

INVESTIGATION THE DYEABILITY OF HYPERBRANCHED POLYMER MODIFIED POLYPROPYLENE FIBERS WITH NATURAL DYES

HİPERDALLANMIŞ POLİMER İLE MODİFİYE EDİLMİŞ POLİPROPİLEN LİFLERİNİN DOĞAL BOYALARLA BOYANABİLİRLİĞİNİN İNCELENMESİ

Asım DAVULCU

Department of Textile Engineering, Erciyes University, 38039, Kayseri, Turkey

Received: 13.10.2014

Accepted: 19.01.2015

ABSTRACT

Polypropylene (PP) fiber dyeable with natural dyes was produced with the inclusion of hyperbranched polymer (HBP) via melt spinning technique. Walnut shell (*Juglans regia* L), oak gall (*Quercus infectoria*), dyer's camomile (*Anthemis tinctoria*), sage tea (*Salvia officinalis* L) and cehri (*Rhamnus petiolaris*) are selected as natural dye sources. The effect of HBP concentration on K/S values of natural dyed PP fibers was investigated. The wash fastness and Fourier Transform Infrared (FTIR) spectroscopy results of fiber samples were also studied. Furthermore, the percent crystallinity of fiber samples was determined by differential scanning calorimeter (DSC) and the morphological analyses were performed with scanning electron microscopy (SEM). It was observed that the addition of HBP enhanced the dyeability of PP fiber with walnut shell, oak gall and cehri significantly compared to dyer's camomile and sage dyed ones. The chemical structure of dyes has a great importance in the interaction with HBP. The inclusion of HBP enhanced the dyeability of PP fibers with natural dyes.

Keywords: Polypropylene, dyeability, natural dye, dendrimer

ÖZET

Hiperdallanmış polimer (HBP) eriyik halde lif çekimi esnasında ilave edilerek doğal boyalarla boyanabilen polipropilen (PP) lifi üretilmiştir. Ceviz kabuğu (*Juglans regia* L), palamut (*Quercus infectoria*), papatya (*Anthemis tinctoria*), ada çayı (*Salvia officinalis* L) ve cehri (*Rhamnus petiolaris*) doğal boya kaynakları olarak seçilmiştir. Doğal boyalarla boyanmış PP liflerinin K/S değerlerine HBP konsantrasyonunun etkisi incelenmiştir. Yıkama haslıkları ve Fourier Dönüşümlü Infrared spektrometresi (FTIR) analizleri yapılmıştır. Ayrıca Diferansiyel Taramalı Kalorimetre (DSC) ile liflerin yüzde kristaliniteleri ve Taramalı Elektron Mikroskobu (SEM) ile morfolojik analizleri yapılmıştır. HBP ilavesinin; PP lifinin ceviz kabuğu, palamut ve cehri ile boyanabilirliğini papatya ve ada çayına göre daha çok artırdığı tespit edilmiştir. PP liflerinin doğal boyalarla boyanabilirliği HBP ilavesi ile arttığı görülmüştür.

Anahtar Kelimeler: Polipropilen, boyanabilirlik, doğal boya, dendrimer.

Corresponding Author: Asım Davulcu, adavulcu@erciyes.edu.tr Tel: +90 352 207 66 66/32882

1. INTRODUCTION

Polypropylene (PP) is a versatile and widely used synthetic polymer due to its low cost, high strength, high toughness, light weight, resistance to chemicals and reasonable thermal stability. PP fibers find a broad spectrum of use in apparel, upholstery, medical, geotextiles, various home furnishing sectors, automotive textiles and so on. However, they do not enjoy comparable popularity in the apparel sector of the

textile industry, one of the main reasons being lack of dyeability (1).

Dyeable PP fiber has remained an unsolved problem for decades. The inherent properties including non polar character, high crystallinity and high stereo-regularity of PP hinder dyeability with conventional dyeing techniques. Accordingly, PP is dyed commercially during melt spinning with the inclusion of organic and inorganic pigments. The

mass coloration of PP fibers during spinning limits its wider application and the number of available shades (2,3). However, the lack of high chroma colors, appearance of color streaks, and frequent yarn breaking during the finishing processes are some disadvantages of this technology (4).

The dyeability of PP fibers has been improved by blending or grafting with additives such as polyamide-6 (5,6), metal compounds, inorganic nanoparticles, nano clays, dendrimers, and hyper branched polymers during melt spinning (7-11) and many other additives (12,13).

