.

IV . II. Cross section analysis of dyed fibers

Initially fiber cores were dyed with 5g/L concentration, and small sections of the fiber, 5cm lengths were then viewed under a light microscope at 5x magnification. The figure below shows that light does transmit through the fiber even after 3 hours of dyeing (*Figure 21, j*). What was found in this study is that the fiber became very brittle, and was prone to breaking after 60 minutes (*Figure 21, d*). Also the fiber became very stiff, and thus it was not feasible to dye the fiber to such an extent, since the flexibility of the fiber is the key to integration into fabrics. This method also proved to be inconclusive since it was not possible to have the same calibration settings to measure the dye penetration or even the fiber diameters. It can also be seen from the images that it is necessary to cut the fibers with a better method, since the surfaces in this case will have to be polished smooth in order to get a better image.



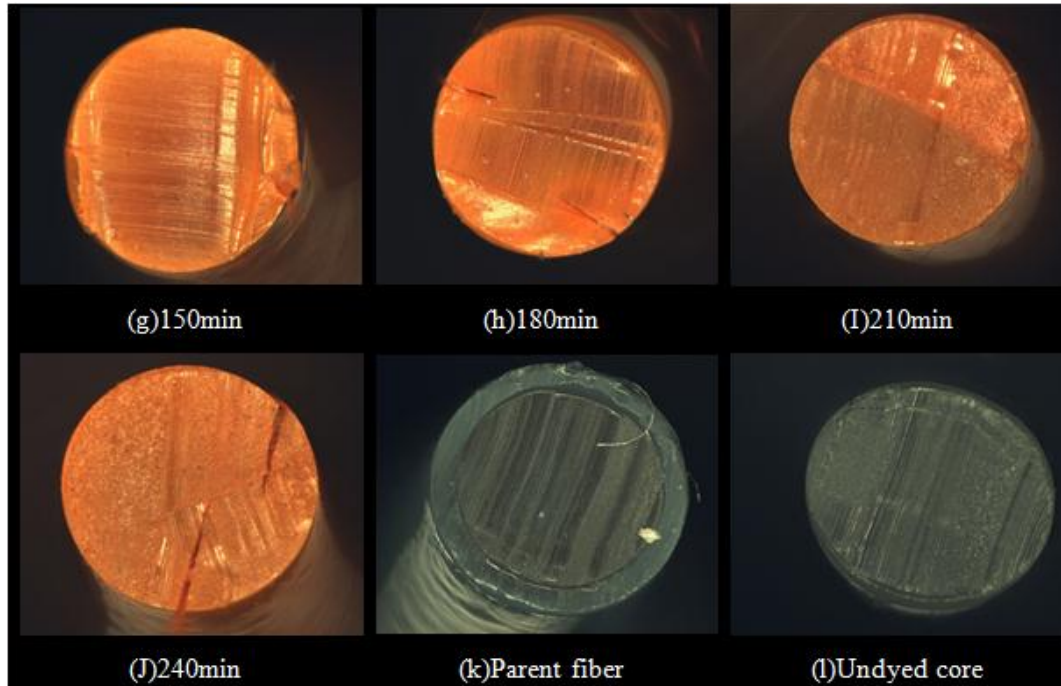


Figure 21: Macroscopic images of dyed optical cores

Referring to the figure below (*Figure 22*), the image shows the macroscopic view of the longitudinal direction of the *Flexi* core. The dyed fiber on the left shows some surface roughness, whilst the untreated core from the parent fiber shows a flawless surface. The dye penetration can be seen clearly also in this image, since a dark portion on the fiber, signifies the black stage to which the fiber was placed. The black stage can be seen clearly through the untreated fiber. This may also be a possible method to measure the dye penetration of the fiber, but largely the problem is due to calibration, since each of these images (*Figures 21 and 22*) required individual processing.

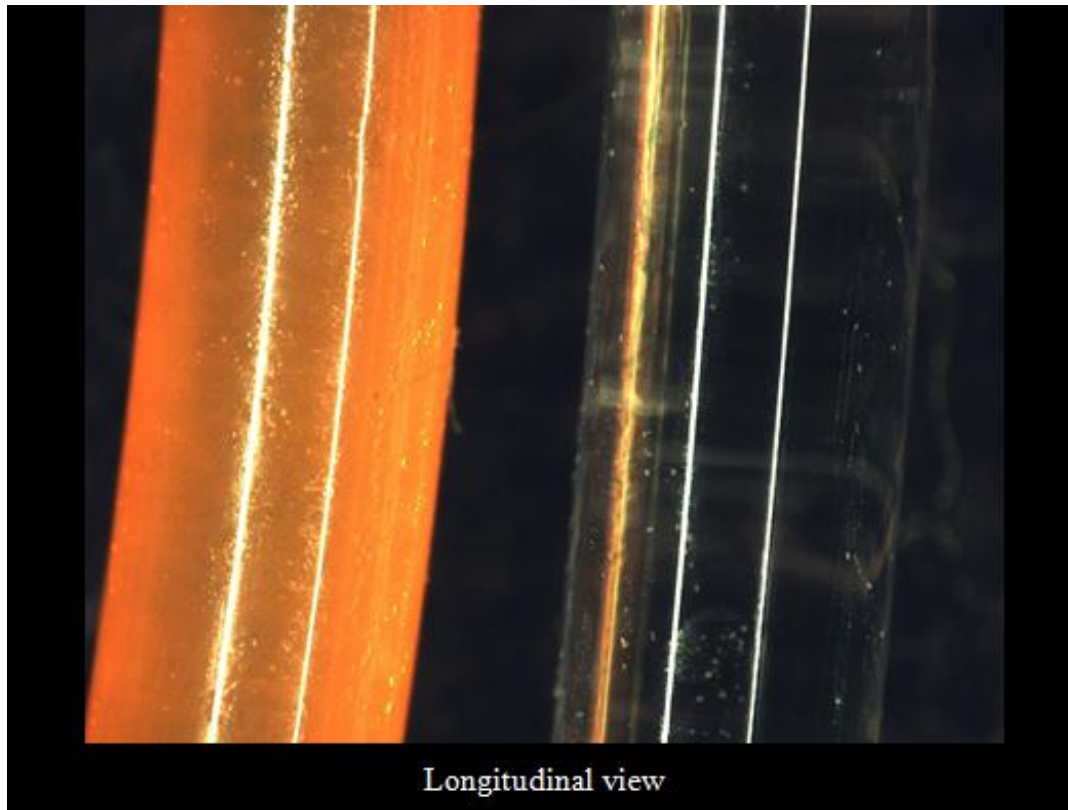


Figure 22: Macroscopic image of longitudinal view - dyed core and parent core

After processing the short fibers, longer lengths were dyed (60cm samples), and the dye time was optimized to 90 minutes for these research purposes. The fibers showed to be difficult to set in wax, since the surface is very smooth, and does not absorb any wax. A solution was found to wrap the fibers in cotton sliver, to aid in some gripping capacity during the cutting of the cross sections. The *Microtome* instrument had a maximum capacity to cut $70\mu\text{m}$ cross sections. This setting was used since there was a lot of damage to the integrity of the fiber diameter when lower cross sections were tried. Cutting was done at a slow rate, unlike conventional fibers which can be cut relatively fast, this was due to the fiber being very rigid, and hard as a material itself. The cross sections below (*Figure 23*) were achieved by calibrations mentioned in the previous chapter. Image analysis was done by means of *NIS-Elements*, which allowed for the diameters and the dye penetration to be measured accurately.

