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Characteristic Properties of Unmodified Polypropylene Fabric Dyed with Pigment Dyes in Aqueous Medium for Medical Uses

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AN easy and direct method was adopted for dyeing unmodified polypropylene (PP) fabric using pigment dyes blue15 and green 7 in aqueous medium. The dyes are based on phthalocyanine groups containing copper in their chemical structure in presence of 2 % anionic dispersing agent and are used for dyeing PP at high temperature (100-115 °C). The dyeing parameters include dye concentration, dyeing time and temperature were studied. Color strength (K/S) and colorimetric data (L*, a* and b*) were evaluated at specific λ_{max}355. In addition washing and light fastness were determined for PP dyed fabric. Antibacterial activity of pigments blue15 and green 7 dyed PP fabric against *S-aureus*, *E-coli* and *C-candida* were evaluated by optical density method. SEM, EDX and FTIR were performed for PP pigment blue 15 dyed fabric. PP dyed fabric with pigment dyes is useful for making staff coat uniforms, patients and others products such as mattress covers, bed sheets in clinics and hospitals. This method for dyeing PP fabric will prevent propagation of diseases in these medical places and the excess can be exported abroad.

Keywords: Polypropylene fabric, Pigment dyes, Aqueous medium, Antibacterial activity.

Introduction

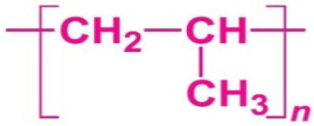

Fig. 1. Chemical structure of Polypropylene.

Polypropylene (PP) is a low price fabric, has chemical resistance and excellent mechanical properties [1]. PP is used in different hygienic and medical applications such as hospital uniforms, bed sheets, surgical masks, diapers, burns, wound healing dressings and hygiene bands. PP has the disadvantages of being hydrophobic in nature, inactive synthetic fabric due to the absence of reactive functional groups in its molecular structure, thus preventing its dyeability [2]. For the above reasons, PP fiber is first modified by different irradiation methods to form free radical centers onto the surface and then graft copolymerization of vinyl monomers and finally dyeing. Different irradiation techniques are used such as plasma discharge, electron beams, ozone, UV, γ- rays and others [1, 2].

PP can be grafted after irradiation with selected monomers including methacrylate derivatives such as 2N -Dimethyl amino ethyl methacrylate [3], 2N- morpholino ethyl methacrylate [4], 2-ethyl methacrylate phosphoric acid [5], 2- hydroxy ethyl methacrylate) [6] acrylic acid [7,9] etc...

Literature review revealed that the chemical structure of nano-clay had produced dye site in nano composites [10]. PP films were dyed using a disperse dye with acceptable fastness and shade which are related to the clay content. PP fibres dyeable with natural dyes were produced with the incorporation of hyper branched polymer (HBP) using melt spinning technique [11]. Bi-functional hydrophobic disperse hydrazonyl cyanide dyes were synthesized and used for dyeing PP under aqueous and supercritical carbon dioxide [12].

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Plasma discharge device is an eco- friendly, dry process, which is usually used for activation of polymers without affecting the bulk properties [13]. Atmospheric pressure plasma and low pressure plasma are well known techniques for enhancing dyeability PP. A plasma discharge exposure of PP fabric followed by grafting monomers results in excellent dyeing properties [14-18].

In this investigation, two hydrophobic pigment dyes were chosen such as pigment blue 15 containing copper and pigment green 7 having copper and chlorine in their chemical structure [17], for dyeing hydrophobic and untreated polypropylene. The dyed PP fabric has antibacterial activity due to presence of copper in the dyes structures.

The dyed PP fabric can be used for staff and patients uniforms in hospitals to prevent infection by diseases.

Materials and Methods

Materials and chemicals

Fabric

Nonwoven polypropylene fabric, needle punched and weighing 26.7 per m^2 was supplied from Egyptex Co. as a gift Cairo, Egypt.

Chemical reagents

An anionic dispersing agent (Setamol WS, BASF) was used during the dyeing process. A nonionic detergent (Triton X-100) was used in soaping and washing fastness tests.

