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Nanostructured ultraviolet resistant polymer coatings

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Abstract

Nanoparticle-embedded acrylic coatings that can absorb copious amounts of UV radiation yet scatter little were developed to protect base fabrics from sun-induced degradation. Zinc oxide and titanium dioxide nanoparticles with diameters ranging from 15 to 70 nm were used. Nanoparticles (5 wt%) were dispersed in acrylic emulsions. Nanoparticle-embedded acrylic films of 10 μm and 20 μm thick were prepared and bonded to Kevlar fabric. Mechanical tests as well as infrared, visible and UV spectroscopy were used to characterize nanoparticle-embedded acrylic emulsions and coated Kevlar fabric.

The changes in mechanical and chemical properties of Kevlar fabric after a day and week of intense UV exposure were assessed using tear and strip tensile testing, UV, visible and infrared spectroscopy, and wide and small angle X-ray analysis. Tear and tensile data, with support from UV results, showed that 20 μm nanoparticle-embedded coatings largely prevented degradation of Kevlar fabric, allowing only 5% of the degradation that occurred in the unprotected fabric after a week of UV exposure.

Keywords: Nanoparticle-embedded coatings; UV protection; Transparent coating; Scattering

1. Introduction

Ultraviolet light, ranging from 280 to 400 nm, represents about 5% of the total radiation reaching the earth's surface. UV radiation has detrimental effects on synthetic polymers as well as on human skin, a natural polymer [1]. High performance fabrics like Kevlar®, Zylon®, and Spectra® are particularly susceptible to degradation by UV radiation. Fabrics made from these fibers lose their strength and other serviceable properties deteriorate [2]. More common polymers, like nylon, polypropylene and polyethylene terephthalate, also degrade surprisingly quickly in sunlight.

The main reason for the outdoor degradation of these polymers is the absorption of UV radiation from sunlight, with energies ranging from 300 to 450 kJ/mol. Simply put, degradation can occur when the amount of energy absorbed exceeds the bond energy of a polymer. Polymers can be protected from degradation by using various UV absorbing and stabilizing agents. They work in different ways, by quenching free radicals or by absorbing high-energy radiation; however, these additives are undesirable in high performance fabrics when they affect physical or mechanical properties [3]. In addition, chemical UV stabilizers have a limited lifetime. On the other hand, it is possible to protect high performance fabrics by coating with UV resistant polymers. Polymeric coatings used to protect base substrates like fabrics can be prepared by adding various UV stabilizers or pigments. The stabilizers or pigments prevent UV radiation from reaching the underlying substrate, perhaps by acting as a sacrificial coating.

Harmful UV radiation can be kept from rapidly degrading skin by applying sunscreens, which form a thin coating on the skin. Sunscreens use various chemical ingredients, such as phenyl salicylate, which absorb UV radiation to protect the skin. Modern sunscreens include more effective and nonreactive physical absorbers, like ZnO or TiO_2 nanoparticles, for UV protection [4]. The particulate additives, besides

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absorbing a wide range of UV radiation, lose the cosmetically undesirable whitening when sufficiently small or nanoparticles are used.

We formulated particle-embedded acrylic coatings that are transparent to visible light but absorb UV radiation. The UV absorption behavior of nano- and micron size particles was studied and explained. Thick coatings of 10 μm and 20 μm were applied to Kevlar fabrics and the mechanical behavior of the fabrics before and after UV exposure was studied to evaluate the performance of coatings. The protection that coatings need to provide clearly exceeds that of a sunscreen in which a short-term solution that may allow a significant fraction of light to pass through is perfectly acceptable.

2. Experimental

2.1. Materials used

U.S. Army Natick Soldier Center provided Kevlar® 29 fabric, style 005. Nanophase Technologies supplied zinc oxide particles 24–71 nm in diameter and titanium dioxide particles 25–51 nm in diameter. Sachtleben Chemie GmbH provided titanium dioxide particles 15–20 nm in diameter. Raffi and Swanson, Inc. supplied acrylic emulsion, 30204 Tecpol. Diversified Biotech Corporation was the source for UV transparent films.