Hyperbranched polymers have a very large number of branches and show similarity with conventional linear polymers. Hyperbranched polymers have received much attention due to their unique chemical and physical properties as well as their potential applications in coatings, additives, drug and gene delivery, macromolecular building blocks, nanotechnology, and supramolecular science (14). Hyperbranched polymers are generally produced by the condensation, addition and ring opening polymerization methods (15). A host of hyperbranched polymers have been presented in the literature: polyphenylenes (16), polyethers (17), polyesters (18), poly(esteramides) (19), poly(ester amines) (20), poly(sulfone amines), polyurethanes, poly(urea urethanes), poly(amine esters), poly(amide amines) (14), polyamides (21), polycarbonates (22) and polycarbosilanes (23). These polymers can provide many functional groups, such as hydroxyl, amine, carboxyl, anhydride, amide etc. The presence of polar groups and aromatic rings will ensure interaction with appropriate dyes. The dyeability of PP with CI. Disperse Blue 56 can be markedly enhanced through the incorporation of hyperbranched macromolecules such as Hybrane PS2550 (hyperbranched polyester-amide) into PP prior to fiber spinning (19).

Although modifications are applied to increase the dyeability properties of PP fibers especially with disperse dyes, only a limited number of studies have been done to increase the dyeability of PP fibers by anionic dyes with the inclusion of

nano clay, amine modifiers (polyamide 6, polyether amine), styrene amine resin (23-25). with natural dyes in the literature.

Natural dyes derived from naturally occurring sources such as plant, insect and mineral extracts are believed to be safe because of their non-toxic, non-carcinogenic and biodegradable nature (26). Natural dyes do not cause pollution and waste water problems (27). Moreover, many of the plants traditionally used in dyeing are credited with medicinal properties (28) and some of these have antimicrobial activity (26-31).

The aim of this study was to determine whether the dyeability of PP with walnut shell (*Juglans regia L*), oak gall (*Quercus infectoria*), dyer's camomile (*Anthemis tinctoria*), sage tea (*Salvia officinalis L*) and cehri (*Rhamnus petiolaris*) could be enhanced through the incorporation of hyperbranched poly(ester amide) (HPEA) into the polymer prior to fiber spinning.

2. MATERIALS AND METHODS

2.1. Materials

PP (Petoplen EH-251) with a melt flow index (MFI, 2.16 kg, 230 °C) of 20-28 g/10 min., was obtained from PETKIM A.Ş in Turkey. Hyperbranched polymer (HPB) dendrimer was donated by DSM corporation (Heerlen, Netherlands), under the trade name HYBRANE PS2550 with an average molecular weight 2500 g/mol in powder form. The chemical structure is shown in Figure 1.

Walnut shell (*Juglans regia L*), oak gall (*Quercus infectoria*), dyer's camomile (*Anthemis tinctoria*), cehri (*Rhamnus petiolaris*) and sage tea (*Salvia officinalis L*) which were cultivated in the Anatolia region were selected as natural dye sources and they were obtained from local markets in Turkey. Some of the chemical structures of the chromophore groups in selected natural dye sources are given in Figure 2.

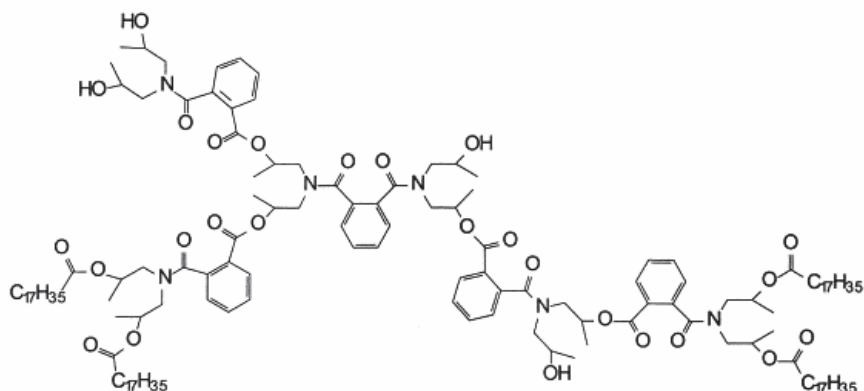


Figure 1. Chemical structure of HYBRANE PS2550 (19)

