Dyeing and Fastness Properties of Acid Dyeable Polypropylene Nanocomposites

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ABSTRACT

PP nanocomposites acid dyeability using three distinct chemical structures, namely, anthraquinone, premetallized and monoazo with four major colors was investigated. The dyeing properties and the wash fastness of the dyed samples prepared under different experimental conditions were studied. The PP nanocomposite was prepared using nanoclay with the aid of ultrasonication. PP nanocomposite films with various clay concentrations were dyed with four acid dyes, which are C.I Acid Blue 80, C.I Acid Orange 74, C.I Acid Red 266, and C.I Acid Yellow 135. The effect of clay add-on, ultrasonication time and dye fixation time on the color yield (K/S) on the PP nanocomposites were examined in relation to dye structures. It was found that increasing the clay content from 0% to 8 % had a significant effect on the dye uptake. Ultrasonication time and dye fixation time had no immediate effect on the color yield of acid dyes although comparatively more uniform dyeing was obtained with increased ultrasonication. Fairly reasonable wash fastness results were achieved with best ratings shown by monoazo dye CI Acid Yellow 135.

Keywords: dyeability, polypropylene, nanoclay, acid dye, color fastness

1. INTRODUCTION

Improper dye or inappropriate dyeing process results in poor appearance of finished products. In the case of polypropylene (PP), these defects appear as non-uniform dyeing, different tints etc. The structural features responsible for the higher strength and thermal stability of isotactic PP limit the internal volume accessible to the dye molecules. Another serious disadvantage is the completely non-polar aliphatic structure of PP.

Modification of PP can impart new properties to the fiber. In the past this was done by grafting various agents or by introducing in PP melt, prior to molding, numerous high and low molecular weight substances that exhibit affinity for particular dyes. Modification methods by fiber treatment can be divided into two groups: chemical treatments, in which the polymer structure is chemically altered, and infusing treatments, in which foreign materials are infused into the fiber to become dye receptors.

Akrman *et al.* extruded modified PP polymer that was a mixture of an additive and the polymer itself [1-3]. The additive was synthesized by reacting styrene maleic anhydride copolymer with a mixture of 3-dimethylaminopropylamine and octadecylamine. Another method of PP modification is to add compounds that form active centers to fix the dye. The modifying additives are compounds of complex forming metals, mostly Ni, Al and Zn [4-5]. The additives introduced do not form bonds with the polymer; instead the metals form chelates with dyes and are fixed on to the fiber. Carpets made from mass pigmented unmodified PP yarns are only suitable for certain indoors uses because of limited light, washing and dry cleaning fastness. The Ni-modified PP allows the use of indoor/outdoor carpets with much better fastness properties when printed with chelatable dyes. However, this technique also has some disadvantages [6]. Therefore, the problem of quality dyeing of PP and various composition based on it is still unsolved.

Nanotechnology has been used to increase the tensile strength, flexural modulus and heat resistance of polymeric materials. Nanoparticles, such as montmorillonite clay, normally reinforce the thermal properties of the nanaocomposite fiber [7-11]. The dyeing of PP using nanoclay holds a lot of prospect and expectation. The dyesites in the PP nanocomposite are expected to be the places where nanoclay particles are located. The low cost of nanoclay incorporation, flexibility, and its low doping levels give it an edge over all other additives that were used in the past to make PP dyeable. This paper is an account of an in depth analysis of the effects of polymer processing (clay concentration and sonification time) and dyeing (fixation time) conditions on the reflectance properties of acid dyed modified PP nanocomposites. The fastness properties of the dyed PP films are also reported.

2. EXPERIMENTAL

2.1 Experimental Design

The following experimental layout (Table 1) was planned in order to investigate the effect of varying the three independent variables (experimental factors) on the K/S values of the acid dyed virgin PP and PP nanocomposites. The hypothesis is that the factors,

clay add-on, ultrasonic time and fixation time are significant. The synthesis procedure and conditions for the preparation of these PP nanocomposites have already been reported [12].