Dyes

Powder pigment dyes blue 15 and green 7 were supplied from the Indian Saya & Friends Co. (Ahmedabad) as follows:-

1. Alfa Pigment blue 15 powder, CI no. 74160, chemical composition: $C_{32}H_{16}N_8Cu$
2. Pigment green 7 powder, CI no. 74260, chemical composition: $C_{32}O_{0\text{-}1}N_8Cl_{15\text{-}16}Cu$

Methods

Dyeing Method

The dyeing of nonwoven and unmodified PP fabric was done in aqueous medium. Dyeing process was carried out in a laboratory-scale HT thermal dyeing machine (Roachs Co. England) using liquor to good ratio 50:1, concentration of dye (1, 2, 3, 4%) on weight fabric (owf) were dissolved in water. Then 2 gm. nonwoven PP fabric (10×10 cm) was introduced into the dyeing machine cups with 2 % anionic dispersing agent (Setamol). The temperature was raised from 35°C to (100, 105, 110, 115°C) respectively for a period of 30 min., and the dyeing process was continued at the above temperatures for (30, 60, 90 and 120 min. respectively). After dyeing, the samples were soaped in a bath containing 2% nonionic detergent at a temperature of 50°C for 30 min., then rinsed with water and dried at room temperature.

Colorimetric measurements

Color strength (K/S):

Color strength (K/S) in the visible region of the spectrum (400- 700 nm) was calculated based on Kubelkae– Munk equation:

$$\mathbf{K/S} = \frac{(1-R)}{2R} - \frac{(1-R_0)}{2R_0}$$

R = Decimal fraction of the reflectance for PP dyed fabric.

R_0 = Decimal fraction of the reflectance for the undyed fabric.

K = Absorption coefficient.

S = Scattering coefficient.

The colorimetric properties of PP dyed fabric were measured with a Hunter Lab DP-9000 Color-Spectrophotometer

Color data CIE LAB space

The total difference CIE (L*, a*, b*) was measured using the Hunter-Lab spectrophotometer (model: Hunter Lab DP-9000).

CIE (L*, a*, b*) between two colors each is given in terms of L*, a*, b* is calculated from:

L* value: indicates lightness, (+) if sample is lighter than standard, (-) if darker.

a* & b* values: indicate the relative positions in CIE Lab space of the sample and the standard, from which some indications for the nature of the difference can be seen.

Antibacterial test

The antibacterial and antifungal studies of treated fabric were accomplished in triplicates according to standard methods (AATCC TM100).

The treated fabric (0.5 g) was introduced into 20 ml nutrient broth and inoculated with the respective bacterial strains followed by overnight (24 hrs) incubation at 37^oC. Growth of the bacterial strain was determined spectrophotometrically (OD 660) in presence of the treated fabric against a blank of un-inoculated sterile medium. Similarly, the fungal strains inoculated into potato dextrose broth was incubated for 48 hrs at 28^{o}C in a shaker incubator followed by measurement of (OD 450) against a blank of un-inoculated sterile medium. Before recording the OD of the respective media after incubation, the culture tubes were shaken thoroughly in order to bring microorganisms into suspension.

Optical density is directly proportional to the number of microorganisms (bacteria or fungi) in the medium. The percentage of reduction of the microorganisms was expressed as follows.

R = (B - A)/B x100

where; R, percentage of reduction of microbial population; B, absorbance of the media inoculated with microbes and A, absorbance of the media inoculated with microbes and treated fabric.

Fastness testing

Washing fastness

Color fastness to washing was determined according to ISO 105-C01:1989 (E) test method. The washing fastness test was conducted in a Launder Ometer (ATLAS–Germany) using 5g/L nonionic detergent at 50^{o}C for30 min. and liquor ratio 1:50. The composite specimen was removed, rinsed with running tap water, squeezed, then opened and dried in air. It included the test specimen and the two adjacent fabrics in contact of the main sample. Gray scale was used to assess the color change of the dyed sample and the staining of the two adjacent white fabrics (cotton and wool).

Light fastness

This test was evaluated according to ISO 105-B02: 1988 test method using a xenon lamp. Samples were exposed to a continuous light for 35 hours in order to determine the degree of color resistance to photo- degradation light.

Scanning Electron Microscope (SEM) and Energy Dispersive X-ray (EDX)

The fabric was well washed with distilled water to remove the unattached particles and then dried before SEM determination. The fabric was measured on SEM (Quanta FEG 250, FEI Co.) working at 20 KV. Then, the fabric was coated with carbon double face and fixed with stubs of Quanta holders and examined in low vacuum.

