

Polyurethane nanocomposite films containing nano-cerium oxide as UV absorber; Part 2: Structural and mechanical studies upon UV exposure

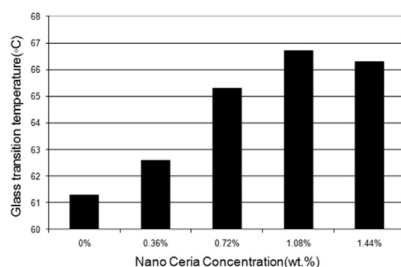
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HIGHLIGHTS

- Degradation of a polyurethane film containing nano-ceria was investigated.
- T_g of nano-ceria embedded films increased with increase in UV exposure time.
- Polyurethane and Polyurea were formed at the surface due to crosslinking reactions.

GRAPHICAL ABSTRACT



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ABSTRACT

Degradation of a water-based polyurethane clear coat containing nano-sized cerium oxide was investigated. Nanoparticles at different concentrations were dispersed in a water-reducible polyol polyacrylate dispersion resin, followed by mixing with polyisocyanate hardener from which wet films of 90 μm thick were prepared. Samples were exposed to 700 h of accelerated artificial weathering (QUV). Their performances were then accessed by DMTA and ATR–FTIR spectroscopy. It was revealed that the glass transition temperature (T_g) of films systematically increased with increase in nano ceria content. Due to UV absorption and decrease in photo-oxidation and chain scission reactions, the storage moduli of clear coats containing nano ceria were shown higher than that of the blank polyurethane after UV exposure. T_g for both pure blank polyurethane and nano-ceria embedded clear coats increased with increase in degradation time. Most of variations in T_g s occurred in the first 150 h of exposure. ATR–FTIR spectra also proved these results by showing depreciation in intensities of C–H and N–H peaks. It was seen that the surface of the clear coats as analyzed by ATR–FTIR was polyurea-rich and contained urea functionality at least as much as polyurethane. During weathering, the photo-oxidation of C–H groups to carbonyl groups occurred.

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1. Introduction

Automotive OEM clear coats based on aqueous 2K–PUR systems, like the other coatings for outdoor applications, require additives, either UV absorber (UVA), hindered amine light stabilizers (HALS) or both for weatherability enhancement. The main drawback of

organic UVAs is their relative high loss rate due to continuous conversion to radicals. Organic UVAs have certain absorption peaks in narrow UV ranges, while inorganic UVAs have relatively wide absorption regions. Titania, silica, zinc oxide and ceria are the most important inorganic UVAs. Moreover, nano-sized particles have no detrimental effect on transparency of coating. Among these, considering energy band gaps and absorption edges, only ceria is a proper UV-B absorber. CeO_2 is a technologically important rare earth material because of its wide applications as polishing materials [1], fuel cells [2] oxygen sensors [3], catalysts [4]

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and UV blockers [5]. In its most stable phase, bulk CeO₂ adopts a fluorite-type Fm₃m crystal structure in which metal cation is surrounded by eight oxygen atoms [6,7]. The band gap of pure ceria is ~5 eV [8,9], but crystal defects or impurities can transform the material into a good n-type semiconductor [7]. Besides, CeO₂ nanoparticles have band gap energies, ranging from 2.9 eV to 3.5 eV depending on their particle sizes (quantum confinement effect) [10].

Cerium oxide shows a UV cut-off threshold at around 370 nm, similar to that of nano titanium oxide. These two oxides are both semi-conductors with a band gap being ca. 3.0–3.2 eV and present the same UV absorption mechanism under UV radiation. The absorption of a photon with a higher energy than the band gap creates an electron-hole pair. In the case of titanium oxide, these holes and electrons migrate to the surface of the particles (rather than recombining together inside the particles). When holes and electrons join the surface, they can react with oxygen, water or hydroxyl groups to form free radicals. These free radicals are oxidant moieties and can cause the degradation of organic molecules, particularly polymers, which aggravate degradation process of protective coatings. In contrast, cerium oxide absorbs UV without being photoactive. Indeed, cerium oxide has a localized electron (4f orbital) while titanium oxide has less localized electrons than cerium oxide (3d orbital). Hence, the cerium–oxygen bonding is more ionic than the titanium–oxygen bonding, and logically, the charge carriers (holes and electrons centers) creation is less in the case of titanium oxide. Moreover, cerium oxide shows a very fast recombination of charge carriers before they can migrate to the surface (due to crystal defects and oxidation–reduction reactions); hence there wouldn't be any further creation of free radicals. Due to the combination of these two phenomena, cerium oxide does not show any photocatalytic effect. Cerium oxide presents property of transparency in the visible spectrum from 400 nm up to 800 nm higher than that of titanium oxide.

