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A new method to increase disperse dyeability of polypropylene fibers: ultrasonic assisted dyeing

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Summary

In this study, a new method to increase the disperse dyeability of polypropylene fibers was investigated. For this purpose, dye bath having liquors to good ratio of 20:1 and dye concentration of 2% owf has been prepared and fabrics from polypropylene fibers were dyed by using ultrasonic energy. These experiments were done at different temperatures (20 ^{0}C, 40 ^{0}C, 60 ^{0}C and 80 ^{0}C) and different time intervals (1, 3, 5, 10, 15, 20, 25, 30 min). In order to evaluate the effect of carrier, dyeing experiments were repeated in the case of 1% carrier addition to the dye bath. Dyeing experiments were also repeated by conventional manner to compare the effect of ultrasonic power as well as the effect of carrier addition. The color strengths of dyed fabrics were examined by K/S values measured by a spectrophotometer. Therefore dyeability of polypropylene fibers was determined according to temperature, time and carrier. According to results, ultrasonic power improves the dyeability and addition of carrier gives better results.

Keywords: *Polypropylene fiber, dyeability, disperse dye, ultrasonic energy*

Polipropilen elyafın dispers boyarmaddeler ile boyanabilirliğinin geliştirilmesi için yeni bir yöntem: ultrasonik boyama

Özet

Bu çalışmada polipropilen elyafın dispers boyarmadde ile boyanabilmesinin arttırılması için yeni bir yöntem incelenmiştir. Bu amaçla, flotte oranı 1/20 ve boyama şiddeti %2 olan boyama banyosu hazırlanmış ve polipropilenden mamul kumaşlar ultrasonik enerji kullanılarak boyanmıştır. Deneysel çalışmalar farklı sıcaklıklar (20 ^{0}C, 40 ^{0}C, 60 ^{0}C ve 80 ^{0}C) ve farklı sürelerde (1, 3, 5, 10, 15, 20, 25, 30 dak) gerçekleştirilmiştir. Taşıyıcının etkisini görebilmek amacı ile boyama denemeleri %1 taşıyıcı içeren boyama banyosunda tekrarlanmıştır. Ultrasonik gücün ve taşıyıcının etkisini kıyaslayabilmek amacıyla normal yöntem ile de boyama denemeleri gerçekleştirilmiştir. Boyanan kumaşların renk şiddetleri spektrofotometre kullanılarak ölçülen K/S değerlerine gore değerlendirilmiştir. Dolayısıyla polipropilenin boyanabilirliği sıcaklık, zaman ve taşıyıcı etkisine göre araştırılmıştır. Araştırma sonuçlarına gore ultrasonik güç boyanabilirliği arttırmaktadır ve taşıyıcının ilavesi çok daha iyi sonuçlara yol açmaktadır.

Anahtar kelimeler: *Polipropilen elyaf, boyanabilirlik, dispers boyarmadde, ultrasonik enerji*

Introduction

Polypropylene (PP) has unique properties such as low density (0.9 g/cm^3, the lowest in all synthetic fibers), good chemical resistance, low cost, ease of processability and good mechanical properties such as high toughness, high elasticity and low abrasion resistance. Polymerization of propylene monomer yields three different configuration polymers, namely atactic, sindiotactic and isotactic polypropylene. Only isotactic form in which all substituent methyl groups located in the same direction is suitable for fiber formation because of its high crystallinity. The crystallinity of isotactic polypropylene ranges between 50-65 % (Lewin, 2007; Broadbent, 2001; Tripathi, 2002; Kocsis, 1999; Needles, 1986).

Polypropylene is, besides polyesters, one of the widely used polymers for producing synthetic fibers, especially for technical applications. However, its sensitivity to photo and thermal oxidation, and the difficulties in dyeing for lack of reactive sites, can be expressed as disadvantages of it. Sensitivity to heat and light can be dissipated by additives (Lewin, 2007; Broadbent, 2001; Tripathi, 2002; Kocsis, 1999; Needles, 1986). High crystallinity is required for strength of the fiber but also it is one of the main reasons for difficulties in dyeing.

PP is available in monofilament, multifilament and staple fiber, fibrillated yarn as well as non-woven fabric. It enjoys manifold applications, as exemplified by medical fabrics, industrial sewing threads, cordage, artificial turf, carpeting and geotextiles; little is used in apparel (Lewin, 2007; Broadbent, 2001; Tripathi, 2002).