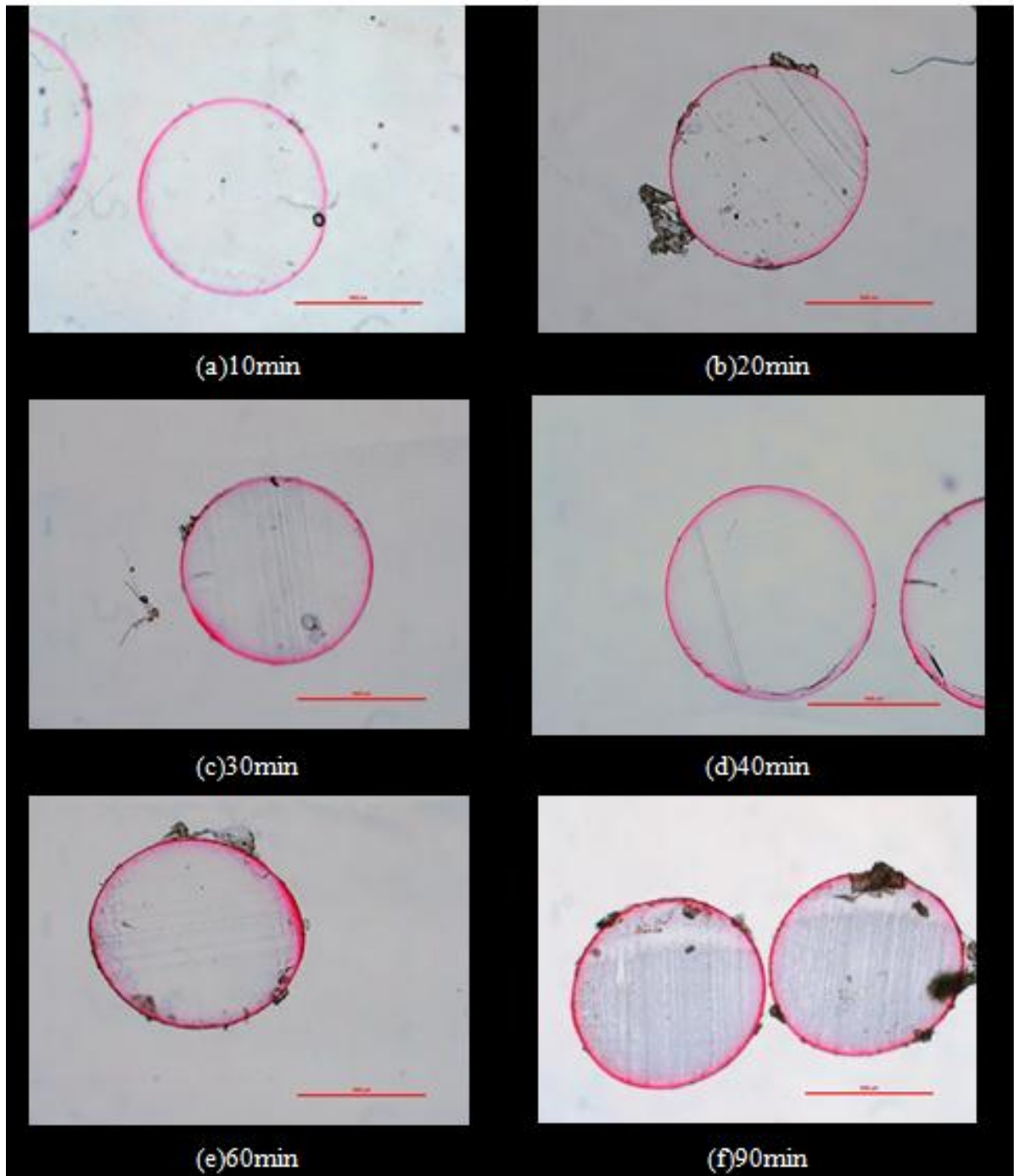


Figure 23: Optical fiber cross sections of 70µm

Using the images, it is quite easily distinguished the difference between where dye stuff is present and absent. Thus using subjective evaluation of image analysis the following results were obtained

Table 11: Objective measurements of fiber radius and diameter by image analysis

Time[min]	Radius[μm]	Diameter[μm]
10	764.83	1529.66
20	789.17	1578.33
30	743.38	1486.76
40	804.12	1608.25
60	790.42	1580.83
90	764.05	1528.1
Average	776.00	1551.99
Standard deviation	22.38	44.75

Referring to the table above, the radius of the fibers were consistent with the expected diameter of *Flexi*, which was 1.5mm in diameter. Some distortion may have been caused whilst removing the core from the cladding of the fiber. Variations may also be due to the heating of the fiber over a prolonged period. It is noticed that the diameter of the 40 minute sample, is significantly higher than the other samples. It may be possible that at this time there is a structural change in the fibers composition (PMMA). Referring to *Figure 24, d* ; the sample after 40 minutes of dyeing, shows a much more full and circular shape, correlating with the results found via image analysis. Taking the average diameter, 1551.99 μm , the result is consistent with what is expected, and the standard deviation was 44.75.

The dye penetration into the fiber was measured subjectively by image analysis, by taking the distance from the fiber edge, to the furthest perpendicular point showing coloured dye-stuff. Looking at the cross sectional images (*Figure 24*) the dye penetration showed graphically to be uniform around the fiber.

Table 12: Dye penetration measurements by image analysis

Time [min]	Colour penetration [um]
10	37.05
20	41.08
30	62.12
40	77.35
60	148.89
90	152.17

In this respect the measurement was taken at random points along the circumference of the fiber cross sections. The results show an increasing trend, which is more easily seen graphically below

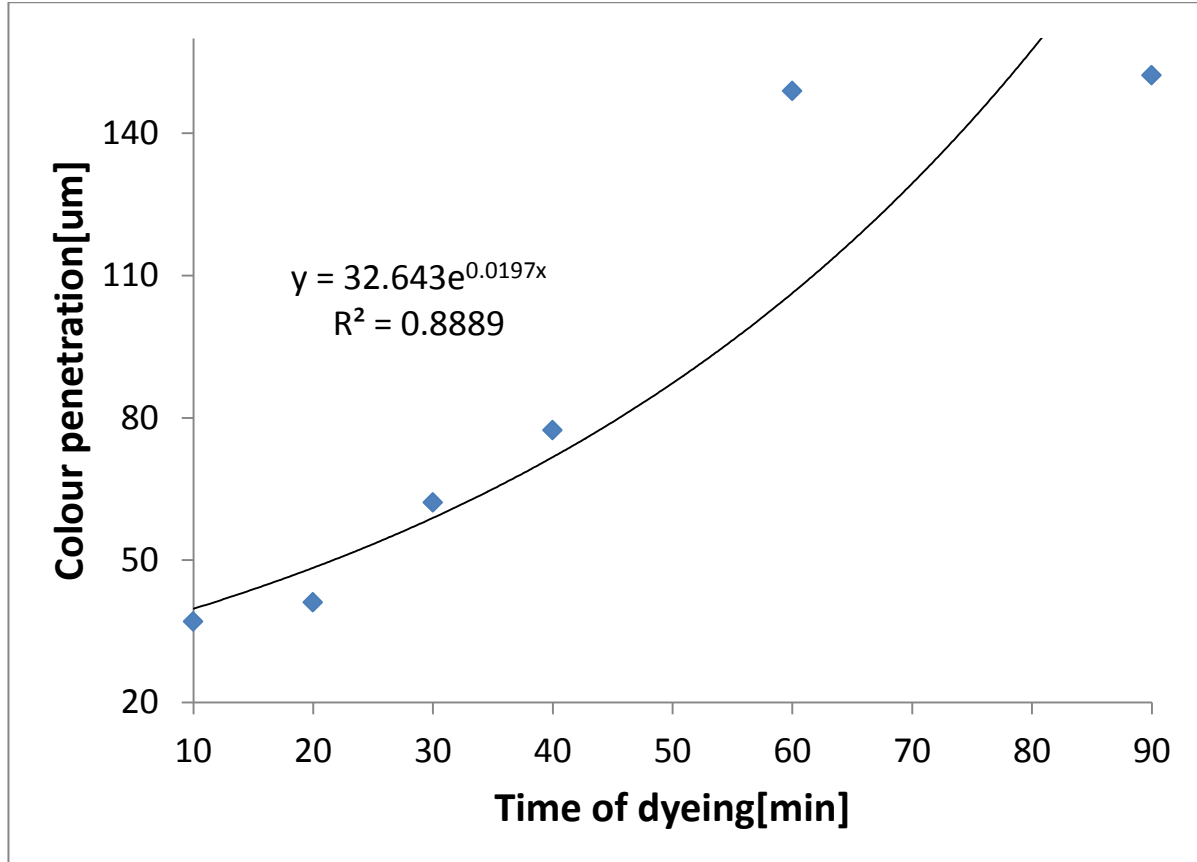


Figure 24: Graphical interpretation of dye distribution in flexi core

Referring to the above figure, the graph shows the increasing trend in dye penetration with the increase in dye bath exposure, correlation= 0.8889. The dye penetration is proportional to the dye time, since these fibers were dyed using the same dye bath concentration (5g/L). If comparing the results of fibers for 30 minutes and 60 minutes, the dye penetration was found to be 62µm and 148µm respectively. The dye penetration more than doubles in depth; which provides a conclusive result for dye penetration and time.

IV . III. Dyeing of Core

After dyeing the PMMA core, and cross section analysis the following results were obtained

