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Properties of Photochromic Textiles

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SUMMARY OF THE THESIS

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ABSTRACT

Textile materials are one of the basic needs for the human life after food and shelter. It can be applied in various forms from clothing to high tech applications such as protective textiles, medical textiles, geo textiles and sports textiles. Due to the environmental changes, there is a high chance of getting skin cancer, eye damages and immune system damages due to ozone layer depletion. Skin cancer is one of the most effective threaten to the human being and everyone is cringed in these regards. Therefore, it gives immense inspiration to prepare the UV sensor based on incorporating the various photochromic pigments in to textile materials. In this regard, take more attention to prepare the mass colored polypropylene filaments and sol-gel coated with photochromic pigments and which can able to use as flexible UV-sensor. For the production of mass coloration, metallocene catalyst polypropylene (miPP) filaments were chosen due to many features. The mass colored filaments were produced with various concentrations as well as different color. Also, the filaments were produced with different cross-sections. On other hand, different precursors are used to preparing the sol-gel solution along with photochromic pigment which later applied to PET fabrics. After production, it applied to different drawing ratio, object of this research to investigate how the drawing ratio is affected the various optical properties like *K/S* functions, changes in optical density, color difference by ΔE^* (CIE 1976), half-life of color change in during exposure and reversion phase, rate constant, color intensity in beginning, at half of the cycle and color intensity at infinitive were studied. Apart from optical properties, it also investigated the various physical properties like tensile strength, elongation at break, flexural rigidity and bending modulus. In the case of sol-gel coating, since different precursors are used, therefore it is required to investigate the precursors impact on the various optical properties as like the same properties which above mentioned was analyzed. Thermal analysis was done with pigments by TGA to get an idea for the thermal properties and DSC analysis could be done with produced filaments to know the impact on drawing ratios. The laser scanning confocal microscope analysis helps to find the surface roughness after the coating process. Finally, SEM analysis could be done to understand the surface modifications of both filaments and fabrics. The overall photochromic response is depending on the drawing ratio on the filaments, whereas the fabric is depending on the precursors which used in the sol-gel coated fabric. The miPP filaments generally showed a good stability of photocoloration during the color measurement and the optical density have been reduced with increasing the fineness of the miPP filament. Thermal degradation is varied with respect to the photochromic pigments it can be confirmed by TGA results, it is due to their structures, highest degraded pigment shows less photochromic response than another one. In fact, the thermal analysis can give an idea that how the drawing ratio changes its crystallinity % and melting temperature, however, the drawing ratio positively increased all these properties. The surface characterization confirms that there is no change in case of unpigmented and colored filaments. In some case, it shows some micro fibrils, which is due to their cross sections and nor on the pigment addition or process conditions. On other hand, the photochromic response for the fabric was depending on the precursor and its combinations, in some case the reflectance spectrum was shifted, which denoted as hypsochromic shift. This shift is due to the polarity of the precursors. Also, the precursors have a strong influence on the physical and handle properties. The surface

characterization confirms that there is a deposition of precursors in the fabrics, laser scanning confocal microscopy analysis showed significant changes in the surface micro-roughness after coating.

Key words: Drawing process, Mass coloration, Halflife, PET, Photochromism, Photochromic textiles, Rate constant, Sol-gel technology, Ultraviolet Sensor.

ANOTACE

Textilní materiály jsou jednou ze základních potřeb lidského života po jídle a přístřeší. Tyto materiály mohou být využity v různých formách oděvů až po high-tech aplikace jako jsou ochranné textilie, textilie využívané v medicíně, geo-textilie nebo sportovní textilie. Vzhledem ke globálním změnám klimatu se zvyšuje možnost onemocnění rakoviny kůže, poškození očí a imunitního systému v důsledku snížení ozónové vrstvy. Rakovina kůže je jednou z nejefektivnějších rakovin, která ohrožuje lidské bytí a každý je v tomto ohledu ohrožen. Tento fakt poskytuje inspiraci pro přípravu UV senzorů/čidel založených na zabudování různých fotochromních pigmentů do textilních materiálů. Tato práce se věnuje především přípravě barvených polypropylenových filamentů ve hmotě a materiálům s povrchově nanesenými fotochromními pigmenty, které mohou být využity jako flexibilní UV-senzory. Pro barvení ve hmotě byly vybrány, vzhledem k mnoha svým vlastnostem, metalocen-katalycké-polypropylenové (miPP) filamenty. Výsledné filamenty byly vyrobeny s různou koncentrací a stejně tak i s různým odstínem, jakožto i s různým příčným řezem. Na druhou stranu, pro přípravu sol-gel roztoků byly použity různé prekurzory společně s fotochromními pigmenty, které byly následně aplikovány na polyesterové tkaniny. To bylo aplikováno s různým dloužícím poměrem. Cílem tohoto výzkumu je studium, jak dloužící poměr ovlivňuje různé optické vlastnosti, např. Kubelka-Munkovu funkci, změnu optické propustnosti, barevný rozdíl ΔE^* vyjádření pomocí CIE 1976, poločas barevné změny během osvitové a reverzní fáze, rychlostní konstantu, intenzitu odstínu na začátku, v polovině a na konci cyklu. Vedle optických vlastností byly zkoumány různé fyzikální vlastnosti jako pevnost v tahu, prodloužení při přetržení, ohybová tuhost a pevnost v ohybu. V důsledku použití různých prekurzorů u sol-gelů, bylo zkoumáno, jak tyto prekurzory ovlivňují optické vlastnosti, tak i fyzikální vlastnosti uvedené výše. Tepelná analýza byla provedena pomocí termogravimetrické metody ke zjištění tepelné degradace filamentů. Diferenční skenovací kalorimetrie byla použita pro zjištění, jak tepelná degradace ovlivňuje dloužící poměr filamentů. Konfokální laserová skenovací mikroskopie (SEM) byla použita pro zjištění povrchových drsností způsobených nanášecím procesem. SEM analýza může být provedena pro pochopení povrchových modifikací filamentů a tkanin. U filamentů závisí celková fotochromní změna na dloužícím poměru, zatímco u tkanin s aplikovaným sol-gelem je tato změna závislá na použitém prekurzoru. Polypropylenové filamenty obecně vykazovaly dobrou barevnou změnu během měření a optická hustota se snižovala se zvyšující se jemností použitých polypropylenových filamentů. Tepelná degradace se liší s ohledem na typ fotochromního pigmentu, což lze potvrdit výsledky TGA analýzy na základě jejich struktury. Více degradovaný pigment vykazuje nižší fotochromní odezvu než ostatní. Na základě

tepelné analýzy lze získat myšlenku, jak změna dloužícího poměru může ovlivnit krystalinitu a teplotu tání. Avšak dloužící poměr pozitivně zvyšuje všechny tyto vlastnosti. Povrchová analýza potvrdila, že v případě nepigmentovaných a barevných filamentů nedochází k žádným změnám. V některých případech se objevují mikrofibrily, které nemají díky svému příčnému řezu vliv na procesní podmínky. Povrchová analýza potvrdila, že není žádný rozdíl mezi nepigmentovanými a barvenými filamenty. V několika případech (8-cípé) se mikrofibrily objevily na povrchu filamentů. Avšak analýza prokázala, že neexistuje vztah mezi přidáním pigmentů a generací těchto mikrofibril. Na druhé straně lze říci, že fotochromní odpověď závisí na typu prekurzoru. V několika případech došlo k posunu maximální vlnové délky směrem k nižším vlnovým délkám. Hypsochromní posun je způsoben polaritou prekurzorů. Prekurzory mají velký vliv na fyzikální a povrchové vlastnosti. Povrchová analýza potvrdila, že v tkaninách dochází k ukládání prekurzorů. SEM analýza ukázala významné změny povrchové mikrostruktury po nanášení sol-gelů.

Klíčová slova: proces kreslení, hmotnostní zbarvení, polovina života, PET, fotochromie, fotochromní textilie, rychlostní konstanta, technologie sol-gelů, ultrafialový senzo

Contents

List of Figures

List of Tables

1. Introduction

One flourishing field in photochemistry is photochromism and the photochromic behavior of both organic and inorganic materials [1]. Innovation in the textile industry has been increased day by day and there is no limit in the field of functional textiles, photochromism in textiles are one among them. Recent research manuscripts were rapidly increased with the interest on the application of photochromic compounds in textile materials, though comparatively few reports are there in this specified area [2–5]. Photochromic colorants are a class of unusual colorants which undergo reversible color change stimulated by applying light of different wavelengths which is an example of color changeable materials. Due to the color changing properties, it is shown that potential applications such as ophthalmic sun-screening applications, flexible sensors, security printing, optical recording and switching, solar energy storage, nonlinear optics and biological systems. However, the production of photochromic textiles offers color changeable fabrics which may be used as fashionable textiles, security prints and ultraviolet (UV) sensitive textiles such as a visual alarm for a signal indicating the high levels of UV radiation in specific areas. There are many photochromic materials, spirooxazines (SPO) having significant interest since it has good fatigue resistance and relative ease of synthesis towards to their intense color generation properties. Due to a ring-opening reaction, the existing range of products generally undergoes positive photochromism, a light-induced transition from colorless to color [6–10].

2. Purpose and the aim of the thesis

The aim of this research work is to find the impact of different drawing ratio on physical, mechanical and optical properties of mass colored photochromic polypropylene filament as well as the impact of the precursor on optical and physical properties of sol-gel photochromic coated fabrics. For mass coloration, polypropylene (PP) was chosen since it is most versatile polymer available currently with the huge potential application, such as plastics, filaments, textile fabrics, medical devices and etc. The advantages of PP, it has good resistance to the chemicals, solvents, having good impact strength and excellent abrasion resistance. Since, non-polar in nature, and having the aliphatic structure, high stereoregularity and high crystallinity, therefore, coloration of polypropylene is very difficult on classical methods of dyeing as like other fibers. Nevertheless, mass coloration can solve such issues and helps to make coloration of PP textiles. However, this technique provides better dispergation and homogenization properties of dyed PP textiles. Based on these advantages and the fact behind the dyeability of PP, it is decided to produce photochromic polypropylene filaments through mass coloration techniques. The end product of polypropylene is mainly depended on the degree of orientation, which can be obtained by the drawing process with different ratios. SPO based photochromic pigments were used for this study, the pigments are formulated with many additives which include, hindered amine light stabilizer (HALS). However, these additives are not only impaired the tensile strength but also show some significant changes in the optical and physical properties. The second technology which is used to produce the photochromic materials are sol-gel coating technology, by using this technology, photochromic pigments can be incorporated into textile fabrics. Polyethylene terephthalate

(PET) was chosen for the sol-gel coating since it has many advantages as compared other synthetic fibers, particularly more resistant to wear and tear, good durability, good resistance to chemicals except strong alkalis. In this work, different types of precursors are used to study on their impact of optical, physical properties.

3. Overview of the current state of the problem

As discussed in the previous section, photochromism is a reversible color change brought about whilst the material undergoes UV irradiation, the speed of coloration and discoloration is dependent on many factors which are UV irradiation index, the molecular structure of the pigment, properties of materials & their structure and etc. The production of photochromic textile material can be possible in different techniques, but the mass colorations and sol-gel coating techniques are better in terms of durability and other subsequent properties. The major problem when we produce the photochromic synthetic filaments (PP) via mass coloration techniques, it is necessary to carried out the drawing process to enhance the filament physical and mechanical properties. During the drawing process, it increases the molecular orientation for both crystalline and amorphous phase of the filaments. However, in other end, there is a reduction of optical properties and it indirectly proportional to the drawing ratio. Generally, when the photochromic materials are applied to the flexible UV sensorial material, the various optical properties like photochromic behavior under UV radiation is very important. Therefore, it is necessary to know how much the reduction of optical properties with respect to the drawing ratio, perhaps, this research work can provide the elaborated results to know the above issues and also it provide the solution for the same.

In the case of sol-gel coating, the nature and amount of the organic groups (*R*) in the silica matrices determine the polarity of the inner surface of the pores, where the photochromic pigments are located. Therefore, the spectral and kinetic properties of sol-gel coated fabrics are purely affected by the polarity of precursors, which means, it affects the absorption spectrum of the colored form of merocyanine. Due to these modifications in the silica matrices, photochromic colorants can be affected and it changes its own absorption maxima spectrum. Therefore, the same pigment produces a different color when it coated with different precursors. Generally, the precursors directly influence the optical and kinetic properties of photochromic materials. Therefore, the photochromic response is purely dependent on the chemical structure of silane, size and shape of silica network. First, the amount of light reflection during the color measurement is marginally depends on the presence of available dye which is covered by the sol networks in the fabric with respect to the unit area. In this case, the precursors having the rigid network and followed by the structural transformation, which results in the reduced absorption of light under the UV irradiation. In other words, light reflection is decreased where the sol network is in a rigid manner. The precursors with flexible network along with photochromic dyes has less steric hindrance effect on the dyes, therefore, this structural arrangement allows dye to undergo the photochromic reaction easily. Apart from these modifications, the silica matrices also influence on the various physical properties of coated materials. The physical properties of coated fabric are depending on the type of precursors and its chemical structure.

4. Methods used, studied material

4.1 Mass coloration of miPP filaments

There are two different technology were used to develop the photochromic textile materials, the first one is polypropylene multifilaments via mass colorations techniques. In this case, Metallocene catalyst isotactic polypropylene was procured from Lyondell Basell, Italy. In this study, three different photochromic pigments were used, these pigments are commercially available in the market (Matsui Shikiso Chemical Co., Ltd, Japan), the list is given in Table. 1.

Table. 1: Photochromic pigments used for the production of mass colored miPP filaments.

Color	Abbreviation	Chemical name
Blue	MPB	1,3,3-trimethylspiro [indolino-2,3'- (3H)naphtho(2,1-b)(1,4)-oxazine] [11, 12].
Purple	MPP	5-chloro-1,3,3-trimethylspiro[indoline-2,3'-(3H) naphtho(2,1-b) (1,4)-oxazine] [11, 12].
Yellow	MPY	3,3-diphenyl-3H-naphtho[2,1-b]pyran [11, 12].

4.1.1 Production of photochromic filaments

Two varieties of miPP filaments were produced (i.e. with and without pigment), during the production, miPP dried chips were used with standard conditions which could be specified by the manufacturer. For the production of colored filaments, first 100% colored miPP was produced like a tape/ribbon form, therefore photochromic pigments and miPP dried chips (un colored) were mechanically mixed before it melts, finally, it can be dried and converted into chips form. The single-screw tape extruder was used to produce the tape, although it has three different temperature zones, the same temperature was maintained in all the zones at 220°C (i.e. photochromic pigment is sensitivity towards temperature if more than 230°C), after extruding the colored tapes passed through water bath immediately and then dried to make chips. Later, these air-dried colored chips were vacuum dried for 2 hours at 105°C, then these chips (colored chips) were mixed to colorless chips with four different concentrations (0.25; 0.50; 1.50 and 2.50 on weight % of the chips (wt.%)) to produce colored photochromic filaments. The filaments were produced by laboratory scale single-screw melt extruder (melt spinning) with the diameter of 16*mm*, L/D ratio of 30 with the MFI of 2.66 $g.min^{-1}$. The spinneret has 13 orifices and each having the diameter of 0.5*mm* (i.e. the spinneret designs are varied according to the shape of filament produced) [1, 13, 14]. The miPP filaments was produced with different cross sections, namely circular, triangle, 5-star and 8-star.

3.2.2 Post spinning process

In this research, six different drawing ratios (*DR- 1.0; DR-2; DR-2.5; DR-3; DR- 3.5 and DR- 4.0*) was applied under 120°C. After the drawing process, the filaments were winded on the gray cardboard with uniform tension as well as sufficient thickness, therefore six layers of the filaments can be winded on the cardboard. The color of the cardboard is gray and there no addition of fluorescing agents in the cardboard and it can be confirmed by subsequent tests.

