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Dyeing of PET Fibers in Ionic Liquids

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***Abstract*—The dyeing of textile materials is still accompanied with several economic and ecological disadvantages resulting in a high consumption of water, energy and chemicals. In particular the dyeing of polyester fibers (PET) - beside cotton the most important fiber type - is accompanied with additional disadvantages, because it needs high process temperatures of more than 130 °C enabling the disperse dye stuffs to penetrate the fiber matrix above the glass transition temperature of PET. Therefore, an aqueous dyeing liquor would evaporate if open systems were used. Due to this, in praxis the dyeing of PET fibers is carried out in special pressure vessels, which results in another cost intensive factor. Thus, since many years textile researchers around the world are looking for alternative dyeing techniques for all kind of fiber types but especially for PET. In this context, ionic liquids (IL) can play an important role. IL are salts with a melting point lower than 100 °C and they are often thermo-stable far beyond 200°C. IL excel by their extremely low vapor pressure, which makes them easy to handle in contrast to typically used organic solvents. Moreover, IL show high and temperature related dielectric constants, therefore showing outstanding solvent power for different textile-related substances, such as cellulose, keratin, and silicones. In addition, preliminary work at DTNW has shown that IL are suitable as dyestuff medium for textiles (e.g. for disperse dyestuffs, cationic dyestuffs, reactive and metal complex dyestuffs). Now, the DTNW has developed an innovative operational technique to dye various fibers in IL. This has been systematically investigated for the commercially most important fiber PET. Our dyeing procedure allows a pressure-free dyeing at high temperatures with minimal air pollution, which enables the textile industry in future to carry out their business with new methods avoiding high consumption of energy, water and chemicals.**

***Index Terms*—Dyeing, Ionic Liquids, PET, Polyester, Textiles.**

I. Introduction

The dyeing of textile materials is one of the most important finishing processes and looks back on a several thousand years old tradition. For instance, in ancient Egypt, Greece, and Rome chromophore natural materials such as indigo, Tyrian purple or henna were used, which were produced by complex processes. Thus, in former centuries gaudy clothing and accessories were only available for the prosperous society. Nowadays, more or less all textile products are dyed. This is due to many important discoveries and developments starting in the middle of the 19^{th} century, which results in the production of the first synthetic dye stuffs, e.g. azo dyes and synthetic indigo. Today, synthetic dyes for the dyeing of all known natural and synthetic fiber materials are available in manifold colors and shades. Prominent examples are reactive dyes, direct dyes, vat dyes, disperse dyes and acid resp. basic dyes. Depending on the dye category and the textile substrate to be dyed different water based dyeing processes exists, which are all accompanied with the following economic and ecological disadvantages:

- high process water demand,
- therefore, high quantities of waste water,
- high energy demand (e.g. for drying the textile after dyeing),
- high demand on auxiliaries and
- necessity of waste water treatment

Especially the dyeing of polyester fibers with disperse dyes - beside cotton the most important fiber type - is accompanied with additional disadvantages, because it needs particular high process temperatures of more than 130 °C enabling the dyestuffs to penetrate the fiber matrix above the glass transition temperature of polyethylene terephthalate. This means, that the aqueous dyeing liquor would evaporate if open systems were used. Therefore, in praxis the dyeing of polyester fibers takes place in special complex and, therefore, expensive apparatuses under pressure, which results in another cost intensive factor besides the already high energy demand for heating.

Thus, since many years textile researchers around the world are looking for alternative dyeing techniques for all kind of fiber types but especially for polyester and cotton (the main fibers types) to overcome some of the mentioned drawbacks.

In this context, the DTNW achieved a significant success in the early 1990^{th} by the invention of polyester dyeing in supercritical carbon dioxide [1-2]. In doing so the supercritical fluid acts as a novel solvent for conventional disperse dyes, which are able to penetrate the polyester fibers at high pressure and temperatures in an absolute water-free system. The process needs no water and, therefore, no costs appear for the drying of the textiles and the wastewater treatment. At the same time, supercritical carbon dioxide can be used for the extraction of disturbing spinning auxiliaries and oligomers [3].

