The Degradation of Nylon in Acid Dyeing

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The degradation of nylon 6 in acid dyeing at pH 3.60 and 2.50 at 90°C has been studied. The acid dye-stuff, aniline → R-acid (DAR) and its model compounds, R-acid (RA) and 1,5-naphthalenedisulfonic acid (NDS) were used. Nylon fabric was treated in aqueous solutions of these compounds and its tensile strength was determined. Nylon treated with RA and NDS shows a remarkable decrease in tensile strength compared with DAR. Viscosity measurements indicate a similar trend in decreases. These organic acids, especially RA and NDS are clearly responsible for the catalytic hydrolysis. The mechanism of the degradation is discussed.

(Received September 29, 1987)

Keywords: fiber degradation, nylon dyeing, acid dyeing.

Introduction

The degradation of nylon fibers in acid dyeing has been examined by many workers in relation to overdyeing as well as the mechanical stability of fabrics after dyeing. Hydrogen ions in the dyebath appear to be responsible for the hydrolysis of the fiber and the presence of dye-stuff anions sometimes accelerates hydrolysis.

Bhatt and Daruwalla measured the rate of dyeing of nylon 6,6 in the presence of five acid dyestuffs of different affinities in dyebath at pH 1 and 2, at 60, 68 and 75°C and found that the dyestuffs catalyse the depolymerization of nylon to an extent depending on their affinity for the polymer substrate.

In our previous work we examined the chemical stability of nylon 6 in presence of acid dyestuffs, naphthionic acid → β-naphthol, naphthionic acid → G-acid and α-naphthylamine → G-acid by measuring terminal end amino group contents of the fiber. The results indicate that there were no detectable changes of amino end group contents of the fiber under conditions when the amount of dyestuff sorbed at pH 3.60, at 90°C for 6 hr is lower than the original terminal amino group content.

Recently, Masuko et al. carefully investigated the amino end group contents of nylon 6 filament after dyeing with four acid dyestuffs at 100°C for 1 to 6 hr. The pH of the bath was varied from 1 to 4. The amino contents in undissolved nylon were determined with ninhydrin method. They reported that the hydrolysis was accelerated in the overdyeing region and the dyestuffs with a larger number of sulfonic groups increased hydrolysis.

In the present work, to elucidate the mechanism of the hydrolysis reaction, we investigated the degradation accelerated by organic acids including a typical acid dyestuff.

Experimental

Materials. Nylon 6 fabric taffeta (70 d/48 f) scoured was used for the tensile strength measurements. Nylon 6 films was used for viscosity measurements as the determination of sorbed organic acid can be done directly by spectrophotometry. Nylon in both fiber and film was the same characteristics. The terminal amino group content was 4.0 × 10^-5 and carboxyl 5.0 × 10^-5 Eq·g^-1. The water content of the conditioned sample (65% RH, r.t.) was 3.3%.

The dyestuff used, aniline → R acid (2-naphthol-3,6-disulfonic acid) was synthesized by the diazo coupling and purified by a conventional method. R-acid (extra pure grade) was kindly supplied by Daiwa Kasei Co., and used without further purification. Naphthalene-1,5-disulphonic acid (chemi-
cal pure grade) was obtained from Tokyo Kasei Co. and purified by repeated precipitation with ethanol from an aqueous solution. The chemical structure of the organic acids are given in Fig.1.

Tensile properties measurement. Three g of nylon fabric was dyed in a bath containing 2 g of organic acid in 580 ml of water. The pH of the bath was adjusted to 3.60 or 2.50 by the addition of HCl. Before dyeing the fabric was treated in aqueous HCl solution at the same pH of the dye bath at 90°C for 1 hr. The dyeing was performed at 90°C for 3 hr. At the end of dyeing the fabrics were removed from the bath, rinsed with cold water, dried and conditioned at 20°C at 60% RH. Tensile properties were measured with a Tensilon RTM-100, Orientec Corporation, with a 6.0 cm gauge length and 30 mm/min strain rate. Each tensile property value in this work represents a ten-break average. Tensile strength is calculated as the stress at break in kg divided by the width of the test pieces, 2 cm. Elongation is defined as the percent residual elongation-to-break, i.e., 100 × ([length at break] − [original length])/[original length]).