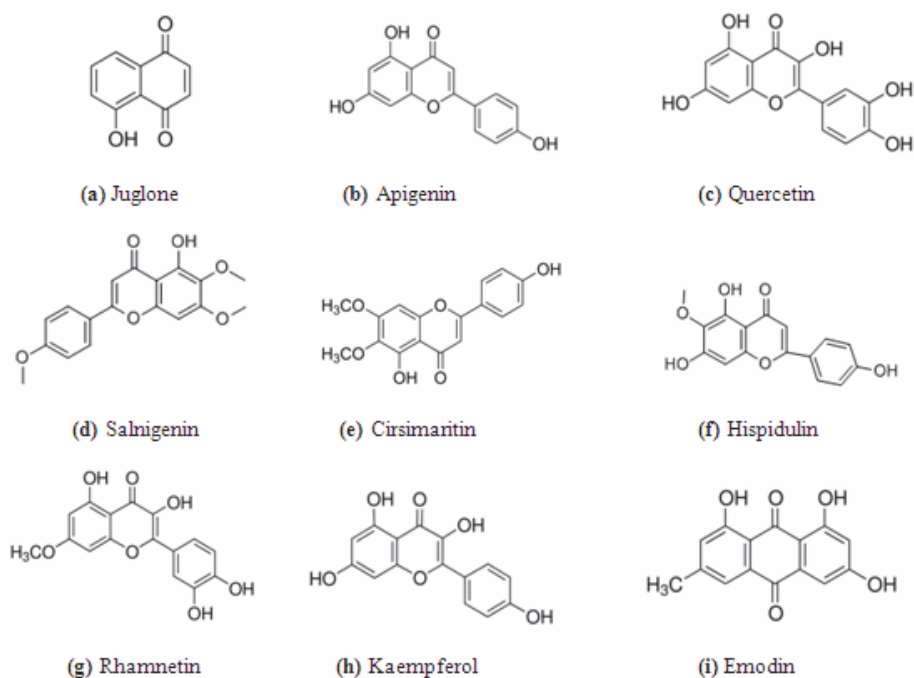


Figure 2. Chemical structure of some natural dyes.

2.2. Preparation of Monofilament PP Fibers

PP was dried at 80 °C for 8 hours before fiber the spinning process. The mixing of PP with HBP 1 wt% and 3 wt% was conducted in a twin screw microextruder (15 ml microcompounder®, DSM Xplore) coupled with winding unit (DSM Xplore) at 100 rpm at 230 °C. After mixing was complete, the twin screw extruder was brought to force controlled mode which ensures a uniform polymer melt flow. The diameter of the die is 0.25 mm. The spinning speed was 200 m/min. After the spinning process, as-spun monofilaments were obtained with varying diameters of 55-60 µm for PP fiber. No additional cooling was applied to the extrudate except for the ambient conditions (25 °C). The as spun fibers were drawn at 125 °C with a draw ratio of 3.5.

2.3. Dyeing Procedure

All dyeing processes were carried out according to the exhaustion technique in a laboratory type dyeing machine (Termal, Turkey) at a liquor ratio of 1:20 at pH 7-7.5, at 98 °C, for 60 minutes. Dyeing was performed using 100 % owf (on weight of fiber) walnut shell, oak gall, dyer's camomile, sage tea and cehri dye plants. The dried-ground forms of these natural dye sources were directly added to the dyeing bath as a kind of natural dyestuff. After dyeing, the fiber samples were removed from the dye baths and rinsed for 10 min., washed with a washing agents at a concentration 0.5 g/l at 70 °C for 10 minutes and then given a warm rinse twice at 70 °C for 10 minutes and finally a cold rinse with soft mill water, respectively.

2.4. Characterization Methods

Morphology Characterization: The surface morphology of the fiber samples was examined with scanning electron microscopy (SEM) (LEO 440 computer controlled digital, 20 kV). All specimens were sputter-coated with Au/Pd before examination.

Tensile Strength Measurement: In order to determine the tensile properties of the modified PP fibers, a tensile test was performed according to the standard ASTM D 3822 on Shimadzu AG-X tensile testing machine with a load cell of 10 N.

DSC Analysis: Differential Scanning Calorimeter (DSC) analyses were carried out on Perkin Elmer Diamond at a heating rate of 10 °C/min up to 200°C under nitrogen a flow of 50 ml/min. DSC analyses were performed on the PP and modified PP fiber samples in order to determine the melting point (T_m) and X values. The X values of the fiber samples can be determined from the following equation:

$$X (\%) = (\Delta H_c / (1-\Phi) * \Delta H^0_m) * 100$$

ΔH_c : Measured enthalpy of crystallization,

ΔH^0_m : Enthalpy of 100 % crystalline PP (209 Jg⁻¹)

Φ : Weight fraction of POSS nanoparticle in fiber sample

Color Measurement: The color strength (K/S) values of samples were measured using a spectrophotometer (Minolta 3600d, Japan) coupled to a PC under D65 illuminant/10° observer with UV and a specular component included mode for all measurements. The reflectance measurements expressed as K/S value were determined by the Kubelka-Munk equation:

$$K/S = (1-R)^2/2R$$

where K is the absorption coefficient, S is the scattering coefficient and R is the reflectance. Thereafter, the K/S values corresponding with wavelength of maximum absorption (λ_{max}) are reported as the color strength parameter.

FTIR Spectroscopy: Fourier Transform Infrared (FTIR) spectroscopy is a tool for identifying various functional groups present in the compound FTIR (Fourier transform

infrared spectroscopy) analysis of fabrics was carried out with a Perkin Elmer Spectrum 400.

Fastness Assessment: The wash fastness of fiber samples was tested using the method described in ISO 105 C06 B1S (32).

3. RESULTS AND DISCUSSION

3.1. Morphological Analysis

The SEM images of unmodified the PP and 3% HBP modified PP (MD-PP) fiber samples at a magnification of 1000× are shown in Figure 3. The unmodified PP has a smooth surface and the inclusion of HBP does not change the surface of the fiber. This proves that HBP is equally dispersed in the PP matrix. It can be seen that the average diameter of the PP and HBP modified PP fibers are nearly the same.