Later, DTNW has demonstrated successfully that - besides supercritical carbon dioxide - Ionic Liquids (IL) are another alternative medium for the dyeing of textile substrates, with which it is possible to proceed textile dyeing under atmospheric conditions [4]. Ionic liquids - often indicated as “green solvents” - are ionic substances, which are liquid in the temperature range of room temperature up to ~ 100 °C [5]. Most are thermo-stable even above 200 °C without

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showing a significant vapor pressure and no emission of volatile organic compounds (VOC), which allows an easy and non-hazardous handling compared to common organic solvents. Moreover, they exhibit high dielectric coefficients what results in amazing dissolving power for manifold monomeric and polymeric compounds (cellulose, keratins, silicones etc.) [5-7]. In addition, they have a low inflammability and show a high heat capacity. Like common salts, IL consist of cations and anions, e.g., imidazolium, pyridinium, phosphonium plus ammonium (cations) and alkyl sulfate, hexafluoro phosphate, tetrafluoro borate plus halogenides (anions). These two components can be varied to design Ionic Liquids for a specific end use or to possess a particular set of properties. Properties such as melting point, viscosity, density, and hydrophobicity can be varied. In addition, Ionic Liquids have unique dissolving properties in the presence of organic compounds. In the non-textile sector Ionic Liquids find many potential and already realized applications. Examples are solvents (catalysis, organic syntheses, polymerizations, synthesis of nano particles), electrolytes (batteries, fuel cells, sensors), separation techniques (membranes, gas separation, extractions), analytics (gas chromatography, protein crystallization), lubricants and fuel additives [8-16]. IL can replace conventional solvents in many applications and, as mentioned above, IL are useful as solvents for textile dyestuffs too. Some potential species are already identified within the successful pre-studies at DTNW - namely methylimidazolium acetate (MIMAC), ethylmethylimid azolium chloride (EMlM-Cl), allylmethylimidazolium chloride (AMIM-Cl), and piperidium acetate (PIPAC). By using these species various fiber materials could be dyed yielding colorations with high fastness towards light, rubbing and washing. Successful examples are the dyeing of polyester with disperse dyes (e.g. teratoto blue), cotton with reactive dyes (e.g. serilene red), polyamide with metal complexes (e.g. isolane green) and polyacrylonitrile with cationic dyes (e.g. methylene blue) [4].

Now, we have widened the investigations to generate more information on the general feasibility of the dyeing of polyester fibers in these promising "green solvents". This included the identification of commercially available IL and the testing of their inherent properties with respect to the needed requirements in the envisaged textile dyeing process.

II. Experimental

A. Materials

The standard PET fabric (170 g/m^2, weave L 1/1) and the PET/cotton blend (50:50, 127 g/m^2, weave L1/1) were purchased from wfk Testgewebe GmbH (Brüggen, Germany). For the dyeing experiments the Ionic Liquids 1-Ethyl-3-methylimidazolium acetate (Sigma-Aldrich), 1-Ethyl-3-methylimidazolium diethyl phosphate (IoLiTec), 1-Ethyl-3-methylimidazolium chloride (Sigma-Aldrich), Tris(2-hydroxyethyl)methylammonium methyl sulfate (Sigma-Aldrich), 1-Ethyl-3-methylimidazolium ethyl sulfate (Sigma-Aldrich), and Tributylmethylammonium methyl sulfate (Sigma-Aldrich) were used. The IL were used without further purification. Commercial disperse dyestuffs for PET Dianix® Green CC, Dianix® Blue CC, Dianix® Red CC, Dianix® Yellow CC plus Dianix® Black CC-R were purchased from Dystar (Frankfurt, Germany). The pure disperse dyestuffs Seriplas® Yellow 3GL-TPS, Seriplas® Red 2BL-TP, Seriplas® Blue 2GN-TP are without any auxiliaries and were purchased from Yorkshire Farben GmbH (Krefeld, Germany). The pure fluorescent dyestuffs for PET Maxilon® Flavine crude was purchased from Huntsman (Langweid a.L., Germany) and the pure reactive dyestuffs without auxiliaries for cotton Jettex® R. Marine BS was purchased from Dystar (Frankfurt, Germany).