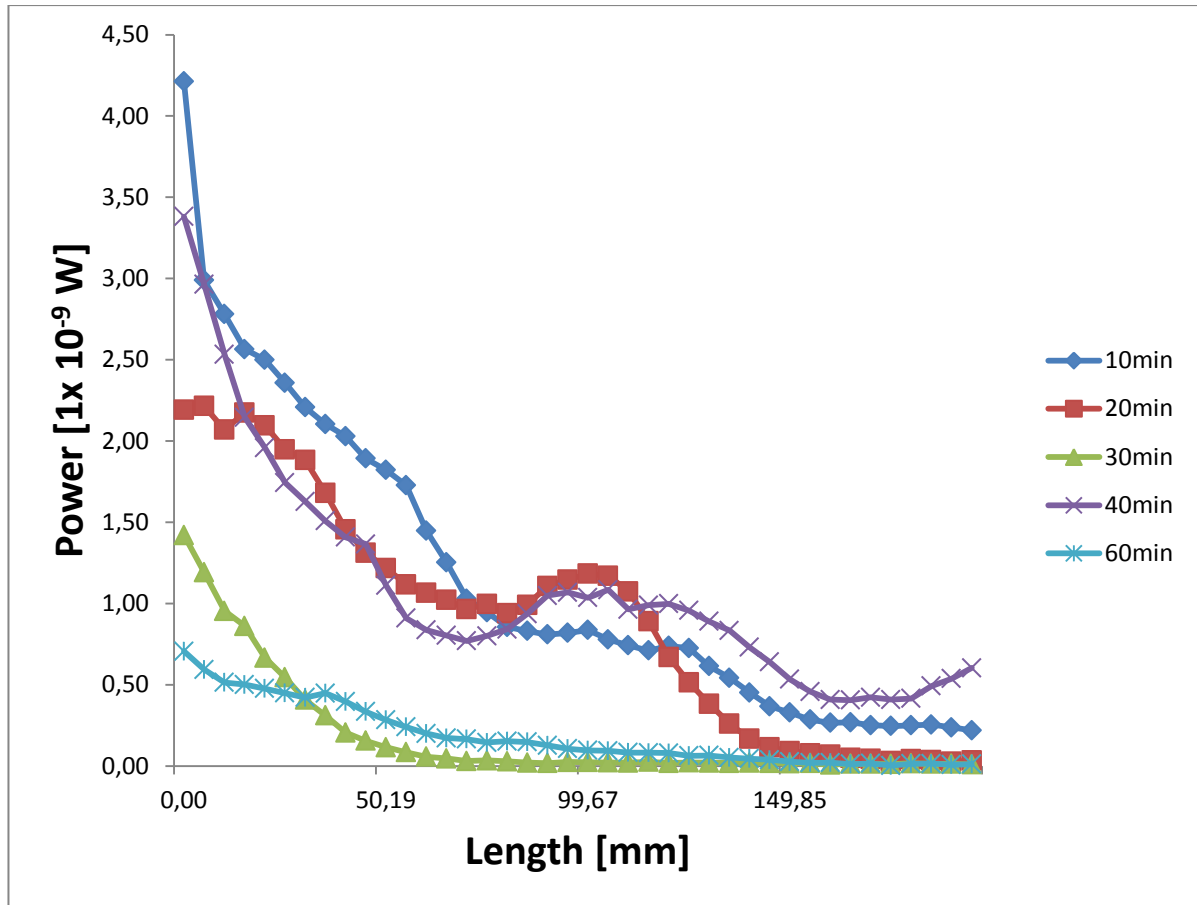


Figure 25: Effect of time in dye bath

Although the parent fiber, *Flexi* could not be dyed by this method, it was possible for the penetration of dye into the core of the fiber. Although the fiber samples were dyed till a time of 120 minutes initially, it was found that the fiber became extremely brittle as the effect of time at a constant temperature increased. This may have been due to the dye completely penetrating the fiber and changing the chemical characteristics of the PMMA core completely.

It was then found the 60 minutes should be the maximum exposure in the dye stuff, to maintain some integrity of the fiber. It may be observed from *Figure 25*, that the side emission decreases exponentially with respect to light attenuation, which could be observed for all time intervals. The side emission gradually decreases as the dye time moves from 10 minutes to 30 minutes, but the emission suddenly increases at 40 minutes. This may be due to the fact the dye is somewhat forming a suitable cladding for the PMMA core, thus light is able to remain in the fiber over a longer attenuation. The emission once again decreases for the 60 minute interval.

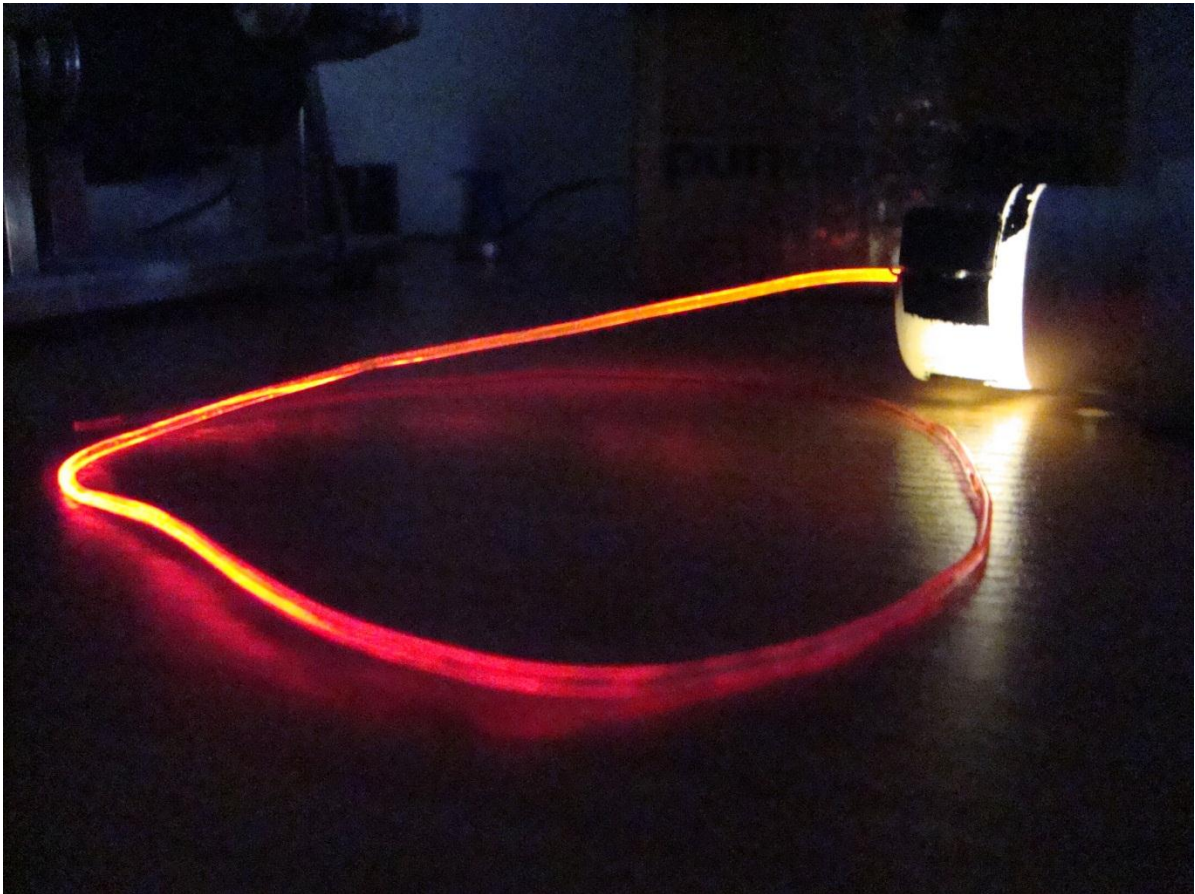


Figure 26: Illuminted dyed fiber with Light source one

IV . IV. Effect of time for a constant temperature on core of *Flexi*

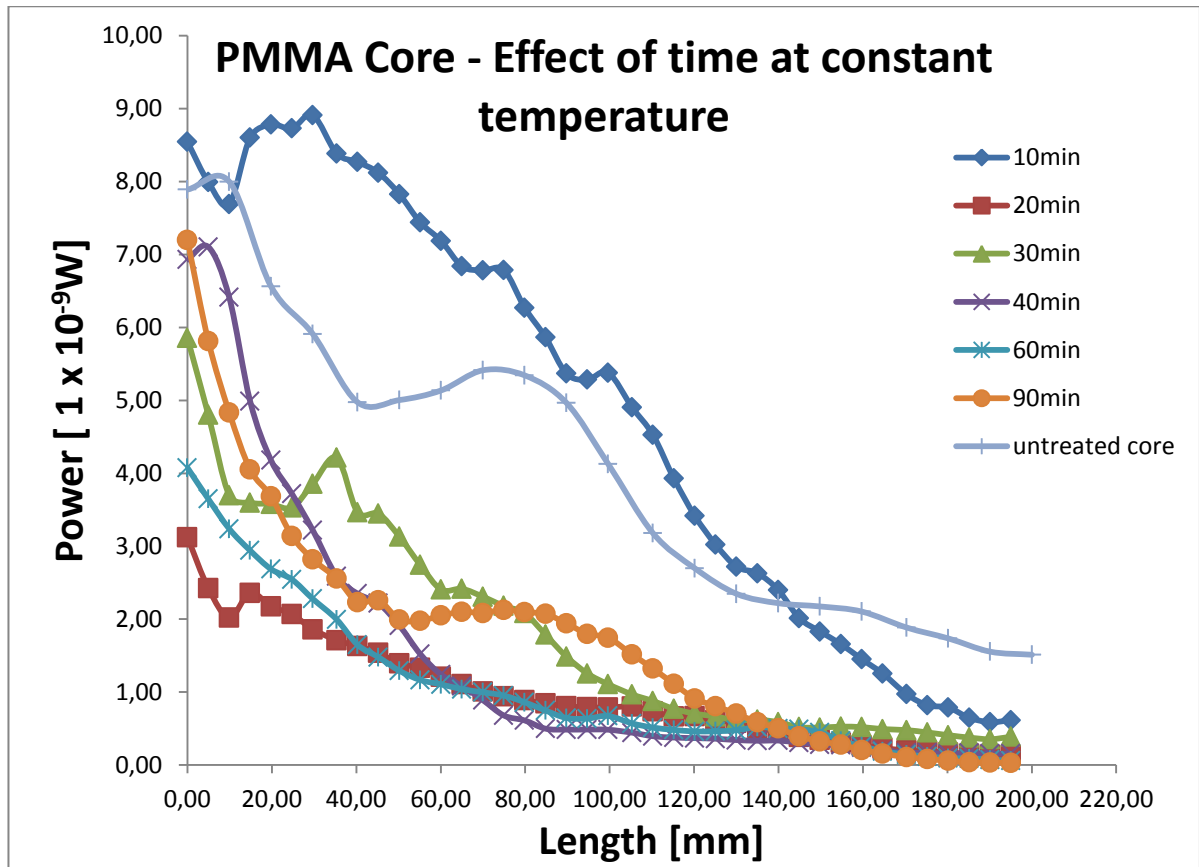


Figure 27: Effect of time at constant temperature for PMMA Core

The fiber shows the best attenuation and side emission, after the lowest time influence of 10minutes. As the time is increased there is a gradual decrease in light emission, till 40 minute interval is reached. Similar to that of the dyed core, the phenomena could be due to penetration of water, such that a portion of the cross-section, forms a radial cladding, thus increasing the fibers side emission and attenuation of light. As time increases, the power emission and attenuation decreases proportionally, but once again increases at 90 minutes.

