Available online at www.sciencedirect.com

ScienceDirect

Dyes and Pigments 75 (2007) 199–206

DYES and PIGMENTS

www.elsevier.com/locate/dyepig

Process analysis and optimization for the ionic interactions of quaternary ammonium salts with nylon 66 fibers using statistical experimental design

K. Ravikumar, Young-A. Son*

BK21 FTIT, Department of Organic Materials and Textile System Engineering, Chungnam National University, Daejeon, 305-764, South Korea

Received 15 December 2005; received in revised form 24 March 2006; accepted 30 April 2006
Available online 10 July 2006

Abstract

A 2^4 response surface central composite design was successfully formulated using statistical software to establish the optimum process conditions for developing durable antimicrobial nylon 66 fibers through interactions with two different types of quaternary ammonium salts (QASs) namely cetylpyridinium chloride (CPC) and benzyldimethylhexadecyl ammonium chloride (BDHAC). The treatment conditions such as pH, temperature, concentration and time were studied for % exhaustion and thoroughly analyzed by analysis of variance (ANOVA) statistical concept. Appropriate predictable empirical models were developed incorporating interaction effects of all variables and then optimized. The significance of the mathematical model developed was ascertained using Microsoft Excel regression (solver) analysis module. The theoretical optimum conditions for 100% exhaustion were found to be pH 10.83, temperature 79 °C, concentration 1.63% omf and time 57 min for CPC and those for BDHAC were 10.75, 85 °C, 1.85% omf and 77 min, respectively. However, at the optimum conditions, maximum % exhaustion of 97.32% for CPC and 94.56% for BDHAC was achieved experimentally.

Keywords: Optimization; Nylon fibers; Quaternary ammonium salts; % Exhaustion; Statistical experimental design

1. Introduction

The production of textile fibers is a global industry and the end-uses for textile-based materials continue to expand every year as the unique properties of textile fibers are utilized in many industries. So, in recent days, many studies for improving the qualities as well as incorporating new functional groups into the fibers are being carried out by means of chemical or physical modifications. Durable wrinkle-free cotton [1,2], durable fire resistant cotton [3,4], durable antimicrobial cottons [5,6], antimicrobial wool [7] are examples of the chemical modifications of fibers. Acrylic fibers become dyeable by incorporating a co-monomer containing sulfonate or carboxylate groups that are interactive with cationic dyes [8]. Shrink proof wool was developed by acid chlorination of the wool or by the application of permonosulfuric acid (PMS), followed by a biopolymer application [9]. Electron beam modification was done on cotton, cotton/polyester film and nylon 6 by coating with polyvinyl alcohol (PVA) and acrylic acid [10]. Coloration of nylon fabrics with acid dyes was carried out using the ionic interactions between protonated amino end groups of the polyamides and sulfonate or carboxylic acid groups of the dyes [11]. By incorporating the halamine structures [12,13] and also by the addition of the reactive agents [14] that are interactive with the incorporated acid dyes, attempts were previously made to develop antimicrobial nylon fibers.

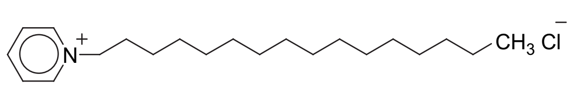
With similar approach, a durable antimicrobial nylon 66 fiber was successfully developed through ionic interaction of cationic antimicrobial functional agents with the carboxylic end groups of the nylon 66 by the author [15]. Quaternary ammonium salt (QAS) is widely accepted as a strong

* Corresponding author. Tel.: +82 42 821 6620; fax: +82 42 823 3736.
E-mail address: yason@cnu.ac.kr (Y.-A. Son).