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectrometer (Nicolet Magna-IR 560) was used to analyze the spectrum. The transmittance between 400 and 4000 cm^{-1} was recorded for the 15 blue pigment dye onto PP.

Results and Discussions

Effect of dye concentration on color strength and colorimetric data of polypropylene fabric dyed with pigment dyes

Figure 2 represents the effect of dye concentration on the color strength of pigments dyed nonwoven polypropylene fabric. It can be concluded that the color strength (K/S) of polypropylene fabric dyed with 15 blue

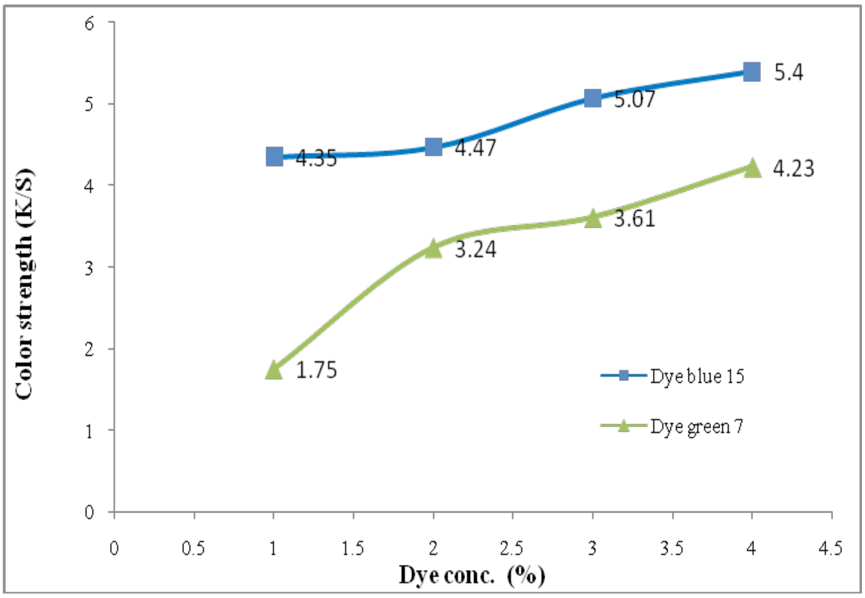


Fig. 2. Effect of pigment dye concentration on color strength of dyed polypropylene fabric.

pigment dye is higher than the color strength of polypropylene fabric dyed with 7 green pigment dye. Also, the color strength of polypropylene fabric dyed with 15 blue pigment dye and 7 green pigment dyes is increased with increasing the dye concentration.

Table 1 shows the results of L*, a* and b* of polypropylene fabric dyed with 15 blue and 7 green pigment dyes using different concentrations (1-4% dye).

From the results of L* values, it can be concluded that polypropylene dyed fabric becomes darker with increasing the dye concentration (1-4 %) for both pigment dyes. The fabric dyed with 15 blue pigment dye are darker than the fabric dyed with the 7 green pigment dye. Also, the results of a* and b* values for the fabric dyed with 15 blue pigment dye is shifted towards the blue co-ordinate in green blue zone of CIE Lab color space, while the fabric dyed with 7 green pigment dye is shifted towards green co-ordinate in green blue zone of CIE Lab color space.

The effect of dyeing temperature on color strength and colorimetric data of polypropylene fabric dyed with pigment dyes

Figure 3 illustrates the effect of dyeing temperatures on the color strength of dyed nonwoven polypropylene fabric. It can be concluded that the color strength of polypropylene fabric dyed with 15 blue pigment dye is higher than the color strength of polypropylene fabric dyed with 7 green pigment dye. Also, the color strength of polypropylene fabric dyed with 15 blue pigment dye and 7 green pigment dye is increased with increasing the dye concentration.