IV . V. Effect of time at constant temperature on *Flexi* with cladding

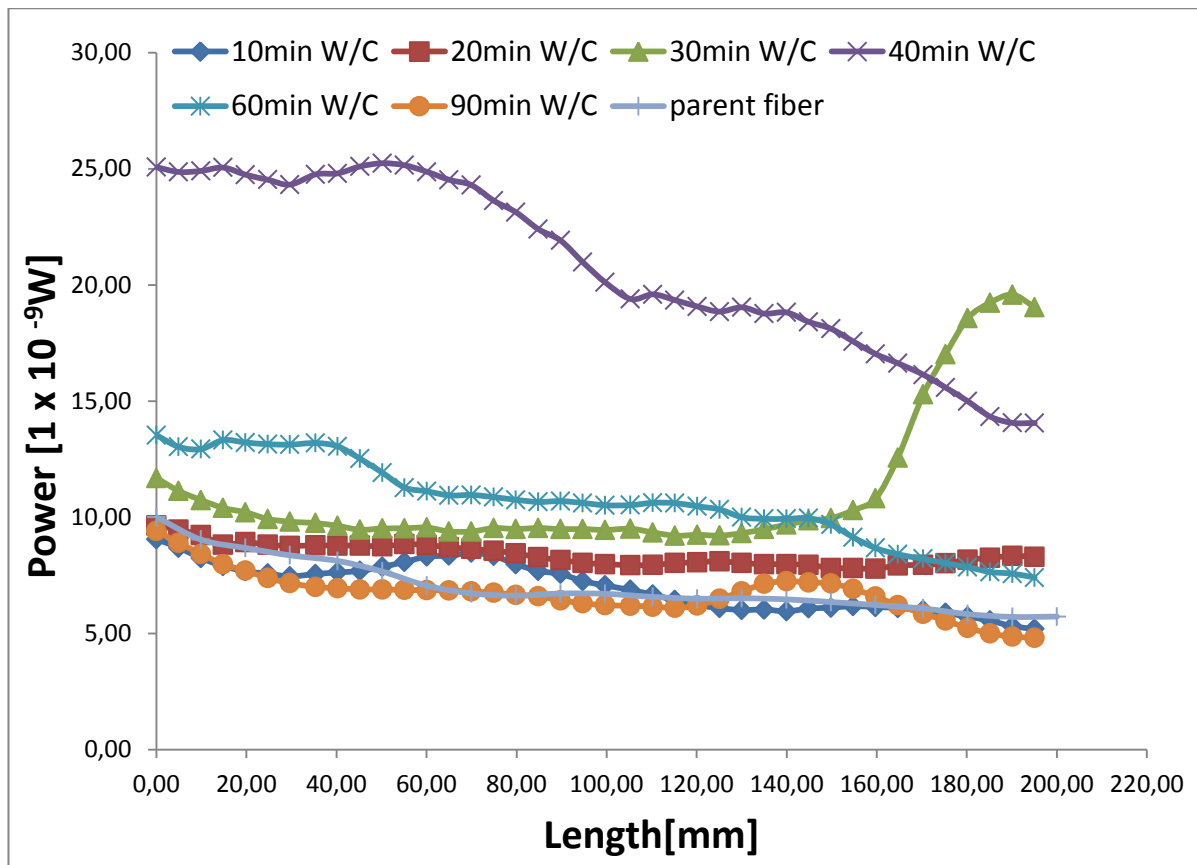


Figure 28: Effect of time at constant temperatures on flexi with cladding

There are very small differences between the 10minute interval, in comparison with the other samples, with the exception of 40 minutes of treatment at 98°C bath temperature. There is a significant decrease in emission after 90 minutes of treatment, which may be due to the degradation of the fiber, since the melting temperature of the fiber is around 160°C. It was also noted that the fiber became significantly softer by touch, after some influence of heat. Treatment after 40minutes once again shows a significant increase, as compared to the other samples. Ideally for an optic fiber to have better attenuation, firstly the refractive index of the cladding, will have to be lower than that of the core, secondly, to have better side emission, some of this internal reflection cause by the difference in refractive indices, will

have to be lost. Thus the refractive index of either the core or the cladding may have changed due to the effect of constant temperature due to time.

IV . VI. Surface treated fibers

Flexi fibers were treated as mentioned in Chapter 3.1 and 3.2, after this treatment, the side emission was measured, and the following results were obtained,

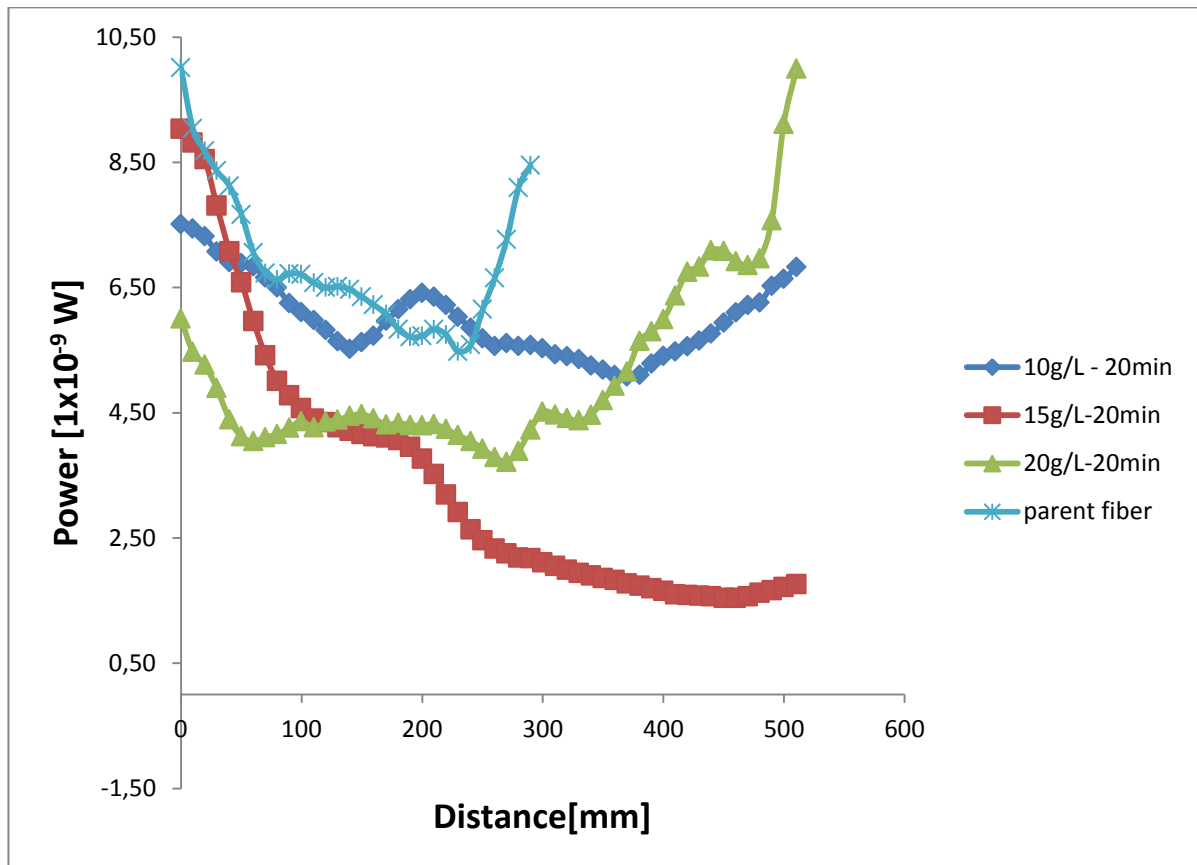


Figure 29: Surface treated fibers after dyeing

The fibers were found to have good propagation of light. Since these were 1 meter samples, the side emission would decrease as the length increases. This trend is noted graphically above, that the side emission does decrease gradually, for example in the sample for 15g/L for 20 minutes of dyeing, the power of side illuminated light initially starts at $9.03 \times 10^{-9} \text{W}$, and decreases steadily to $1.76 \times 10^{-9} \text{W}$ after 510mm. In this case the difference is a marginal

$7 \times 10^{-9}W$. Although this may seem like a large value of loss in side emission, due to the internal reflection achieved in the *Flexi* fiber, visually the fiber does not show the intensity loss.



Figure 30: 15g/L after 20min of dyeing, showing length of fiber illuminated

Referring to *Figure 29*, the trend of the highest dye concentration, 20g/L, showed similar characteristics to the parent fiber, but the difference was that the trend was over 510mm in comparison to the parent fiber which was only measured till 300mm. Although the result may be still inconclusive, because in the difference of lengths, the sample was the only evidence of a comparison to the parent fibers behavior, such that the side emission does not only decrease as length is increased. Factors which may have affected the high concentration sample, may be due to sufficient surface modification, with respect to dye stuff.

A comparison of variability of time was also processed, by taking the 15g/L sample and dyeing the samples for 20 and 40 minutes respectively.