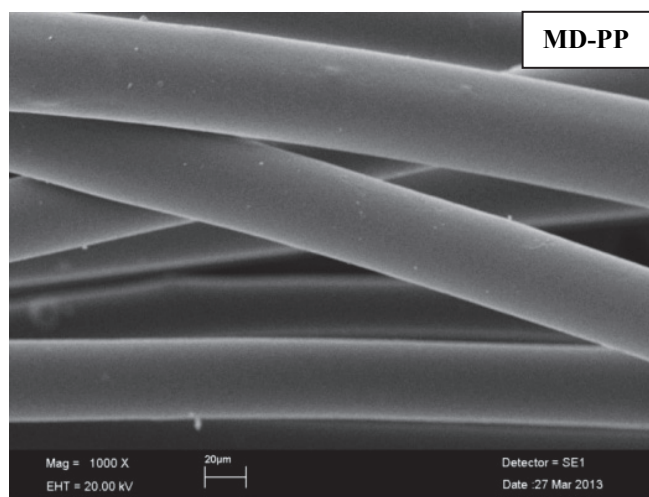
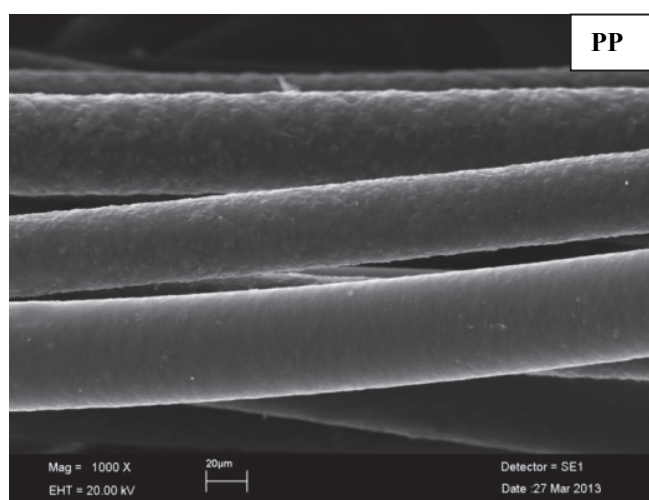


Figure 3. SEM images of fiber samples at magnification of PP (unmodified polypropylene) and MD-PP (3% HBP modified polypropylene)

3.2. DSC Analysis and Tensile Properties

Tensile tests on the monofilament fiber samples were made to investigate the effect of HBP on the mechanical properties of fibers. The stress at break values (σ) and elongation at break values (ϵ) are listed in Table 1. The incorporation of HBP causes a reduction in both the σ and ϵ values.

Table 1 Tensile and DSC data of fiber samples

SAMPLE	σ (MPa)	ϵ (%)	T_m (°C)	X (%)
Unmodified PP	34.2±1.4	91±16	164.3	39.9
1%modified PP	32.4±1.4	79±12	164.1	39.1
3%Modified PP	30.2±1.5	68±12	163.4	38.6

σ : Stress at break, ϵ : Percentage strain at break
 T_m : Melting point X: Percent crystallinity

One of the parameters that affects the dyeability of synthetic fibers is the percent crystallinity (X). It is known that the dye molecules diffuse into the amorphous region of synthetic fibers (33,34). The DSC data of fiber samples are listed in Table 1. The addition of HBP slightly decreases both the T_m and X of PP fiber. The added HBP is less crystal compared to polypropylene and incompatible with polypropylene matrix which leads to a reduction in total crystallinity may reduce T_m and X. Considering the dyeability, adding HBP to PP increases the amount of interfaces and reduces the degree of crystallinity, thereby, increasing the number of accessible active sites for fixation of dyestuff molecules (4).

3.3. Effect of HBP concentration on K/S values

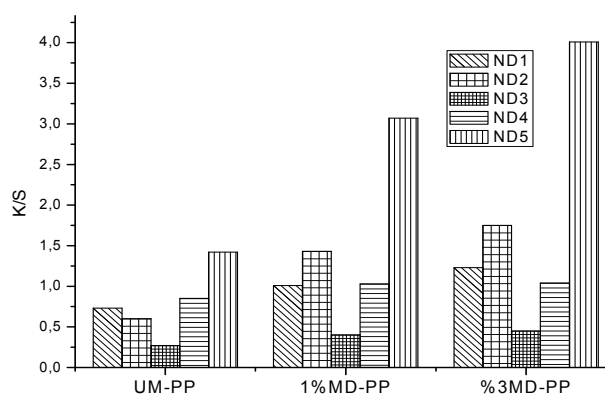


Figure 4. The effect of HBP concentration on K/S values of natural dyed fiber samples (MD: Modified, UM: Unmodified, PP: polypropylene, ND: Natural Dye, ND1: Walnut shell, ND2: Oak gall, ND3: Dyer's chamomile, ND4: Sage tea, ND5: Cehri)

