

Factors That Influence Disintegration of PFD Cover Fabrics

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SYNOPSIS

Six fabrics used as the cover component of personal floatation devices (PFDs) were evaluated during exposure to laboratory-simulated accelerated weathering. Factors that influence the disintegration were examined including fiber type, coloring agents, water type, and length of exposure. Disintegration was determined by monitoring changes in physical properties. Fabrics of similar fibers, yarn construction, and fabric construction but of different colors had significantly different disintegration rates. The fabrics that were neon-colored degraded significantly faster than did two of the non-neon-colored fabrics in the study. The white fabric degraded the most rapidly. Various water types including simulated sea water, lake water, and deionized water resulted in no significant differences in the disintegration rate of the fabrics. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The stabilization of polymers found in various outdoor environments has been of concern since synthetics have been incorporated into these end uses. In many cases, the concern is related to the longevity of the product and its ability to remain functional over the expected life of the product. This is of paramount importance when the product is a lifesaving device, such as a personal floatation device (PFD), designed to be used outdoors in water. Weathering of many polymer systems have been completed, but no studies have examined the weathering of PFDs as they are today. The United States Coast Guard (USCG) developed standards for the cover fabric component in the 1970s based on studies completed at that time. However, the materials used for the cover fabrics today have changed dramatically. In the past several years, there have been complaints forwarded to the USCG concerning the failure of the cover fabric after limited use.¹ Failure was a result of disintegration of the fabric. To study this disintegration, it is important to have an understanding of those weathering actions and polymer variables that influence the performance of the system in an anticipated environment of use.

Weathering

Weathering is a complex system that can include one or any combination of actions on the substance by living organisms, light, heat, oxygen, water, ionizing radiation, or chemical reagents. Of these, sunlight, specifically, radiation in the ultraviolet (UV) region, 290–400 nm, has been shown to be damaging to some polymers. There are four principal factors that may affect the photostability of commercially pigmented systems: (1) the chemical and physical nature of the polymer, (2) the environment in which the polymer is used, (3) the chemical and physical nature of the pigment, and (4) the presence of antioxidant and UV stabilizers.² Breakdown of the polymer outdoors results primarily from free-radical chain oxidation which can cause cleavage of the polymer backbone, unsaturation, crosslinking, or the formation of small molecular fragments.^{2–4} Another degradative process is oxidative photodegradation due to the presence of singlet oxygen. The degradation can originate from radical ions or excited states. The initiation of the process can be attributed to the formation and reaction of electronically excited molecules, free radicals and ions, or radical ions. This can be enhanced by the presence of UV light-absorbing compounds.⁵

Compounds commonly used in the coloration of polymeric materials have been linked with accelerating the photodegradation of the polymer. Inor-

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ganic metal oxides and salts are examples of these. Iron oxides are commonly used in the coloration of polymers. If a pigment with photosensitivity is incorporated into the polymer, degradation reactions are likely to occur at the pigment/polymer interface.² The presence of iron oxides in the coloring agent have resulted in accelerated degradation.⁶ Various nitrogen-containing chromophores, azo, nitrosom, and aromatic amino compounds decompose to radicals when excited by UV light, hence causing initiation of the degradation process. These compounds are commonly used in the coloration of polymers.

PFDs

Cover fabrics used in personal floatation devices were made of cotton and were orange in color for many years. The USCG developed PFD component acceptance procedures and standards in the early 1970s with the most recent edition drafted in 1979.⁷ The initial testing of the cover fabric component was based on the traditional orange cotton fabric.

Many changes have occurred in the materials used in the cover component of the PFD since the 1970s. Some of these changes are a result of technological advances and others are due to consumer demand. Today, the most prominent fabric used in the production of PFD covers is produced from nylon fibers vs. the cotton that USCG acceptance procedures are based on. Currently, there is no source for the traditional cotton PFD fabrics. Nylon is usually less expensive than is cotton and has greater resistance to degradation due to microorganism attack. However, nylon is more susceptible to deterioration as a result of exposure to UV.