Table 2 represents the results of L*, a* and b* of polypropylene fabric dyed with 15 blue and 7 green pigment dyes using different dyeing temperature (100-115°C). The results of L* values has indicated that polypropylene dyed fabric becomes darker by increasing the dyeing bath temperature for PP fabric dyed with both pigment dyes. The color of PP fabric dyed with 15 blue pigment dye becomes darker than the fabric dyed with 7 green pigment dye. Also, the results of a* and b* values for PP fabric dyed with 15 blue pigment dye is shifted towards the blue co-ordinate in blue green zone of CIE Lab color space. While the fabric dyed with 7 green pigment

TABLE 1. Effect of pigment dye concentration of dyed PP fabric on colorimetric data at λ_{max} 355.

Dye concentration %	Blue dye15, λ_{max}			Green dye 7, λmax		
	L*	a*	b*	L*	a*	b*
1	52.13	-12.93	-33.45	62.56	-12.65	-23.80
2	51.15	-12.70	-32.86	55.42	-13.25	-30.69
3	49.40	-11.56	-34.82	54.10	-12.81	-31.72
4	49.38	-11.83	-35.73	51.91	-12.64	-32.84

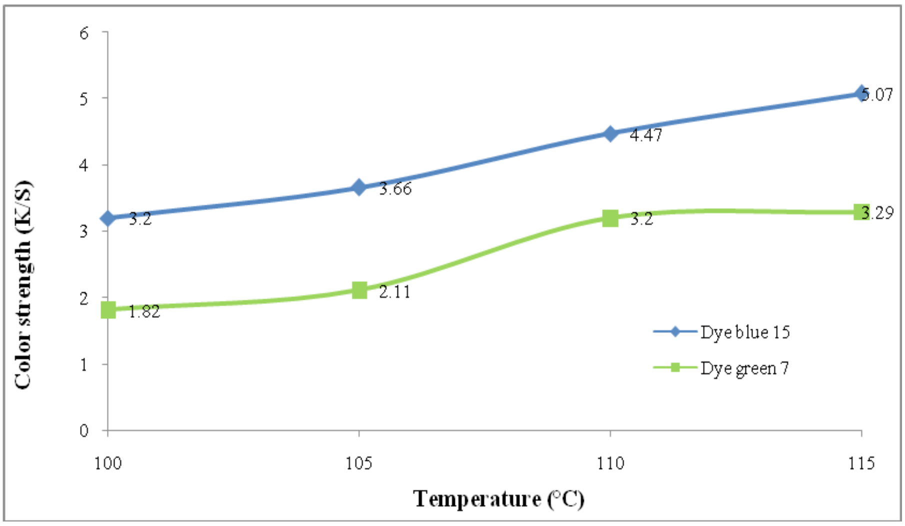


Fig. 3. Effect of dyeing temperatures on color strength of pigment dyed polypropylene fabric.

TABLE 2. Effect of dyeing temperature on dyed PP fabrics.

Dyeing Temperature	15 Blue dye			7 Green dye		
	L*	a*	b*	L*	a*	b*
100 °C	54.85	-12.92	-29.08	67.41	-35.56	2.66
105 °C	53.2	-13.7	-28.62	67.04	-30.77	1.97
110 °C	51.15	-12.70	-32.86	66.95	-26.43	1.84
115 °C	48.50	-11.22	-34.21	62.99	-37.49	1.83

dye is shifted towards the green co-ordinate in green yellow zone of CIE Lab color space.

Effect of dyeing time on color strength and colorimetric data of polypropylene fabric dyed with pigment dyes

Figure 4 clarifies the effect of dyeing time on the color strength of dyed nonwoven PP fabric. It shows that the color strength of PP fabric dyed with 15 blue pigment dye is higher than the color strength of PP fabric dyed with 7 green pigment dye. Also, the color strength of nonwoven PP fabric dyed with 15 blue pigment dye and 7 green pigment dye is increased with increasing the dyeing time.

Table 3 shows the results of L*, a* and b* of nonwoven PP fabric dyed with 15 blue and 7 green pigment dyes using different dyeing times (30-120 minutes). The results of L* values demonstrates that polypropylene dyed fabric becomes darker by increasing the dyeing time of nonwoven PP fabric for both pigment dyes. The color of nonwoven PP fabric dyed by 15 blue pigment dye was darker than the fabric dyed with 7 green pigment dye. Finally, the results of a* and b* values for nonwoven PP fabrics dyed with 15 blue pigment dye is shifted towards the blue coordinate in blue green zone of CIE Lab color space. The fabric dyed with 7 green pigment dye is shifted towards the green coordinate in green yellow zone of CIE Lab color space.