B. Dyeing Procedures

Dyeing procedures for PET in IL

In 15 g of each IL 600 mg of the respective dyestuffs were dissolved. A piece of PET textile (2 cm x 2 cm) was put into the preheated solution and heated for one hour at a given temperature (100 °C, 120 °C, 140 °C resp. 160 °C) without stirring or for 5, 10 resp. 15 min at 160 °C under stirring. After the dwell time the fabric was removed from the dyeing bath and was put into a beaker with water. Afterwards the fabric was rinsed with running water till the water was clear. Then the fabric was dried overnight at room temperature. All colored textile materials were rinsed additionally with acetone to remove excessive dyestuffs.

Dyeing procedure for PET/cotton blends in IL

The PET/CO fabrics were dyed according to the dyeing procedure for PET at 140 °C in Tris(2-hydroxyethyl)methyl ammonium methyl sulfate. For the dyeing of the PET/cotton blends the pure reactive dyestuff Jettex® R. Marine BS and the disperse dyestuff Dianix Red CC were used.

Conditions of the conventional PET dyeing (HT process)

To compare the IL dyeing procedure common PET dyeing, PET was additionally dyed under pressurized conditions in water (HT process: starting temperature 40°C, heating rate 2°C/min, final temperature 130°C, hold for 60 minutes, liquor ratio 1:10, dyestuff Serilene Red 2BL 200, concentration 0.5% dyestuff). After the dyeing procedure the PET was not treated reductively, but treated as described for the dyeing in IL. The pH value at the beginning and at the end of the dyeing was 4.3.

C. Analytics

UV-VIS-Spectroscopy and colorimetric measurements

UV-Vis spectra of the samples were evaluated using a Cary 5E spectrophotometer (Varian GmbH, Waldbronn, Germany). The colorimetric measurements were conducted using a Colorlite sph850 (Colorlite GmbH, Katlenburg-Lindau, Germany). Note: The mentioned color distances are the differences between the uncolored and the colored textile materials.

Determination of maximum force and elongation at maximum force

The maximum force and elongation at maximum force were measured according to DIN EN ISO 13934-1 [17] using a ZMART pro Typ 1455 (Zwick GmbH&Co KG, Ulm, Germany) (standard atmosphere: 20°C, 65% rel. humidity, clamping length: 200 mm, bandwidth: 30 mm, speed of testing: 100 mm/min, preload force: 5 N).

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Fastness

The fastness to washing was conducted according to DIN EN ISO 105-C06 [18] using a Linitest plus (Atlas Material Testing Technology GmbH, Linsengericht-Altenhasslau, Germany). The fastness to rubbing was conducted according to EN ISO 105-X12 [19] using a Crockmeter (Crockmaster, James Heal, UK) (standard atmosphere: 20°C, 65% rel. humidity, conditioning: 4 h, cone for rubbing: cylindrical (16mm), weight of 9 N, absorption of water: 95% - 100 %). The light fastness was evaluated according to DIN EN ISO 105-B02 [20] using a Xenotest 150 S (Atlas Material Testing Technology GmbH, Altenhasslau, Germany).

Fiber cross sections

To evaluate fiber cross sections of the dyed textile material single fiber filaments were removed from the fabric and embedded in instant adhesive between two PP plates. Thin slices of the cured sample were cut off and put on object plates. The samples were examined by microscopy and photos were taken using a microscope of Olympus, Type BH-2 (Olympus Deutschland GmbH, Hamburg, Germany).

Effective temperatures

The effective temperatures were determined by differential scanning calorimetry (DSC). The sample quantity was nearly 4 mg and the heating rate was 10 °C/min. The measurements were carried using model Q20 from TA Instruments (USA).

III. RESULTS AND DISCUSSION

A. *Pre-selection of Ionic Liquids*

The work included a study on available IL with properties, which meet the basic requirements for their use in the envisaged dyeing procedures. Essential properties of the IL are a high dissolving power for various dyestuffs, a thermo-stability of at least 150 °C, and a very low vapor pressure. Other properties such as non-flammability and high heat capacity would be appreciated but are not absolutely essential. This task foresaw a market study on available IL, which are offered by the stakeholders in this field, e.g. BASF, Merck, Aldrich, and IoLiTec. Some potential species are already identified within the successful pre-studies at DTNW [5].