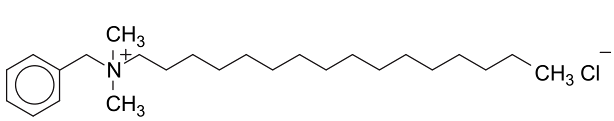
0143-7208/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2006.04.022

antimicrobial agent as it contains a positively charged nitrogen atom in its chemical structure as shown in Fig. 1. The quaternary ammonium salts (QASs) were used as cationic antimicrobial functional agents which impart strong antimicrobial property and the effects of four process variables namely pH, temperature, QAS concentration and finishing time were studied in detail [15]. But, the traditional methods of experimentation were followed to study the effects of all variables which are lengthy, random processes and also require large number of experimental combinations to obtain the desired results. In addition, obtaining the optimum conditions i.e., the point at which maximum % exhaustion could be achieved, is almost beyond the scope.

The traditional step-by-step approach, although widely used, involves a large number of independent runs and does not enable us to establish the multiple interacting parameters. This method is also time consuming, material consuming and requires large number of experimental trials to find out the effects, which are unreliable. So, specifically designed experiments to optimize the system with lesser number of experiments are the need of the hour. These limitations of the traditional method can be eliminated by optimizing all the affecting parameters collectively by statistical experimental design such as response surface methodology (RSM) [16]. So, in this research article, experiments were designed by incorporating all important process variables namely pH, temperature, concentration and finishing time using Statistical Design Software i.e., MINITAB 14 (PA, USA). Experimental design allows a large number of factors to be screened simultaneously to determine which of them has a significant effect on % exhaustion. A polynomial regression response model shows the relationship of each factor towards the response as well as the interactions among the factors. Those factors can be optimized to give the maximum response (% exhaustion) with a relatively lower number of experiments. In this context, a new approach using statistically designed experiments for developing durable antimicrobial nylon 66 fibers through interactions with two different types of quaternary ammonium salts (QASs) namely cetylpyridinium chloride (CPC) and benzyldimethylhexadecyl ammonium chloride (BDHAC) was discussed in detail. The corresponding interactions among the variables were studied and optimized using response surface methodology.



Cetylpridinium chloride (CPC)



Benzyldimethylhexadecyl ammonium chloride (BDHAC)

Fig. 1. Molecular structure of quaternary ammonium salts.

2. Experimental

2.1. Reagents and materials

All chemicals used were of analytical grade and doubly distilled water was always used. Nylon 66 was purchased from Korea Apparel Testing and Research Institute (KATRI).

The two different quaternary ammonium salts CPC and BDHAC were purchased from Aldrich Chemical Co.

2.2. Apparatus

A Hewlett Packard UV–vis spectrophotometer, model HP8452 was used for measuring the absorbance and recording the normal and derivative spectra. A Corning model 220 pH meter was used for pH measurements.

2.3. Factorial experimental design and optimization of the variables

Temperature, pH, concentration and finishing time were chosen as independent variables and the % exhaustion as dependent output response variable. Independent variables, experimental ranges and levels for CPC and BDHAC are given in Table 1. The formulated design matrix, shown in Table 2, is a response surface central composite design consisting of 31 sets of coded conditions. It comprises a full replication of 2^4 (=16) factorial design plus seven center points and eight star points. All the variables at the intermediate level (0) constitute the center points and the combinations of each of the variables at either its lowest (−1) level or highest (−1) level with the other three variables at the intermediate levels constitute the star points. Thus, 31 experimental runs allowed the estimation of the linear, quadratic and two-way interactive effects of the process variables on the % exhaustion. Experimental plan showing the coded value of the variables together with % exhaustion of both CPC and BDHAC is given in Table 2. For statistical calculations, the variables X_i were coded as x_i according to the following relationship:

$$x_i = \frac{X_i - X_0}{\delta X} \tag{1}$$

The results of the experimental design were studied and interpreted by MINITAB 14 (PA, USA) statistical

Table 1
Experimental ranges and levels of process variables for % exhaustion of CPC and BDHAC onto nylon 66

Independent variables	Range and level				
	$-\alpha$	−1	0	1	$+\alpha$
pH (X_1)	9	10	11	12	13
Temperature (°C, X_2)	41	60	80	100	117
Concentration (%omf, X_3)	2.25	0.5	3.25	6	8.75
Time (min, X_4)	15	10	35	60	85