4.2 Silica Sol-Gel Synthesis and Coating on PET fabrics

The second techniques were used to develop photochromic textiles is sol-gel coating, Therefore, Pre-treated, 100 % PET plain structured fabric was used for this study. Triacetoxyvinyl-precursor (TAS); Octyltriethoxyprecursor (OTES); Phenyltriethoxyprecursor (PhTES); aminopropyltriethoxy precursor (APS) and MPP (photochromic pigment). All the chemicals were purchased from Sigma-Aldrich, USA. Deionized water was used for the preparation of sol solutions. First, the MPP was added into the prepared sol slowly to ensure the proper mixing, after mixing it could be stirred until getting the clear solution. Two pieces of PET fabrics (*30cm×12cm*) were dipped into the solution and then withdrawn vertically at a constant speed (~10$mm.sec^{-1}$). The fabrics were dried in atmospheric condition and then cured at 110°C for 10 minutes. Before measurement, the coated fabric was left in atmospheric condition for 24-48 hours to ensure complete stabilizing of the silica matrices, followed by washing two times as per the standard washing procedure.

4.3 Analysis of optical and physical properties

4.3.1 Measurement of Kinetic properties of photochromic materials

Photochrom-3 has already made with the activation light source of Edixeon UV LED EDEV-3LA1 with radiometric power (Φ_V)=350mW with adjustable minimum peak wavelength. The minimum peak wavelength for the pigment MPB and MPP incorporated filaments are measured at 385nm, whereas MPY incorporated filaments measured at 365nm. The Photochrom-3 having the construction of dual light source with the shutter over the exciting light source makes the continuous measurement of photochromic materials with the UV energy density of 675± 50 $\mu W.cm^{-2}$. Due to the easy control over excitation with light sources by using the shutter, it becomes possible to examine the photochromic properties of materials with respect to single or multiple cycles. The produced photochromic miPP filaments have been measured five cycles both exposure and reversion phase. One measurement cycle consists of 5 min exposure under UV and 5 min of reversion phase (i.e. without UV-radiation) and totally 10 min per cycle. Average value of the five repetitive measurements was used for statistical data treatment. Generally, photochromic colorants are sensitive towards the temperature, therefore a thermostat was used to maintain the temperature at 22±2°C and the relative humidity is 45 ± 10%. The reflectance values can be utilized to find out the color strength and another related parameter, the color strength (*K/S* function) values can be computed as following equation Eq.1;

$$\frac{K}{S} = \frac{(1-R)^2}{2R} \qquad (1)$$

where *R*- reflectance factor, *K*-absorption and *S*-scattering of colorant. The changing in optical density (ΔOD) were calculated using the Eq.2;

$$\Delta OD = K/S_{\lambda \max G \max} - K/S_{\lambda \max D \min} \qquad (2)$$

where $K/S_{\lambda maxGmax}$ is the maximal value of *K/S* function at a wavelength of absorption maxima during exposure phase and $K/S_{\lambda maxDmin}$ is the minimal value of *K/S* function at a wavelength of absorption maxima during reversion phase. The ΔE^* of drawn and undrawn filaments are computed through simple CIE lab formula in the Eq.3.

$$\Delta E^* = \sqrt{\left(\Delta L^*\right)^2 + \left(\Delta a^*\right)^2 + \left(\Delta b^*\right)^2} \quad (3)$$

From the first order kinetics, the half-life ($t_{1/2}$) of color change and rate constant (k) for the photochromic miPP filaments can be calculated by using the Eq.4 & 5 respectively.

$$t_{1/2} = \frac{ln2}{k} \quad (4)$$

$$k = \frac{ln2}{t_{1/2}} \quad (5)$$

4.3.2 Thermogravimetry analysis of miPP filaments

To find out the thermo-chemical behavior of photochromic pigments, the thermogravimetry analysis could be done in Mettler Toledo TGA analyzer. Therefore, the samples weighing between 7-8mg were used for analysis to heat from 25°C to 300°C with a heating rate of 5°C.min^{-1} under the nitrogen atmosphere.

4.3.3 Differential scanning calorimetry of miPP filaments

In this research work, the DSC analysis were performed on Perkin Elmer based on ASTM standard D3418-08. In the DSC analysis, the produced colored miPP filaments were heated at a rate of 10°C.min^{-1} from 25°C to 200°C (melting phase), later it cooled from 200°C to 25°C (cooling phase). After the measurement the data was collected for both heating and cooling phase. The measurement can be done under the nitrogen atmosphere in the rate of 20 mL.min^{-1}. Based on the DSC data, the various thermal properties can be calculated such as melting temperature (T_m) and melting enthalpy (H_m), change in melting enthalpy (ΔH_m). Change in entropy (ΔS_m) can be calculated through Eq.6.

$$\Delta S_m = \frac{\Delta H_m}{T_m} \quad (6)$$

The crystallinity ($Xc\%$) of the produced filaments were computed from the Eq.7, where ΔH_m° is 209 $J.g^{-1}$ [15],

$$Xc(\%) = \frac{\Delta H_m}{\Delta H_m^o} \times 100 \quad (7)$$

4.3.4 Physical & Mechanical properties of miPP filaments

The mechanical properties have been determined through Instron instrument according to the international organization for standardization (ISO) standard 2062:1993. The various mechanical properties namely tenacity, elongation, Young's modulus was investigated. During the testing, clamping length of 12.5cm was maintained with clamp speed of is 350 m.min^{-1}.

4.3.5 Microscopic analysis

The surface morphology of control and photochromic materials were observed by using TS5130 Vega-Tescan scanning electron microscope (SEM). In the measurement, the electron column was kept at vacuum and other following parameters were used; 20 kV accelerating voltage and 500x magnification levels with a vacuum of 7.8×10^{-3} *Pa*. The working distance between the sample and objective lens can be adjusted according to the image resolution.

The flexural rigidity and bending modulus of coated fabrics were calculated from the Eq.8 and 9 in *mg.cm* and *kg.cm*$^{-2}$ respectively.

$$G = 0.1MC^3 \quad (8)$$

where M is the mass per unit area (*g.m*$^{-2}$) and C is the bending length (*cm*) of the fabric;

$$Q = \frac{\left(12G \times 10^{-6}\right)}{g_2^3} \quad (9)$$

where Q is the bending modulus in (*kg.cm*$^{-2}$), G is the flexural rigidity and g is the fabric thickness (*cm*).

5. Summary of the results achieved

5.1 Results of miPP filaments (circular)

5.1.1 Effect of photochromic response on drawing ratio of photochromic filaments

In this study, three different photochromic pigments were used to produce the miPP filaments. Photochromic materials are sensitive towards to the amount of UV energy; therefore, it is necessary to ensure the amount of UV energy during the measurement. So, amount of UV energy was measured under exposure and reversion phase, the value of energy is 675±50 $\mu W.cm^{-2}$, 2.26±0.8 $\mu W.cm^{-2}$ respectively.

Figure 1 shows the photographs of original color (i.e. colorless) and developed the color of the filament under the UV exposure. The kinetic measurement of photochromic materials can be done in Photochrom-3 under the reflectance mode, based on these results the various optical properties of photochromic materials are analyzed, namely, color build-up analysis through *K/S* function, *K/S* (max) at exposure phase, changing in the optical density (ΔOD), color difference analysis via L^*, a^*, b^* & ΔE^* (under CIELAB 1976), half-life of color change in both exposure and reversion phase, rate constant and color intensity at beginning, half and infinitive.

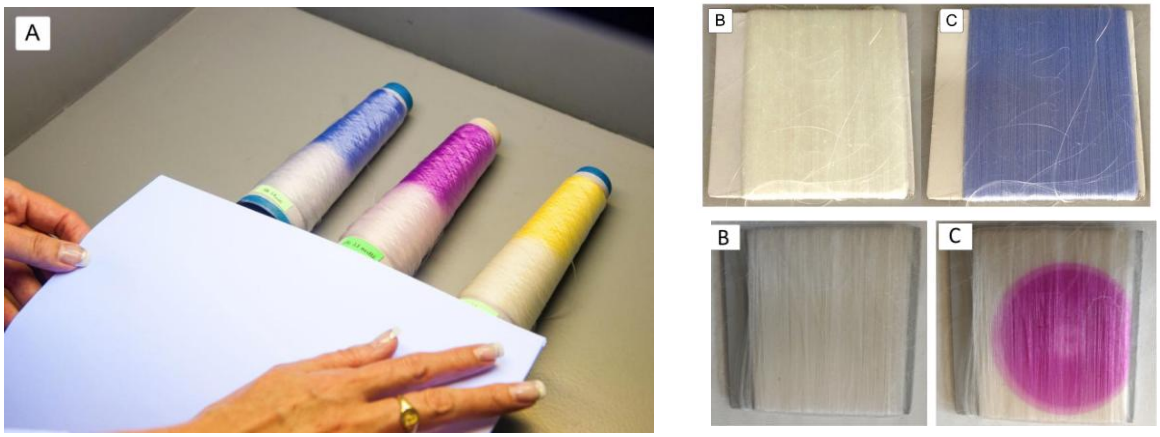

Figure 1: Produced photochromic miPP filaments (A); filament winded on cardboard B & C (B-UV off; C-UV on).

The *K/S* values of both exposure and reversion phase with respect to the time and wavelength interval are plotted in Figure 2 and Figure 3 respectively for the filament with MPP pigment,

it gives the information on the individual spectra curves, in the case of exposure phase shows overlapping *(A→B)*, on the other hand, it gives good separation of spectra curves under reversion phase *(B→A)*. These graphs provide the information on the influence of *K/S* values with respect to the UV radiation. It is evident from these two graphs are, positive acceleration of *K/S* values under UV exposure required less time than the negative acceleration of *K/S* under reversion phase, it is due to the structure of photochromic pigment (MPP) which having the higher half-life. In other words, conversion of colored form to the colorless form required more time, which is slightly depended on the time, whereas reverse phase is independent on the time. The reason behind this is, during the exposure phase, the photochromic compounds get faster reconversion of the original chemical structure (i.e. conversion of original form to merocyanine form), in case of reversion phase, it becomes slower reconversion of merocyanine form to original form.

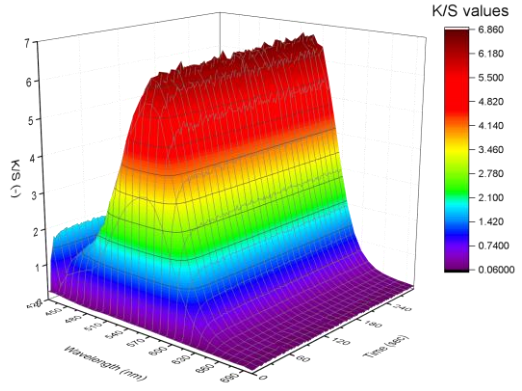

Figure 2: K/S values of miPP filaments (MPP-2.5 wt.%) (exposure phase).

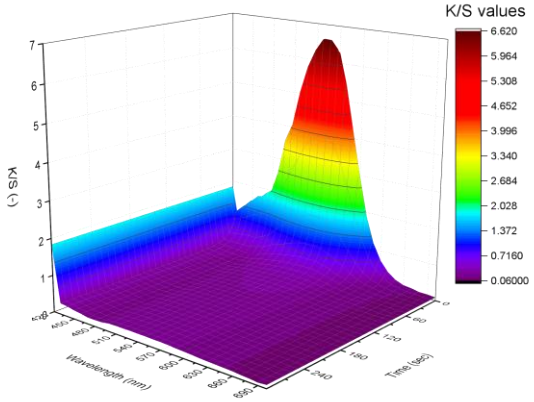

Figure 3: K/S values of miPP filaments (MPP-2.5 wt.%) (reversion phase).

The results of *K/S* values for five cycles of exposure and reversion phase for the highest and lowest concentration of photochromic miPP filaments on circular cross-sections were plotted in Figure 4. Results significantly show the reduction of *K/S* values with increasing the fineness of filament (i.e. increasing the drawing ratio). Therefore, *K/S* values are depending on the drawing ratios of respective filaments, in a simple way, it could be, amount of light reflection during the color measurement is marginally depends on the presence of pigment in the filament with respect to the unit area. Therefore, light reflection is decreased with increasing the drawing ratio. During the drawing process, there is an extension of filaments towards to the drawing direction (i.e. length wise), in other word, increasing the length of filaments causes to the reduction of the diameter. In the mass colorations, the pigments are mixed thoroughly with the polymer in the molten state, when it extrudes, the pigments are incorporated with the filaments since the amount of pigment per unit area could reduce according to the drawing ratio in the drawing process. Apart from this fact, the thickness of filament layers also influences the light reflection, for all drawing ratio, the filaments are wind uniform number of layers (i.e. six layers) on the gray board, the thickness of layers is decreased with increasing the drawing ratio, this is due to the reduction of filament fineness.

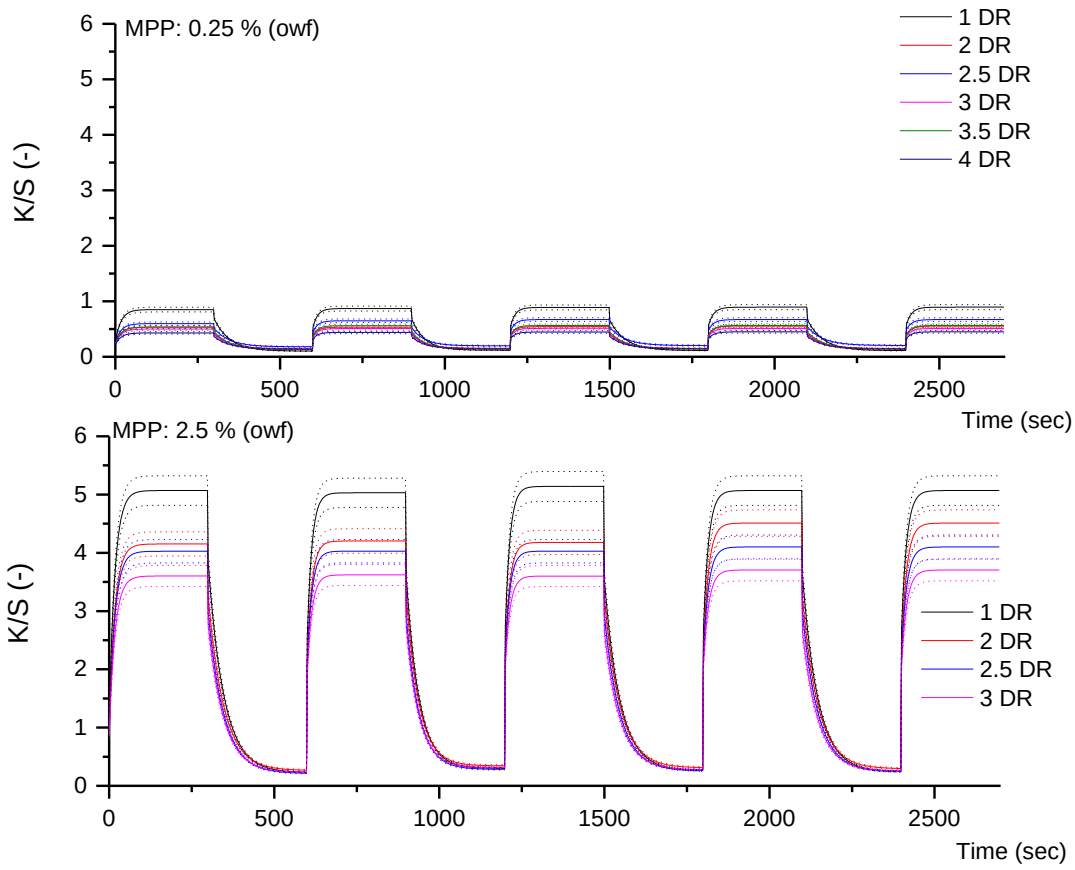

Figure 4 Dependence of color strength (*K/S* values) on photochromic miPP filaments.