IL No.	IL	Molecular weight	Density $[g/cm^3]$	pH value	water-soluble	mp [°C]
1	1-Ethyl-3-methylimidazolium acetate	170.21	1.027 (25°C)	5.4 (100 g/l)	yes	< -20
2	1-Ethyl-3-methylimidazolium diethyl phosphate	264.26	1.157	./.	yes	19-21
3	1-Ethyl-3-methyl imidazolium chloride	146.62	1.112 (80°C)	7.7 (100 g/l)	yes	77-79
4	Tris(2-hydroxyethyl) methylammonium methyl sulfate	275.32	1.32 (20°C)	7.0 - 8,0 (20 g/l)	yes	< -20
5	1-Ethyl-3-methylimidazolium ethyl sulfate	236.29	1.239 (20°C)	8.2 (100 g/l)	yes	< -30
6	Tributylmethylammonium methyl sulfate	311.48	./.	7.5 (300 g/l)	yes	62

Table 1. Properties of the used IL.

The nature of each IL is documented in order to determine the starting conditions for future dyeing. Their properties are given in Table 1. All used IL are soluble in water. Two IL show a melting point above room temperature. For their use it was necessary to melt them. The pH values were determined after solving a certain amount of the IL in water. All investigated IL show a sufficient dissolving power for typical disperse dyestuffs (Fig. 1).

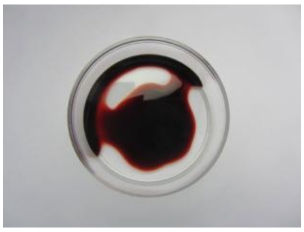
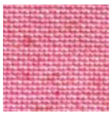
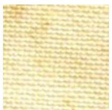
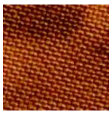


Figure 1. Photograph of a typical used dyeing liquor consisting of an IL and the dissolved disperse dyestuff.

We started the experiments with a pre-selection of the most promising Ionic Liquid for the waterless and non-pressurized dyeing of polyester fibers. Therefore, a standard PET fabric was dyed with various commercial disperse dyestuffs (Dianix series) in the six selected IL at certain temperatures between 100 °C and 160 °C. Exemplarily, Table 2 (bad result) and Table 3 (good result) show photographs of the dyed fabrics after washing. The photographs give a first impression of the color depth and the equality of the colorations.

Table 2. Photographs of PET dyed in IL 1-Ethyl-3-methyl imidazolium diethyl phosphate (IL 2).

Dyestuff	Dyeing temperature			
	100°C	120°C	140°C	160°C
Dianix Green CC				
Dianix Blue CC				
Dianix Red CC				
Dianix Yellow CC				
Dianix Black CC-R				

The results of the dyeing in IL 2 are very poor (Table 2). At no dyeing temperature a satisfactory result was observed. Comparable bad results were found for IL 1 (accompanied with fiber damage at high temperature), while IL 3, IL 5 and IL 6 gave slightly better dyeing effects.

The dyeing in Tris(2-hydroxyethyl)methylammonium methyl sulfate (IL 4), however, shows very good results (Table 3). The effects became better with rising temperature. Best results were obtained at the dyeing temperature of 140°C (e.g.

blue or yellow) and 160°C (black). Lower temperatures yield no sufficient coloring.

To visualize the dyeing performance fiber cross sections of the dyed material were prepared and pictures were taken. Table 4 shows the cross sections of PET fibers after dyeing in IL 4 with Dianix Red and Yellow. It can be clearly seen that the integral coloration became more completely with the increase of the dyeing temperature. These results are in-line with the visual impressions of the dyed materials (Table 3). After this pre-selection we decided to conduct all following PET experiments with the most promising IL 4.

Table 3. Photographs of PET dyed in Tris(2-hydroxyethyl)methyl ammonium methyl sulfate (IL 4).