Effect of antimicrobial activity of PP fabric dyed with pigment dyes

The antibacterial activity in Table 4 of nonwoven PP fabric with 3% pigment dyes shade such as blue 15 which was revealed by optical

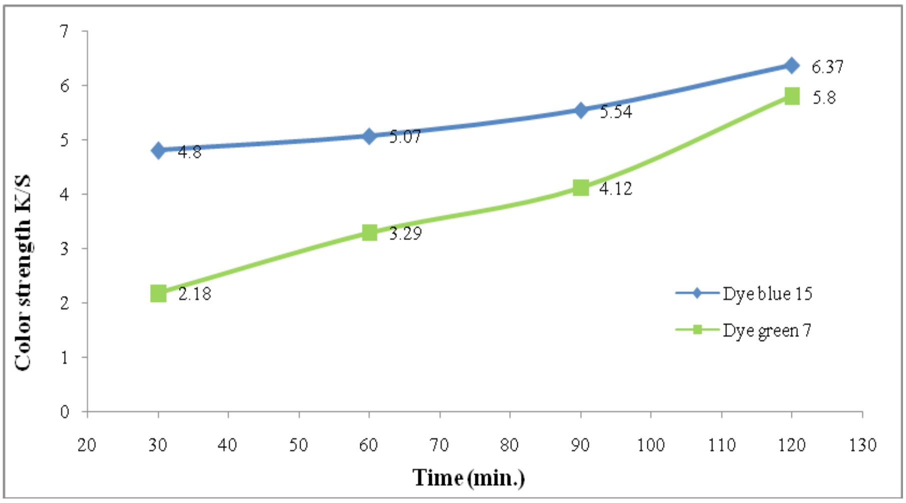


Fig. 4. Effect of dyeing time on color strength of pigment dyed fabric.

TABLE 3. Effect of dyeing time on colorimetric data.

Dyeing Time (minutes)	15 Blue dye			7 Green dye		
	L*	a*	b*	L*	a*	b*
30	49.40	-11.56	-34.82	62.99	-37.49	1.83
60	48.50	-11.22	-34.21	61.52	-40.27	3.38
90	47.26	-9.75	-35.33	60.25	-38.84	3.28
120	46.26	-10.90	-36.76	58.11	-44.80	3.77

density tests (OD) and gave excellent 100% reduction activity against *E-coli* and *C. candida*, but only a reduction of 44% against *S. aureus* was obtained. This is explained by the content of copper in the 15 blue pigment dye. While the 7 green pigment dye showed only 22% reduction for *E-coli* and was inactive against *S. aureus*, and *C. candida* [20].

Effect of fastness properties of PP dyed fabric with pigment dyes

Table 5 illustrates color fastness properties of dyed nonwoven PP fabric for the two pigment dyes (15 blue pigment dye and 7 green pigment dye). By comparison of the colorfastness properties for the two dyes, it is clear that color fastness to washing is very good to excellent, while color fastness to light is excellent. These results are similar for nonwoven PP fabric dyed with the two 15 and 7 pigment dyes.

SEM and EDX of PP 15 blue dyed fabric

Figures 4 (a, b) and 5 of SEM and EDX for PP 15 blue dyed fabric confirmed the presence of Cu, N and C in the dyed PP fabric with pigment 15 blue, which is an indication of the presence of the molecular elements of 15 blue pigment dye. The presence of oxygen in EDX is due to partial oxidation of the original undyed PP fabric.

TABLE 4. Effect of Antibacterial activity of PP fabric dyed with pigment dyes.

Dyed fabric	*S. aureus*	*E. coli*	*C. Candida*
15 Blue pigment dye	44	100	100
7 Green pigment dye	0	22	0

TABLE 5. Effect of fastness properties of PP fabrics dyed using pigment dyes.