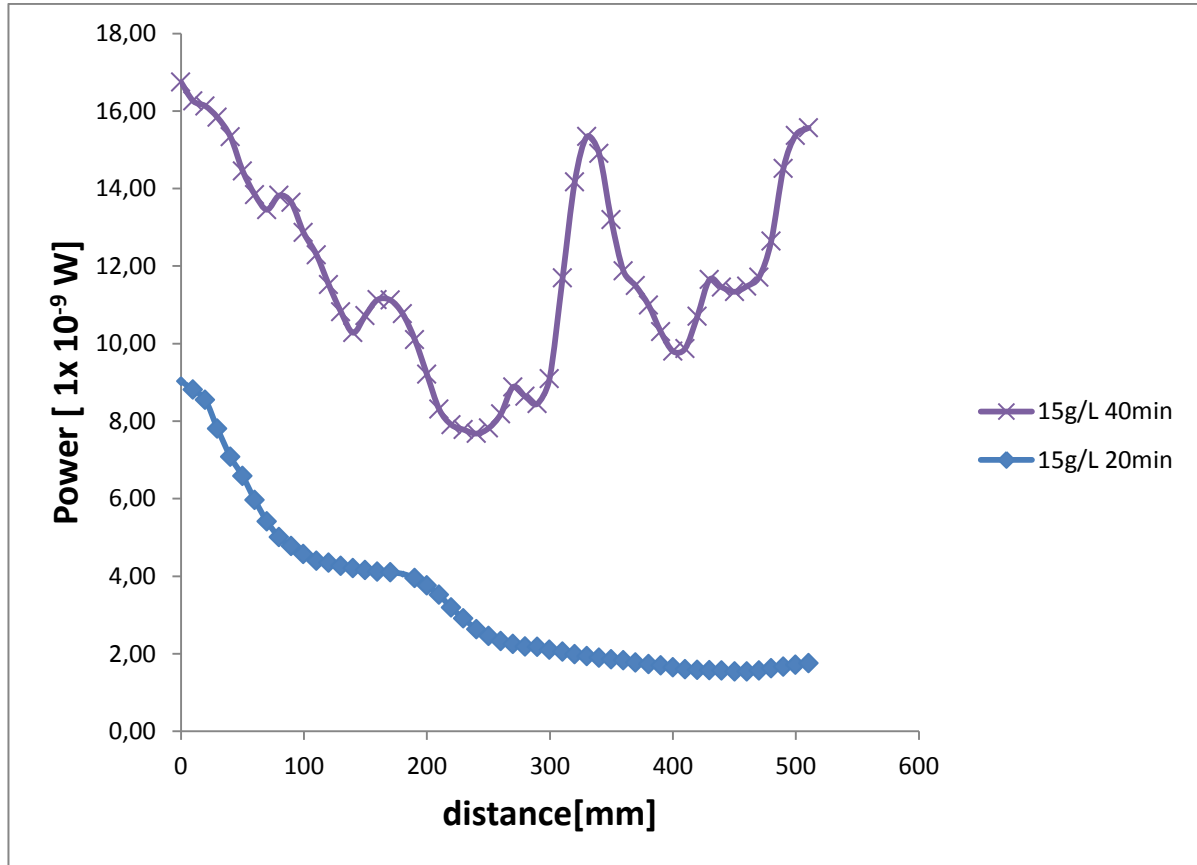


Figure 31: Effect of dyeing time on the side emission of fiber

As discussed earlier, it was found that an increase in dye time will increase the dye distribution into the fiber, since it is a proportional relation. In the above figure, the dye time was doubled. The resulting side emission for the 40minute dyeing, showed a more than significant increase, the initial power output was $16.75 \times 10^{-9}\text{W}$, and after a lot of variability in emissions, the output after 510mm was found to be $15.56 \times 10^{-9}\text{W}$. In comparison the sample with lower dye time, showed an initial output of $9.03 \times 10^{-9}\text{W}$ and final of $1.76 \times 10^{-9}\text{W}$. These results provide more evidence of the effect of time that heat has on the fiber, showing that side emission is increased with extended exposure to heating.

IV . VII. Comparison of light sources

A second, high intensity LED light source was used to see the effect of light intensity on the samples dyed.

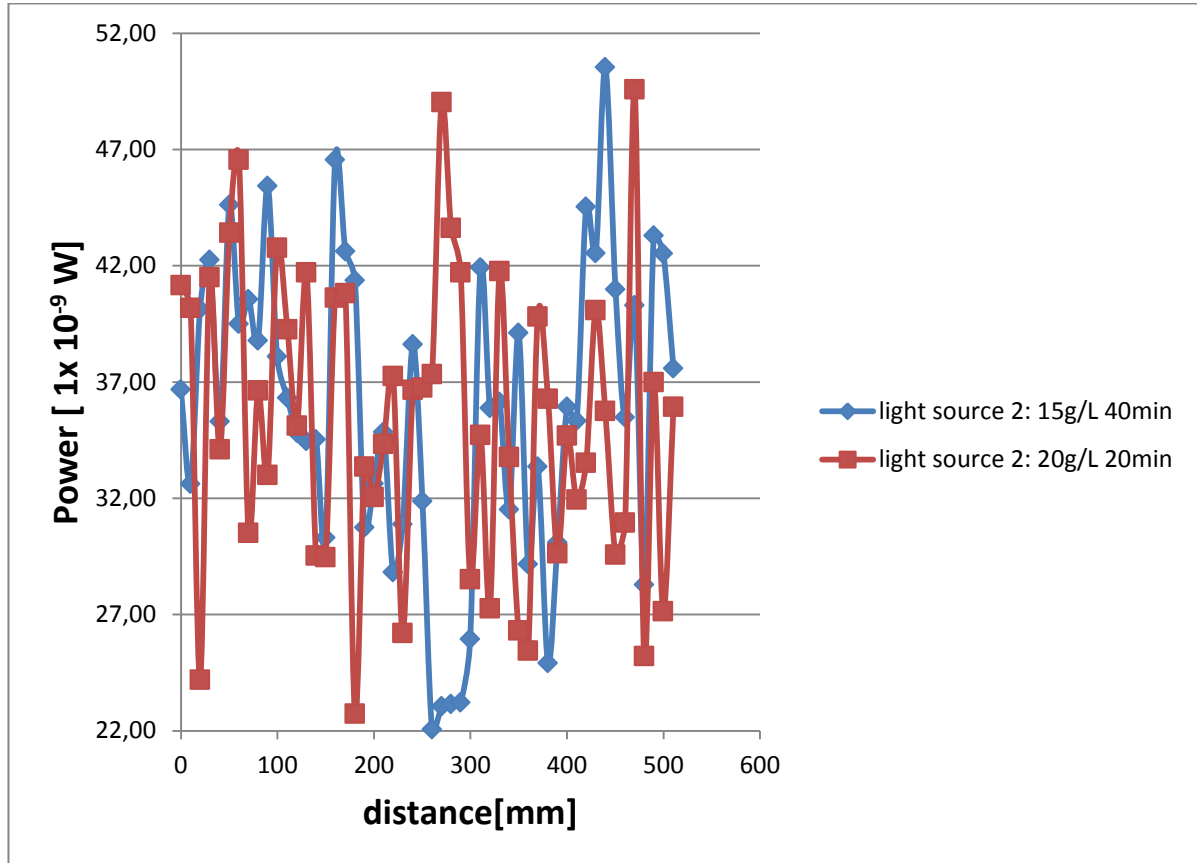


Figure 32: Light source 2, high discharge LED

The same method was used to measure side emissions of the fiber samples. It was found that there was far more disturbances compared to the expected trend, where the intensity should have decreased as the length was increased away from the light source. Although the light source power was kept constant, like the previous source used in experiments, the smaller, higher intensity light, showed a difference in the colour of the emitting fiber as well. The colour difference can be explained in terms of the temperature of the light source. *Wiens law*, explains the following

$$\lambda \cdot T = 2890$$

Where λ : wavelength of light [nm]

T: temperature of light [K]

If the temperature were to increase, the emitting wavelength will be lower, hence an inverse proportion. The light source initially used was white light, warm temperature ($\approx 5000\text{K}$), whilst the second light source was a higher intensity light, with more blue-white light, signifying a temperature approximately 6000K . An increase in temperature of light resulted in a shorter wavelength as expected, thus the fiber had more internal reflection. In this case, simply it meant that there were more light rays able to bounce off the surface of the fiber, resulting in variations of intensity due to attenuation (loss of power) in some points, whilst other points in the fiber had some amplification.