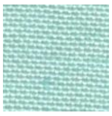
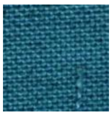
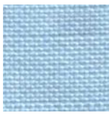
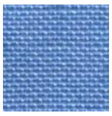
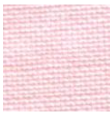
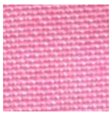
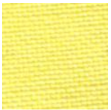
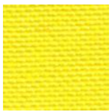
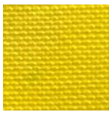
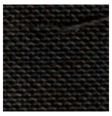
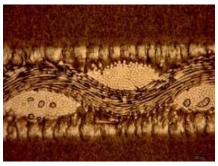
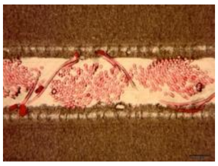
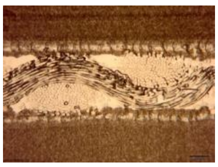
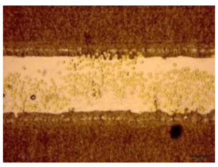
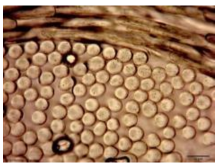
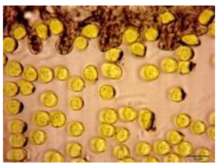
Dyestuff	Dyeing temperature			
	100°C	120°C	140°C	160°C
Dianix Green CC				
Dianix Blue CC				
Dianix Red CC				
Dianix Yellow CC				
Dianix Black CC-R				

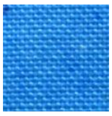
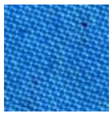
Table 4. Fiber cross sections of PET fibers after dyeing in IL 4 with Dianix Red and Yellow.

dyestuff	120°C	160°C
Dianex Red CC (lower magnification)		
Dianex Red CC (higher magnification)		
Dianex Yellow CC (lower magnification)		
Dianex Yellow CC (lower magnification)		

B. Comparison of dyeing PET in IL with dyestuffs with and without auxiliaries

After the decision on the IL to be used we focus on the dyestuffs. Formulated commercial disperse dyestuffs for the dyeing of PET fibers contain typically nearly 50 % auxiliaries. One goal of our study was the total abandonment of such chemicals in terms of environmental protection. Moreover, an undesired enrichment of the auxiliaries in the IL dyeing bath can occur under repeated use. Therefore, we conduct comparative experiments on the dyeing of PET with formulated commercial dyestuffs (with auxiliaries) and pure dyestuffs (without auxiliaries). For a better comparability in each case the same absolute dyestuff amount was used. Therefore, the experiments with the pure dyestuff (here 300 mg) were conducted using only the half amount of the commercial product (here 600 mg). Typical results for two shades of color are shown in Table 5.

Table 5. Photographs of PET dyed with red (above) and blue (below) dyestuffs with and without auxiliaries at different concentrations in IL 4 at 160°C.

pure (without auxiliaries)				commercial (with auxiliaries)
10 mg	30 mg	60 mg	300 mg	600 mg
				
				

No fundamental differences between the colorings with dyestuffs with or without auxiliaries were observed. Therefore, the dyeing of PET in IL generally succeeds even with pure dyestuffs. No auxiliaries are necessary. In addition, a set of experiments was conducted with lower dyestuff concentrations in order to minimize the needed amount for a sufficient color depth. Additional photographs of PET samples dyed at lower concentrations are presented in Table 5. It is obvious that even a 20 times lower concentration (30 mg) leads to a satisfying color depth, while 10 mg results in pale shades.

C. Repeated use of the IL dyeing liquor

Another goal of the study was the characterization of the dyeing results using the same dyeing liquor repeatedly. Therefore, we have conducted 10 repeated dyeing cycles (each 1 h, 160 °C) in IL 4 at various dyestuff concentrations. Fig. 2 summarizes the color-metric measurements (color distance) of PET for Dianix Red. All dyed samples start with a high color distance ΔE of ca. 77 and no broad dependence on the initial dyestuff concentration was observed. Moreover, the color distance stays more or less constant over all dyeing cycles and only a slight decrease in color depths was found. In addition, the corresponding VIS-spectra of the fabrics dyed at a Dianix Red concentration of 100 mg Dianix Red at 160°C in IL 4 are depicted exemplarily in Fig. 3. As expected from analytics above all curve shapes appear very similar.

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Therefore, our innovative approach allows the repeated use of IL dyeing bathes generally.