Dyed fabric	Washing fastness			Light fastness
	Alt	St*	St**	
15 Blue pigment dye	4	4-5	4-5	6
7 Green pigment dye	4	4-5	4-5	6

St.* staining on cotton St. ** staining on wool Alt. alteration

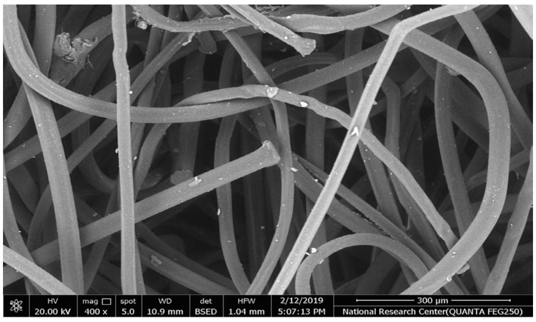


Fig. 4 (a). SEM of PP dyed fabric usingusing 15 blue pigment dye (400 x).

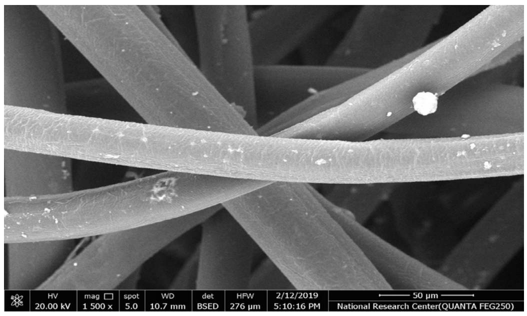
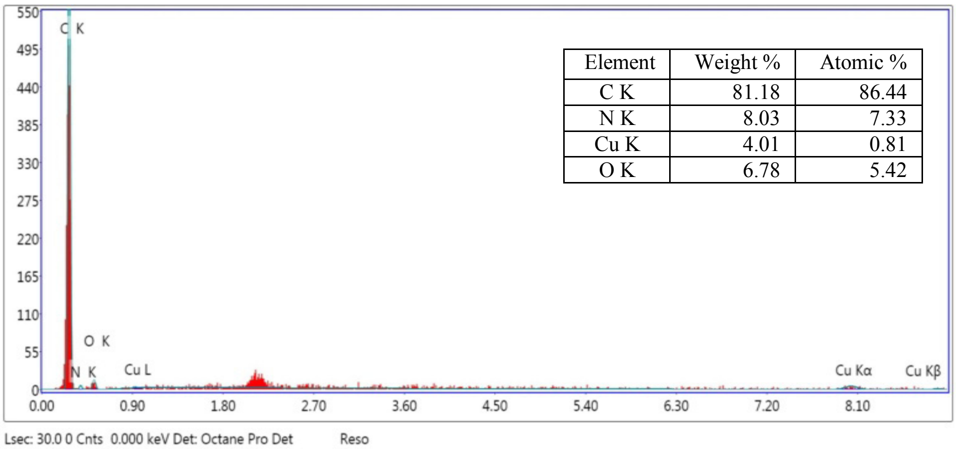


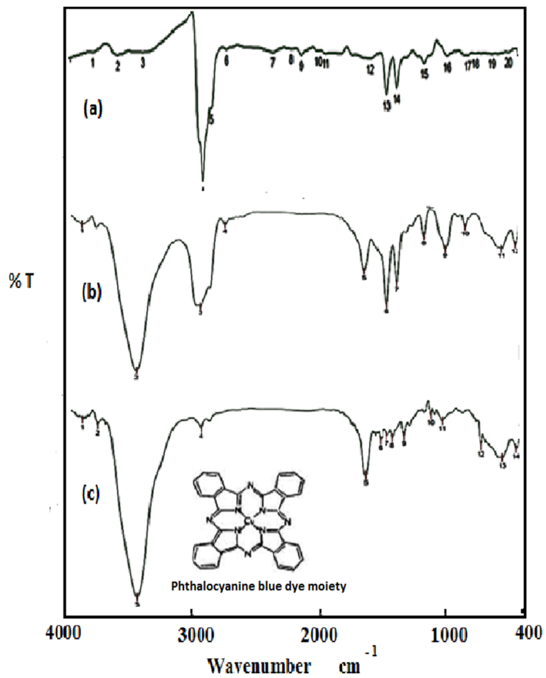
Fig. 4 (b). SEM of PP dyed fabric using 15 blue pigment dye (1500 x).