In recent years, there have been complaints that many of the bright neon-colored fashion fabrics currently used as PFD cover material faded rapidly and lost strength during use, resulting in performance failures. In one such failure, the cover fabric tore upon impact and the foam blocks were lost, resulting in little floatation assistance for the wearer.¹ Many of the cover fabric are colors described by the PFD manufacturers as fluorescent or neon. These colors are produced by molecules that absorb light in the UV range and emit it at a higher wavelength.⁸ Therefore, these coloring agents play an important role as initiators in the photochemical degradation processes. The USCG is in the process of reviewing and revising the standards based on the performance of materials currently available and used as the cover fabric component.

In a previous study, 10% of the fibers used in PFDs were found to contain a delustrant, titanium dioxide (TiO_2). Titanium dioxide is available in two forms: anatase and rutile. They each have high refractive indexes which result in the reflection of light, therefore inhibiting light from initiating photodegradation mechanisms. However, they have low reflectance in the UV region of the spectrum.⁹ The anatase form is more photoactive than is the rutile form and is known to be a photosensitizer. It has been proposed that the anatase form of TiO_2 will quench the phosphorescence emission and this quenching effect has been linked with the photosensitizing effect on the polymer.¹⁰

The environment in which the polymer is used has also been identified as a principal factor that affects the photostability of a commercially pigmented system.² As PFDs are used in both marine and aquatic environments, it is necessary to identify the effects of these environments on the weathering process. Previous studies have evaluated dry samples that may be misted with water in the confines of the laboratory apparatus. Typically, this equipment requires deionized or distilled water free from the impurities that are present in fresh or sea water. There have been no published studies evaluating the effects of various water types on the disintegration of the cover fabric. However, studies evaluating other polymeric materials have shown that water systems do influence the disintegration rate.¹¹

This study was designed to evaluate selected fabrics currently used as PFD covers during exposure to laboratory-accelerated weathering. The independent variables included the length of exposure to accelerated weathering, water type, and fabric.

EXPERIMENTAL

Six different fabrics were exposed to laboratory-accelerated weathering. Physical properties commonly used to monitor disintegration of polymeric systems were measured at predetermined intervals during the accelerated weathering process.

Fabrics

The fabrics evaluated in this study are currently used as PFD covers (Table I). Fabric A was produced from polyester filament yarns and the remaining five fabrics were produced from nylon filament yarns. All fabrics in this study were plain weave and had similar yarn counts. Three of the fabrics were considered to be bright neon colors (D, E, and F) and

Table I Fabric Descriptions

Fabric Descriptions			
Code	Color	Yarn Size	Fiber
A	Orange	150 denier	Polyester
B	Orange	210 denier	Nylon
C	White	200 denier	Nylon 6
D	Rocket Red	200 denier	Nylon 6
E	Orbit Yellow Widgold Uracoat	N/A	Nylon T6
F	Purple Widgold Uracoat	N/A	SD nylon T6

three were not (A, B, and C). Information regarding the specific nylon (6 or 6, 6), possible additives (de-lustrants), methods of coloration, or coloring agents used for all fabrics were not available from the fabric dyers.

Exposure to Weathering

Accelerated weathering was completed in accordance with ASTM G53-91: Standard Practice for Operating Light- and Water-Exposure Apparatus (Fluorescent UV-Condensation Type) for Exposure of Nonmetallic Materials as prescribed in the testing procedure by the Personal Floatation Device Manufacturers Association (PFDMA), USCG, and Underwriters Laboratory (UL) (dated October 14, 1990) for a maximum of 150 h.¹² Specimens were exposed in a QUV accelerated weathering tester using UVA-340 lamps and misted with deionized water in the confines of the weathering apparatus. The QUV accelerated weathering apparatus was selected after communication with USCG and PFDMA representatives. Although it is recognized by the authors of this article that xenon arc lamps produce a spectral distribution most similar to natural sunlight, the QUV was the tester of choice because of its current availability and use in industry at the time of this study. Specimens were removed for physical property testing at 50, 100, and 150 h exposure intervals. After removal, specimens were conditioned as specified in ASTM D1776-90: Standard Practice for Conditioning Textiles for Testing.

To determine the effects of sea and fresh water on the fabrics, simulated sea water was produced using the commercially available product Instant Ocean® at a salinity of 1.021 ± 0.002 . The fabrics were immersed in the water until complete wetting occurred and then removed and immediately placed in the accelerated weathering equipment for the

predetermined exposure period (50, 100, 150 h). Misting of the fabric samples occurred once every 24 h during exposure. Exposure to fresh water followed the same protocol with water obtained from local lakes used to initially saturate and mist the fabrics.