Nowadays, PP fiber is colored with a method called masterbatching or mass pigmentation. In this technique, pigments are added to melt polymer prior to extrusion, and by drawing and annealing, pigments remain in between crystalline regions of the polymer. This technique is only available for large amounts production. It is very difficult to obtain different colors and re-obtain the same color with this technique and also fiber cannot be dyed anymore after production (Lewin, 2007; Kocsis, 1999; Needles, 1986). Poor repeatability and color unevenness in different thicknesses can also be explained as inadequacies of this technique.

Studies to overcome the dyeability problem of the fiber have been present in the literature. These can be classified as blending with other polymers containing reactive sites, chemical modification of the fiber and copolymerization (Burkinshaw et al., 2002). The main

purpose of all studies can be explained as interact the fiber with dye molecules by supplying reactive dye sites. Blending with other polymers is the most used technique in dyeability studies.

Ultrasonic power, 18 kHz-10 MHz frequency, is used in several applications in industry such as underground studies, metallurgical studies, medicines, military, surface processing, and automotives (Peters, 1996). However its use in textile processes is a new area. It is used in textile area as cleaning, dye extraction from various plants and dyeing. By this purpose, ultrasonic baths and ultrasonic probes can be used but ultrasonic baths have the advantage of low cost and they are the most used equipments (Öner, 2002).

Sonic waves play an important role in relaxation and squeezing in molecular structure of the fiber thus an interaction between dye molecules and fiber can be achieved.

The effect of ultrasonic power can be explained as the phenomenon called cavitation. Cavitation can be defined as local evaporation and condensation of liquid. The microbubbles that is forming in the liquid, condenses abruptly so high temperature points form that makes possible bonds in between the molecules to move. Therefore ultrasonic power causes molecular relaxation and squeezing (Peters, 1996; Öner, 2002).

Shukla and Mathur (Shukla&Mathur, 1995), have studied about the dyeability of silk fiber by cationic, acid and metal-complex dyes at low temperatures. They used 26 kHz ultrasonic power in their study. In order to compare the effect of ultrasonic power, they have been also done the same dyeing experiments without ultrasonic power. According to results, dyeing temperature reduced from 60 ^{0}C to 45-50 ^{0}C, while dyeing time also reduces from 1h to 15 min. for the same dye uptake.

Kamel et al. (Kamel et al., 2005), have studied the ultrasonic power in extraction of lac (a natural dye), and in dyeing of wool with this dye. According to their results, ultrasonic offers 41% increase in extraction and 47% increase in dyeing.

A study about the use of ultrasonic power in dyeing of wool with a natural dye obtained from Acer pectinatum plant has been done by Vankar et al (Vankar et al., 2008). Effectiveness of dyeing was expressed as 50% time and 30% cost reduction.

Akalın et al. (Akalın et al., 2004), have studied the washing fastness of wool fabrics dyed with the assistance of ultrasonic power. According to researchers, darker colors were obtained in the case of ultrasonic dyeing compared to conventional dyeing technique.

Değirmenci (Değirmenci, 2005), has reported an increase in dyeing efficiency in the case of ultrasonic assisted dyeing of 60%/40% PES/PA with disperse dyes.

It can be said that by the light of these literature, ultrasonic energy offers lower temperature and shorter time dyeings therefore it can provide cost savings in textile wet processes.

Color strength of the dyed textile material can be measured using a spectrophotometer and using Kubelka-Munk equation (Equation 1). K/S is known as color strength and its value is directly proportional to the amount of dye in the fiber (Broadbent, 2001):

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

Material and methods

In this study a narrow woven fabric made of 100% polypropylene was used. Before dyeing it was cut into 4 cm x 5 cm pieces and washed with 1% aqueous solutions of Na_2CO_3 for 20 min then 1% acetic acid solution for 20 min. in order to remove preparation waxes and other dirtiness, and then atmospherically dried.

Dyestuff used in this study was Disperse Blue 56 (from Setaş Chemical Co.). Dye was used without purification and contains dispersing agents and blending oil.

In this study a carrier (commercial name, Setacarrier ECO, from Setaş Chemicals Co.) was used. More than half of it is composed of Bip Phthalimides. Besides 9% isobutylalcohol and 10 % LABSA and monopropylene glycol is included.

An ultrasonic bath (Bandelin Sonorex, RK-255H) was used as dyeing equipment.