5.1.2 K/S (max) of photochromic miPP filaments during exposure phase

Figure 5 shows the *K/S* (max) for all three pigments with same drawing ratio (i.e. DR-2), overall *K/S* (max) is increased with increasing the pigment concentration. The results of *K/S* (max) for all the data was used to fit with linear regression and MPP shows the R^2=0.98; MPB is R^2=0.99 and MPY provides R^2=0.92, it confirms there is a strong linear relationship between the pigment concentration and *K/S* (max) values. The results of Δ*OD* for three pigments shown in Figure 6 with same drawing ratio (i.e. DR-2), the Δ*OD* is increased with increasing the pigment concentration, the trend was observed for three pigments. The results of Δ*OD* for all the data was used to fit with linear regression and MPP shows the R^2=0.98; MPB is R^2=0.99 and MPY provides R^2=0.89, it confirms there is a strong linear relationship between the pigment concentration and Δ*OD*. Among of three pigments, MPP shows highest and MPY shows lowest *K/S* (max) values and even in Δ*OD*, for the same concentration. This purely depends on the dyeability of photochromic pigment with respect to the miPP filament, there are many parameters which influence the dyeability, namely, stability of pigment towards to the heat, chemical structure of pigments, adverse interactions between the additives like stabilizers (HALS and others), other impurities present in the pigments, these factors may have caused to reduction of dyeability. These unforeseen reactions will reduce the *K/S* values among the pigments. Figure 13 shows the thermal properties of three different photochromic pigments. Among three pigments, MPY shows the highest degradation in

terms of weight loss towards to the specific temperature, it can be seen in TGA measurement. In the mass coloration, heat stability for the colorants decides the dyeability.

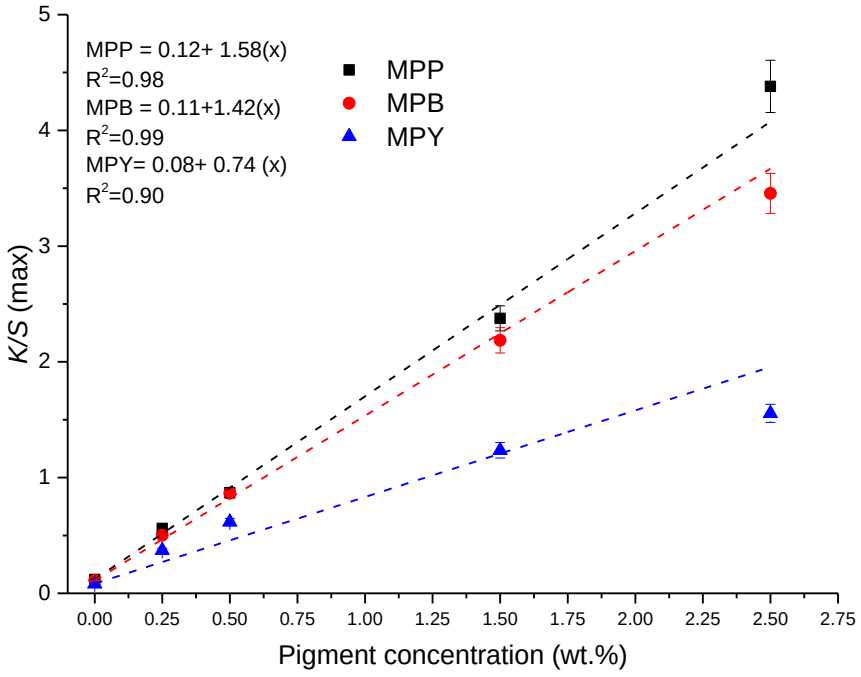

Figure 5: Dependence of *K/S* (max) for miPP filaments (DR-2) under exposure phase.

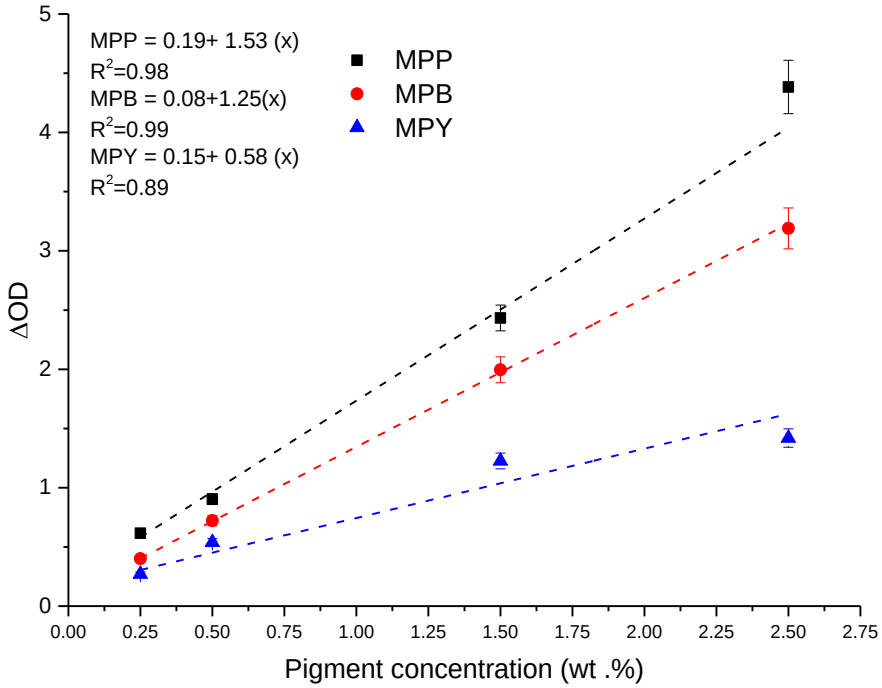

Figure 6: Dependence of Δ*OD* on the miPP filaments (DR-2).

5.1.3 Half-life of color change for photochromic miPP filaments

Figure 7 shows the half-life of color change of photochromic miPP filaments with respect to the pigment concentration under the exposure phase, results are evident that purely depends on the concentration of pigments, the trend of the result is same as for all the pigments. The

half-life for color change during exposure is approximately two times less than the reversion phase. The results of the half-life of color change and rate of reaction varied with respect to the type of pigment, even though in same concentrations. In the concentration of 0.25 wt.%, results of the half-life of color change during the exposure phase shows 34*s*, 24*s*, 15*s* for the pigment MPP, MPB and MPY respectively. So, it confirmed that the filament with the pigment MPY shows faster reaction which is nothing but shorted half-life as compared to other pigments. Similarly, the pigment MPP provides the longer half-life color change, which denotes the slower reaction. During the exposure phase, all the pigments show half-life of color change has been reduced linearly with increasing the concentration of pigments from 0.25 to 2.5 wt.%. It was observed, miPP filament with MPP shows 34*s* when the concentration is 0.25 wt.%, the same filaments were reduced to 24*s* when the concentration has been increased to 2.5 wt.%, Similarly the lowest half-life of color change was found in filaments with MPY, 14*s* and 5*s* respectively with the above-mentioned concentration, these data were fitted with linear regression and the goodness of fit was found R^2=0.91. The observed linear trend is same for another pigment too. The goodness of fit for MPB and MPY shows R^2=0.89, R^2=0.91 respectively. The variability of error shows higher in case of filaments with MPP and lower with MPY. Overall the results conclude that filament with MPP shows longer half-life which denotes slower reaction, on other hand filaments with MPY shows shorter half-life of color change, which is nothing but faster reaction. The half-life of color change for all three pigments in the order of MPP>MPB>MPY. Figure 8 described the half-life of color change of photochromic miPP filaments under the reversion phase, it is clearly described that the results are depending on the pigment concentration, which is similar to the exposure phase. The results of the half-life of color change during reversion phase has been reduced linearly by increasing the concentration of pigment, it can be observed for all three pigments. In the concentration of pigments at 0.25 wt.%, MPP incorporated filament shows 71*s*, when the concentration is increased to 2.5 wt.%, the half-life of color change could be reduced to 45*s*. This trend is same for other pigments too, overall results during the reversion phase were found that filament with MPY shows the lowest half-life, 23*s* for 0.25 wt.%, in case of 11*s* for 2.5 wt.%. The results of the half-life of color change during reversion phase with respect to the pigments in the order is MPP>MPB> MPY. There are many parameters which influence the half-life of color change, such as, amount of UV radiation and its absorption rate of pigment, concentration of photochromic colorant, available form of colorant, chemical structure of the colorant, number or type of functional groups present in the colorant, position of functional group, surface area of reactant, temperature of the system, reaction rate and type of substrate. However, it is generalizing the statement and it is difficult to particulate the specific parameter which influences on the half-life of color change. However, one conclusion can be proposed from these results, increasing concentration makes faster reconversion of the original form of photochromic pigment into merocyanine form.

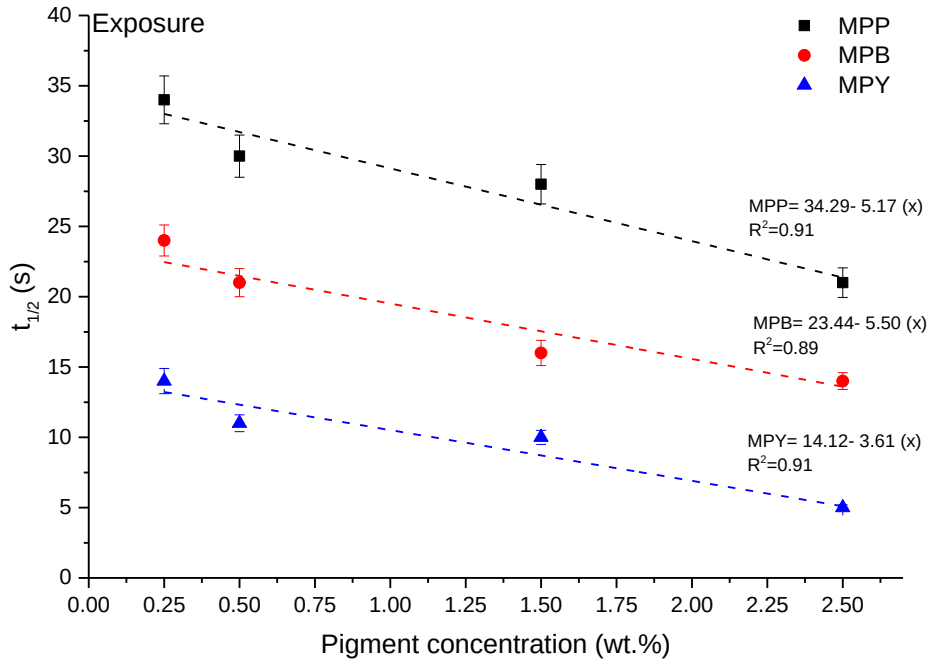

Figure 7: Half-life of color change on miPP filaments under exposure phase (DR-2).

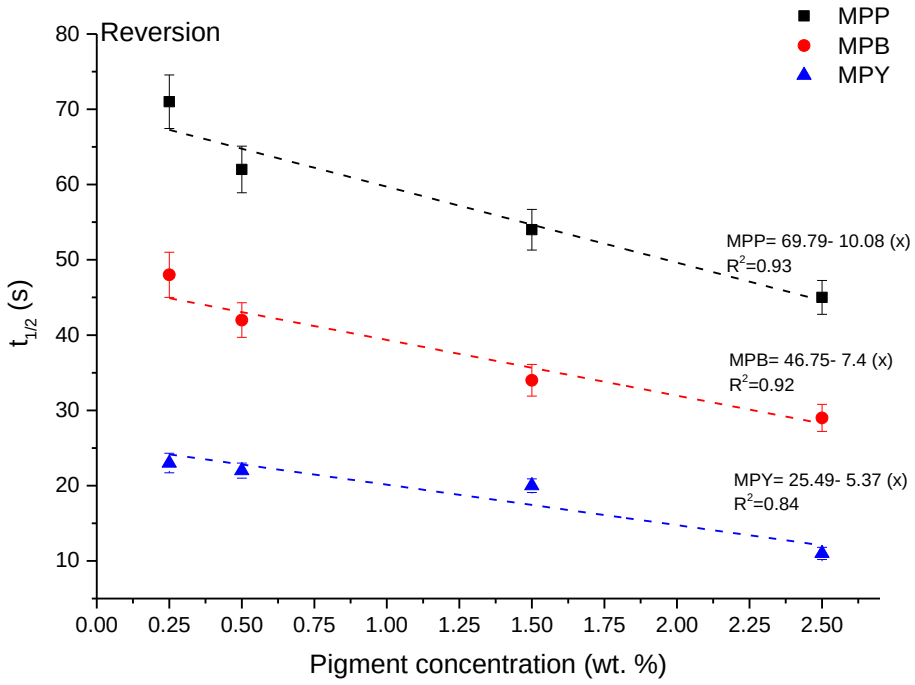

Figure 8: Half-life of color change on miPP filaments under reversion phase (DR-2).

5.1.4 Color difference analysis of miPP filaments

The residual ΔE^* can be calculated as per the CIELAB 1976 color space and the results are plotted in Figure 9 to Figure 10. Perhaps, the color difference ΔE^* can explain the changing of hue, shade intensity or shifting of the lightness of the color which is produced by the photochromic materials. These colorimetric properties were analyzed with respect to the residual ΔE^* values which explains the visible color difference on the photochromic

filaments and it is depended on the physiology of the human vision, nevertheless, when these filaments are used as a sensorial application for the determination of UV (i.e. when it applied to the UV sensor) in the atmosphere, there is an important requirement which ability to recognize the specific color difference for the human visual evaluation. For human eyes can identify the discernible color differences, when the residual ΔE^* values is higher than 0.4. Overall the results found that the maximum residual ΔE^* values are ~2.5 units and minimum is ~0.02. Also, the maximum residual ΔE^* values are found for the lowest drawing ratios, however, these residuals ΔE^* values are a significantly nonlinear relationship with respect to the concentration of pigment and drawing ratio, the residual ΔE^* values are marginally increased with increasing the concentration of pigment, it can be observed for all three pigments. Among three photochromic miPP filaments, coloration with MPB shows higher residual ΔE^* values (~2.5 units) when the drawing ratio is 2. The data were fitted with an exponential function to find the goodness of fit, which show R^2=0.95. It conveys that there is a non-linear relationship between the residual ΔE^* and the concentration of pigment. The goodness of fit for another drawing ratio also shows above 0.95, which conveys that there is a non-linear relationship between the concentration and residual ΔE^* values. The photochromic miPP filament with MPY pigments observed lowest ΔE^*, it can be seen in the lowest drawing ratio as well as in the highest concentration of pigment too.

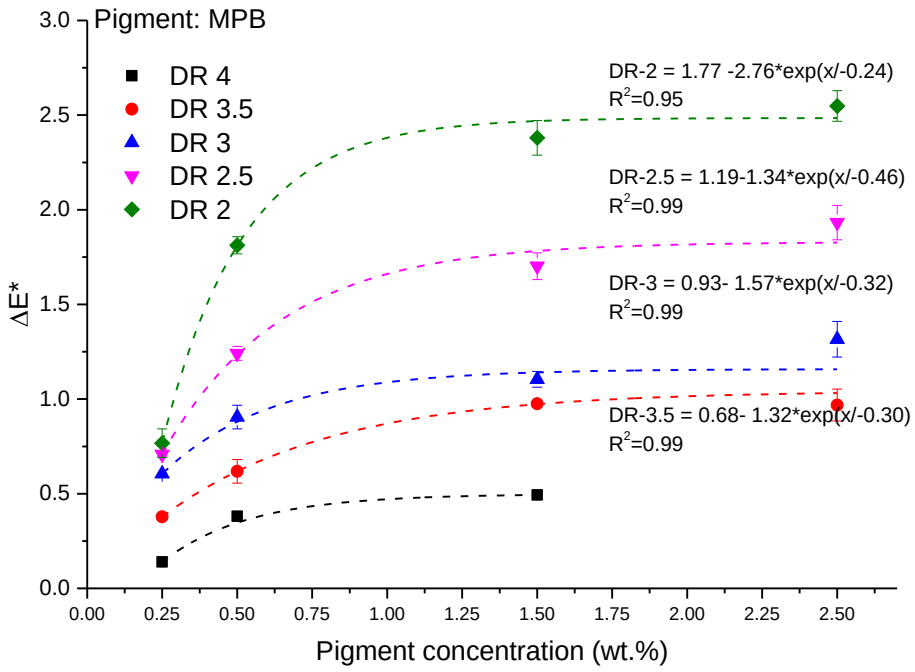

Figure 9: Residual ΔE^* values for photochromic miPP filament with MPP.

