



Fluorinated organozirconiums: Enhancement of overcoming oxygen inhibition in the UV-curing film

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ABSTRACT

Organozirconiums had been studied as the peroxy radical scavenger in UV-curing coatings, which had varied performance in overcoming oxygen inhibition. Herein we modified the complex of zirconium with organic fluorides in order to increase its efficiency of peroxy radical scavenging. A formulation consists of two conventional monomers (Ebecryl 270 and TPGDA) and an oxygen-sensitive photoinitiator TPO was employed in this study. With different content added in the formulation, the UV-cured coatings had different depth conversion profiles, which were measured by confocal Raman microscopy. Moreover, the standing time for the enrichment of fluorinated organozirconium products to the surface of the coatings and two irradiation sources (Hg-Xe lamp and UV-LED lamp) were adopted to emphasize their properties against oxygen inhibition. Finally, it is shown that fluorinated organozirconiums can lead to tack-free coatings, while the cured films from neat formulation remain tacky.

1. Introduction

UV curable coatings based on the radical polymerization of acrylates have gained popularity comparing with traditional solvent-borne coatings and have been widely used in the automotive, packaging and wood industry. Photoinitiator is the key factor for fast curing and low energy consumption in UV-curing systems, which absorbs UV radiation and generates active radicals to initiate the polymerization. The predominate using of acrylate monomers and oligomers offers high curing rate, high degree of optical clarity, low volatile organic compound (VOC) and varied rheological properties [1,2]. Many low-volatile acrylate monomers used as reactive diluents to adjust the viscosity of coatings have been available commercially, such as tripropylene glycol diacrylate (TPGDA), trimethylolpropane triacrylate (TMPTA), hexanediol diacrylate (HDDA) and pentaerythritol tri-, tetra acrylate (PETA) etc.

Notwithstanding the numerous advantages of UV-curing technique mentioned above, the free radical polymerization undergoes oxygen inhibition upon exposure in air, resulting in an inhibition period, longer irradiation time and incomplete conversion. The oxygen diffuses from the atmosphere into the formulation and reacts with excited species and radicals, forming an unreactive peroxy radical. This quenching is critical on the surface of the coatings, which can also be considered as the

interface between air and the liquid formulation. The incompletely cured coatings generally exhibit diminished mechanical performance and tacky surface.

Many factors, physical and chemical, impact the behavior of UV-curing process towards oxygen inhibition [3]. The physical factors include type and intensity of irradiation [4], atmosphere [5], and temperature, while the chemical factors have been discovered such as photoinitiator and/or co-initiator [6], formulation viscosity and structure of monomer [7–9]. To overcome the problem of oxygen inhibition, many researches have been done not only referring to those factors, but also employing oxygen scavengers [10]. Borane complexes have been [11,12] introduced as efficient co-initiators to generate boron-centered initiation radicals in a UV-curing formulation, the photopolymerization of which was almost unaffected under aerated conditions. Similar properties had been discovered in silyl radicals [13]. Triphenylphosphine (TPP) has been employed as an efficient peroxy radical scavenger and the mechanism of peroxy radical scavenging by TPP has been deeply investigated [14]. Thiol-ene chemistry in photopolymerization is also an approach to reduce the oxygen inhibition due to the hydrogen donation from thiols to peroxy radicals. Several thiol compounds have been adopted with different functionalities in the formulations to study the photopolymerization kinetics and depth conversion profiles [15]. It has been shown that thiol content had

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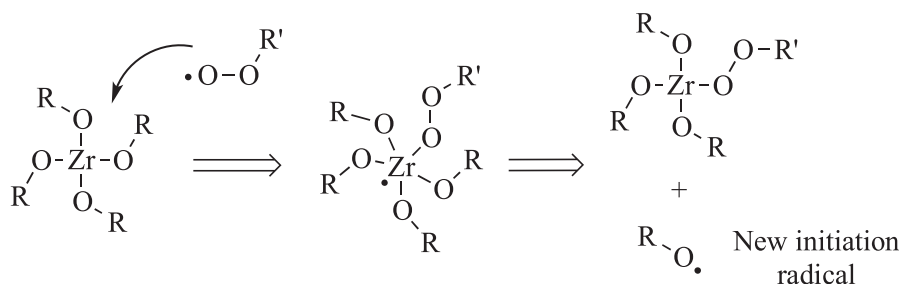


Fig. 1. The mechanism describing the peroxy radical scavenging of organozirconiums.

significant effect on the surface conversion of acrylate-based formulation. Moreover, taking advantage of the biochemical nature of sugar, glucose oxidase has been used as an oxygen scavenger, which could eliminate the oxygen in a waterborne formulation before irradiation [16]. Another interesting methodology to counteract the effect of oxygen inhibition is concentrating certain compounds on the surface of the applied coating, where the diffused oxygen gathers. Polysiloxanes and highly-fluorinated alkane are typical candidate structures owing to their low surface energy. 2-Hydroxyl-2-methylpropiophenone, known as photoinitiator Darocur1173, was modified with pentadecafluoro group [17] while benzophenone was grafted on polysiloxane [18,19].