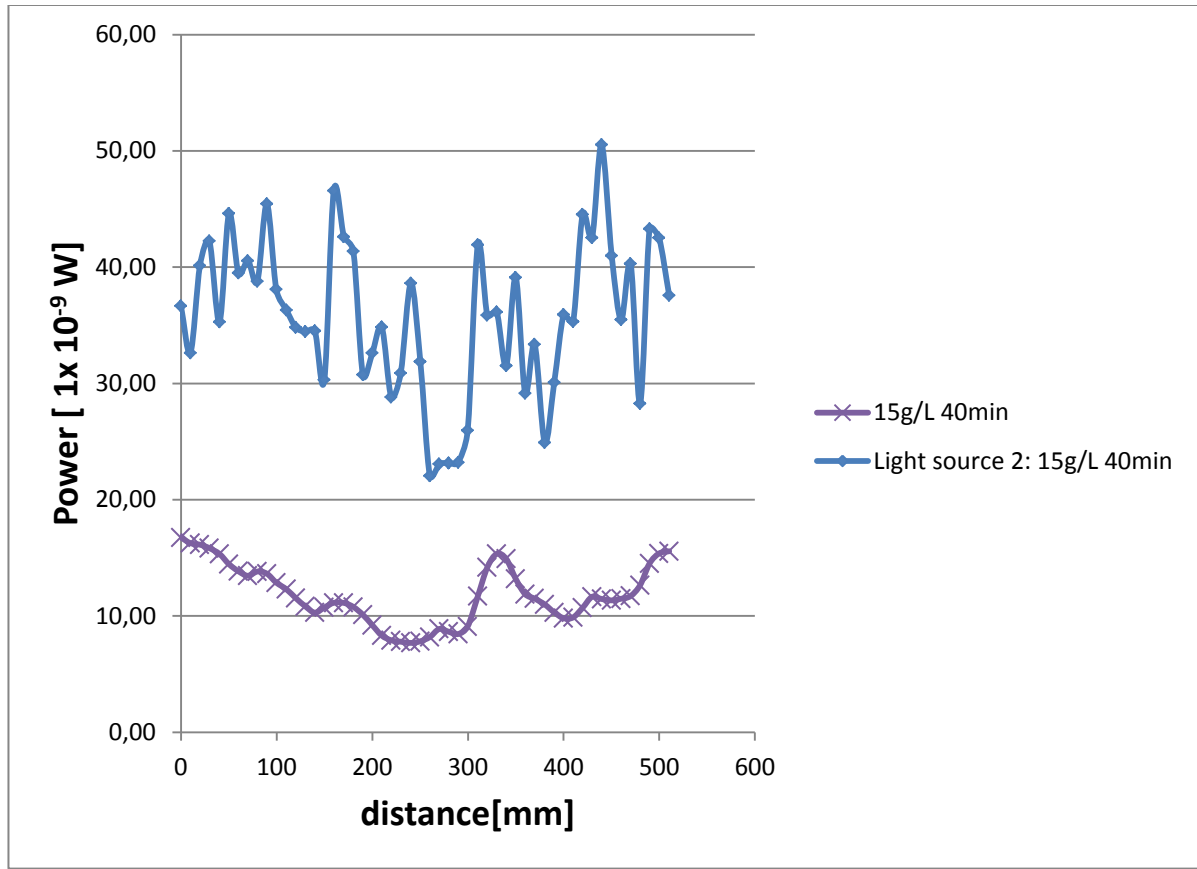


Figure 33: Comparison of light source on sample

From *Figure 33*, the variations can be clearly seen when comparing the same sample with different light sources. It is evident from this interpretation that the power emitted by the second light source is far higher than the initial source used. Power is related to temperature by the *Stefan-Boltzmann law*:

$$j^* = \sigma T^4$$

Where j^* = energy flux [W/m^2]

σ = Boltzmann constant [$\text{W}\cdot\text{m}^{-2}\cdot\text{K}^{-4}$]

T = Temperature of emitting object [K]

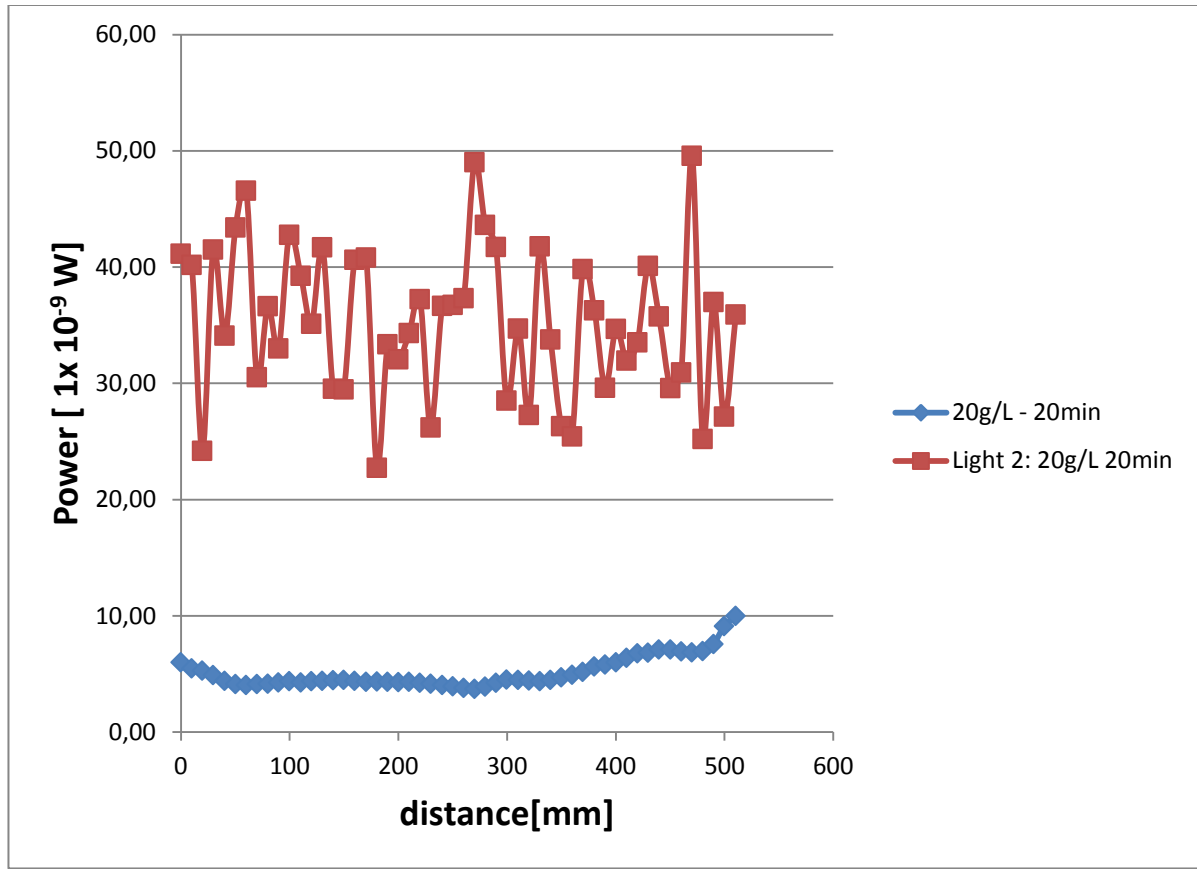


Figure 34: Light source 2 vs. Light source 1, comparison of 20g/L after 20minutes of dyeing

Using the same understanding between power and the temperature of the light sources, *Figure 34*, shows the comparison once again for another sample (20g/L after 20min dyeing). The trend for the lower power light source, shows loss of power due to attenuation, whilst the power of light source 2, produces shorter wavelengths of light, hence more disturbance and interference in the power output, over the measured length of the fiber.

Chapter V Conclusions

Cross-section analysis revealed that dye penetration into the fiber relies on the duration of dye time. Dye penetration significantly increases when comparing the difference between 40minutes and 60minutes, the result is more than double the dye penetration. In contrast the time period between 20 and 40minutes does not show much difference, although it is the same time window.

The core of the *Flexi* fiber is able to be dyed with no additional chemical treatment. The fibers are simply dyed with disperse dye and water as a solvent. After 40minutes of dyeing, the fiber exhibits an increase in side emission, and can be compared with the side emission of the fiber dyed for only 10minutes, meaning that during the dye period of 20 and 30 minutes there is sufficient degradation in side emission, but due to some hydrolysis by heating, the fiber regains its side emitting behavior after 40min.

The parent fiber, *Flexi* and its PMMA core, after heat treatment in boiling water, exhibit different characteristics. The PMMA core shows gradual degradation after exposure to boiling water, but showed the same behavior as the dyed fiber, in the sense that the side emission gained after 40minutes. *Flexi* showed an increase in side emission after exposure to boiling water. The parent fiber initially had a value of 10×10^{-9} W, whilst after 40minutes of heat treatment, the side emission increased to 25.07×10^{-9} W. Thus it can be concluded that the PMMA based optical fiber, shows an improvement in side emission after heating in water for a period of 40minutes, provided that there is some type of cladding formed in the case of the dyed core. The hydrolysis by water, causes the refractive index of the core to decrease, thus causing more side emission.

The surface treated fibers, showed that the surface was etched to some extent by ethyl acetate. The results also yielded that an increase in dye concentration also increases the side emission significantly. The time factor was tested once again with 15g/L dye concentration for 20 and 40minutes respectively. The 40minute treated sample yielded an increase in side emission once again, confirming prior theories.

A second light source was used to make a comparison between the effect of the power output of a light source to the fibers side emission. The change in light source, i.e. a light source with a higher temperature rating, proved to be beneficial in increasing the side emission of the surface treated fibers. This concludes that by *Stephan-boltzmann law* the power will increase with an increase in color temperature, meaning that the light source moves away from warmer light, to a cooler hue, creating a shorter wavelength, which in turn causes more internal reflection because of the higher frequency of the light waves.