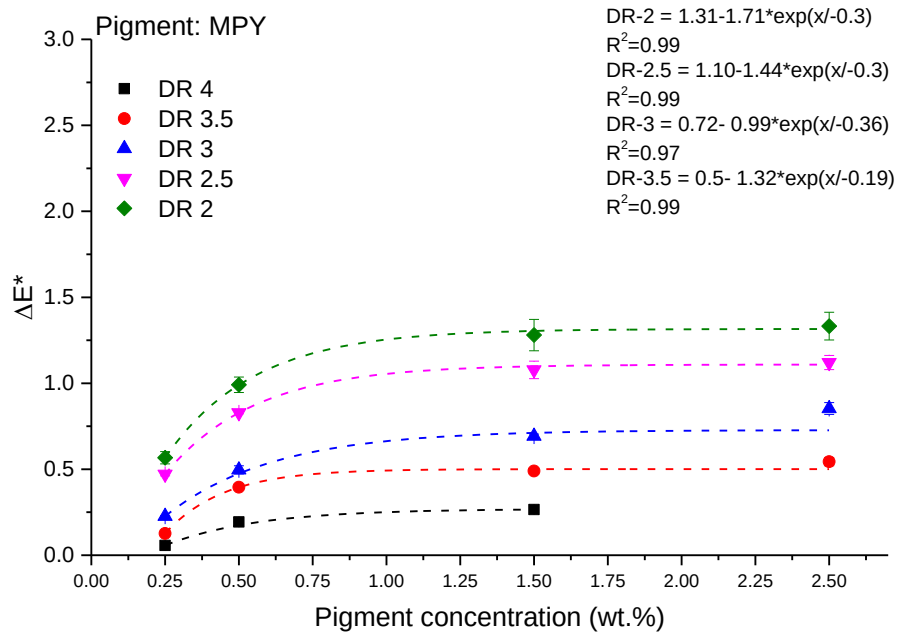

Figure 10: Residual Δ*E** values for photochromic miPP filament with MPY.

5.1.5 Physical and mechanical properties of photochromic miPP filaments

After the drawing process linear density of miPP filaments are decreased with increasing the drawing ratio, it can be seen in Figure 11. The linear density of 45.3±0.3 *tex* for the drawing ratio of 1, and when the drawing ratio is 4, the linear density can be 14±0.17 *tex*. There is an exponential trend was observed when increasing the drawing ratio between the linear density, the goodness of fit was found R^2=0.98, it confirmed that there is an exponential relationship between drawing ratio and linear density. There is interesting fact was observed, the addition of photochromic pigment can cause to decreasing the linear density (Figure 12). The linear density of 45.3±0.3 *tex* for the concentration of 0 wt.% (i.e. without the addition of photochromic pigment) and when the concentration 2.5 wt.% the linear density was reduced to 34.2±0.22 *tex*, it concludes that linear density was reduced 24% by addition of pigment. Figure 11 shows the dependence of tensile strength on the drawing ratio, where the tensile strength of 10.51 cN/tex for the drawing ratio of 1, and when the drawing ratio is 4, the tensile strength of 31.94 $cN.tex^{-1}$. The goodness of fit (0.96) was confirmed that there is strong relationship between the tenacity and drawing ratio. In general, the addition of spinning additives can reduce the tenacity and elongation at break, it can be studied [16–18], in this research, results confirms that the addition of photochromic pigment causes to reduce the tensile strength and elongation at break, which is shown in Figure 12. Results of tenacity have been reduced 28 % between the concentration from 0.25 wt.% to 2.50 wt.%. According to the reference [19], addition of additives like pigments are usually affects their strength and structure, which also confirmed from our research too. Figure 11 shows results of elongation at break with respect to the drawing ratio. There is an exponential relationship between the drawing ratio and elongation at break. The elongation at break 260.3% for the drawing ratio of 1, and when the drawing ratio is increased to 4, the elongation at break was found 39.9%,

which confirms there is a reduction of 84%. The Young's modulus of photochromic miPP filaments was plotted in the Figure 11. Results show that significant improvement in Young's modulus, it was increased 65% from drawing ratio 1 to 4, nevertheless, it is due to the molecular arrangements and followed by the variation in the crystalline region of the filament.

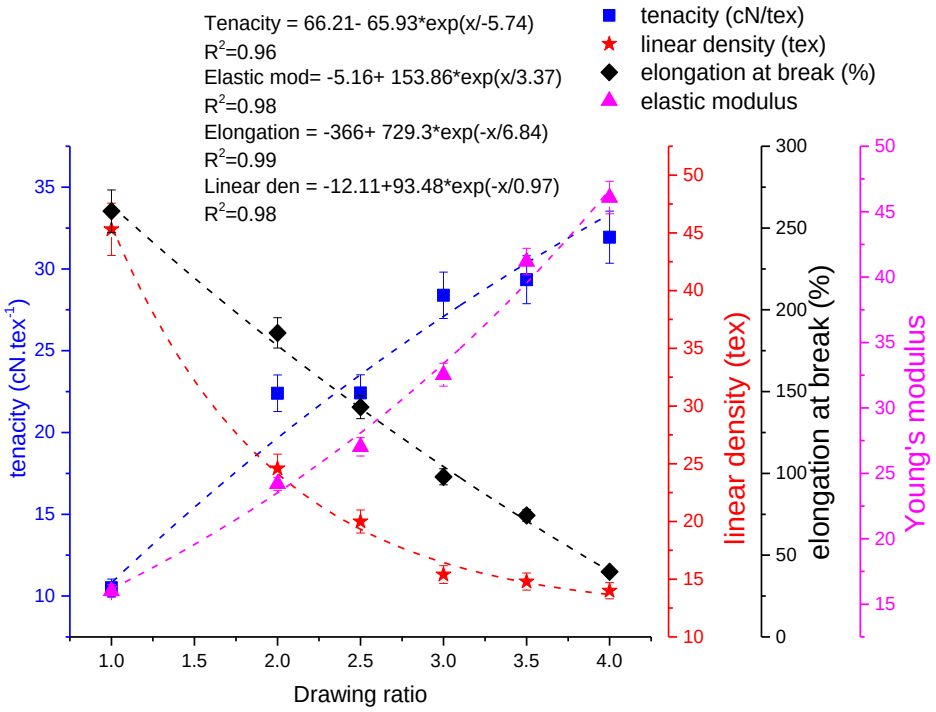

Figure 11: Effect of drawing ratio on various physical properties (MPP-0.25 wt.%).

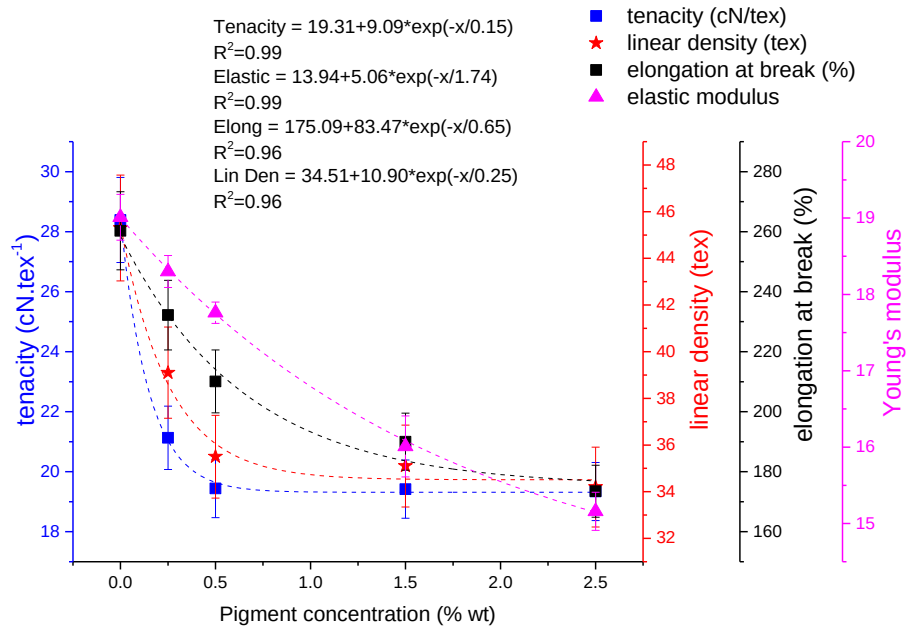

Figure 12: Impact of pigment concentration on various physical properties (DR-1).

5.1.6 Thermogravimetric Analysis of miPP filaments

In this study, three different photochromic pigments were used to analyze their thermal properties and the results are shown in Figure 13. First all the pigments started degradation at 50 to 130°C, however this is due to the HALS and other residual additives present in the pigments, thereafter it sustains for higher temperature and start complete degradation, for MPY pigments degrade significantly during heating and degrade 76% of weight loss by 325°C, whereas MPB and MPP is much better and weight loss of 62% and 53% respectively.

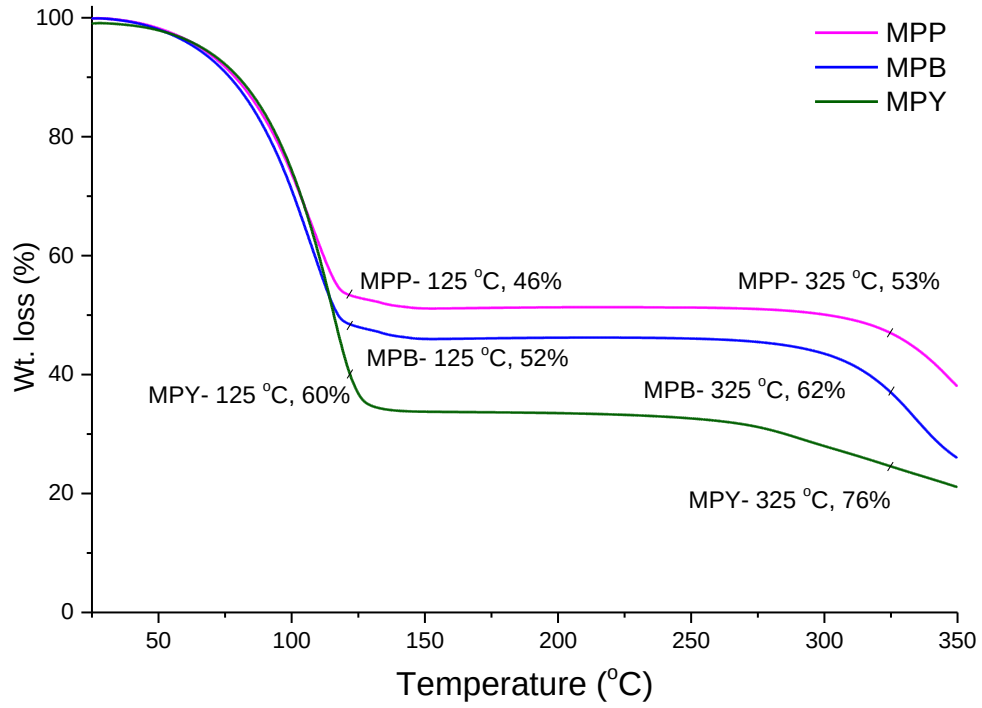

Figure 13: TGA analysis of photochromic pigments.

5.1.7 Differential scanning calorimetry analysis on miPP filaments

The results reveal the difference in the melting peak temperature dependence on the drawing ratio. The melting temperature (T_m) of undrawn filament shows 146.65°C, whereas the drawing ratio 4 shows 150.28°C (Figure 14), this is due to the thermal demonstration of the components during the crystallization of the polymer which may create the supermolecular structure of the polymer. In general, the liquid phase may reduce the distance between adjacent chains and therefore it increases the fraction of lower energy trans conformation. The melting temperature miPP filaments with photochromic pigments are increased ~2°C with increasing the photochromic pigment concentration (Figure 15). The melting temperature miPP filaments with photochromic pigments are increased ~2°C with increasing the photochromic pigment concentration (Figure 15). Of course, the drawing ratio is highly responsible for the increasing of melting temperature, it can be seen in Figure 16. However, it is desired and expected effects on the photochromic filaments. In the drawing ratio 4, there are two melting peaks were visible, it is due to the during the DSC measurement the mass colored miPP was exposure to set conditions or may be melting of less stable β crystallites formed during the measurement. The crystallinity of photochromic filaments was increased

with increasing the drawing ratio, therefore, the higher rate of crystallization makes many modifications in the filament, mainly the α, β modification of morphological structure.

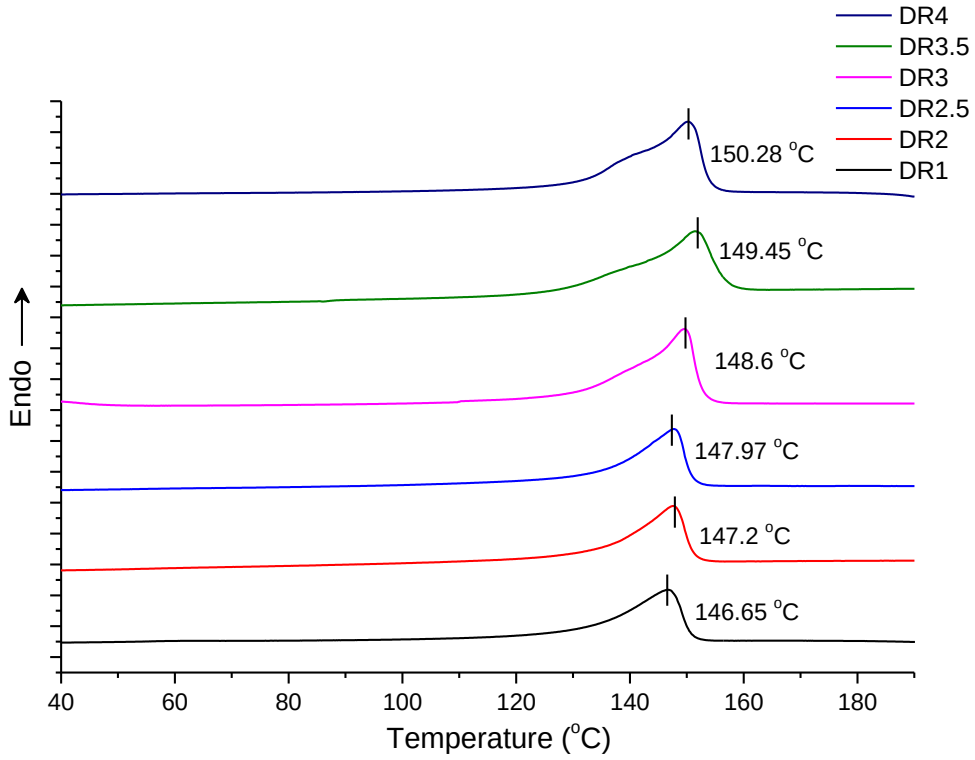

Figure 14: Normalized DSC curves for miPP filaments, (MPP=0.0 wt.%).

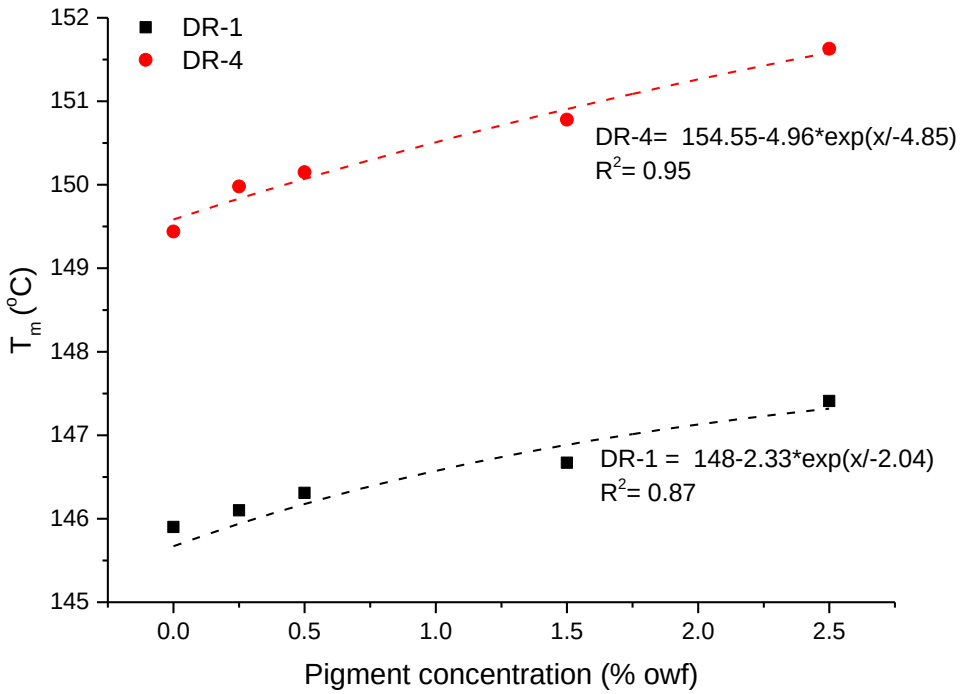

Figure 15: Effect of pigment concentration on T_m.