Dyeing procedure

Dyeing bath was prepared with liquors to good ratio of 20:1, and dye concentration of 2% owf. The fabric was put inside the bath for dyeing at different temperatures (20 ^{0}C, 40 ^{0}C, 60 ^{0}C ve 80 ^{0}C) for 15 minutes. After dyeing fabric was dried and washed with 1% Na_2CO_3 solution for 30 min., then with tap water for 30 min. Fabrics were atmospherically dried again

and so they were ready for color measurements.

In order to determine the effect of carrier, dyeing experiments were repeated at the same conditions with the addition of 1% (v/v) carrier.

Dyeing experiments with the same dyebath conditions were repeated in conventional manner to be able to compare the efficiency of ultrasonic technique.

Besides, in order to obtain the dependence of dyeing to time and to get the optimum dyeing time, both carrier and non-carrier dyeing as well as the conventional dyeing were done for different time intervals (1, 3, 5, 10, 20, 25 and 30 min).

Color measurements

The reflectance of dyed fabrics at λ_{max} of the dye (620 nm) was measured by a spectrophotometer (Gretag, Color Eye 7000 A). Relative color strengths (K/S values) were determined using the Kubelka-Munk equation (Eq. 1).

Color measurements were done by using 10^0 standart observer, D_{65} illuminant. An undyed fabric sample was used as reference. CIELab values (L*, a*, b*, ΔL*, Δa*, Δb*, ΔE) for all samples were determined and given in Table 1.

Fastness measurements

Washing fastnesses of dyed fabrics were determined by ISO test. Dyed fabrics were attached to a multifiber and were washed with an alkaline soap in liquors to good ratio of 50:1 at 50 ^{0}C temperature and for 30 min. After washing off with distilled and then tap water they were atmospherically dried. Then washing fastness values of the samples were obtained by using grey scale.

Results

Effect of dyeing technique and dyeing temperature

Colorimetric measurements of dyed fabrics were given in Table 1.

Table 1. CIELab of dyed fabrics with different methods

Sample		L*	a*	b*	ΔL*	Δa*	Δb*	ΔE
Conventional dyeing	20 ^{0}C	72.88	-5.88	-11.41	11.39	-5,84	-11.34	20.24
	40 ^{0}C	75.72	-5.40	-8.27	-8.55	-5,37	-8.20	15.54
	60 ^{0}C	73.44	-5.84	-9.65	-10.83	-5,80	-9.57	17.83
	80 ^{0}C	70.22	-6.22	-13.51	-14.05	-6,18	-13.43	23.54
Ultrasonic dyeing	20 ^{0}C	68.78	-5.61	-15.53	-15.49	-5,57	-15.45	26.13
	40 ^{0}C	69.27	-6.00	-15.09	-15.00	-5,96	-15.01	23.80
	60 ^{0}C	69.97	-5.56	-13.97	-14.30	-5,52	-13.89	25.68
	80 ^{0}C	66.11	-4.74	-17.03	-18.16	-4,70	-16.95	28.11
Ultrasonic dyeing (with carrier)	20 ^{0}C	62.31	-2.72	-20.53	-21.96	-2,68	-20.45	33.02
	40 ^{0}C	61.63	-3.13	-21.74	-22.64	-3,09	-21.66	34.97
	60 ^{0}C	58.73	-1.48	-23.32	-25.54	-1,45	-23.24	37.34
	80 ^{0}C	47.85	2.25	-25.49	-36.42	2,29	-25.41	41.77

ΔE values show the total vectorial color difference in between two samples. According to results in conventional dyeing experiments, these values were slightly decreasing and then increasing with increasing temperature. In the case of ultrasonic assisted dyeing same pattern was observed while by the addition of carrier uniform increase has been seen with increasing temperature. In dyeing experiments with carrier, carrier is firstly absorbed by the fiber and forms a surface for dye absorption. Therefore increase in dye absorption with increasing temperature shows smoother line in this case. From Table 1 it can be concluded that in all cases as temperature increases ΔE values increase that means that amount of dye absorbed by the fiber increases.

Dye uptake of the fiber was interpreted according to color strength values, K/S. Color strengths of the dyed fabrics by ultrasonic power (with and without carrier) and by conventional dyeing was given in Figure 1.