Physical Testing

Disintegration of polymeric systems can be monitored by evaluating changes in the properties of strength, elongation at break, and tensile energy at break. These properties were measured in accordance with ASTM D1682-64: Standard Test Methods for Breaking Load and Elongation of Textile Fabrics using an Instron 1130 with an Instron Series IX automated materials testing system. Properties were measured at 0, 50, 100, and 150 h of exposure.

The values were converted to percent retained so that comparison of disintegration rates was possible. Percent retained values were used in the statistical analysis. Analysis of variance (ANOVA) was used for analysis. Duncan's Multiple Range post-hoc analysis was performed when appropriate.

RESULTS AND DISCUSSION

The percent retained values for breaking strength, elongation at break, and toughness are in Tables II-IV. All fabrics showed a significant loss of breaking strength, elongation at break, and toughness after exposure to accelerated weathering. Based on ANOVA, there were significant differences between fabric and exposure intervals, but no significant differences between the two fabric directions (warp and fill) or treatment types (simulated sea water, lake water, or deionized water). Therefore, data from the

Table II Tensile Strength Retained at Predetermined Exposure Intervals

Fabric	Exposure (h)		
	50	100	150
A	69.93	55.80	49.59
B	89.47	70.69	54.91
C	10.42	4.70	0.67
D	14.68	5.08	2.79
E	15.11	5.09	2.78
F	19.24	8.60	3.99

Table III Elongation—Percent Retained at Predetermined Exposure Intervals

Fabric	Exposure (h)		
	50	100	150
	Elongation—Percent Retained (%)		
A	58.84	44.87	36.62
B	93.11	73.63	66.12
C	12.80	7.87	5.51
D	17.43	8.57	4.74
E	18.89	8.30	5.07
F	25.61	11.89	8.67

warp and fill directions and all water-type treatments were combined for further analysis.

Breaking Strength

The percent of strength retained decreased throughout the exposure period for all fabrics, indicating continued disintegration with continued exposure (Table II). The fabrics were ordered as follows with respect to breaking strength percent retained (\gg indicates significantly greater than; $>$ indicates greater than but not significantly different):

Fabric B \gg Fabric A \gg Fabric F $>$ Fabric E
 $>$ Fabric D $>$ Fabric C

Fabric B had the greatest percent breaking retained followed by Fabric A. Fabrics C–F all had less than 10% breaking strength retained after 150 h of exposure and differences in strength retention between these fabrics were not statistically significant.

Elongation at Break

All fabrics showed a decrease in percent elongation at break retained at each testing interval (Table III). The fabrics order was as follows for breaking elongation—percent retained at the final testing interval (150 h):

Fabric B \gg Fabric A \gg Fabric F $>$ Fabric D
 $>$ Fabric E $>$ Fabric C

Toughness

Toughness at break represents the energy required to break the sample. Toughness retained percentages are shown in Table III.

Fabric B had a significantly greater percent toughness retained at the testing intervals than had the other fabrics in this study. The fabric with the second greatest percent toughness retained was A. The fabric order was as follows for toughness at break—percent retained at the final testing interval (150 h):

Fabric B \gg Fabric A \gg Fabric F $>$ Fabric E
 $>$ Fabric D $>$ Fabric C

By the 100 h testing interval, Fabrics C–F had retained less than 5% of their original toughness value (Table IV).

Polymers are susceptible to degradation through oxidation and hydrolysis. For the end use of the fabric examined in this study, PFDs, it is probable that both of these mechanisms play a role in the material degradation. The oxidative process is most likely a combination of photooxidation and thermal oxidation. In those instances where the polymer contains a significant hydrocarbon segment, oxidation by the radical-initiated chain mechanism can contribute to the overall degradation process. It is believed that the colored agents used in the production of the fabrics contained a catalyst that resulted in the initiation of the degradation process.

Both polyamides and polyesters can also be degraded by hydrolysis. Reaction with water cleaves primary bonds between the repeating units, reducing the molecular weight. Acidic products formed by hydrolysis can also catalyze hydrolysis.¹³ The longer the hydrocarbon chain segment, the more resistant the polymer is to degradation by hydrolysis. However, the hydrocarbon chains are susceptible to oxidative degradation, as previously mentioned. The rate of hydrolysis is also limited by diffusion of water into the polymer bulk.