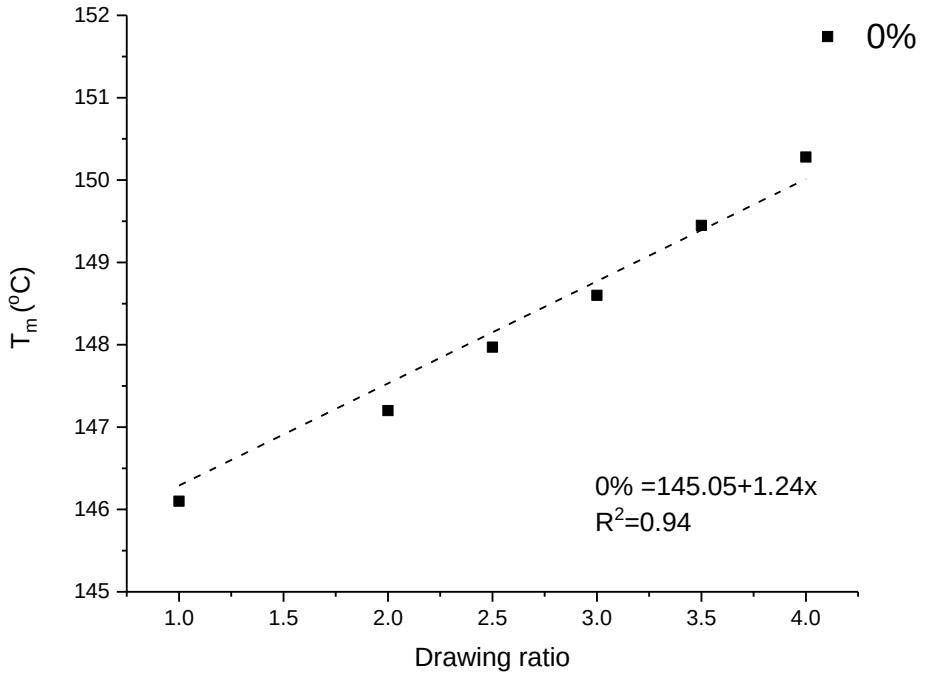

Figure 16: Effect of drawing ratio on T_m.

5.2 Results of miPP filaments (non-circular)

5.2.1 Optical properties

Table 2&3 shows *K/S* (max) values to the different drawing ratio of photochromic miPP filaments on non-circular cross-sections. Due to the limited options, it manufactured with only one concentration by each pigment, therefore it is very difficult to make a graphical representation with limited independent and depended on values. Results describe the circular cross-sectional filament shows higher *K/S* (max) values than the non-circular filaments even in all the drawing ratios as well as in the same concentration of pigment. In over all, results of *K/S* (max) values were observed that it varied with respect to the cross-sectional shape of the filaments. The results of *K/S* (max) values on the filaments with MPP pigment, 8-star and 5-star cross-sectional filaments show 63% and 72% less *K/S* (max) values than the circular cross-sections in the same drawing ratios. The results trend is similar to other pigments too, so, it evidenced and confirmed that the shape of cross-sections plays a vital role in the optical properties of produced filaments.

Table 2: The *K/S* (max) on the different cross-sections of the produced filament (DR-1).

Cross- sections	Pigment concentrations 1.5 wt.%					
	MPP	$CV\%_{K/S\ (max)}$	MPB	$CV\%_{K/S\ (max)}$	MPY	$CV\%_{K/S\ (max)}$
Circular	3.230	82.2	2.835	112.4	1.397	229.7
5-star	0.949	95.4	0.4969	249.6	0.544	160.0
8-star	1.229	80.1	0.6024	67.0	0.948	183.3
Triangle	-	-	-	-	0.688	120.9

Table 3: The *K/S* (max) on the different cross-sections of the produced filament (DR-2).

Cross- sections	Pigment concentrations 1.5 wt.%					
	MPP	$CV\%_{K/S\ (max)}$	MPB	$CV\%_{K/S\ (max)}$	MPY	$CV\%_{K/S\ (max)}$
Circular	2.523	135.6	2.201	90.7	1.229	190.8
5-star	0.704	153.9	0.415	101.2	0.502	112.2
8-star	0.945	118.2	0.520	95.1	0.495	118.7
Triangle	-	-	-	-	0.479	116.1

5.2.2 Surface morphological analysis of miPP filaments

SEM characterization was used to investigate surface characteristics of the produced photochromic miPP filaments with the influence of photochromic pigments and their distributions, the results are shown in Figure 17. The outer surface for all the filaments (i.e. colored and uncolored) looks similar with a smooth surface, which means that there is no significant influence on the pigments with its distribution of filaments on surface characteristics.

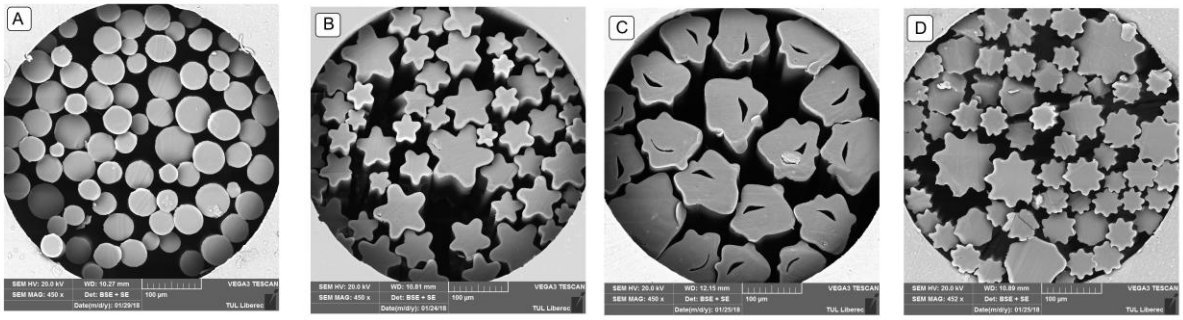

Figure 17: Cross sectional view of circular and non-circular photochromic miPP filaments, (A) circular (B) 5-star; (C) Triangle; (D) 8-star (all are 2.5 wt.% MPP with DR-1).

5.3 Results of sol-gel coated photochromic fabrics

The photochromic pigment was successfully incorporated on to the PET fabric via sol-gel coating treatment. Figure 18-(A&B) shows the photographs of original color (i.e. colorless) and developed color of the photochromic fabric under the UV influence. Figure 18-(B) shows the visual observation of the color change of produced photochromic fabrics where the original color of the pigment is purple. The color strength values of the photochromic fabrics with respect to different precursor compositions were shown in Figure 19. Results indicates, in the same concentration pigment derived different *K/S* values and it depends on the type of precursor. Therefore, *K/S* values are purely depending on the type of precursor used during the sol-gel coating process. From the observed results, the precursor having the strongly influence the photochromic pigment and their optical properties.

Figure 18: Photochromic sol-gel coated fabric, (A) fabric coated with APS precursor and (B) fabric coated with OTES precursor (Colored portion indicates the influence of UV radiation).

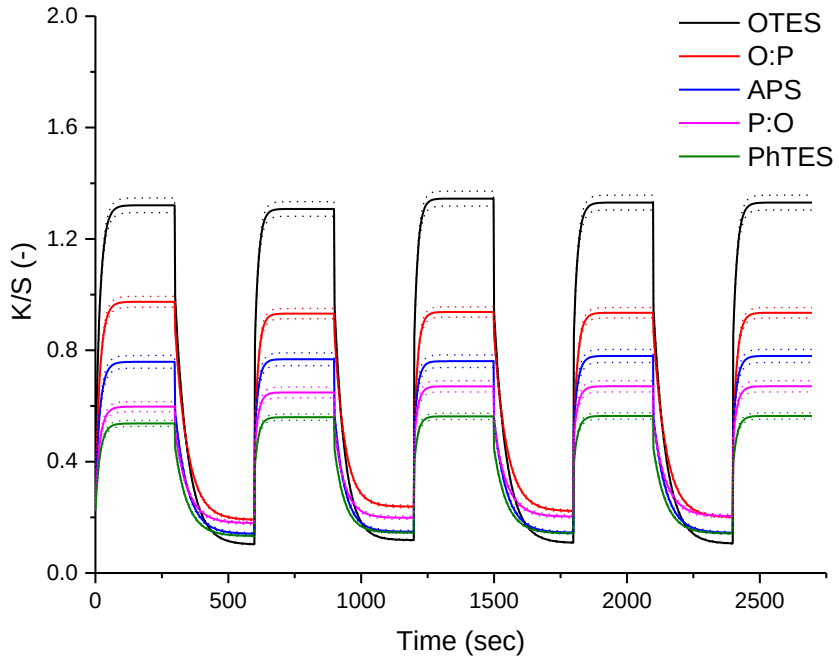

Figure 19: Effect of the precursor on the K/S values of coated fabrics (MPP-2.0 wt.%).

5.3.1 K/S (max) functions on sol-gel coated fabrics

K/S (max) of produced photochromic fabrics with different precursor combinations was plotted in Figure 20 and the Δ*OD* were plotted in Figure 21. Δ*OD* can be measured on the coated fabric without the addition of photochromic pigment and fabric coated with photochromic pigment. Results are significantly increasing the *K/S* (max) and Δ*OD* values with increasing the concentration of pigment.

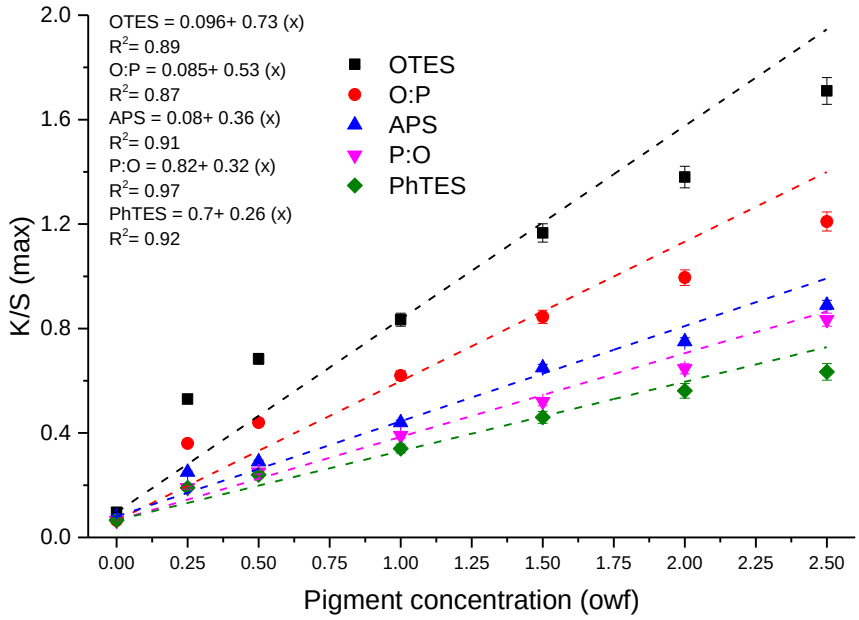

Figure 20: Dependence of *K/S* (max) on the sol-gel coated fabric.

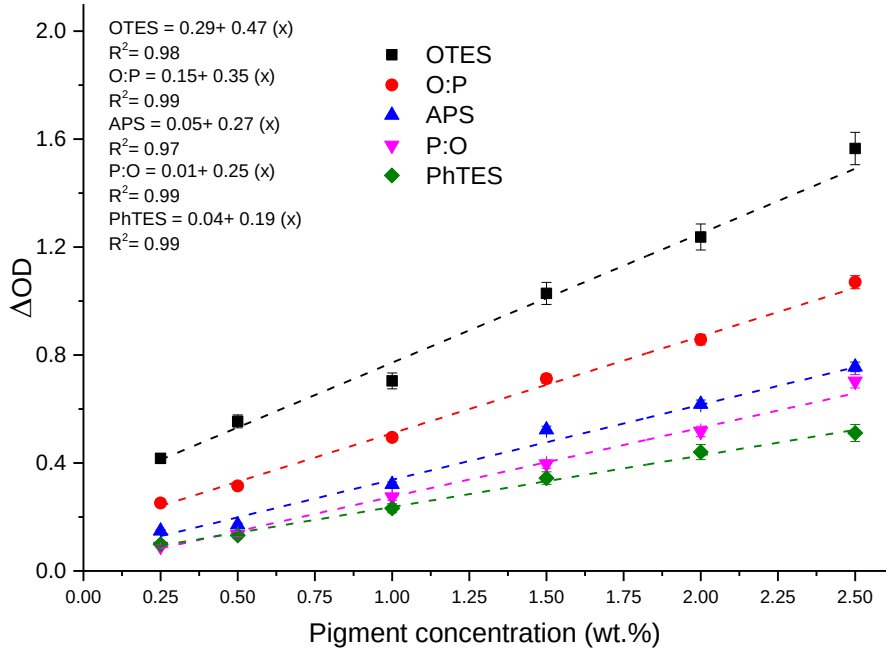

Figure 21: Dependence of Δ*OD* on the sol-gel coated fabric.

Therefore, *K/S* (max) and ΔOD are depending on the concentration of photochromic pigment, of course, it is a well-known effect. On other hand, *K/S* (max) and Δ*OD* is purely depended on the precursor and its combinations, since precursor has strongly influenced on the color strength values and followed by changes in the optical density. The data for the *K/S* (max) was fitted with linear regression, it concludes the goodness of fit all the precursors is above 0.98, which strongly recommend that there is a linear dependency of both the variables.

5.3.2 Color difference analysis of sol-gel coated fabric

The color difference (residual Δ*E**) of photochromic coated fabric was analyzed and the results are shown Figure. 22. In this work, highest residual Δ*E** was found ~3.1 units and lowest was ~0.1 units. In all the concentration photochromic fabric with OTES precursor shows highest Δ*E**, which confirms that there is a visible color difference since a human can identify the color difference if Δ*E** is more than ~0.4 units. The main objectives to produce these fabrics to determine the UV in the environment, which act as a flexible UV-sensor, therefore the residual Δ*E** values are more important to consider. The fabric coated with PhTES shows lowest Δ*E** values it can be seen in all the concentration. On other hand APS based precursor shows moderate (~1 units at maximum concentration). All the results are fitted with exponential functions to find the goodness of fit, all the results show more than 0.98, which strongly recommend that there is a significant dependency on Δ*E** values and the concentration of pigment as well as precursor types.

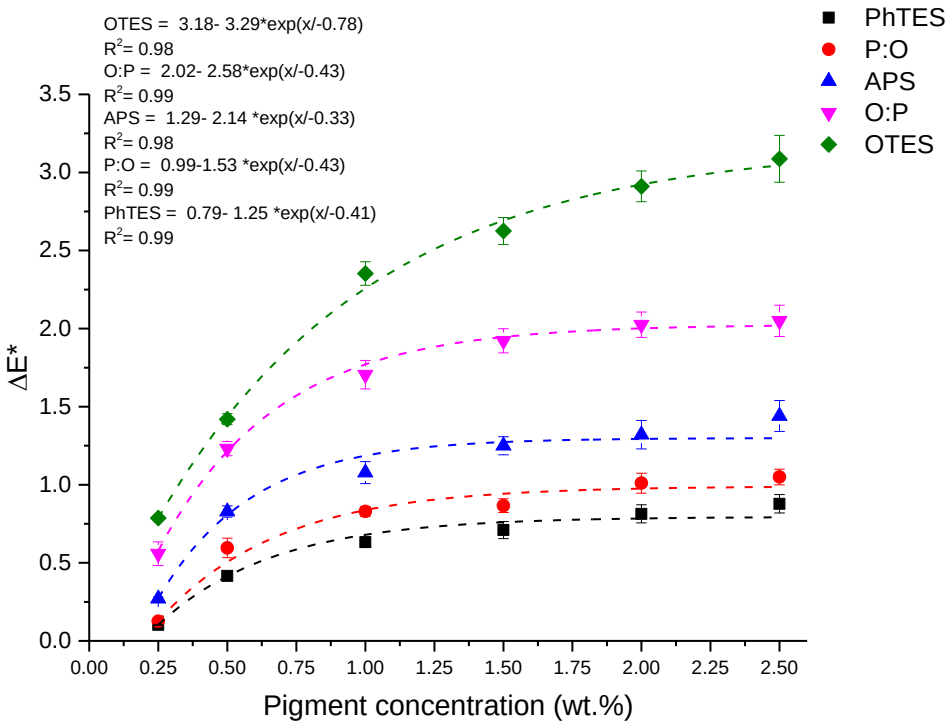

Figure. 22: Residual Δ*E** for the sol-gel coated fabric.