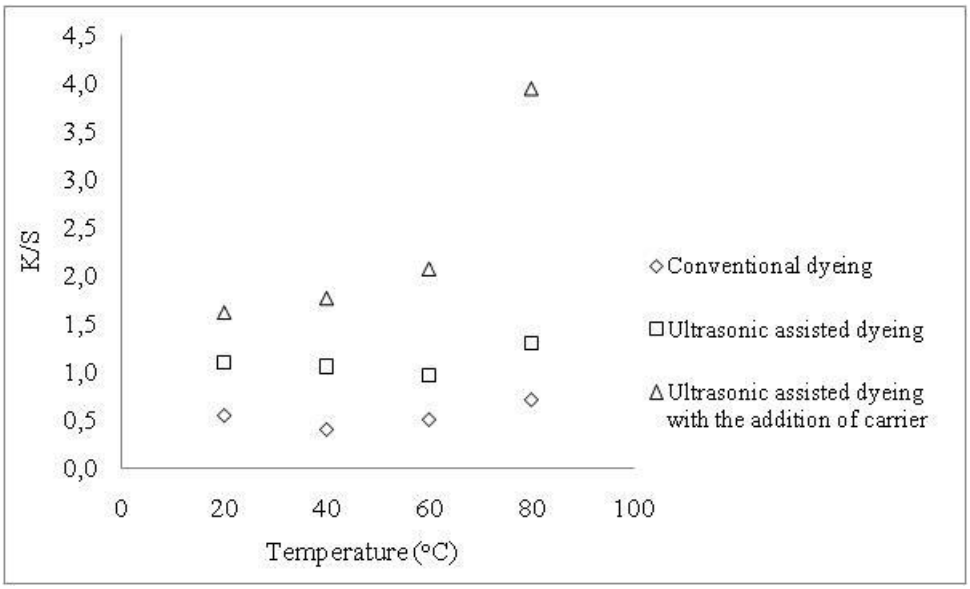

Figure 1. Color strengths of the dyed fabrics by ultrasonic power, by addition of carrier and by conventional dyeing at different dyeing temperatures.

From Figure 1 one can say that K/S values increase with temperature increases in all cases, ultrasonic energy provide bigger K/S values while carrier addition leads to the biggest K/S values. From this figure it is also obvious that ultrasonic energy improves dyeing. For dye molecules to absorb by the fiber, dye molecules should first diffuse into the fiber. As temperature increases fiber swells therefore dye diffusion enhances. In the case of ultrasonic dyeing (both with and without carrier) as well as the increase in temperature ultrasonic power plays an important role for dye molecules to disperse and to deaggregate. Therefore in this case better color strength values were obtained. Carrier addition to dyebath while ultrasonic energy was used has a greater possitive effect on color strength values since carrier is tought to be firstly absorbed by the fibre and the dye molecules tied on it. From Figure 1 it can be said that increase in K/S values is bigger after 60 ^{0}C in all cases.

Effect of dyeing technique and dyeing time

In order to obtain the optimum dyeing time, experiments for different time intervals (1, 3, 5, 10, 15, 20, 25 and 30 min) have also been done. The results of these studies can be seen in Figure 2.

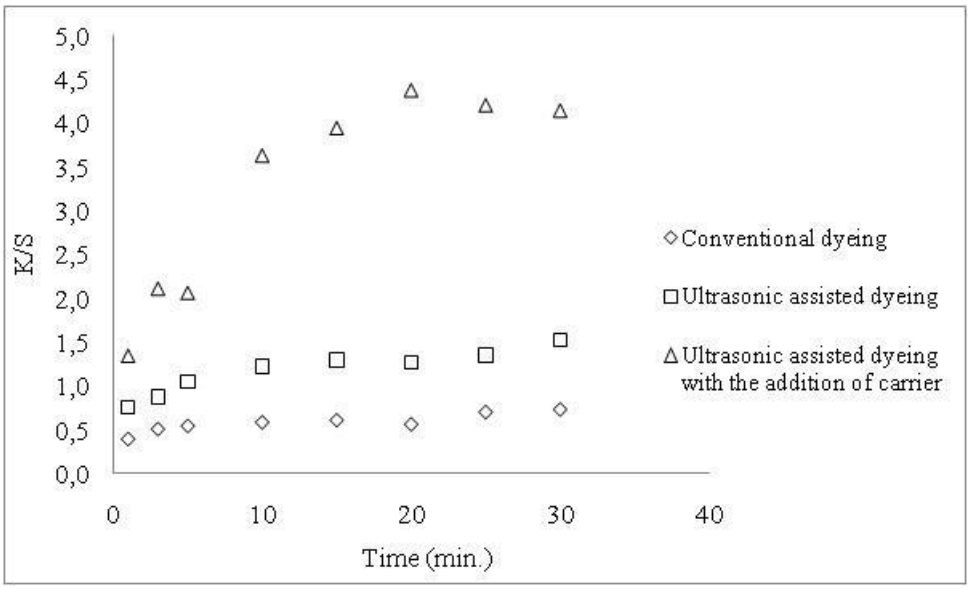

Figure 2. Color strengths of the dyed fabrics by ultrasonic power, by addition of carrier and by conventional dyeing at different dyeing times.