The K/S values of unmodified, 1% HBP modified and 3% HBP modified PP fibers dyes with walnut shell, oak gall, dyer's chamomile, cehri and sage tea are given in Figure 5. The extracts of green walnut shells and walnut leaves consist of 5-hydroxy-1,4-naphthoquinone juglone (35) (Figure 2a). The dye uptake of modified PP fibers increased with the increasing of the HBP concentration (Figure 5). Walnut shell is generally used in wool dyeing (36). The cationic character of wool provides dyeing with walnut shell with a good color strength. In contrast to wool, cotton is less dyeable with juglone due to its anionic character. The cationic character of Hybrane PS 2550 may enhance the dyeability with walnut shell dyeing.

The color strength of oak gall dyed modified PP increased as the HBP concentration increased. The photochemical studies signified that oak gall (*Quercus infectoria*) consists of tannic acid (gallotannic acid, the principal constituent, 50-70%), gallic acid, syringic acid, ellagic acid, /f-sitosterol, amentoflavone hexamethyl ether, isocryptomerin, starch, essential oils, anthocyanins, methyl-betulate, methyl-oleate, hexagalloyl glucose, and polygalloyl-glucose (37). The term "tannin" by extension is widely applied to any large

polyphenolic compound containing sufficient hydroxyls and other suitable groups (such as carboxyls) to form strong complexes with various macromolecules (38). The color strength of modified PP fibers may be considerably higher than unmodified PP fiber due to these groups.

Flavonoids (flavones and flavonols) are the main chromophores in the most extensively used yellow dyes (39). The main flavonoids in dyer's camomile are apigenin and quercetin (40) (Figure 2b,c). There was a little increase in K/S values in MD-PP fibers when compared to unmodified PP fiber even when the HBP concentration was increased. Like dyer's camomile dyeing, the K/S values of sage tea dyed modified fibers did not show a significant increase even if the HBP concentration was increased. The main flavonoids in sage tea are salvigenin, cirsimaritin and hispidulin (Figure 2d,e,f). These flavonoid groups probably have little effect on the formation of secondary bonds with HBP molecules. The highest K/S values were obtained from cehri dyed modified PP fibers. Quercetin, rhamnetin and kaempferol dyestuffs are classified as flavonoids and emodin is an anthraquinone (39,40) (Figure 2c,g,h,i). The dyeability of PP with dispers dyes including the anthraquinone group was markedly enhanced through the incorporation of hyperbranched polyester-amide modified PP fiber (19). Emodin, having anthraquinone group, enhances the interaction between HBP so the K/S values of 3% HBP modified PP fibers reach to highest value. Moreover it can be thought that the reason of the highest value obtained by cehri can be related with the hydroxyl group amount (Figure 2).

The presence of certain functional groups in suitable positions in the dye molecule causes its coordination to the functional groups on fiber. When the HBP concentration was increased, the K/S values of all natural dyed PP fibers increased. HBP concentration raises the polar character of PP fiber thus the color strength of natural dyed PP fibers is enhanced. It is obvious that the color strength (K/S) of HBP modified PP fibers is higher than that of unmodified PP fibers.

3.4. FTIR analysis

The ATR-FTIR spectrum of the unmodified PP fiber shows four large peaks in the wave number range 3000–2800 cm^{-1} . The strong peaks at 2949 and 2867 cm^{-1} are attributed

to CH_3 asymmetric/symmetric stretching vibrations, and those at 2916 and 2837 cm^{-1} are assigned to CH_2 asymmetric/symmetric stretching vibrations (41,42). There are also two intense peaks at 1454 and 1375 cm^{-1} , which are assigned to CH_3 asymmetric deformation vibrations or CH_2 scissoring vibrations, and CH_3 symmetric deformation vibrations, respectively (41-43).

The ATR-FTIR spectrum of PP shows two intense peaks at 1460 and 1378 cm^{-1} : the peak around 1460 cm^{-1} is caused by CH_3 asymmetric deformation vibrations or CH_2 scissor vibrations, while the peak at 1379 cm^{-1} is due to CH_3 symmetric deformation vibrations in the amorphous region of PP (43,44). The peak at 1166 cm^{-1} can be attributed to C–C asymmetric stretching, CH_3 asymmetric rocking and C–H wagging vibrations in the crystalline regions. The peaks around 842 and 810 cm^{-1} are due to CH_2 rocking vibrations in the crystalline regions. Many smaller peaks are shown in the spectrum in the region 1200–800 cm^{-1} , which is characteristic for polypropylene (41,43). In general, it was observed that no significant differences were available in the bands and intensities of unmodified and HBP modified PP fibers.

3.5. Fastness Properties

The wash fastness of unmodified PP and 3 wt % HBP containing fibers dyed with walnut shell, oak gall, dyer's camomile, sage tea and cehri are shown in Table 2.