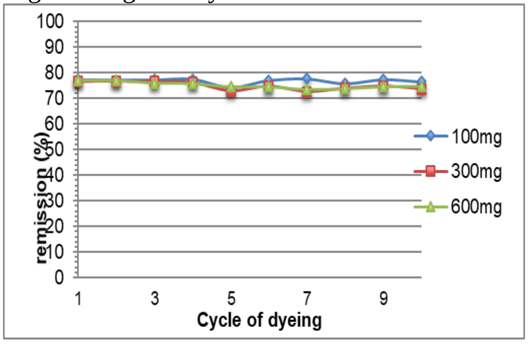


Figure 2. ΔE values of dyed PET after 10 dyeing cycles at 160°C colored with different concentrations of Dianix Red in IL 4 (multiple use of the same dyeing liquor).

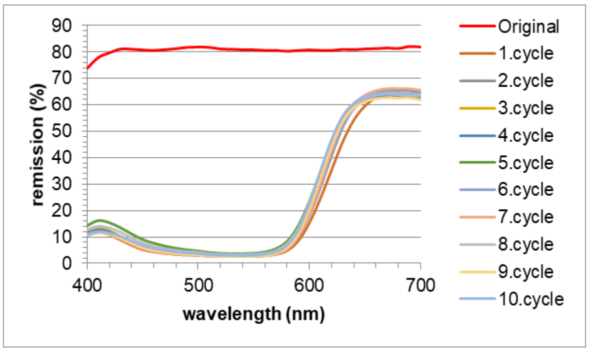


Figure 3. VIS-spectra of PET fabrics dyed one by one in the same liquor with100 mg Dianix Red at 160°C in IL 4.

D. Comparison dyeing in IL vs. standard HT-dyeing process

To introduce a new innovative dyeing procedure into the market the quality of the dyeing must meet the requirements of the state-of-the-art. Therefore, we compare our IL process with conventional HT-dyeing. We have investigated the most important parameters colorization, mechanical properties and fastness to rubbing, washing plus light. The dyeings were conducted with a disperse dyestuff. The HT-process was carried out with the commercial dyestuff (with auxiliaries), while the IL process was carried out with the pure dyestuff. Exemplarily, Table 6 shows photographs of PET dyed with red color. It can be seen clearly that the color depth of both samples differs and the IL sample is dyed deeper. Generally, impressive results can be obtained using our innovative IL process.

Table 6. Photographs of conventionally dyed PET (HT-dyeing, left) and PET dyed in IL 4 at 160 °C.

HT dyeing	Dyeing in IL
	

Another important quality characteristic of the dyeing process is the exclusion of fiber damage during treatment. Table 7 summarizes the tensile strength of HT and IL dyed PET fabrics compared to the untreated material.

Table 7: Tensile strength of the blank material, the samples dyed by HT-process and dyed by the IL process (width of the measured samples: 3cm).

sample	direction	maximum force [N]			
		single values			mean
blank	warp	734	610	564	636
	weft	562	604	585	583
HT	warp	821	750	787	786
	weft	632	685	677	665
IL	warp	582	783	678	681
	weft	681	658	604	648

Under both dyeing conditions the maximum forces (warp and weft) of the fabrics dyed with the HT-process and the IL-process are higher than the corresponding results of the raw material and no significant fiber damage was observed. In addition, the results of the maximum force elongations of HT- and IL-dyed samples are very similar.

Table 8 shows the corresponding fastness results of the IL-dyed PET fabric to washing, rubbing, and light exposure compared to the values for classical HT-dyeing. All values are equal and no differences between the both dyeing procedures were observed. In conclusion all measured parameters of the IL-dyed PET fabrics are in the same range as the conventional HT-dyed material.

Table 8. Fastness to laundry, rubbing and artificial light of PET samples dyed by HT-process and dyed by the IL-process (CA = Acetate, CO = Cotton, PA = Polyamide, PAN = Polyacrylonitrile, PET = Polyester, WO = Wool).