2.2. Nanocomposite coating formulation

We prepared the following coating formulations by dispersing 5 wt% nanoparticles in the acrylic emulsion:

(1) ZnO nanoparticles (2.5 g) were added to 95 g of acrylic emulsion, which consisted of 50% of solids. Dispersion was achieved by adding 0.5% non-ionic dispersing agent (Trycol 5952) and by mechanically stirring for 3 h followed by ultrasonication for 10–15 min. Ultrasonication was performed in a cold bath (i.e., water at room temperature) at 35% amplitude using a Cole-Parmer CPX 750 ultrasonic processor. The dried coating contained 5 wt% nanoparticles.

Trycol 5952 is an ethoxylated aliphatic alcohol $CH_3(CH_2)_8CH_2O(CH_2CH_2O)_6H$: $O(CH_2CH_2O)_6H$ being the hydrophilic moiety and $CH_3(CH_2)_8CH_2$ being the hydrophobic moiety. The hydrophilic moiety is compatible with nanoparticles and the hydrophobic moiety is compatible with acrylic polymer coating. Thus, in theory, the dispersing agent helps to improve mixing of the nanoparticles in the acrylic resin.

Similarly,

(2) TiO_2 nanoparticles (5 wt%) were added to the acrylic emulsion. The process used for dispersing zinc oxide particles was repeated.

(3) Also, 5 wt% Hombitec RM 220 grade TiO_2 nanoparticles were added to the acrylic emulsion using the same process.

We anticipate that the selected nanoparticle-embedded acrylic coatings will be durable, since neat acrylic coatings are durable and widely used [5,6]. The addition of 5 wt% nanoparticles may actually improve durability and strength.

2.3. Coating process

The wire wound, or Meyer rod, method was used for coating. Nanoparticle-embedded emulsions were applied to the UV transparent films, not only to insure a uniform coating but also to allow testing after weathering that was free of complications associated with having coating bonded to and impregnating the fabric. We also did apply the coating directly on the Kevlar fabric to insure results using UV transparent films that corresponded to what may become commercial practice, which is coating directly on the fabric.

We conducted a crude analysis that showed the minimum thickness of dried coating that could block UV radiation from reaching the base substrate (i.e. a perfect monolayer of particles) was about 5 μm. Our coating thicknesses were 10 μm and 20 μm. The nanoparticle-embedded emulsions were applied using nos. 8 and 16 wire wound rods. The coated film was dried at 40–50 °C overnight in a circulating air oven.

The average dry coating thickness was calculated by weighing the films before applying the coating and then again after applying and drying the coating. The average thickness of the dried coatings was calculated using the formula:

$$\text{Thickness} = \frac{W\left(\text{g/cm}^2\right)}{\rho\left(\text{g/cm}^3\right)}$$

where, W is the basis weight, or areal density, of the coating and ρ is the density of coating; the density of the coatings was calculated using the rule of mixtures.

These coated films were then attached to the Kevlar fabric using tape. The tape was outside the area of fabric exposed to UV light. A summary of the samples prepared for UV treatment is shown in Table 1. The first sample is the control. The next three have 10 μm coatings and the last three have 20 μm coatings.

Table 1
Samples for UV treatment

Samples
Kevlar fabric bonded to UV transparent film
Kevlar fabric bonded to 10 μm thick 5 wt% of ZnO nanoparticle-embedded acrylic coating on UV transparent film
Kevlar fabric bonded to 10 μm thick 5 wt% of TiO_2 nanoparticle-embedded acrylic coating on UV transparent film
Kevlar fabric bonded to 10 μm thick 5 wt% of RM 220 grade TiO_2 nanoparticle-embedded acrylic coating on UV transparent film
Kevlar fabric bonded to 20 μm thick 5 wt% of ZnO nanoparticle-embedded acrylic coating on UV transparent film
Kevlar fabric bonded to 20 μm thick 5 wt% of TiO_2 nanoparticle-embedded acrylic coating on UV transparent film
Kevlar fabric bonded to 20 μm thick 5 wt% of RM 220 grade TiO_2 nanoparticle-embedded acrylic coating on UV transparent film