5.3.3 Half-life of color change for sol-gel coated fabric

The relationship between in the half-life of color change and rate constant on the pigment concentration & precursor influences was studied, the results significantly depend on the pigment concentration & precursor combination, this trend is same for both exposure and reversion phase.

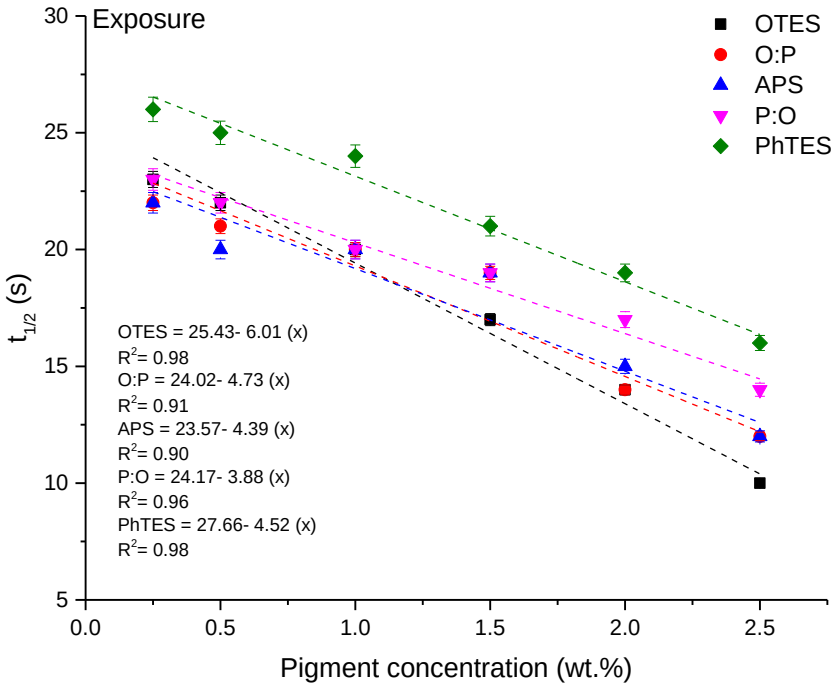

Figure 23: Half-life of color change during exposure phase of coated fabric.

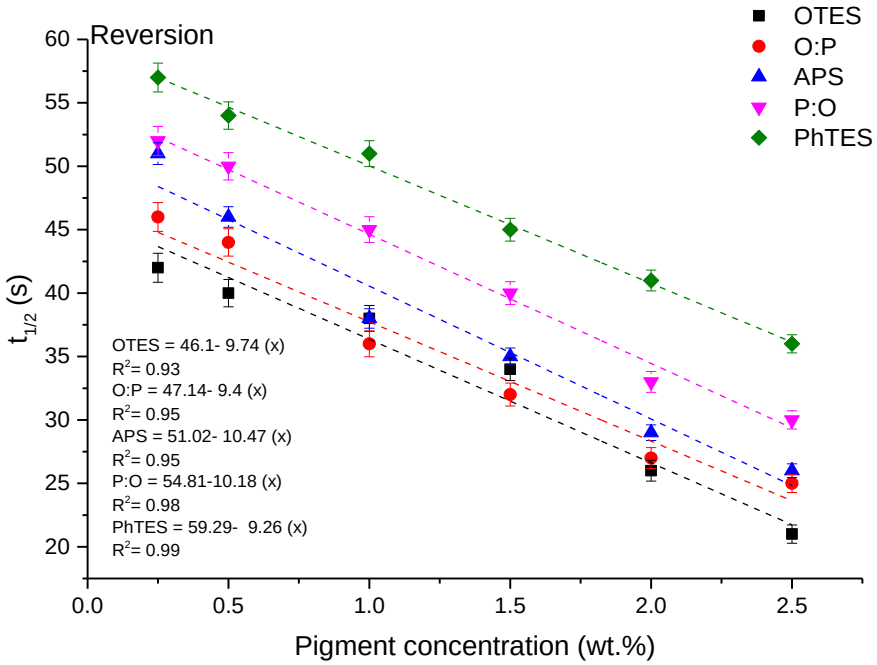

Figure 24: Half-life of color change during reversion phase of coated fabric.

Figure 23 shows the half-life of color change of sol-gel coated PET fabric with respect to the pigment concentration under the exposure phase, results are evident that purely depends on the concentration of pigments and precursor types. From the results, it is confirmed that the fabric coated with OTES, APS shows faster reaction than the PhTES & its combination. Figure 24 described the half-life of color change of photochromic fabric under the reversion

phase, it is clearly described that the results are depending on the precursor types and pigment concentration. The half-life of color change during reversion phase shows higher than the exposure phase, this is due to the structural modification of pigment during the isomerization reaction. Generally, structural conversion in to merocyanine is take lower half-life than the structure of merocyanine is converting into their original structure. To find the statistical dependency, the data were fitted with linear regression and it shows the better coefficient determination values (<0.95).

5.3.4 Hypsochromic shift

The nature and amount of the organic groups (*R*) in the silica matrices determine the polarity of the inner surface of the pores, where the photochromic pigments are located. Therefore, the spectral and kinetic properties of sol-gel coated fabrics are purely affected by the polarity of precursors, which means, it affects the absorption spectrum of the colored form of merocyanine. Thus, the hypsochromic shift of ~40nm was observed (absorption maxima are shifted from 610nm to 570nm), when the fabric is coated with OTES/PhTES or its combinations with 5-chloro-1,3,3-trimethylspiro[indoline-2,3'-(3H) naphtho(2,1-b) (1,4)-oxazine]. The reflectance spectrum of both precursors is given in Figure 25 and the produced fabric under UV radiations are given in Figure 18- (A&B). A colorless 5-chloro-1,3,3-trimethylspiro[indoline-2,3'-(3H) naphtho(2,1-b) (1,4)-oxazine] (i.e. MPP) can be isomerizes to purple colored merocyanine form in presence of APS precursor, whereas same pigment isomerizes to blue colored merocyanine when the PET fabric coated with the help of OTES or PhTES based precursor. Chemically the OTES/PhTES containing the methoxy groups which generally the electron donating in nature which are the prime reason for the hypsochromic shift of coated fabric from 610nm to 570nm. Apart from the electron donating groups, the polarity of the precursors in the OTES/PhTES major reason for the hypsochromic shift, since it is less than the precursor APS and it confirmed by the visual appearance of fabric under UV radiations. As per the Kellmann et al. [20] hypothesis, the ground-state weakly polar molecule of 5-chloro-1,3,3-trimethylspiro[indoline-2,3'-(3H) naphtho(2,1-b) (1,4)-oxazine] could approach to the configuration of quinoid form. The polarity of both precursors OTES/PhTES plays a vital role in terms of solvatochromism and it is sensitivity towards to the precursors polarity with respect to the electron donating groups of 5-chloro-1,3,3-trimethylspiro[indoline-2,3'-(3H) naphtho (2,1-b)(1,4)-oxazine]. Due to the precursors polarity, the energy level of ground state declines more sharply than the excited state. Therefore, the result shows the energy between two different merocyanines, which has been produced during the UV radiations.

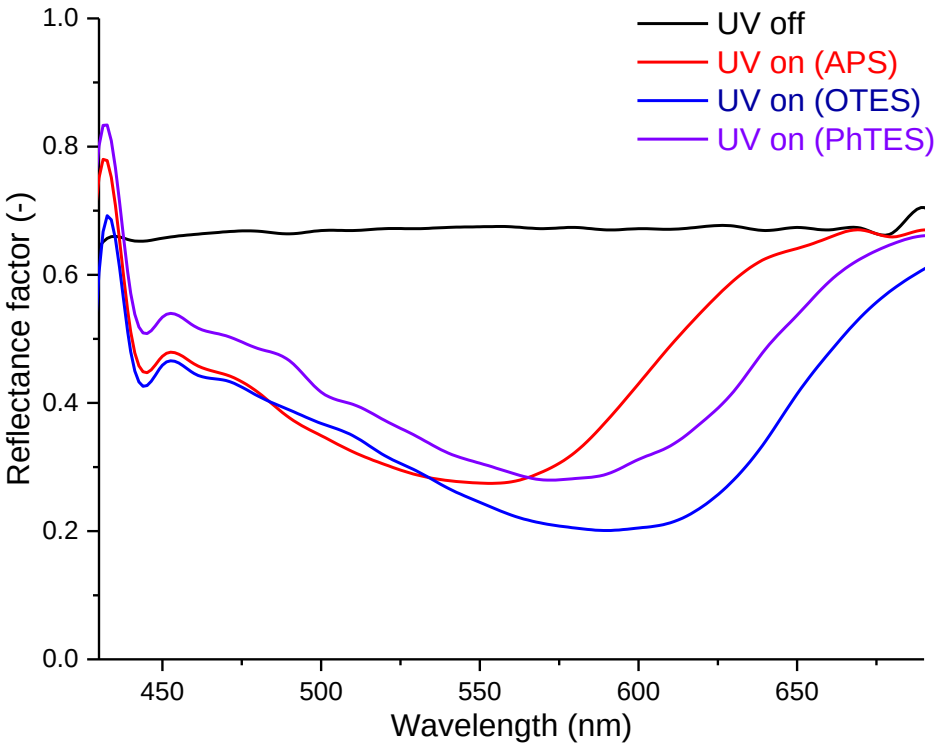

Figure 25: Reflectance spectra of coated fabric with different precursors (MPP-2.5%).

5.3.5 Flexural rigidity and bending modulus of coated fabrics

Flexural rigidity and bending modulus of fabrics are calculated and the results are depicted in Figure 26 and Figure 27 respectively. As a result, a significant increase in the stiffness is caused by APS, PhTES and combination of PhTES based sol-gel treatment. OTES is the only treatment which did not cause a significant increase in the flexural rigidity and bending modulus. The coating with OTES has the long aliphatic chain which ensures the softness of fabric without affect the fabric bending and flexural rigidity as like other precursors and its combinations. PhTES and APS coated fabric were observed higher bending modulus and flexural rigidity, which says that most rigid fabric. On the contrary, O:P (2:1) combination did not show higher bending modulus and flexural rigidity, whereas, P:O (2:1) has shown higher, the reason is the higher contribution of PhTES. In overall, if the precursors contain PhTES, phenyl groups containing PhTES increase the rigidness of coated fabric. Since, APS having the different chemical groups, therefore it is not used for statistical fit which is demonstrated in the Figure 26 and Figure 27. This results also confirmed by LSCM images. The results of APS coated fabric shown an increase in flexural rigidity and bending modulus, chemically APS containing the propyl groups which is purely rigid in structure, which is the prime reason for the increasing the rigidness of fabrics. In both the warp and weft direction, the increasing trend of flexural rigidity and bending modulus was found.

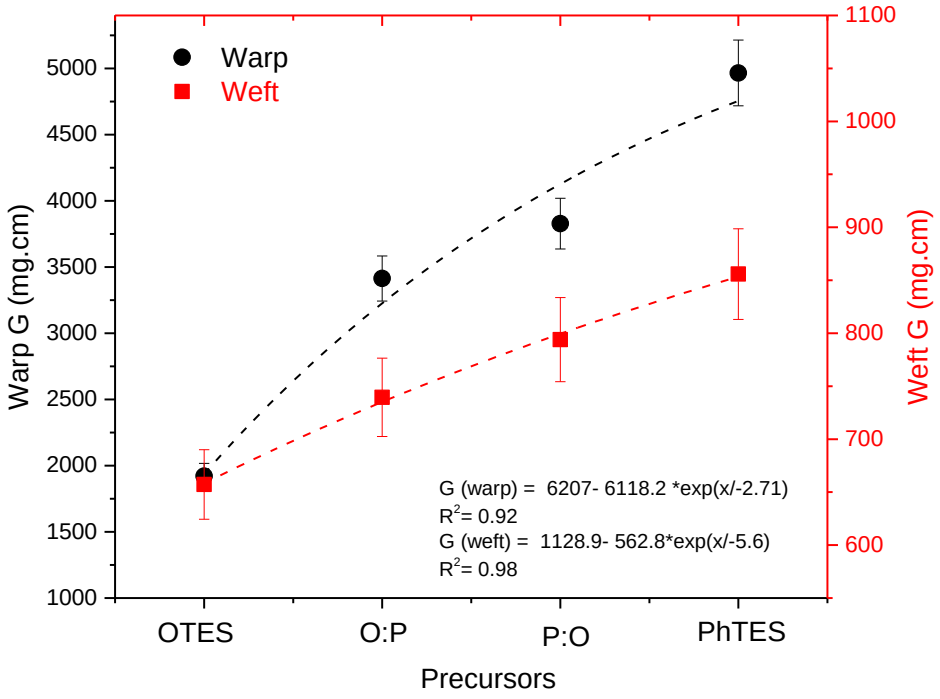

Figure 26: Flexural rigidity of sol-gel coated fabric (MPP-2.5 wt.%).

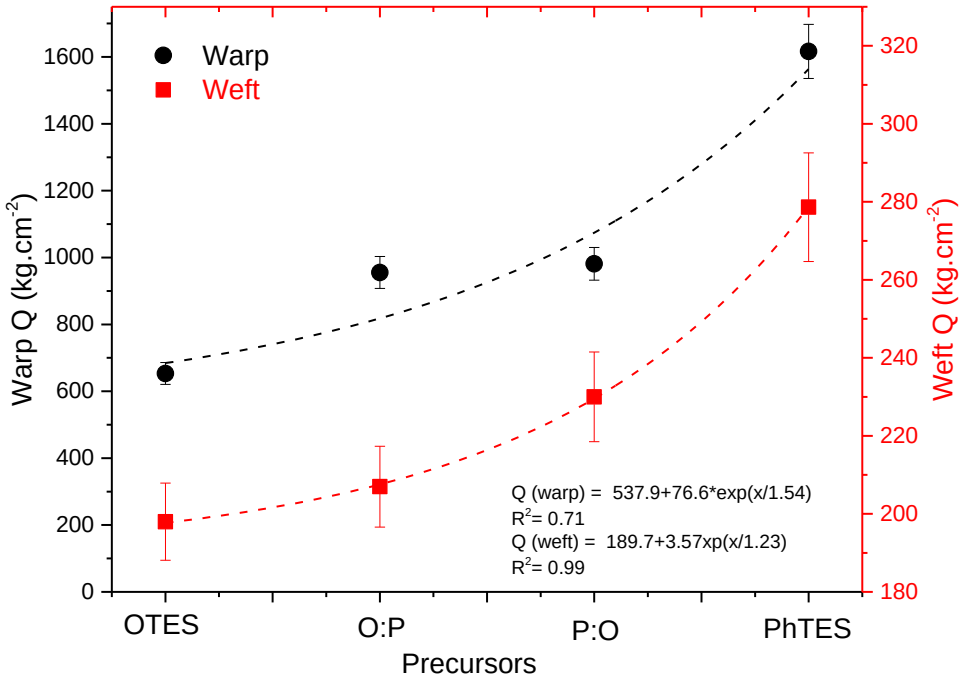

Figure 27: Bending modulus of sol-gel coated fabric (MPP-2.5 wt.%).

5.3.6 Surface morphological analysis on sol-gel coated fabric

The surface of coated and uncoated PET fabric samples was observed using SEM. Figure 28 shows the surface characteristics of PET fabrics with the different precursor. Uncoated PET (i.e. control sample) sample has plain surface without any deposition of chemicals. In

contrast, such characteristic completely disappeared on the surface of coated PET samples. It is apparent from the micrographs that a thin film was formed on the coated fiber surface and the film thickness increases by changing the precursor, as compared to another precursor, PhTES shows higher deposition of sols and it formed like film, since phenyl groups in the sol networks and makes thick film formation this is the main reason why it changes the handle and other physical properties of coated samples. In fact, all coated fabrics (i.e. fibers) are covered with a continuous layer of sols, these layer formation on the fiber surface could be confirmed that the pigments containing sols were successfully coated on the PET fabrics.