The change in color for cehri dyed unmodified PP fibers is the highest as the color strength of dyed fiber is high. Although the color strength of cehri dyed modified PP fiber is high, the change in color is low. The color change in modified PP dyed with walnut shell, oak gall, dyer's camomile, and sage tea is similar to that in unmodified PP dyed ones. Natural dyes mostly require a mordant like alum, copper sulphate, potassium dichromate, iron salts and stannous chloride to be fixed onto the fiber in order to enhance fastness properties (45). The staining on multifiber for unmodified PP fibers dyed with walnut shell, oak gall, dyer's camomile, and sage tea are similar to each other as their color strength values are low. For cehri dyed unmodified PP fiber, staining on multifiber is high as the color strength is high. HBP added to PP enhanced the wash fastness properties.

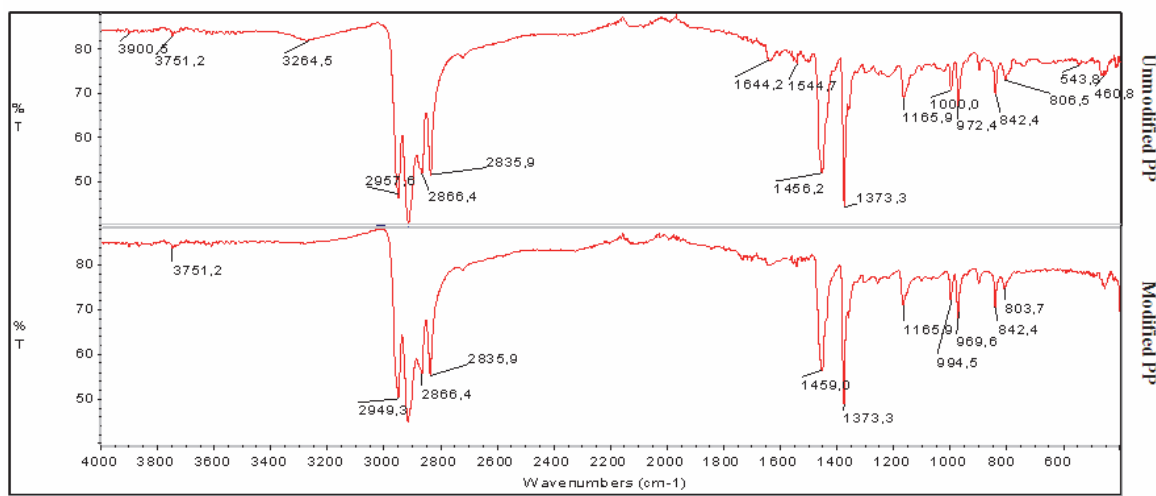


Figure 5 FTIR of unmodified and 3% HBP modified PP fibers.

Table 2 Wash fastness properties of fiber samples (¹: walnut shell, ²: oak gall, ³: dyer's camomile, ⁴: sage tea, ⁵: cehri).

Sample	Shade Change	Acetate	Cotton	Staining on			
				Nylon	Polyester	Acrylic	Wool
¹ Unmodified PP	3-4	4-5	4	4	4-5	4	4
¹ MD-PP	4	4-5	4-5	4-5	5	4-5	4-5
² Unmodified PP	3-4	4	4	4	4-5	4	4
² MD-PP	4	4-5	4-5	4-5	5	4-5	4-5
³ Unmodified PP	3-4	4-5	4-5	4-5	5	4-5	4
³ MD-PP	4	4-5	4-5	4-5	5	4-5	4-5
⁴ Unmodified PP	3-4	4-5	4-5	4	4-5	4-5	4
⁴ MD-PP	4	4-5	4-5	4-5	5	4-5	4-5
⁵ Unmodified PP	3	4	3-4	3	4-5	3-4	2-3
⁵ MD-PP	4	4-5	4-5	4	5	4-5	3-4

4. CONCLUSION

In this study, PP is modified with hyper-branched poly(ester amide) in order to enhance dyeability with walnut shell, oak gall, dyer's camomile, sage tea and cehri. The K/S values of all modified PP fibers dyed with natural dyes increased. The highest K/S values were obtained from cehri dyed modified PP fibers. The color strength of walnut shell and oak gall dyed modified PP fibers was higher than those of the dyer's camomile, and sage tea dyed samples. The color strength of all natural dyed modified PP fibers increased with increasing HBP concentration. The chemical structure of natural dye has a great effect on the color strength of modified PP fibers. The polar structure of HBP enhanced interaction with the functional groups in natural dye sources.

It is observed from the SEM images that the HBP uniformly dispersed into the PP matrix. The incorporation of HBP causes acceptable reduction at both stress at break values (σ) and elongation at break values (ϵ). The T_m and X values of modified fiber samples are almost close to those of the unmodified PP fiber. The experimental results indicated that HBP also enhanced the wash fastness properties when compared to unmodified PP fibers. It is thought that this study offers a new approach to improve the dyeability of PP fiber with natural dyes.