From Figure 2 it can be said that as time increases K/S values increase in all cases. Ultrasonic dyeing yields bigger K/S values compare to conventional dyeing and carrier addition gives the biggest K/S values. From this result effectiveness of ultrasonic method can also be interpreted. Increase in K/S values were recorded as time increases and after a certain time values does slightly change. This result can be tought that as time increases much dye can diffuse into the fiber, and after a certain time no noteworthy effect has been seen. Therefore it can be concluded that approximately 15-20 min.is the optiumum dyeing time.

Washing fastnesses of dyed fabrics

Washing fastness tests have been done to the ultrasonically dyed (with and without carrier) samples. According to color strength values, fabrics dyed at 80 ^{C}C temperature and 20 and 25 min. time were selected to make washing fastness analysis. According to this analyze 1 indicates poor fastness while 5 indicates good fastness. Results can be seen in Table 2.

Table 2. Washing fastnesses of dyed fabrics

Sample		Wool	Acrylic	Polyester	Polyamide	Cotton	Acetate
Ultrasonic dyeing (without carrier)	20 min	2	4-5	2-3	1	3	1
	25 min	2	4	2-3	1	3	1
Ultrasonic dyeing (with carrier)	20 min	1	4	2	1	2	1
	25 min	1-2	4-5	2-3	1	3	1

Washing fastness results of samples were poor to moderate. Although good color

strength values were obtained by new dyeing technique, washing fastness results show that these dyeings need to be fixed on fiber surface.

Discussion

In this study a new method for dyeing of polypropylene fiber was investigated. Color strength values (K/S) are directly proportional to the amount of dye on fiber. Therefore color strength values were used to understand the effectiveness of this new dyeing method. As it can be seen from Figure 1, color strength values of ultrasonically dyed samples (both with and without carrier) were bigger than conventionally dyed samples that shows that ultrasonic energy plays a positive role in dyeing. Ultrasonic energy is tought to have an effect on fiber swelling as well as dye dispersion and deaggregation.

In order to obtain optimum dyeing temperature, K/S values of fabrics dyed according to three different methods namely, ultrasonic, ultrasonic with carrier and conventional, were examined. In all three methods as temperature increases color strength values increase and a sudden increase could be seen after 60 ^{0}C (Figure 1). This increase may be attributed to swelling of fiber by temperature increase and therefore dye molecules can easily diffuse to areas between fiber. The bigger K/S values were obtained in the case of ultrasonic dyeing with carrier. The difference in K/S values obtained by ultrasonic dyeing both with and without carrier shows the effectiveness of this technique.

In Figure 2, dyeing time was plotted against color strength values. In all cases color strength values increase while time increases and approximately after 15-20 min. no noteworthy increase has been seen. According to these results, the optimum dyeing time can be suggested as about 15-20 min.

As for the washing fastnesses of fabrics, low-medium fastness to washing values were obtained. Therefore it can be said that successive processes is required for dye fixation.

In conclusion, dyeability of polypropylene fiber was improved by ultrasonic power. Color strength values showed an increase with temperature and time, and optimum dyeing temperature and time were suggested about 60 ^{0}C and 15-20 min. respectively. In comparison to conventional dyeing K/S values of ultrasonic dyeing are very big. Thus ultrasonic dyeing can provide both time and energy saving, therefore economy.

Nomenclature

owf : On the weight of fiber

K/S : Kubelka-Munk function (color strength)

PP : Polypropylene

PES : Polyester

PA : Polyamide

R : Reflectance

LABSA : Linear Alkyl Benzene Sulfonic Acid

λ_{max} : Wavelength of maximum absorption

D_{65} : Daylight illuminant

L* : Light-Dark axis in CIELab color space

a* : Red-Green axis in CIELAb color space

b* : Yellow-Blue axis in CIELAb color space

ΔL* : Magnitude of difference in color in L axis

Δa* : Magnitude of difference in color in a axis

Δb* : Magnitude of difference in color in b axis

ΔE : Magnitude of total difference in color

ISO : International Organization for Standardization

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