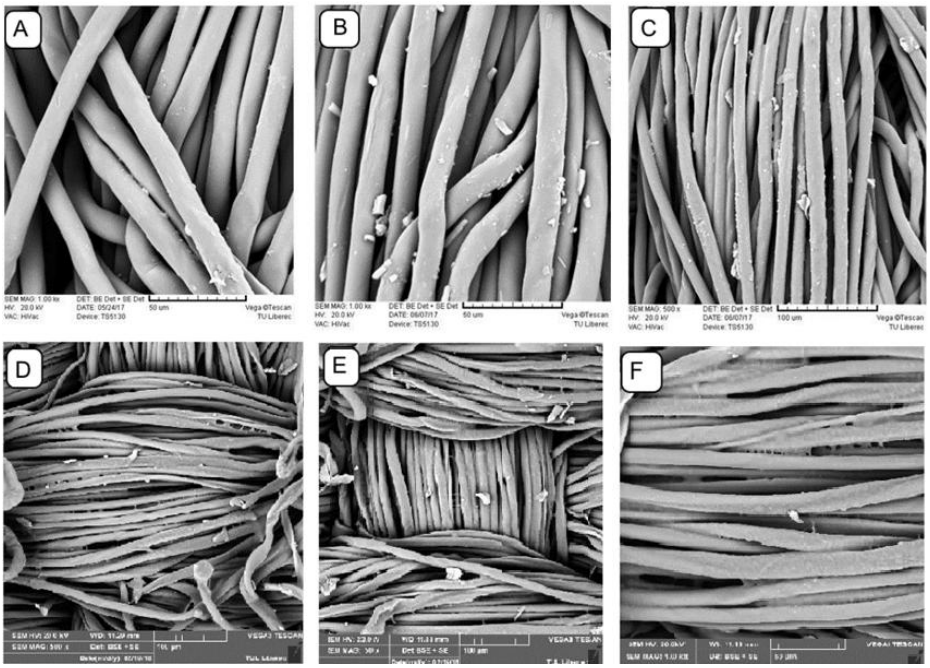

Figure 28: Surface morphological characterization of sol-gel coated fabric,
(A)-control PET fabric and modified with (B) OTES; (C) O:P (2:1); (D) P:O (2:1) (E) APS and (F) PhTES precursors (MPP-2.5 wt.%).

5.3.7 Surface roughness analysis on sol-gel coated fabrics

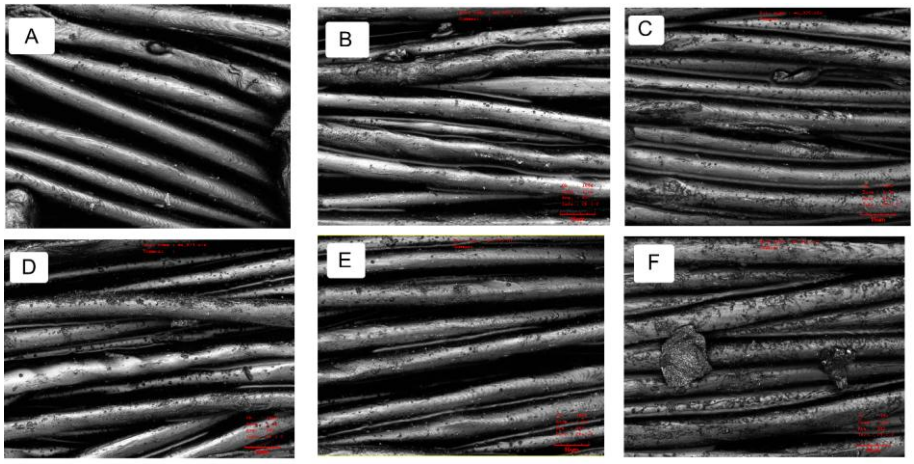

Figure 29: LSCM images photochromic fabrics with (A) control PET fabric and modified with (B) OTES; (C) O:P (2:1); (D) P:O (2:1) (E) APS and (F) PhTES precursors (MPP-2.5 wt.%).

The coated fabric shows different handle properties; consequently, it is necessary to analyze their surface characteristics. For visual scope, the LSCM images are given in the Figure 29 (A-F) and it shows the surface property of fabrics before and after the sol-gel coating. These pictures were confirmed that sol-gel coating made significant changes in the surface by creating the roughness. Sols prepared with PhTES and APS containing photochromic pigment made more roughness than the sols prepared OTES alone or its combinations, which is due to the chemical groups presented in the precursor and its structure. However, OTES having the flexible long alkyl chain groups provided the significantly less roughness, although APS could not produce the roughness as like PhTES or its combinations.

5.4 Kinetics response of photochromic change on a different substrate

The photochromic pigment was incorporated on two different substrates with different techniques which they are the mass coloration of miPP filaments and sol-gel coating on PET fabrics. To get a better idea of the application technology, it is required to compare both in terms of optical characteristics, which gives an immense idea regarding the techniques involved and the type of substrate.

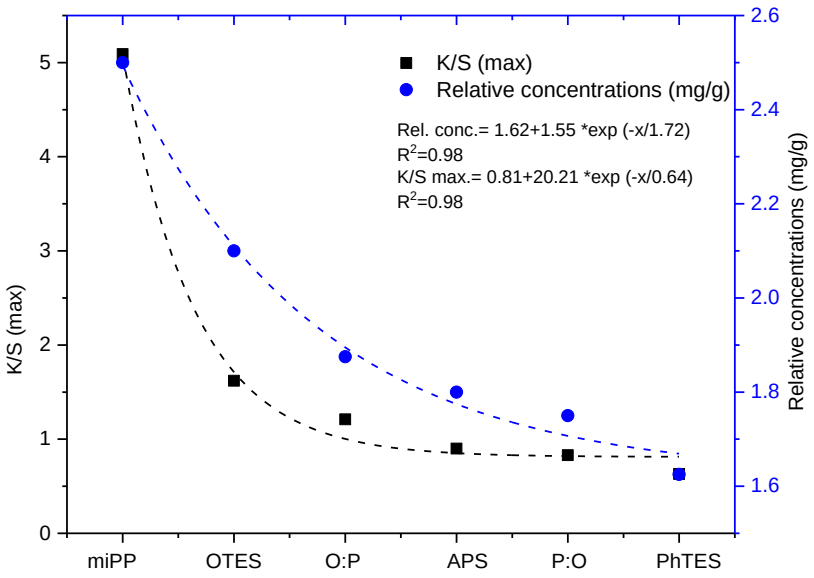

Figure 30: *K/S* (max) of photochromic textiles with different technique with respect to their relative concentrations.

Figure 30 describe the photochromic response for the mass colored miPP filaments and sol-gel coated PET fabrics, in this case, the same concentrations of pigment (i.e. MPP-2.5 wt.%) was used. Figure 30 shows the comparison results of photochromic textiles, among two different techniques, mass colorations produced a highest photochromic response. Overall the sol-gel coated fabric shows a lowest photochromic response in the all the case, also, the photochromic response is purely depending on the precursor types. Generally, in mass coloration, the pigments are mixed with the molten polymer solution, whereas in the sol-gel coating it just applied on the surface, secondly, the medium of the substrate is different in terms of their optical properties.

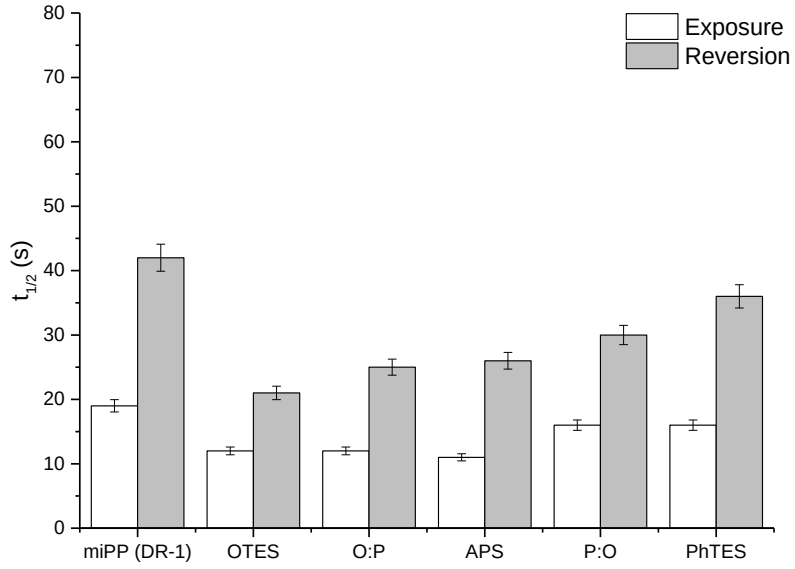

Figure 31: Half-life of color change photochromic textiles (i.e. MPP-2.5 wt.%).

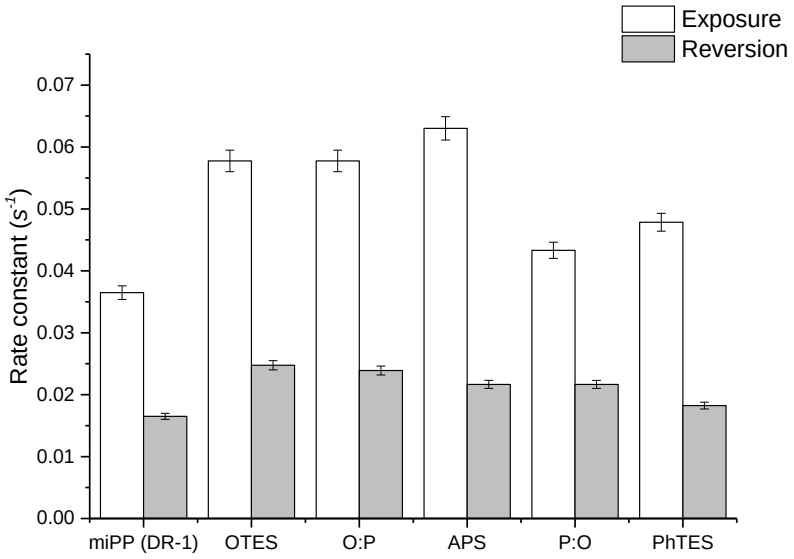

Figure 32: Rate constant of photochromic textiles (i.e. MPP-2.5 wt.%).

Figure 31 shows the half-life of color change for the MPP incorporated textiles and results of the rate constant of various photochromic textiles have been demonstrated in the Figure 32, the rate constant of sol-gel coated fabrics varies with respect to the precursors. Obviously, it is due to their size of the structure, size of the pore, which is directly proportional to the photochromic response, rate constant is one among it, however miPP filament has slow rate than the sol-gel coated fabric, the observed trend is same for both exposure and reversion phase. The predicted reason could be, the sol-gel coating can provide the thin layer on the surface of PET fabric along with the photochromic pigments, which is nothing but, the fabric has the photochromic pigments only on its surface, whereas the mass coloration provides the good penetration of the colors along with the polymeric structure. Therefore, the miPP

filaments required more time to undergo the molecular collision, which directly influenced on the lower speed of reaction (i.e. low rate constant) compared to the sol-gel coated fabrics. Among the sol-gel coated fabric, precursors like APS and OTES shows the highest rate than other fabrics.

6. Evaluation of results and new findings

On the basis of this research it was observed that, Kubelka-Munk functions are purely depending on the drawing ratios of produced photochromic miPP filaments, it is confirmed through the *K/S* values, that decreased with increasing the drawing ratio. The *K/S* (max) values for MPP incorporated miPP filaments with different cross-sectional, 8-star and 5-star cross-sectional filaments shows 63% and 72% less *K/S* values than the circular cross-sections respectively. The results trend is similar to all other pigments. So, it evidenced that the shape of cross-sections plays a vital role in the optical properties of produced miPP filaments. The *K/S* (max) and ΔOD values have been reduced with increasing the drawing ratio, it has the non-linear relationship between the drawing ratios of produced filaments. The residual ΔE^* values were observed to be maximum at ~2.5 units and minimum at ~0.02 units. With increase in drawing ratios, the residual ΔE^* values decrease and confirming that the drawing ratio which is lowest has highest residual ΔE^* values. With respect to the concentration of pigment and the drawing ratio the ΔE^* values significantly have nonlinear relationship. It is observed in all the three pigments that the residual ΔE^* values are marginally increased with increase in the concentration of pigment. In order to find the color difference, the prime intends to determine the residual ΔE^* values as the vision of humans able to identify the color difference due to the residual ΔE^* is more than 0.4 units. Henceforth, the drawing ratio which is lowest have the color difference to be highest can be easily visible by human vision. During the exposure, the color build-up was significantly increased with respect to the time, later on systems gets saturated with minor stabilization, this trend was observed in all the concentration as well as drawing ratios of the particular pigment. In case of reversion phase, significantly decreased with respect to the time. The observed trend is same for other pigment, only time requirement is different. Therefore, the positive acceleration of *K/S* values under UV exposure required less time than the negative acceleration of *K/S* under reversion phase. Generally, the stabilization causes the measured errors in the exposure phase shows higher than the reversion phase, which means that the error from reversion phase is invisible, this is due to the higher variability in exposure phase and lower variability in reversion phase. The half-life of color change for all three pigments in both exposure and reversion phase in the order of MPP>MPB>MPY. Due to the thermal degradations of pigment during the melt extrusion, with respect to pigment types the color build-up varies as then filaments with MPY 220% less *K/S* (max) values than filament with MPP even in the same concentration and also MPY pigment forms two transoid isomers of the quinoid forms during the isomerization which are the essential motive for the reduction of color build-up of MPY incorporated miPP filament. In case of thermogravimetric analysis, based on the chemical structure of the pigment, the degradation % is varied and it directly influenced on the dyability of the filaments. The changing of melting enthalpy is increased with increasing the drawing ratio, from 56.16 to 84.20 $J.g^{-1}$ for drawing ratio 1 and 4 respectively (i.e. without pigmentation).

Addition of pigment shows that there no much influence on the melting temperature of filament, however it varies the changing in enthalpy as well as the crystallinity %. With and without pigmentation, the longitudinal views of photochromic miPP filaments produced looks similar in the micrographs. Considering the different shapes of the filament, on the triangular and in 5-star there is a smooth surface and as in 8-star it contains some microfibers leading to generating the fibrillation on the surface. With the study of the cross-sectional view of the filament it is observed in case of 5-star shape there are some effects, some of the filaments never drawn, based on the size of other filaments in this group comparatively some filaments are larger than other filaments in the same groups.

Depending on the types of precursor the same concentration pigment derives different *K/S* values. Henceforth, depending on the usage of the type of precursor the *K/S* values are pure which is used in the sol-gel coating process. As of the observance of the results, the photochromic pigment and their optical properties are strongly influenced by the precursor. Compared to the sol prepared from APS & PhTES alone or its combinations, OTES and its combination produce higher photochromic response even though at the same concentration of photochromic pigment. With increase in the concentration of pigment, *K/S* (max) and ΔOD values are significantly increasing apart from them. As it is well known that the *K/S* (max) and ΔOD depends on the concentration of photochromic pigment. On other hand, *K/S* (max) and ΔOD is purely depending on the precursor and its combinations, due to the strong influence of precursor on the color strength values and followed by changes in the optical density. Due to the strong influence of the results, the color difference and half-life for color change of the coated fabrics depends on the precursors. Higher photochromic response is provided by the OTES based precursor based on the long flexible chains creating more pore space along with flexible silica network. Henceforth the photochromic pigment to undergo isomerization reactions without any interreference is allowed by it and also flexible octal chains surrounds the pores obtained by the OTES based precursors. Phenyl groups in PhTES lead to a more rigid pore shell due to the presence of long alkyl aliphatic chain and due to the phenyl groups are rigid in nature. In this work, the hypsochromic shift of ~40nm was observed (absorption maxima are shifted from 610nm to 570nm), when the fabric is coated with OTES/PhTES or its combinations with 5-chloro-1,3,3-trimethylspiro[indoline-2,3'-(3H) naphtho(2,1-b) (1,4)-oxazine], in case of APS coated photochromic fabric shows the original color. So, the coated fabric is under UV radiations, it turns to Blue color instead of its original color (i.e. Purple). From this result it is confirmed that the spectral and kinetic properties of sol-gel coated fabrics are purely affected by the polarity of precursors, which means, it affects the absorption spectrum of the colored form of merocyanine. With respect to the abrasion resistance and washing durability, the photochromic response was analyzed and the results depends on the precursors. By analyzing various physical properties in the case of thickness on the precursors there is a significant influence. APS PhTES and combination observed the increased stiffness of coated fabric. In the flexural rigidity and bending modulus, the treatment which does not cause a significant increase is OTES. With the different precursor surface morphology of PET fabrics is shown by the SEM characterization. Without the deposition of chemicals, the uncoated PET sample has a plain surface. On the contrary, on the surface of the coated PET samples such characteristic completely gets disappeared. By

creating the rough surface sol-gel coating made significant changes is confirmed by the LSCM pictures. It is shown that for the two different techniques of compared results of photochromic textiles, mass colorations produce the highest photochromic response than that of sol-gel coating. On the whole, in every case the sol-gel coated fabric shows lowest photochromic response and also the photochromic response depends on the precursor types purely. In general, the pigments are mixed with molten polymer solution in mass coloration, whereas in the sol-gel coating it just applied on the surface. the medium of substrate is different because of their optical properties. Comparatively, the rate constant for photochromic miPP show is less than the sol-gel coated fabrics and with respect to the precursors the rate constant of sol-gel coated fabrics varies. Evidently, it is directly proportional to the photochromic response due to their size of the structure, size of the pore at the rate constant which is one among them.