A water-born coating based on an acrylic-polyurethane dispersion containing nano-cerium oxide has been used for wood coatings [11]. It has been claimed that the durability of UV absorption function has improved. Moreover, the surface mechanical properties (hardness and scratch resistance) were clearly improved by cerium oxide nanoparticles. The use of fine particles of cerium oxide has also been effectively used for personal sunscreen care products compared with titanium and zinc oxides containing ones [12]. The use of such nanoparticles in PP matrix has also been reported [13]. It has been shown that the addition of 1 wt% of CeO₂ improves the resistance of the PP matrix to UV exposure due to the screening effects offered by these particles.

In our recent work [14] the influence of nano cerium oxide particles on UV resistance of a water-base polyurethane lacquer has been reported. Stabilized particles dispersed in nanocomposite films were studied using light scattering and small angle neutron scattering techniques. It was shown that a monolayer of stabilizer was grafted at the surface of nano cerium oxide out of which uniformly distributed mono-disperse particles in the films were prepared. Films were then exposed to 700 h of accelerated artificial weathering. Their optical performances were then accessed by UV–vis spectroscopy. Clear coats containing nano-ceria showed less deterioration in UV exposure test compared to the blank polyurethane film.

In addition to the effective UV screening of ceria nanoparticles, the variations of structural and mechanical performances of coatings upon UV radiation need further investigations. The current paper is a continuation of the above work and is aimed at evaluating the structural and mechanical properties of these nanocomposite films upon UV exposure as revealed by ATR–FTIR spectroscopy, Vickers hardness and DMTA analysis.

2. Experimental

2.1. Materials

Nanobyk-3810, a suspension of nano ceria, was provided by BYK (Germany) and used as received. It consists of an 18% w/w pre-dispersed nano ceria suspension in water, with an average particle size of 10 nm. The ceria nanoparticles have been previously stabilized using poly(oxy-1,2,ethanediy1)- α -(3-phosphonopropyl) omega hydroxyl as reported in reference [14].

Materials used for preparation of nanocomposite films including main resin and hardener together with the required additives are listed in Table 1.

2.2. Preparation of nano ceria embedded nano composite coatings

Various amounts of modified nano ceria suspensions were separately added to acrylic polyol resin in such a manner that the concentrations of nano ceria in the final solid films would turn out to be 0.36%, 0.72%, 1.08% and 1.44% (w/w) based on total solid resin. A proper dispersion (judged based on high optical transparency of films) was achieved by dispersing at 2000 rpm using a Dispersmat AE3-C for 1 h, followed by pearl milling the mixture for 30 min. The blade was a high-shear saw-tooth one whose diameter (6 cm) was two-third of the container and the torque at the end of impeller remained constant at about 5 N m.

The additives, excluding coalescing agent mixture, were then added and agitated at 2000 rpm for 20 min. This mixture (Part A) was left to de-aerate for one day. The hardener (Part B), was primarily diluted down to 80% solid content by EEP (see Table 1). The coalescing agent mixture was then added to diluted hardener and agitated for 10 min using Dispersmat. Finally part B was added to part A and dispersed at 1000 rpm for 10 min. The mixing ratio of NCO:OH was 1.2:1. The coatings with wet thicknesses of 90 μ m were applied onto cleaned glass plates and left to cure for 15 min at ambient conditions, followed by drying for 25 min at 40 °C and then 2 days in dust free chambers at room temperature. The pure polyurethane clear coat (labeled as 0%) was used as a control to elucidate the effect of nano ceria addition.

2.3A. Accelerated weathering tests

The artificial weathering was carried out using a QUV-Spray accelerated weatherometer (Q-Panel Co.) according to the ASTM G154 standard. The QUV chamber was equipped with fluorescent UV lamps (UV-A) with UV emission from wavelength of 365 nm down to 295 nm, having a peak emission at 340 nm, which provides the best possible simulation of sunlight in the critical short wavelength region. Specimens were exposed to repeated cycles composed of 8 h of UV radiation at 60 °C, followed by 4 h of water vapor condensation at 50 °C in cyclic manner for 700 h.

2.4. ATR–FTIR spectroscopy

ATR–FTIR spectra of free films in transmission mode were recorded and analyzed using an FTIR spectrometer model Equinox X-55, collecting 35 scans in the 400–4000 cm⁻¹ range with 4 cm⁻¹ resolution.

2.5. Mechanical Studies

Micro-harnesses were measured using a Leica VMHT MOT hardness tester by the Vickers indenter at 49 mN at a constant time-period of 12 s. Average of five replicates were then reported. Storage modulus and Tan δ curves were recorded using a Triton DMA analyzer model Tritec 2000 in the temperature range from –50 °C to

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