Table IV Toughness—Percent Retained at Predetermined Exposure Intervals

Fabric	Exposure (h)		
	50	100	150
	Toughness Percent Retained (%)		
A	46.23	29.52	22.93
B	92.33	72.02	42.60
C	1.58	0.38	0.20
D	3.23	0.76	0.35
E	3.92	0.64	0.27
F	5.78	1.52	0.70

For a significant reaction to occur, water must be absorbed at the surface and then permeate into the subsurface region. Flexibility of polymer chains also contributes to hydrolytic instability by opening the structure to moisture penetration. Hydrolysis is believed to occur primarily in amorphous regions which are more readily penetrated by water molecules.

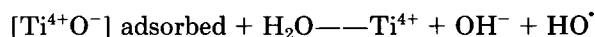
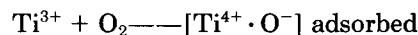
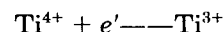
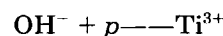
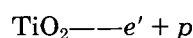
Fabric A was the only fabric in this study produced from polyester fibers. The initial physical property values for this fabric were lower than for the fabrics produced from nylon fibers. However, polyester had less loss of the properties measured (strength, elongation and toughness) than had the nylon fabrics. Polyester is less sensitive to polymer cleavage as a result of exposure to UV light but does experience degradation due to hydrolysis.

Influence of Color on Physical Properties

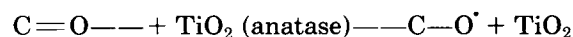
Fabric B had the least amount of disintegration, with Fabric A showing only slightly more disintegration than did fabric B. The property loss of these two fabrics was significantly less than for any of the other fabrics produced from nylon fibers. Both of these fabrics were orange, but not neon.

Fabrics D-F were all neon colors and lost physical properties more rapidly than did Fabric B, a non-neon-color nylon fabric. The colors here are produced from fluorescent dyes and pigments and absorb light at one wavelength and emit some of it at longer wavelengths. These coloring agents work on the principle of absorbing UV radiation (less than 380 nm) and then emitting it in the visible region.⁸ The conversion of invisible radiation to visible light produces a color brighter than a nonfluorescent material; however, the fluorescent coloring agents are designed to absorb UV light, which could lead to degradation of the polymer.

Fabric C, the white fabric, had the poorest resistance to disintegration. It showed the lowest retained percentage of the measured properties of all fabrics evaluated in this study. Although the specific additives in these fibers are not known, it is expected that the fabric contains TiO₂ as part of the coloring agent, as this is commonly used to impart a white color to polymers. The high refractive index of TiO₂ which results in the reflection of light, therefore, inhibits light from initiating photodegradation. Although several mechanisms of the photosynthesized oxidation have been proposed, the following, proposed by Allen et al., is the most favorable^{2,10,14,15}:



The OH⁻ ion remains on the surface of the pigment to complete the cycle. Both the ·OH and the HO₂ radicals then cause oxidation of the polymer substrate.² It has also been proposed that the anatase form of TiO₂ will quench the phosphorescence emissions and this quenching effect has been linked with the photosensitizing effect on the polymer.¹⁰ The following mechanism was proposed assuming the phosphorescent species are carbonyl in nature:



The carbonyl radical anion may then proceed to attack the polymer. Various nitrogen-containing chromophores, azo, nitrosom, and aromatic amino compounds decompose to radicals when excited by UV light, hence causing initiation of the degradation process.

SUMMARY

The results of this study show that fabrics of similar fibers, yarn construction, and fabric construction but of different colors had significantly different disintegration rates. Although information on the specific coloring agents was not available, this is suspected to be the primary variable resulting in the various disintegration rates of the fabrics when exposed to accelerated weathering procedures. Previous research has shown that the chemical composition of the coloring agents can act as a catalyst initiation and in accelerating the disintegration of the polymer. The three fabrics that were neon-colored degraded significantly faster than did two of the non-neon-colored fabrics in the study. The white fabric, likely to be colored with TiO₂, degraded the most rapidly. Various water types, simulated sea water and lake water, resulted in no significant differences in the disintegration rate of the fabrics.

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