Chapter VI References

[1] Firecomms, Simply pof:high-end connectivity with plastic optical fiber, technical papers, <http://www.firecomms.com/downloads/tech%20papers/SIMPLY%20POF%20R1.pdf>
Accessed: 17 November 2011

[2] Paschotta, R., Physical principles and applications of different types of Optical Fibers, , Optik & Photonik, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, June 2008

[3] Omar, X. A., Brief history and overview of optical fiber technology in telecommunications, 2010

<http://haxr.org/omar/papers/PDF/Omar%20X.%20Avelar%20-%20Brief%20History%20and%20Overview%20of%20Optical%20Fiber%20Technology%20in%20Telecommunications.pdf>

Accessed: 16 November 2011

[4] Lanshack, cabling and connectivity superstore, Optical fiber tutorial

<http://www.lanshack.com/fiber-optic-tutorial-fiber.aspx>

Accessed: 15 January 2012

[5] Appajiah, A., Climatic stability of polymer optical fibers, University of Potsdam, Germany, 2004, p 7

[6] Leno, S. P., Basic Geometrical Optics, Fundamentals of Photonics, module 1.3, International society for optics and photonics, Wales

<http://spie.org/x17229.xml>

Accessed: 15 January 2012

[7] Electrical Wholesaling, The basics of fiber optics, part 2

http://ewweb.com/mag/electric_basics_fiber_optics_2/

Accessed: 15 January 2012

[8]Peatross, J., Ware, M., Physics of light and optics, Brigham Young University, Utah, 2008, p62

[9]ee, F. P. van der, Anaerobic azo dye reduction, Wageningen University, Netherlands, 2002, p 2

[10]Zee, F. P. van der, Anaerobic azo dye reduction, Wageningen University, Netherlands, 2002, p 3

[11]Broadbent, A. D, Basic principles of textile coloration, Society of Dyers and Colourists, West Yorkshire, 2001, p 307

[12]Broadbent, A. D, Basic principles of textile coloration, Society of Dyers and Colourists, West Yorkshire, 2001, chapter 21, p 427

[13]Zubia, J., Arrue, J., Plastic optical fibers: an introduction to their technological processes and applications, Optical fiber technology 7, 2001, p101-140

[14] Methyl methacrylate

http://en.wikipedia.org/wiki/Methyl_methacrylate

Accessed: 20 November 2011

[15] Organic chemistry, Jonathan Clayden, Nick Greeves, Stuart Warren, Peter Wothers - Oxford University Press (2001), Chapter 52, Pages 1460-1461

[16]Poly(methylmethacrylate),

http://en.wikipedia.org/wiki/Poly%28methyl_methacrylate%29

Accessed: 20 November 2011

[17]Density of glass,

<http://hypertextbook.com/facts/2004/ShayeStorm.shtml>

Accessed: 12 December 2011

- [18] Meryova, B., Measurement of light intensity of optical fibers, Dana Kremenakova, 2012, p70.

Chapter VII Appendix

Table 13: Side emission of dyed fibers, with respective time intervals in dye bath- 65mm
maximum measured

distance[mm]	Power [W x 10 ⁻⁸]					
	10[min]	20[min]	30[min]	40[min]	60[min]	90[min]
0.00	0.42	0.90	0.40	0.84	0.20	2.00
4.95	0.42	0.90	0.41	0.68	0.15	1.46
9.90	0.46	0.88	0.49	0.63	0.09	0.87
14.84	0.47	0.87	0.48	0.59	0.05	0.49
19.79	0.46	0.82	0.56	0.56	0.03	0.34
24.74	0.45	0.81	0.74	0.49	0.03	0.28
29.69	0.42	0.77	0.81	0.42	0.02	0.23
35.34	0.38	0.69	0.95	0.37	0.02	0.22
40.29	0.34	0.61	0.89	0.35	0.02	0.22
45.24	0.29	0.54	0.74	0.33	0.02	0.19
50.19	0.27	0.49	0.62	0.36	0.02	0.20
55.13	0.30	0.45	0.59	0.36	0.02	0.19
60.08	0.26	0.41	0.60	0.40	0.02	0.21
65.03	0.27	0.37	0.59	0.41	0.02	0.23

Table 14: Effect of time at a constant temperature - parent fiber - length 200mm

Distance[mm]	Power [W x 10 ⁻⁹]					
	10[min]	20[min]	30[min]	40[min]	60[min]	90[min]
0.00	9.06	9.65	11.69	25.07	13.53	9.41
4.95	8.69	9.46	11.13	24.86	13.03	8.91
9.90	8.24	9.24	10.74	24.91	12.94	8.43
14.84	7.90	8.82	10.40	25.05	13.32	7.98
19.79	7.68	8.93	10.21	24.74	13.22	7.70
24.74	7.57	8.82	9.93	24.53	13.15	7.39
29.69	7.46	8.77	9.81	24.32	13.13	7.16
35.34	7.56	8.79	9.75	24.76	13.20	7.01
40.29	7.63	8.78	9.63	24.80	13.05	6.95
45.24	7.69	8.78	9.46	25.10	12.52	6.89
50.19	7.87	8.75	9.52	25.24	11.92	6.89
55.13	8.08	8.84	9.53	25.15	11.28	6.87
60.08	8.31	8.81	9.56	24.87	11.12	6.86
65.03	8.35	8.71	9.39	24.52	10.94	6.85
69.98	8.47	8.64	9.39	24.29	10.96	6.81
74.93	8.33	8.56	9.53	23.63	10.87	6.75
79.87	7.98	8.44	9.50	23.13	10.75	6.66
84.82	7.69	8.28	9.54	22.40	10.66	6.60
89.77	7.56	8.16	9.49	21.91	10.70	6.43
94.72	7.26	8.04	9.49	20.98	10.62	6.30
99.67	7.07	7.98	9.45	20.11	10.52	6.22
105.32	6.87	7.94	9.51	19.39	10.52	6.19
110.27	6.67	7.95	9.35	19.59	10.62	6.15
115.22	6.44	8.03	9.21	19.35	10.61	6.10
120.17	6.22	8.06	9.24	19.07	10.47	6.20
125.11	6.09	8.11	9.21	18.85	10.34	6.49
130.06	6.01	8.03	9.32	19.04	10.00	6.81
135.01	6.03	7.98	9.49	18.77	9.93	7.14
139.96	5.95	7.98	9.68	18.82	9.93	7.25
144.91	6.07	7.95	9.86	18.41	9.96	7.19
149.85	6.11	7.82	9.96	18.11	9.69	7.16
154.80	6.17	7.81	10.30	17.56	9.13	6.92

159.75	6.14	7.78	10.81	17.03	8.68	6.59
164.70	6.09	7.93	12.57	16.63	8.41	6.22
170.35	6.00	7.95	15.29	16.14	8.21	5.85
175.30	5.88	8.02	17.02	15.58	8.03	5.56
180.25	5.72	8.18	18.57	14.99	7.85	5.24
185.20	5.55	8.25	19.24	14.33	7.65	5.00
190.14	5.31	8.33	19.58	14.06	7.57	4.86
195.09	5.20	8.30	19.04	14.06	7.40	4.82

Table 15: Side emission of dyed fibers, with respective time intervals in dye bath- 200 mm maximum measured

Distance[mm]	Power [W x 10 ⁻⁹]					Distance[mm]	Power [W x 10 ⁻⁹]
	10[min]	20[min]	30[min]	40[min]	60[min]		Untreated core
0.00	4.21	2.19	1.42	3.38	0.71	0.00	7.89
4.95	2.99	2.21	1.19	2.96	0.59	9.90	8.00
9.90	2.78	2.07	0.95	2.53	0.51	19.79	6.56
14.84	2.56	2.18	0.86	2.14	0.50	29.69	5.91
19.79	2.50	2.10	0.67	1.96	0.48	40.29	4.97
24.74	2.36	1.95	0.54	1.74	0.45	50.19	5.00
29.69	2.21	1.88	0.41	1.63	0.42	60.08	5.14
35.34	2.10	1.68	0.31	1.51	0.45	69.98	5.41
40.29	2.03	1.46	0.21	1.41	0.40	79.87	5.34
45.24	1.89	1.31	0.16	1.37	0.33	89.77	4.97
50.19	1.82	1.22	0.12	1.11	0.28	99.67	4.13
55.13	1.73	1.12	0.08	0.91	0.24	110.27	3.18
60.08	1.45	1.07	0.06	0.84	0.20	120.17	2.70
65.03	1.25	1.02	0.05	0.80	0.17	130.06	2.35
69.98	1.03	0.96	0.03	0.77	0.17	139.96	2.22
74.93	0.95	1.00	0.03	0.80	0.14	149.85	2.17
79.87	0.86	0.94	0.03	0.84	0.15	159.75	2.10
84.82	0.83	0.99	0.02	0.94	0.15	170.35	1.88
89.77	0.81	1.11	0.02	1.05	0.13	180.25	1.74
94.72	0.82	1.15	0.02	1.07	0.11	190.14	1.55
99.67	0.84	1.18	0.02	1.04	0.10	200.04	1.51
105.32	0.78	1.17	0.02	1.08	0.09	209.94	1.62
110.27	0.74	1.07	0.02	0.96	0.08	219.83	1.64
115.22	0.71	0.89	0.03	0.99	0.08	229.73	1.60
120.17	0.74	0.67	0.02	1.00	0.08	240.33	1.62
125.11	0.73	0.52	0.02	0.96	0.06	250.23	1.46
130.06	0.61	0.38	0.02	0.89	0.06	260.12	1.30
135.01	0.54	0.26	0.02	0.83	0.05	270.02	1.20
139.96	0.45	0.17	0.02	0.73	0.04	279.92	1.15
144.91	0.37	0.11	0.02	0.64	0.04	289.81	1.08