Viscosity measurements. Decimal five g of nylon 6 film was immersed in an aqueous solution at 90°C adjusted to pH 3.60 with HCl, containing 2.0 g[l]−1 DAR, RA and NDS. Times were varied from 1 to 48 hr. At the end of dyeing the films were removed from the solution, rinsed with small amounts of cold water and dried in a dessicator containing silica gel. The pH of the bath was between 3.60 to 3.67. The limiting viscosity [η] of m-cresol solution of the dyed nylon films was determined at 25°C with a modified Ubbelhode Viscometer. Viscosity average molecular weight $M_v$ was calculated using the following equation.

$$[\eta] = K \cdot M_v^n$$  \hspace{1cm} (1)

Where $K$ is 0.320 (ml/g) and $n$ is 0.62 at 25°C.10

Sorption rate measurements. The sorption rate curve of NDS by nylon 6 was determined by measuring the absorbance of the sorbed film species at 291 nm.

Results and discussion

Change of the tensile properties

The tensile strength of dyed fabric was less than of untreated fabrics as shown in Fig.2. The results clearly indicate catalytic degradation by the organic acids. The effects of RA and NDS on the degradation are much clear than that of DAR. The fabrics treated with NDS at pH 2.50 show a remarkable decrease of the tensile strength. The decrease of the elongation was the same tendency as given in Fig.2.

Mechanism of the degradation

The decrease of molecular weight with time is illustrated in Fig.3. Hydrogen ion alone produces degradation of the polymer but the addition of
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organic anions clearly accelerates hydrolysis. As is found in this figure, the molecular weight decreases gradually with time in both of the presence and absence of the organic acids.

In Fig. 4 the rate of sorption of NDS by nylon 6 film is shown. At first, sorption of NDS is rapid and it continuously increases even after 50 hr which indicates a gradual increase in the number of sorption sites for acid anions.

The depolymerization reaction has been interpreted for various systems; for example, ultrasonic, oxidative, thermal, mechanical and chemical depolymerization.\textsuperscript{11} -\textsuperscript{13} Sakurada \textit{et al.} gave a kinetic expression for the depolymerization by hydrolysis.\textsuperscript{10}

When the polymer with a number average degree of polymerization $N$ decomposes to give a number average degree of polymerization $P$, the number of scission $s$ is given by Eq.2.

$$s = (N/P) - 1.$$  \hspace{1cm} (2)

In the present work the degree of polymerization is weight average and the corresponding equations should be written as Eqs.(3) and (4)\textsuperscript{10} for $n = 1$ and 2 in Eq.1, respectively.

\begin{equation}
N/P_v = (2/s^2)[s - 1 + (1/e^s)], \hspace{1cm} (3)
\end{equation}

\begin{equation}
N/P_v = (6/s^2)[s - 2 + ((2 + s)/e^s)], \hspace{1cm} (4)
\end{equation}

where $P_v$ is the weight average degree of polymerization. Bearing in mind $P_v/N = 1$ at $n = 0$, with the aid of the Eqs. (3) and (4), a theoretical relation, $N/P_v$ against $s$ at $n = 0.62$ is drawn by the method presented in ref. 14). The curve thus obtained is given in Fig.5. Using the curves of Fig. 3 with the aid of Fig. 5, the plots of the number of the polymer chain scission, $s$ against time were given as Fig. 6. This figure shows the
increase in the number of scissions with time. At pH 3.60, after 30 hr, in the absence of NDS the number of scission per molecular chain is approximately two whereas in the presence of NDS ten scissions occurs.

Steinhardt and Fugitt investigated the catalytic hydrolysis of amide and peptide linkage of the proteins \(^{15}\) and found that amide and peptide bonds are broken over 100 times easier than hydrolysed with certain strong monobasic acids of high molecular weight than with hydrochloric acid. They suggested a mechanism of enhanced catalytic hydrolysis in the presence of anions of high affinity. According to those authors, higher affinity anions promote the combination of hydrogen ions with basic groups. It is worthwhile mentioning here that our results show the greatest decrease in viscosity in the presence of NDS which has much smaller affinity than DAR. We can therefore conclude that the chemical structure of the organic acids is an important factor in accelerating the hydrolysis of nylon chain.