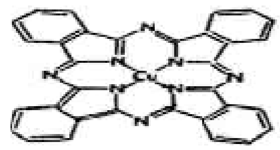


Element	Weight %	Atomic %
C K	81.18	86.44
N K	8.03	7.33
Cu K	4.01	0.81
O K	6.78	5.42

Fig. 5. EDX of PP dyed fabric using 15 blue pigment dye .

Fourier Transform Infrared Spectroscopy (FTIR)





Phthalocyanine blue dye moiety

Fig. 6. (a) FTIR analysis of PP fabric, (b) PP fabric dyed using pigment blue 15 and (c) 15 blue pigment dye (Wave number cm^{-1}).

From Fig. 6 a, b and c for FTIR, it can be noticed that the important peaks are observed at the following values: Cu at 440.65, 547, 719 cm^{-1}, Aromatic C-C stretch bond and C-H bonds in benzene ring at 1165.76, 1458.89, 1635.34 and 1331.61cm^{-1}.

Conclusion

Polypropylene fabric has low price, excellent chemical and mechanical resistance properties. But, PP is difficult to be dyed by normal dyestuffs due to the absence of polar active groups in its chemical structure. For this reason PP must be modified by physical means followed by grafting selected monomers. In this investigation, an easy method was adopted for dyeing PP using 15 blue pigment and 7 green dyes at high temperature. The dyed PP fabric acquired high fastness properties to washing and light.

Dyed PP fabric using 15 blue pigment dye is antimicrobial active and gave 100% reduction for *E-coli*, *C. candida* and 44% for S. *aureus* due to the presence of copper in its molecular formula and can be used for staff and patients uniforms, mattress covers and bed sheets in hospitals and the excess exported abroad.

SEM and EDX have confirmed the presence of the molecular elements of 15 blue pigment (C, N and Cu). FTIR revealed the dyeing of PP by 15 blue pigment dye.

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الخواص المميزة لأقمشة البولي بروبيلين الغير معالجة والمصبوغة بصبغات البيجمنت فى الوسط المائى للاستخدامات الطبية

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شعبة بحوث الصناعات النسجية - المركز القومى للبحوث - القاهرة - مصر.

أجريت دراسة حديثه لصباغة أقمشة البولي بروبيلين الغير منسوجة والغير معالجة كيميائيا بطريقه مباشرة وعاديه بأستخدام صبغات البيجمنت ١٥ و البيجمنت الخضراء ٧ في وسط مائى وتحت ضغط ودرجات حرارة عالية. وقد أشتمل البحث على دراسة بعض العوامل المؤثرة على عملية الصباغة مثل تركيز الصبغة ودرجة الحرارة وزمن عمليه الصباغة. كما تم قياس مقاومة الاقمشة المصبوغة لبعض انواع البكتريا مثل: *S-aureus.*, *E-coli*, *C-Candida* وقد أعطت أقمشة البولي بروبيلين المصبوغة بصبغة البيجمنت الزرقاء ١٥ مقاومة ممتازه للبكتريا، مقارنه بالأقمشة المصبوغة بصبغة البيجمنت الخضراء ٧. ويرجع السبب لأحتواء صبغة البيجمنت الزرقاء ١٥ على عنصر النحاس بكميه كبيرة وملحوظه فى تركيبها الكيميائي. واهتم البحث بقياس البيانات اللونية وشدة اللون (K/S) للأقمشة المصبوغة بالأضافه لقياس مقاومتها للغسيل والضوء. واثبتت التجارب المعملية سهوله صباغه أقمشة البولي بروبيلين والذي يعد من أرخص الأقمشه في السوق، بطريقة مباشره بأستعمال صبغات البيجمت بعمق لون يتروح بين ١-٤٪ وعند درجه حرارة عالية تتراوح من ١٠٠-١١٥°م وأعطت الأقمشة المصبوغة مقاومة كبيرة للغسيل والضوء. ويمكن استخدام أقمشة البولي بروبيلين المصبوغة بالطريقة السابقة بدلا من إستيرادها من الخارج لتوفير العمله الصعبه. وتستخدم هذه الاقمشة لتصنيع ملابس الاطباء والمرضى والعاملين في المستشفيات والعيادات الخاصة وكذلك فى تصنيع غطاءات مراتب الأسرة لمقاومة ومنع انتشار الميكروبات في هذه الأماكن وكذلك تصدير الفائض منها للخارج.