Fastness to laundry							
sample	change of color	staining of					
		WO	PAN	PET	PA	CO	CA
HT	4 - 5	5	5	5	5	5	5
IL	4 - 5	5	5	5	4 - 5	5	5
Fastness to rubbing							
sample		staining of cotton (dry)			staining of cotton (wet)		
HT (warp & weft)		4 - 5			4 - 5		
IL (warp & weft)		4 - 5			4 - 5		
Fastness to artificial light							
sample		Results					
HT		> 4					
IL		> 4					

E. Process Optimization

Up to now all examinations were carried out over a dyeing period of 1 h according to typical industrial procedures in conventional HT-dyeing (high temperature, pressurized process) of PET. In order to optimize the envisaged IL dyeing process in terms of costs, productivity and ecological aspects, in the following, experiments on the time reduction were conducted. Table 9 shows the results of PET dyed with two disperse dyestuffs (Dianix Red and Black) in IL 4 at 160 °C over 15, 30, and 60 minutes. Both, photographs and color distances demonstrate that the best results can be achieved at longest dyeing time of 60 min. However, the color depths at shorter times are acceptable and a time reduction seems to be feasible generally.

Table 9. Photographs and corresponding colour distances (ΔE) of the time-depending dyeing of PET at 160°C with disperse dyestuffs (Dianix) in IL 4.

dyestuff	dyeing time [min]		
	15	30	60
Dianix Red			
	ΔE = 72.0	ΔE = 70.4	ΔE = 75.3
Dianix Black			
	ΔE = 66.3	ΔE = 71.7	ΔE = 72.9

The studies on the dyeing of PET carried out so far were conducted under static conditions. The IL with the dyestuff was preheated and the PET textiles were placed in the dyeing bath for a given time. On the other hand, as expected an acceleration of the dyestuff penetration into the fibrous material can be promoted by stirring the system because of a better mixing of the components at the phase boundary. Thus, we have conducted a study on dyeing under stirring conditions for 5, 10, and 15 minutes in comparison to the dyeing under static conditions after 60 minutes. Table 10 shows photographs and color distances of in such a way dyed PET fabrics. It is obvious, that the stirring has a significant impact on the needed dyeing time. Already after 5 minutes a ΔE value of 73.7 was reached and the coloring is nearly complete after 10 minutes. The corresponding VIS-spectra show very similar results (Fig. 4) and largely confirm the results from the ΔE values.

Table 10. Photographs and color distances of PET fibers dyed under stirring in IL 4 at 160°C with Dianix Red at different times (on the right side: static conditions for 60 minutes).

with stirring for			static
5 min	10 min	15 min	60 min
			
ΔE = 73.7	ΔE = 75.2	ΔE = 75.1	ΔE = 75.8

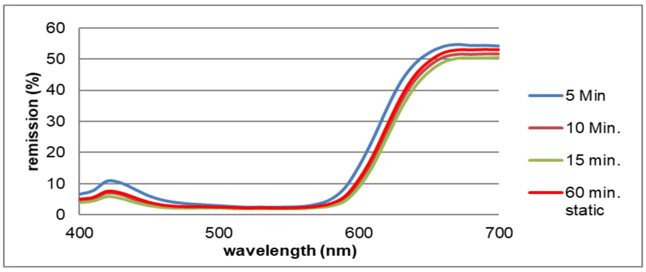


Figure 4. VIS-spectra of PET fabrics dyed with Dianix Red in IL 4 at 160°C under stirring for 5, 10, and 15 minutes and under static conditions.

F. Dyeing of PET with fluorescent dyestuffs

In addition to classical disperse dyestuffs we have performed a set of experiments using a pure fluorescent dyestuff (Maxoline) without auxiliaries. Table 11 shows photographs of PET fabrics dyed in IL 4 at various temperatures (120°C, 140°C, and 160°C). The achieved fluorescent effect was visualized by UV light of different wavelengths.

Table 11. Photographs of PET dyed in IL 4 with pure fluorescent dyestuff (Maxoline) under UV light of different wavelengths.

254 nm	
366 nm	

G. Determination of the effective temperature of PET after IL dyeing (thermal effects)

During our study the question raised, if the high temperature dyeing of PET in IL has an (desired or undesired) influence on the effective temperature of the treated polymer. If so, the industrial dyeing of PET could be combined with the conventional fixation step in a stentering frame, which should be accompanied with a dramatic reduction of energy demand and, therefore, a reduction of costs. On the other hand, the heat setting could lead to irreversibly fixed folds in the treated textile, which reveals the necessity of a well-defined process. Therefore, we measured the effective temperatures of the dyed PET after treatment (Table 12) and the expected results were found. The determined effect temperatures reflect the respective treatment temperatures. This has to be kept in mind for a following up-scale and commercialization of our IL process.