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8. List of Publications

Research Manuscripts

[1] Periyasamy Aravin Prince, Vikova Martina, Vik Michal. 2016. Optical properties of photochromic pigment incorporated into polypropylene filaments. *Vlakna a Textil* 23:171–178. *[Impact factor=0.3]*

[2] Vikova Martina, Periyasamy Aravin Prince, Vik Michal and Ujhelyiová Anna. 2017. Effect of drawing ratio on difference in optical density and mechanical properties of mass colored photochromic polypropylene filaments. *Journal of Textile Institute* 108:1365–1370. *[Impact factor=0.8]*

[3] Periyasamy Aravin Prince, Vikova Martina, Vik Michal. 2017. A review of photochromism in textiles and its measurement. *Textile Progress* 49:53–136. *[Scopus and Thomson Reuters included]*

[4] Seipel Sina, Yu Jhu, Periyasamy Aravin Prince, et al. 2017. Characterization and optimization of an inkjet-printed smart textile UV-sensor cured with UV-LED light. *IOP Conference Series of Material Science Engineering* 254:1–4. *[Scopus and Thomson Reuters included]*

[6] Periyasamy Aravin Prince, Vikova Martina, Vik Michal. Photochromic polypropylene filaments: Impacts of physical and mechanical properties on kinetic properties. *Fibers Textile Eastern Europe. Under review [Impact factor =0.45]*

[7] Periyasamy Aravin Prince, Vikova Martina, Vik Michal. Organosilica coated photochromic polyethylene terephthalate (PET) fabrics with their kinetic and physical properties. *Journal of Sol-Gel Science Technology. Under review [Impact factor =1.68]*

[8] Seipel Sina, Yu Jhu, Periyasamy Aravin Prince, et al. Optimization of an inkjet-printed smart textile UV-sensor cured with UV-light using production process parameters. *Applied Surface Science. Under review [Impact factor =3.44]*

[9] Seipel Sina, Yu Jhu, Periyasamy Aravin Prince, et al. Inkjet printing and UV-LED curing of a smart textile UV-sensor using photochromic dye. *Journal of Materials Chemistry C. Under review [Impact factor =5.96]*

Book Chapter

[10] Seipel Sina, Yu Jhu, Periyasamy Aravin Prince, et al. 2018. Resource-Efficient Production of a Smart Textile UV Sensor Using Photochromic Dyes: Characterization and Optimization. In: Kyosev Y, Mahltig B, Schwarz-Pfeiffer A (eds) Narrow Smart Textile. *Springer International Publishing*, Cham, pp 251–257

Book

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[12] Vik Michal, Vikova Martina, Periyasamy Aravin Prince. Influence of SPD on Whiteness value of FWA treated samples. *21st International Conference Light SVĚTLO 2015*, Brno Univ. Technol. Czech Republic, Vol. 1; 2015, p.5.

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Article: Viková M, Periyasamy AP, Vik M, Ujhelyiová A (2017) Effect of drawing ratio on difference in optical density and mechanical properties of mass colored photochromic polypropylene filaments. *Journal of Textile Institute* 108:1365–1370.

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Article: Periyasamy Aravin Prince, Vikova Martina, Vik Michal (2017) A review of photochromism in textiles and its measurement. *Textile Progress* 49:53–136.

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1. Babonneau Dina, Diop Beco, et al. (2018) Real-time investigations of structural and optical changes in photochromic Ag/TiO_2nanocomposite thin films under laser irradiation. *Nano Futures* 2:1, pages 015002.
2. Periyasamy Aravin Prince, Ramamoorthy Sunil, Rwawiire Samson, Zhao Yan (2018) Sustainable Wastewater Treatment Methods for Textile Industry. In: Muthu SS (ed) *Sustain. Innov. Appar. Prod.* Springer Singapore, Singapore, pp 21–87

9. Curriculum Vitae

PERSONAL INFORMATION

Aravin Prince Periyasamy

Harur, Dharmapuri, TN, India.
+420 775 48 60 50
aravinprince@gmail.com
http://aravinprince.weebly.com/
Sex Male | Date of birth 10/06/1983 | Nationality Indian

WORK EXPERIENCE

Aug 2011- Nov 2014 — *Assistant Professor*
DKTE Textile Engineering Institute, Ichalkaranji, MH, India
- Teaching and Research in the field of Textile chemical processing.
- Color chemistry, Chromic materials, Denim processing.

July 2007- July 2009 — *Production Executive*
Texport Syndicate, Bangalore, India
- Production & Research activities on denim processing textile dyeing.
- Sustainability in wet processing, LCA on denim processing.

May 2003- June 2004 — *Production Executive*
MS Dyeing House, Tirupur, India
- Handling with textile fabric dyeing and finishing.

EDUCATION

December 2014 – Dec 2018 — Ph.D in Textile Techniques and Material Engineering
Technical University of Liberec, Czech Republic.
- Working on the photochromic materials and their kinetics.
- Sol-gel coating, properties of photochromic materials.

Aug 2009 - July 2011 — Masters in Textile Technology
Anna University, Chennai, India.
- Developments in fiber formation, Advanced chemical processing.
- Sustainability in textiles, LCA, Green fashion.
- Defibrillation on Lyocell fiber.

July 2004 - July 2007 — Bachelors in Textile Technology
Anna University, Chennai, India.
- Fiber formation, Spinning, Weaving, Chemical processing, Garmenting.
- Sustainable processing.

PERSONAL SKILLS

Communication skills
- Good communication skills gained through my previous experiences.

Organizational managerial skills
- Leadership (Motivating & Inspiring my teams through positive attitude)
- Mentoring (Conducted the mentoring activity to group of my students).
- Organization (Conducted technical symposium and conference).

Digital competence
- Good command of office suite.
- Good command of statistical and analytical software's like Originlab, MATLAB, SPSS, Minitab, Graph pad and ANSYS.
- LCA software’s like Umberto GaBi, SimaPro and openLCA

10. Brief description of current expertise, research and scientific activities

Doctoral Studies: Full-time student at the Faculty of Textile Engineering, Department of Material Engineering.
Specialization: Material Engineering

Exams:

[1]. Optics of materials	(29-06-2015)
[2]. Structure and Properties of Fibers	(06-05-2015)
[3]. Textile Chemistry	(26-02-2015)
[4]. Mathematical Statistics and Data Analysis	(29-06-2016)
[5]. Experimental Technique of the Textiles	(12-06-2017)

SDE State Doctoral Exam completed on 04-12-2017 with the overall result passed.

Research Projects: Participant in SGS Project at 2015.

Research activities:

- Development of Photochromic textiles materials.
- Optical measurement and Kinetics of photochromic textiles.
- Sol-gel synthesis.
- Sol-gel coating on textiles with functional dyes.
- Sol-gel coating for protection.

Other activities:

- Contributed six book chapters, apart from dissertation topics.

11. Record of the state doctoral exam

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Fakulta textilní

ZÁPIS O VYKONÁNÍ STÁTNÍ DOKTORSKÉ ZKOUŠKY (SDZ)

Jméno a příjmení doktoranda: **Aravin Prince Periyasamy, M.Tech.**

Datum narození: **10. 6. 1983**

Doktorský studijní program: **Textilní inženýrství**

Studijní obor: **Textile Technics and Material Engineering**

Termín konání SDZ: **4. 12. 2017**

prospěl **neprospěl**

Komise pro SDZ:

		Podpis
Předseda:	prof. RNDr. Oldřich Jirsák, CSc.	
Místopředseda:	doc. Ing. Maroš Tunák, Ph.D.	
Členové:	doc. Ing. Ladislav Burgert, CSc.	
	doc. Ing. Ludmila Fridrichová, Ph.D.	
	doc. Ing. Tomáš Novák, Ph.D.	
	Ing. Michal Černý, Ph.D.	
	Ing. Jaromír Marek, Ph.D.	

V Liberci dne 4. 12. 2017

O průběhu SDZ je veden protokol.

12. Recommendation of the supervisor

Supervisor opinion on PhD thesis of Aravin Prince Periyasamy

I am writing this recommendation letter for Mr. Aravin Prince Periyasamy for his PhD defense. Mr. Aravin Prince Periyasamy has been a PhD research scholar under my supervision since 2015. Throughout his studies, I observed that he is highly intelligent and has good analytical skills.

The main aim of this PhD work is to find the impact of different drawing ratio on physical, mechanical and optical properties of mass colored photochromic isotactic polypropylene filament as well as the impact of the precursor on optical and physical properties of sol-gel photochromic coated PET fabrics.

The PhD thesis quite comprehensive and which satisfy the objects outlined in his thesis. The thesis has written clearly and according to the specified format with a high-level language. The candidate has done all his work systematically with specific objectives. Experimental data are in thesis is organized, analyzed logically and the results are discussed in an accurate manner. He has shown adequate ability to explain analytically to a various complex of scientific problems of photochromic incorporation in mass coloration as well as in the sol-gel coating. The results obtained from his thesis provides great importance not only scientific community also for the tycoons.

His publication is quite worthy and published four papers in impact factor journals (as far now, one more is accepted and one is under review), three book chapters, one book in esteemed publishers and seven articles in conference proceedings. By concluding this opinion, I can say from his work finds the relationship between the drawing ratio on the various optical properties of mass colored photochromic isotactic polypropylene filaments, which purely depends on. On another hand, the precursor plays a vital role in the optical and physical behaviour of photochromic textiles, in some case interesting effect called "hypsochromic shift" was found. In overall, the results are interesting, novelty and ready to use practically.

Therefore, I strongly recommend the thesis for the final defense.

Liberec, 12. June 2018

doc. Ing. Martina Vikova, Ph.D.
Supervisor

13. Opponent's reviews

Title of the dissertation: **Properties of Photochromic Textiles**

Author of work: **Aravin Prince Periyasamy, M.Tech.**

Referee: **prof. Ing. Radim Hrdina, CSc.**
Institute of Organic Chemistry and Technology
Faculty of Chemical Technology, University of Pardubice, Czech Republic

Opponent's review

The present dissertation deals with the incorporation of commercial photochromic dyes/ pigments into polypropylene by a process of mass coloration and the application of one dye /pigment by sol-gel process to the surface of PET fibers. The work is very useful for the textile industry because it basically solves the technology of preparing fabrics with photochromic dyes/pigments so that the correct optical effects are achieved.

Formally, the work is written very well by very good English and a reasonable range.

As far as the content is concerned, I will start with the introduction and the literary research part and the philosophy of the whole work. The author of the paper describes nicely the chemistry and photo-physical properties of the photo-chromic dyes and pigments, but the great weakness is that it does not distinguish whether it is a dye or a pigment. The situation is at present such that they are essentially disperse dyes, which are additionally photochromic, and there are very few compounds that are also photochromic in the solid (crystalline) phase - photochromic pigments. For dispersion dyes, it is assumed that inside the hydrophobic fiber is a form of “solid solution”; so that photo-chromic effect is present in individual molecules. On the contrary, pigments are dispersions of crystals inside (or on the surface) of the hydrophobic fiber. So I'll start with an explanatory question. The author used three photochromic compounds, MPB, MPP and MPY in his experiments. Are these compounds photochromic if they are just poured on the surface of the fabric? For polypropylene coloration in mass, the author writes that the pigment has been blended into molten polypropylene (page 35). Has a solution or dispersion been formed? On the contrary, in sol-gel technology (page 89), the author writes that a clear solution has formed which he applied to the surface of PET fabric. If this is true, this suggests that it is a "solid solution" where it is a photochromic of individual molecules.

In the scheme 2 (page 15) is a small error, the product of homolytic cleavage being two radicals.

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chemicko-technologická

The question of whether the pigment or dispersion dye is completely fatal for the photo-resistance (lightfastness) of these photochromic colorants, which is a major problem with the current photochromic compounds. By the way, due to the formation of a triplet excited state.

As for recommendations for future work in this field. And I'll start asking. Did the author of this dissertation work meet the dyes for natural (hydrophilic) fibers that would be soluble in water and would be photochromic after application to these fibers? This is one direction. The second direction is the photochromic of the pigment (photochromic effect in the solid state), as this could solve the problem of low lightfastness.

In conclusion, I can say that the work is very good and I therefore strongly **recommend the work for the defense.**

In Pardubice on 9.10.2018 .....

Prof. Ing. Radim Hrdina, CSc.

Aravin Prince Periyasamy, M.Tech.

PhD. Dissertation:
PROPERTIES OF PHOTOCHROMIC TEXTILES

Review

Dissertation submitted is divided into eight parts. The bottom-line of all of them is the extensive study of photochromic dyes. There are two materials thoroughly studied in the Dissertation. The first one, polypropylene, was used as the polymeric matrix. It was mixed with three commercial photochromic dyes (one with spiropyran skeleton and two with spirooxazine structures) shown on page 33. It is known, that polypropylene can be colored only through mass or spin coloration techniques. The second material to be coloured was PET fabrics using thin surface layer prepared from one photochromic pigment with the help of the sol-gel method.

To keep my review acceptably short, I will concentrate on the chemistry behind the coloration process dealing with the sol-gel photochromic fabric. This part is much more chemistry oriented and it is what I was looking for. It should be stressed that Disertation reports on immense amount of experimental work, mainly connected with the colorationm itself.

Consequently, I have several questions and remarks that follow.

1. The first remark is that I am missing very badly the detailed description of experixments that is usually called experimental part. Such part allows any reader to perform experiments successfully which should summarise the all experimental procedures. On page 35 and 89 we can find something called „process sequence“ and „sequencing process. These descriptions of both types of experiments are not sufficient. The same is true for description of dip coating method on page 85. Expression like „constant speed“ and „for a while“ can be found there.

2. On page 84, there are schematic representation of sol-gel coating method, followed by short description of chemistry behind it on pages 86 – 88 and finally, the whole process on page 89. The chemistry described is shown for dimers only. Is it so, that reaction goes to dimers stage and stops there? Could you show chemical reactions going on in the each step depicted there.

3. It would be also very important to fill all these reaction precisely up to the stage of polymers.

4. There are substantial difference between the structure of photochromic material based on polypropylene and PET as far as the bonds formed are concerned. Could you discuss this in more details.

5. On page 117 the surface roughness characteristics of coated fabric are given. Frankly, I am unable to see any substantial changes among figures 78A – 78F. Could you also estimate, how many molecules of MPP photochromic dyes would fit to max. peak hight shown in Table 16.

6. Could the theoretical (quantum) chemistry be of some help in the study you have described in Dissertations?

Finallly, I can conclude, that Dissertation reports on many experiments done, most of them are carefully interpreted and used for building up the general picture of photochromic textile preparation, structure and application potential.

I am in the position to r e c o m m e n d the Dissertation in question for further process leading to PhD degree.

In Liberec, 29. 10. 2018 Prof. Ing. Ivan Stibor,CSc.