ACKNOWLEDGEMENTS

This work was supported by Erciyes University Scientific Research Unit under grant no: BAP-FBA-10-3316.

REFERENCES

- Toshnival, L., Fan, Q., Ugbohue, S.C., 2007, "Dyeable polypropylene fibers via nanotechnology". *Journal of Applied Polymer Science*, 106, pp: 706-711.
- Burkinshaw, S.M., 1995, *Chemical Principle of Synthetic Fibre Dyeing*, London, Chapman&Hall, 223.
- Needles, H.L., 1986, *Textile Fibers, Dyes, Finishes and Processes*, New Jersey, Noyes Publications, 227.
- Mirjalili, F., Moradian, S., Ameri, F., 2013, "Enhancing the dyeability of polypropylene fibers by melt blending with polyethylene terephthalate", *Scientific World Journal*, Article ID: 46854.
- Ataefard, M., Moradian, S., 2012, "Preparing dyeable PP fiber nanocomposites using the special cubic mixture experimental design". *Journal of the Textile Institute*, 103, p:1169-1182.
- Effenberger, F., Schweizer, M., and Mohamed, W.S., 2010, "Effect of montmorillonite clay nanoparticles on the properties of polypropylene fibres", *Polymer-Plastics Technology and Engineering*, 49, pp: 525-530.
- Arkman, J., Prikril, J., 1996, "Dyeing behavior of polypropylene blend fiber. I. Kinetic and thermodynamic parameters of the dyeing system", *Journal of Applied Polymer Science*, 62, pp: 235-245.
- Li, G., Wang, L., Ni, H., Pittman, C.U., 2001, "Poly oligomeric silsesquioxane (POSS) polymers and copolymers: a review", *Journal of Inorganic and Organometallic Polymers*, 11, pp: 123-154.
- Joshi, M., Bhattacharyya, A., 2011, "Nanotechnology – a new route to high-performance functional textiles", *Textile Progress*, 43, pp: 155-233.
- Butola, B.S., Joshi, M., Kumar, S., 2010, "Hybrid organic-inorganic POSS (polyhedral oligomeric silsesquioxane)/polypropylene nanocomposite filaments", *Fibers and Polymers*, 11, pp: 1137-1145.
- Zeng, J., Kumar, S., Iyer, S., Schiraldi, D.A., Gonzalez, R.I., 2005, "Reinforcement of poly(ethylene terephthalate) fibers with polyhedral oligomeric silsesquioxanes (POSS)", *Advances in Polymer Science*, 17, pp: 403-424.
- Rabiei, N., Haghghat, K., Amirshahi, S.H., Radjabian, M., 2012, "The kinetic and thermodynamic parameters of dyeing of polypropylene/clay composite fibers using disperse dye", *Dyes and Pigments*, 94, pp: 386-392.
- Ataefard, M., Moradian, S., "Investigation the effect of various loads of organically modified montmorillonite on dyeing properties of polypropylene nanocomposites", *Journal of Applied Polymer Science*, 125: pp:214-223.
- Gao, C., Yan, D., 2004, "Hyperbranched polymers: from synthesis to applications", *Progress in Polymer Science*, 29, pp: 183-275.
- Kim, Y.H., 1998, "Hyperbranched polymers 10 years after", *Journal of Polymer Science* 1998; 36: 1685-1698.
- Kim, Y.H., Beckerbauer, R., 1994, "Role of end-groups on the glass-transition of hyperbranched polyphenylene and triphenylbenzene derivatives", *Macromolecules*, 27, pp: 1968-1971.
- Uhrich, K.E., Hawker, C., Frechet, J.M.J., Turner, S.R., 1992, "One-pot synthesis of hyperbranched polyethers", *Macromolecules*, 25, pp: 4583-4587.
- Woolley, K.L., Frechet, J.M.J., Hawker, C.J., 1994, "Influence of shape on the reactivity and properties of dendritic, hyperbranched and linear aromatic polyesters", *Polymer*, 23, p: 4489-4595.
- Burkinshaw, S.M., Froehling, P.E., Mignaneli, M., 2002, "The effect of hyperbranched polymers on the dyeing of polypropylene fibres" *Dyes and Pigments*, 53, pp: 229-235.
- Gao, C., Tang, W., Yan, D.Y., 2002, "Synthesis and characterization of water-soluble hyperbranched poly(ester amine)s from diacrylates and diamines", *Journal of Applied Polymer Science: Part A: Polymer Chemistry*, 40, pp: 2340-2349.