Table 1 Experimental Design

Experimental Factors	Levels			
Clay add-on (%)	0	2	4	8
Ultrasonic time (min)	30		120	
Time at Fixation Temperature (min.)	60		120	

Table 2 PP Nanocomposites Process Parameters and K/S Values at 4% shade

Sample	Clay add-on	Ultra sonic Time	K/S at 4% depth of shade of C. I. Acid Dyes			
	% owp	min.	Orange 74	Blue 80	Red 266	Yellow 135
PP0	0	30	0.5	0.35	0.3	4.7
Nano PP1	2	30	1.8	0.85	2.0	4.9
Nano PP2	4	30	3.5	1.45	3.6	7.4
Nano PP3	8	30	4.1	2.25	5.0	7.8
Nano PP4	2	120	3.4	0.45	1.4	5.7
Nano PP5	4	120	3.0	1.65	3.4	6.8
Nano PP6	8	120	5.3	4.6	5.3	9.4
Nylon			15.0	13.5	15.2	13.0

* *On weight of polymer (PP)*

2.2 Dyeing

The PP nanocomposites were dyed at 2, 4 and 6 % depth of shade. For comparison, virgin PP, polyester and nylon were also dyed at 2, 4 and 6% owf. Dyeing was performed in Ahiba Polymat Lab.dyeing machine. The commercial dyes used without any further purification are listed in table 3.

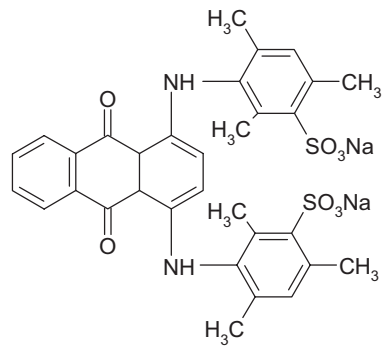
Table 3 Acid dyes and gray scale rating on dyed nylon

C.I. Generic Name	Gray scale rating (GSR) on nylon
C.I Acid Blue 80	3/4
C.I Acid Orange 74	4/5
C.I Acid Red 266	4/5
C.I Acid Yellow 135	3 *

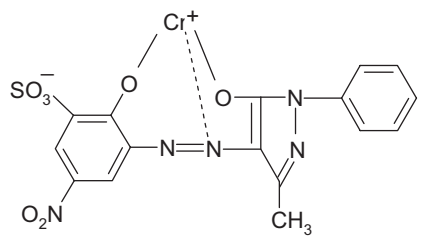
**GSR 5 after syntan aftertreatment*

The dye chemical structures are shown below.

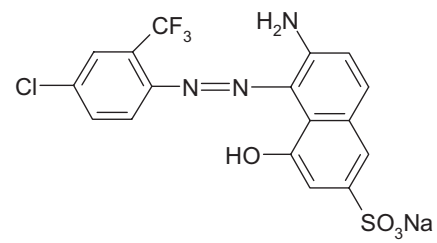
C.I. Acid Blue 80



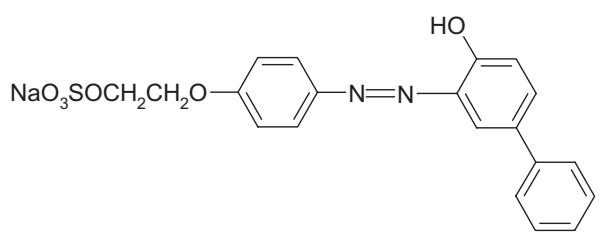
C.I. Acid Orange 74



C.I. Acid Red 266



C.I. Acid Yellow 135



For acid dyeing, the liquor to goods ratio for all the dyeing was 30:1. The pH of the acid dyebath was dependent on dye structure and was varied between 2.5-5.0 using acetic acid (80%). 2g/l of stock dye solution for dyeing was prepared. The remaining dyebath ingredients were weighed as follows: Glaubers Salt (20 g/l), anionic leveling agent (2 g/l). The dyeing tubes were sealed and heated from 30°C to 100°C at the rate of 2°C/min. The temperature was then kept constant for 60 minutes. Finally the dyebath was cooled down

to 40°C. The samples were extracted and washed under cold running water for 5 minutes.

2.3 Measurement of Depth of Shade

The depth of shade was measured on the dyed PP nanocomposites and nylon by determining the K/S value using Kubelka-Munk equation. Reflectance values were obtained by using Macbeth Color Eye 2040 Spectrophotometer and K/S values were calculated according to the following equation:

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

where R is the decimal reflectance value measured from wavelength giving the substrate the maximum absorption.

2.4 Wash fastness

The AATCC Test Method 61-2A was performed on the virgin PP (PP0) and other PP nanocomposites samples dyed at 4% owf depth of shade [13]. The test specimen was prepared by cutting a 10 cm x 5 cm piece of dyed PP nanocomposite film. This was then stapled along one of the shorter edges with the multi-fiber strip (10 cm x 5 cm). The rate of color change of test specimen was evaluated by Gray Scale for Color Change. The amount of staining on multi-fiber test fabric was evaluated by using AATCC Chromatic Transference Scale.