A generally accepted mechanism of the acid hydrolysis of the amide linkage is represented by \(^{16}\):

\[
\begin{align*}
\text{I.} & \quad \text{II.} & \quad \text{III.} \\
\text{R-C}=N-R' & \quad \text{R-C}=N-R' & \quad \text{R-C}=N-R' \\
\text{O} & \quad \text{O} & \quad \text{O} \\
\text{H_2N} & \quad \text{H} & \quad \text{H_2N} \\
\end{align*}
\]

I is the unprotonated form of amide, II the conjugated acid of I. III is the activated complex.

Hill suggested that the protonation of the amide nitrogen predominates during the acid hydrolysis of the amide \(^{17}\) but the protonation species does not alter further discussion.

If we bear in mind the above mechanism, the reason for NDS being most effective in the acceleration of hydrolysis, is that for spatial reasons, it has the highest possibility of approaching to the amide group in the main chain. Strong affinity, as in the case of the dye acid, DAR, immobilizes the anion, and therefore the counterion, \(\text{H}^+\), on the fixed site of the polymer ("site binding"). Hydrogen ions are therefore not efficient in forming species II in such a scheme. On the other hand, in the case of an organic anion of lower affinity, such as naphthalene-disulfonate, it interacts with positively charged fixed sites in a mode of "atmospheric binding." In other words, NDS ions exist in a "Donnan" type of sorption to keep electroneutrality on the polymer phase. Naturally the naphthalene rings interact with the methylene chain of the macromolecule by hydrophobic interaction, leading to a suitable spatial position for the sulfonate group of NDS for the hydrogen ion to be near the carbonyl oxygen atoms of the main chains. It is assumed that R-acid which has a higher affinity than NDS is fixed more firmly, resulting a less favorable location of the sulfonate group for the supply of hydrogen ions. The fact that the sulfonic acid group in NDS are strongly dissociated because of the dipolar effect in the 1,5-position in the naphthalene ring \(^{18}\) may also contribute to the local concentration of hydrogen ions in the reaction area. We can conclude therefore that the catalytic action of organic ions in the degradation of polyamides depends not only on their affinity but also on the chemical structure. The greatest effect should be expected from an ion of optimum affinity.

**Conclusion**

The degradation of fibers in textile dyeing and finishing is a matter of great importance for the quality of textiles. The mechanism of the catalytic action of dyes in acid dyeing of polyamide has been investigated and high affinity of dye is found not to be the sole factor in accelerating degradation. It is suggested that the following two dye properties are most important for catalytic action:

1) an affinity to be sorbed by the polymer in sufficient amounts but not in a firmly immobilized mode, and

2) the \(pK\) value of the ionizable group of the dye must be low.

**References**

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The degradation of nylon in acid dyeing is a complex process influenced by various factors such as pH, temperature, and the nature of the dyeing process. The literature cited in the document highlights the importance of understanding these factors for optimizing dyeing techniques.

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酸性染色におけるナイロンの脆化

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昭和62年9月29日受理

酸性染色におけるナイロン6の脆化をpH3.60とpH2.50, 90℃の条件で, 布の強度低下, 繊維高分子の重合度低下の観点から調べた。酸性染料（アミン→R酸）とそのモデル化合物, R酸と1,5-ナフタレンジスルホン酸を用いた。

ナイロンタフタ織物をこれらの有機酸類の存在下で処理, 染色して引張り強度, 伸度を調べた。R酸とナフタレンジスルホン酸による処理布は強度, 伸度の低下が染料酸の場合よりも著しかった。粘度分子量の測定によりこれら有機酸類のナイロン加水分解の触媒作用を明らかにした。ナイロンの脆化機構と脆化速度について議論した。

キーワード: 繊維脆化, ナイロン染色, 酸性染色.