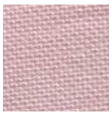
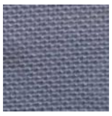
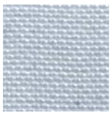
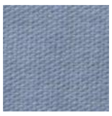
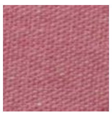
Table 12. Effective temperatures of PET dyed in IL 4 at different temperatures (compared to stentering frame treatment at 160°C).

condition	treatment-T [°C]	effective-T [°C]
stentering frame	160	170
dyeing in IL	100	104
	120	119
	140	144
	160	171

H. Dyeing of PET/cotton blends

In addition, we dyed a mixtures of PET/CO (50/50) in IL 4. We have chosen a dyeing temperature of 140°C because up to now no damage of the cotton was observed and this temperature is high enough for PET dyeing. The dyeings were carried out with a mixture of the dyestuffs Jettex (dyeing for cotton) and Dianix (dyeing for PET). The results show that it is generally possible to dye a mixture of PET and CO in one step. For a more detailed result the textiles (pure CO, pure PET, and PET/CO blend) were subjected to a solution of the pure CO dyestuff, pure PET dyestuff and the mixture of the both dyestuffs. The results of the dyed fabrics are shown in Table 13. As expected, pure cotton has a high affinity to the blue reactive dyestuff Jettex Marine as well as pure PET can be dyed well in red disperse dyestuff Dianix Red. Vice versa, cotton was dyed badly by the red disperse dye, while polyester show a low colour depth using the blue reactive dye. The PET/CO blend shows (visually) half of the intensity in the cases only one dyestuff was used; only the affine part of the blend takes the colour up. Using the dyestuff mixture, both components were dyed yielding a purple-coloured fabric.

Table 13. Fabrics (PET, CO, and PET/CO blend 50/50) dyed with pure dyestuffs Jettex Marine and Dianix Red as well as the mixture of both dyestuffs in IL 4 at 140°C.

sample	used dyestuff (pure and mixture)		
	Jettex Marine (reactive dyestuff)	Dianix Red (disperse dyestuff)	Jettex Marine Dianix Red
cotton			
PET			
PET/CO blend (50/50)			

IV. Conclusion

In recent years, research on Ionic Liquids is growing steadily and some technical applications already arrived the market. However, so far IL play no role in the textile sector. Our new fundamental as well as application-oriented study enlarges the knowledge on the use of Ionic Liquids in general, and helps towards the use of IL in the dyeing of textile materials in particular. The introduction of IL in both textile research and textile processes means a connection to a very actual and strongly expanding work and research field that embraces many technical areas and sectors.

In detail, we have successfully demonstrated, that PET fibers can be dyed in manifold shades with commercial disperse dyestuffs in various IL far above 100 °C using open non-pressurized systems. Compared to conventionally dyed PET, the fibrous material shows no significant differences in terms of mechanical properties and fastness to rubbing, washing and light. In addition, we have optimized several essential process parameters of our innovative dyeing procedure, e.g., process temperature, running time and dyestuff concentration. Moreover, we have successfully demonstrated, that typical auxiliaries of commercial dyestuffs are not necessary within the IL dyeing procedure. Beside the huge potential of saving and the contribution to environmental protection, the abandonment of such chemicals prevents an undesired enrichment of the auxiliaries in the IL dyeing bath, which generally allows the repeated use of the IL dyeing bath. Furthermore, we have shown that PET/cotton blends can be dyed generally in one step using both needed dyestuff types in one dyeing liquor (mixture of reactive dyes for cotton and disperse dyes for PET). This allows a more effective process in terms of costs and environmental protection because only one heating, one washing, and one drying step is necessary.

In summary, we have successfully started and investigated a new innovative IL dyeing process for textile materials in IL, which offers the chance to dye the most important textile fiber PET in open, non-pressurized systems in future. This would be accompanied with several ecological and even economic advantages compared to the classical HT process resp. HT equipment. However, the recycling of the Ionic Liquids used for the dyeing of textiles is the most critical point in our new dyeing process and the development of an appropriate strategy was not part of the study so far. Future R&D work has to focus on this topic.

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