This paper introduces a novel complex substitution of organozirconium, which had been uncovered to be peroxy radical scavenger (Fig. 1) [20,21], with fluorinated alkane groups. The formulations with different organozirconium content were under the irradiation of Hg-Xe lamp or UV-LED lamp, followed by the depth conversion profiling with confocal Raman microscopy (CRM) technique. A short standing time between applying the formulation and the irradiation was also introduced. The polymerization kinetics of those formulations was also analyzed with real-time FTIR.

2. Experimental section

2.1. Materials and methods

Zirconium (IV) propoxide (ZrPrO) was purchased from Sigma-Aldrich. The resin was made from a mixture of 50 wt.% of an aliphatic urethane diacrylate Ebecryl 270 (Eb270, from Allnex) diluted with 50 wt.% of tripropylene glycol diacrylate (TPGDA, from Sartomer). Diphenyl(2,4,6-trimethylbenzoyl)-phosphine oxide (TPO), which used as a Norrish I type photoinitiator in the resin (1.5 mol% with regard to the acrylic double bonds), was obtained from Lamberti. All other chemicals were purchased from TCI as anhydrous grade and used as received without further purification. Real-time FTIR spectroscopies were measured on a Bruker Vertex 70 spectrometer and a Hamamatsu Mercury-Xenon lamp coupled with a light guide or UV-LED lamp

(395 nm). Confocal Raman microscopy measurements were performed on an inVia Reflex Raman microscope from Renishaw which couples a Raman spectrophotometer with a Leica DM2500 microscope. The excitation wavelength was provided by an argon-ionized laser from Spectra-Physics emitting 20 mW at 514.5 nm. Other detailed parameters of CRM can be found in previous research [20]. The conversion of the photopolymerization was determined by monitoring with time the decrease of the 1636 cm^{-1} band corresponding to the C=C stretching vibration using carbonyl group ($1750\text{--}1710\text{ cm}^{-1}$) as internal standard.

2.2. Synthesis of the fluorinated organozirconiums

ZrPrO (1.0 equiv.) was dissolved in moderate anhydrous dichloromethane, and then 1*H*,1*H*-undecafluoro-1-hexanol (5CF-OH) or 1*H*,1*H*-heptafluoro-1-nonanol (8CF-OH) (4.0 equiv.) was added, followed by the removal of volatile solvents under reduced pressure. The products (Zr-O5CF and Zr-O8CF) were obtained as colorless solids.

2.3. Formulations for UV-curing coatings

The purchased reactants, ZrPrO, 5CF-OH and 8CF-OH, were added to the formulation (5.0 mol% with regard to the acrylic double bonds), to make up as the control group. The synthesized fluorinated organozirconiums, Zr-O5CF and Zr-O8CF, were mixed with the resin with the contents from 0.1 to 1.0 mol%. All the formulations were applied to polypropylene films with the thickness of 40 μm .

3. Results and discussion

3.1. Synthesis and structural characterization of Zr-O5CF and Zr-O8CF

The synthesis of the fluorinated organozirconium was a facile substitution of organozirconium (Fig. 2), which had been adopted decades ago. No subsequent purification was conducted due to the absence of catalyst and non-volatile by-product. By removing the volatile content

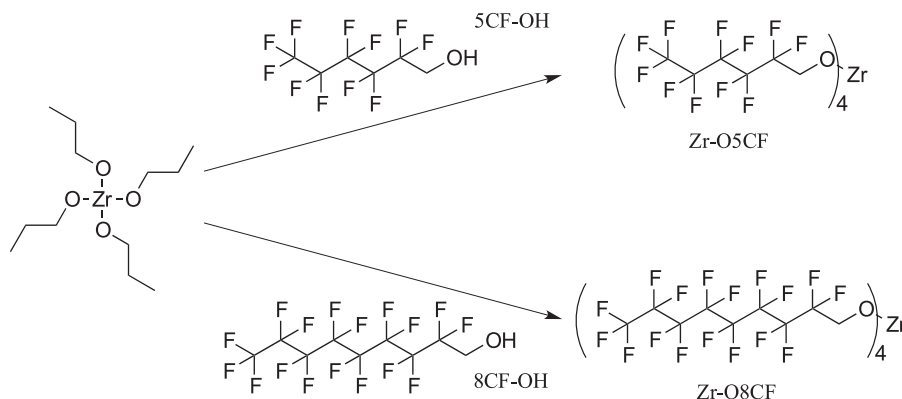


Fig. 2. The synthesis of fluorinated organozirconiums.

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