-
21. Ishida, Y., Sun, A.C.F., Jikei, M., Kakimoto, M., 2000, "Synthesis of hyperbranched aromatic polyamides starting from dendrons as AB_x monomers: effect of monomer multiplicity on the degree of branching", *Macromolecules*, 33, pp: 2832–2838.
 22. Bolton, D.H., Wooley, K.L., 1997, "Synthesis and characterization of hyperbranched polycarbonates", *Macromolecules*, 30, pp: 1890–1896.
 23. Yoon, K., Son, D.Y., 1999, "Synthesis of hyperbranched poly(carbosilarylenes)", *Macromolecules*, 32, pp: 5210–5216.
 24. Razafimahefa, L., Chlebicki, S., Vroman, I., Devaux, E., 2008, "Effect of nanoclays on the dyeability of polypropylene nanocomposite fibres", *Coloration Technology*, 124, pp: 86-91.
 25. Arkman, J., Prikryl, J., 1996, "Dyeing behavior of polypropylene blend fiber. I. Kinetic and thermodynamic parameters of the dyeing system", *Journal of Applied Polymer Science*, 62, pp: 235-245.
 26. Bahtiyari, M.İ., Benli, H., Yavaş, A., 2013, "Printing of wool and cotton fabrics with natural dyes", *Asian Journal of Chemistry*, 25, pp: 3220-3224.
 27. TUTAK, M., Acar, G., Akman, O., 2014, "Natural dyeing properties of wool fabrics by pomegranate peel (*Punica granatum*) peel", *Tekstil ve Konfeksiyon*, 16: 81-85.
 28. Tutak, M., Önal, L., Benli, H., 2013, "Investigation of wicking properties of naturally dyed linen fabrics", *Tekstil ve Konfeksiyon*, 24: 374-380.
 29. Singh, R., Jain, A., Panwar, S., Gupta, D., Khare, S.K., 2005, "Antimicrobial activity of some natural dyes", *Dyes and Pigments*, 66, pp: 99-102.
 30. Ibrahim, N.A., El-Gamel, A.R., 2010, "Gouda M and Mahrous, F. A new approach for natural dyeing and functional finishing of cotton cellulose", *Carbohydrate Polymers*, 82, pp: 1205-1211.
 31. Davulcu, A., Benli, H., Şen, Y., Bahtiyari, M.İ., 2014, "Dyeing of cotton with thyme and pomegranate Peel", *Cellulose*, DOI 10.1007/s10570-014-0427-8.
 32. Anonymous, 1990, *Methods of test for colour fastness of textile and leather*, 5 th ed. Bradford: Society of Dyers and Colourists, 619.
 33. Yan, H., Chen, Y., 2010, "Blends of polypropylene and hyperbranched poly(phenylene sulphide) for production of dyeable p fibres", *Iranian Polymer Journal*, 9, pp: 791-799.
 34. Yu, C., Zhu, M., Shong, X., Chen, Y., 2001, "Study on dyeable polypropylene fiber and its properties", *Journal of Applied Polymer Science*, 82, pp: 3172-3176.
 35. Mirjalili, M., Karimi, L., 2013, "Extraction and Characterization of Natural Dye from Green Walnut Shells and Its Use in Dyeing Polyamide: Focus on Antibacterial Properties", *Journal of Chemistry*, Article ID 375352.
 36. Ghaheh, F.S., Nateri, A.S., Mortazavi, S.M., Abedi, D., Mokhtari, J., 2012, "The effect of mordant salts on antibacterial activity of wool fabric dyed with pomegranate and walnut shell extracts", *Coloration Technology*, 128, p: 473-478.
 37. Hamid, H., Kaur, G., Abdullah, S.T., Ali, M., Athar, M., Alam, S., 2005, "Two new compounds from the galls of *Quercus infectoria*. with nitric oxide and superoxide inhibiting ability", *Pharmaceutical Biology*, 43, pp: 317-323.
 38. Fennemas, D.S., 2014, *Food Chemistry*, 4 th edition, Content Technologies.
 39. Cardon, D., *Natural dyes – sources, tradition, technology and science*, 2007, London, Archetype Publications Ltd, 800.
 40. Özgökçe, F., Yılmaz, İ., 2003, "Dye plants of East Anatolia Region (Turkey)", *Economic Botany*, 57, pp: 454- 460.
 41. Yin, H., Mix, R., Friedrich, J., 2011, "Influence of differently structured aluminium–polypropylene interfaces on adhesion", *Journal of Adhesion Science and Technology*, 25, pp: 799–818.
 42. Sciaratta, V., Vohrer, U., Hegemann, D., Müller, M., Oehr, C., 2003, "Plasma functionalization of polypropylene with acrylic acid", *Surface and Coatings Technology*, 174-175, pp: 805–810.
 43. Morent, R., Geyter, N.D., Leys, C., Gengembre, L., Payen, E., 2008, "Comparison between XPS- and FTIR-analysis of plasma-treated polypropylene film surfaces", *Surface and Interface Analysis*, 40, pp: 597-600.
 44. Socrates, G., 2001, *Infrared and Raman characteristic group frequencies – tables and charts (3rd edn)*, John Wiley & Sons, West Sussex, 362.
 45. Jothi, D., 2008, "Extraction of natural dyes from African marigold flower (*Tagetes erecta* L) for textile coloration", *Autex Research Journal*, 8, pp:49-53.