3. RESULTS AND DISCUSSION

3.1 Effect of Clay Add-on

It is evident from the visual and spectral comparison of the dyeings that nanoclay does create attractive dye sites when dispersed with PP. The acid dye particles adhere to the nanocomposite, primarily due to the ionic attraction between clay particles and the charged chemical group sites in the dye structure [14]. Thus, three different possibilities can be advanced to explain the acid-dyeing phenomenon of PP nanocomposite:

(i) Pores and cracks may occur on the film surface and cross-section during the processing; these submicroscopic voids may allow diffusion of dye into the film;
(ii) Dye diffusion may occur through the wicking process; and
(iii) Dye diffuses through PP nanocomposite in the form of an unionized molecules thus behaving like a disperse dye.

All the above explanations may have a combined role to play in the acid dyeing of PP nanocomposite. The more compatible the clay particles are with PP, the better dyeing properties they impart to the fiber for equivalent number of dyesites. According to Ahmed, the diffusion of dye as unionized molecules through polysolution mechanism does not need support of interphase boundary area for the penetration of dye into the interior of the film [4]. This idea is supported by the fact that acetic acid is better absorbed by acid dyeable PP fibers than strongly ionized hydrochloric acid [4].

3.2 Effect of Ultrasonication Time

The effect of sonification is dependent on a number of factors including but not limited to the amount of organic solvent used for nanocomposite dispersion, timing of clay addition, when to start sonification, rate of evaporation of organic solvent, pulsation rate and amplitude. It is believed that all the above factors have little or no effect on the ultrasonication treatment and thus, were kept constant for all the PP nanocomposites synthesised. To increase the effectiveness of ultrasonication process either one or a combination of the above factors had to be changed.

3.3 Effect of Time of Fixation

In order to find the saturation time for PP nanocomposite, all the samples were dyed at their fixation temperatures for 60 and 120 min. The prime aim was to find an optimum time taken for the dye to attach itself to maximum number of dyesites. For CI Acid Blue 80, at 2% owf, there was circa 1.5 units increase in (K/S) value of the dyed PP nanocomposites as the time was increased from 60 to 120 min. For other dyes mostly there was no change in dye uptake for paler shades.

3.4 Wash fastness

Wash fastness tests were performed on samples dyed at 4% owf. The fastness of dye to wet treatments, such as washing, is a function of kinetic (diffusion) and thermodynamic (affinity) effects. Wet fastness can be divided into two broad categories i.e. (i) Staining on adjacent fabrics and (ii) and the fading/shade change of the sample on washing. All the acid dyes had good wash fastness on nylon and polyester respectively. The figures listed in Table 3 are gray scale ratings on dyed fabrics rather than films. A few samples of acid dyed PP nanocomposites were selected and were after-treated with the synthetic tanning agent to investigate its effect on wash fastness results. This treatment did not have any effect on the fastness rating.

The wash fastness results of acid dyed PP nanocomposites were good except for CI Acid Red 266. Due to color loss of the nanocomposites dyed with CI Acid Red 266, nylon 6,6 was badly stained on multi-fiber strip. The rating of virgin PP is trivial, as it did not absorb any dye that could be washed during the test.

However, the wash fastness rating of the dyes with molecules of same degree of sulfonation would increase with an increase in the molecular weight. The longer alkyl groups in the dye molecules would account for increased hydrophobic interaction between the dye and the substrate causing an improvement in wash fastness. The two sulphonate groups and high molecular weight of CI Acid Blue 80 are associated with its excellent wash fastness on PP nanocomposites. But the CI Acid Red 266 dye being mono sulphonated with low molecular weight was easily washed away due to low dye affinity and diffusion.

4. CONCLUSIONS

The following conclusions are drawn from this study:

- Any change in the color depth of dyed PP nanocomposites can be attributed to the add-on of the nanoclay. The increase in dye fixation time and sonification time for nanocomposite processing did not result in any significant effect on PP dyeability. The amount of clay in the nanocomposite by far is the most dominant factor influencing the dye uptake of PP with polar acid dyes.
- All the PP nanocomposites exhibited better dye uptake than virgin PP. In terms of color yield, the best results were recorded for a monoazo structure, C.I. Acid Yellow 135. At 6% owf and 60 min fixation time, the K/S value for virgin PP was 4.7 while for nanoPP6 it was 9.4.
- Uniform dyeing was only observed on samples dyed at 6% owf depth of shade with a clay add-on of 8%. The values of wash fastness ratings varied significantly. The best ratings were registered for C.I. Acid Blue 80, which is understandable due to its substantivity towards PP nanocomposites. In terms of performance the best compromise is C.I. Acid Yellow 135 with rating around 5.

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