149.85	0.33	0.09	0.02	0.53	0.03
154.80	0.29	0.08	0.02	0.46	0.02
159.75	0.27	0.07	0.01	0.41	0.02
164.70	0.27	0.05	0.01	0.41	0.01
170.35	0.25	0.04	0.01	0.42	0.02
175.30	0.25	0.03	0.01	0.41	0.00
180.25	0.25	0.04	0.02	0.41	0.01
185.20	0.26	0.04	0.01	0.49	0.01
190.14	0.24	0.03	0.01	0.54	0.01
195.09	0.22	0.03	0.01	0.60	0.01

Table 16: Side emission of dyed fiber cores

Distance[mm]	Power [W $\times 10^{-9}$]	Distance [mm]	Power [W $\times 10^{-9}$]					
	Untreated core		10[min]	20[min]	30[min]	40[min]	60[min]	90[min]
0.00	7.89	0.00	8.55	3.12	5.86	6.93	4.08	7.20
9.90	8.00	4.95	7.99	2.42	4.80	7.10	3.65	5.81
19.79	6.56	9.90	7.69	2.02	3.70	6.41	3.24	4.84
29.69	5.91	14.84	8.60	2.36	3.60	4.99	2.94	4.05
40.29	4.97	19.79	8.78	2.17	3.58	4.18	2.69	3.69
50.19	5.00	24.74	8.73	2.07	3.53	3.72	2.54	3.14
60.08	5.14	29.69	8.91	1.86	3.85	3.22	2.28	2.82
69.98	5.41	35.34	8.39	1.71	4.21	2.59	2.00	2.56
79.87	5.34	40.29	8.27	1.63	3.46	2.35	1.65	2.23
89.77	4.97	45.24	8.12	1.54	3.45	2.22	1.48	2.26
99.67	4.13	50.19	7.83	1.39	3.13	1.91	1.29	2.00
110.27	3.18	55.13	7.44	1.33	2.74	1.52	1.17	1.98
120.17	2.70	60.08	7.19	1.21	2.41	1.24	1.11	2.05
130.06	2.35	65.03	6.84	1.11	2.42	1.08	1.04	2.10
139.96	2.22	69.98	6.78	1.01	2.31	0.89	1.00	2.08
149.85	2.17	74.93	6.79	0.94	2.18	0.68	0.95	2.13
159.75	2.10	79.87	6.27	0.89	2.08	0.61	0.86	2.09
170.35	1.88	84.82	5.87	0.85	1.79	0.50	0.75	2.07
180.25	1.74	89.77	5.37	0.81	1.49	0.48	0.64	1.94
190.14	1.55	94.72	5.28	0.79	1.25	0.49	0.64	1.80
200.04	1.51	99.67	5.38	0.79	1.11	0.48	0.67	1.74
		105.32	4.91	0.80	0.97	0.44	0.57	1.52
		110.27	4.53	0.74	0.88	0.39	0.51	1.32
		115.22	3.93	0.67	0.77	0.38	0.48	1.11
		120.17	3.42	0.67	0.70	0.37	0.46	0.91
		125.11	3.02	0.62	0.66	0.36	0.46	0.81
		130.06	2.72	0.58	0.61	0.34	0.48	0.70
		135.01	2.63	0.51	0.62	0.33	0.52	0.59
		139.96	2.40	0.45	0.59	0.33	0.50	0.50
		144.91	2.01	0.38	0.52	0.31	0.49	0.39

		149.85	1.83	0.35	0.51	0.28	0.45	0.32
		154.80	1.66	0.30	0.53	0.27	0.33	0.28
		159.75	1.45	0.27	0.52	0.24	0.26	0.21
		164.70	1.25	0.23	0.49	0.21	0.19	0.16
		170.35	0.97	0.20	0.48	0.17	0.14	0.11
		175.30	0.82	0.19	0.45	0.17	0.12	0.08
		180.25	0.79	0.17	0.41	0.15	0.09	0.06
		185.20	0.65	0.15	0.38	0.16	0.09	0.04
		190.14	0.59	0.13	0.35	0.16	0.07	0.03
		195.09	0.61	0.13	0.39	0.15	0.06	0.03

Table 17: Side emission of dyed parent fibers

	Core	parent		10g/L – 20min	15g/L – 20min	20g/L 20min	15g/L– 40min
Distance[mm]			Distance[mm]	Power [W x 10 ⁻⁹]			
0.00	7.89	10.01	0.00	7.51	9.03	6.00	16.75
9.90	8.00	9.04	9.90	7.44	8.81	5.47	16.26
19.79	6.56	8.68	19.79	7.32	8.55	5.27	16.13
29.69	5.91	8.36	29.69	7.07	7.81	4.89	15.83
40.29	4.97	8.12	40.29	6.90	7.08	4.39	15.33
50.19	5.00	7.66	50.19	6.88	6.58	4.12	14.45
60.08	5.14	7.05	60.08	6.84	5.96	4.05	13.84
69.98	5.41	6.73	69.98	6.66	5.41	4.11	13.45
79.87	5.34	6.63	79.87	6.50	5.01	4.16	13.82
89.77	4.97	6.72	89.77	6.25	4.78	4.26	13.64
99.67	4.13	6.71	99.67	6.10	4.57	4.36	12.87
110.27	3.18	6.57	110.27	5.98	4.40	4.27	12.29
120.17	2.70	6.50	120.17	5.82	4.35	4.36	11.52
130.06	2.35	6.52	130.06	5.64	4.26	4.39	10.82
139.96	2.22	6.47	139.96	5.52	4.21	4.45	10.28
149.85	2.17	6.35	149.85	5.63	4.16	4.47	10.72
159.75	2.10	6.22	159.75	5.72	4.12	4.41	11.13
170.35	1.88	6.07	170.35	5.97	4.10	4.31	11.12
180.25	1.74	5.83	180.25	6.15	4.06	4.34	10.77
190.14	1.55	5.71	190.14	6.31	3.96	4.30	10.11
200.04	1.51	5.73	200.04	6.41	3.77	4.30	9.21
209.94	1.62	5.83	209.94	6.35	3.52	4.32	8.31
219.83	1.64	5.75	219.83	6.22	3.19	4.24	7.91
229.73	1.60	5.48	229.73	6.03	2.91	4.14	7.78
240.33	1.62	5.58	240.33	5.85	2.63	4.04	7.68
250.23	1.46	6.15	250.23	5.69	2.46	3.92	7.82
260.12	1.30	6.65	260.12	5.56	2.33	3.79	8.19
270.02	1.20	7.26	270.02	5.61	2.25	3.71	8.88
279.92	1.15	8.09	279.92	5.56	2.19	3.89	8.64
289.81	1.08	8.45	289.81	5.58	2.18	4.23	8.45
			299.71	5.53	2.11	4.52	9.10

			310.31	5.43	2.05	4.47	11.69
			320.21	5.40	1.99	4.41	14.17
			330.10	5.35	1.94	4.38	15.34
			340.00	5.25	1.90	4.47	14.91
			349.89	5.18	1.86	4.70	13.20
			359.79	5.10	1.83	4.93	11.87
			369.69	5.08	1.77	5.15	11.49
			380.29	5.10	1.73	5.64	10.99
			390.19	5.28	1.70	5.80	10.30
			400.08	5.41	1.65	5.99	9.80
			409.98	5.47	1.60	6.37	9.87
			419.87	5.56	1.59	6.75	10.70
			429.77	5.65	1.58	6.83	11.65
			439.67	5.76	1.56	7.09	11.46
			450.27	5.94	1.54	7.08	11.34
			460.16	6.10	1.54	6.92	11.48
			470.06	6.22	1.56	6.85	11.71
			479.96	6.26	1.63	6.96	12.65
			489.85	6.52	1.67	7.57	14.52
			499.75	6.64	1.72	9.11	15.37
			510.35	6.82	1.76	9.99	15.56

Table 18: Side emission of dyed parent fibers with second light source

Distance[mm]	15g/L – 40min	20g/L – 20min
	Power [W x 10 ⁻⁹]	
0.00	41.16	36.67
9.90	40.18	32.62
19.79	24.18	40.12
29.69	41.49	42.25
40.29	34.09	35.29
50.19	43.41	44.61
60.08	46.56	39.49
69.98	30.51	40.55
79.87	36.63	38.78
89.77	32.99	45.43
99.67	42.77	38.08
110.27	39.26	36.31
120.17	35.12	34.81
130.06	41.70	34.46
139.96	29.53	34.53
149.85	29.46	30.30
159.75	40.62	46.56
170.35	40.81	42.62
180.25	22.73	41.36
190.14	33.35	30.75
200.04	32.05	32.62
209.94	34.33	34.84
219.83	37.24	28.81
229.73	26.20	30.88
240.33	36.66	38.60
250.23	36.75	31.87
260.12	37.33	22.05

270.02	49.02	23.05
279.92	43.62	23.15
289.81	41.71	23.21
299.71	28.51	25.94
310.31	34.71	41.91
320.21	27.26	35.88
330.10	41.77	36.14
340.00	33.77	31.50
349.89	26.30	39.10
359.79	25.44	29.16
369.69	39.81	33.35
380.29	36.27	24.91
390.19	29.62	30.09
400.08	34.69	35.92
409.98	31.94	35.32
419.87	33.51	44.53
429.77	40.09	42.53
439.67	35.75	50.53
450.27	29.57	40.98
460.16	30.94	35.47
470.06	49.58	40.29
479.96	25.21	28.27
489.85	36.98	43.28
499.75	27.13	42.52
510.35	35.92	37.58