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Characterising *in situ* activation and degradation of hindered amine light stabilisers using liquid extraction surface analysis-mass spectrometry

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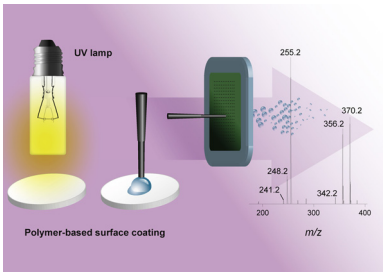
HIGHLIGHTS

- Acrylic polymers with the additive Tinuvin 292 were exposed to heat or UV light.
- Changes to the additive were investigated directly by ambient mass spectrometry.
- Semi-quantitation was achieved using LESA-MRM analyses.
- UV light caused demethylation of piperidinyl nitrogens in Tinuvin 292.
- Demethylation is a necessary step for the antioxidative protection of polymers.

GRAPHICAL ABSTRACT



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ABSTRACT

Changes in the molecular structure of polymer antioxidants such as hindered amine light stabilisers (HALS) is central to their efficacy in retarding polymer degradation and therefore requires careful monitoring during their in-service lifetime. The HALS, *bis*-(1-octyloxy-2,2,6,6-tetramethyl-4-piperidinyl) sebacate (TIN123) and *bis*-(1,2,2,6,6-pentamethyl-4-piperidinyl) sebacate (TIN292), were formulated in different polymer systems and then exposed to various curing and ageing treatments to simulate in-service use. Samples of these coatings were then analysed directly using liquid extraction surface analysis (LESA) coupled with a triple quadrupole mass spectrometer. Analysis of TIN123 formulated in a cross-linked polyester revealed that the polymer matrix protected TIN123 from undergoing extensive thermal degradation that would normally occur at 292 °C, specifically, changes at the 1- and 4-positions of the piperidine groups. The effect of thermal *versus* photo-oxidative degradation was also compared for TIN292 formulated in polyacrylate films by monitoring the *in situ* conversion of *N*-CH_3 substituted piperidines to *N*-H. The analysis confirmed that UV light was required for the conversion of *N*-CH_3 moieties to *N*-H – a major pathway in the antioxidant protection of polymers – whereas this conversion was not observed with thermal degradation. The use of tandem mass spectrometric techniques, including precursor-ion scanning, is shown to be highly sensitive and specific for detecting molecular-level changes in HALS compounds and, when coupled with LESA, able to monitor these changes *in situ* with speed and reproducibility.

1. Introduction

Many commercial polymers contain at least one, if not several additive compounds that reduce manufacturing costs, increase

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service lifetime, or both. The performance of these commercial polymers is often dictated by the performance of the additives. Therefore the detection of these compounds and characterisation of any structural changes at a molecular level are vital to monitoring polymer performance. Some of the most influential polymer additives from a performance perspective are the frequently used class of stabilisers known as hindered amine light stabilisers (HALS). Several empirical studies have shown that the presence of HALS unequivocally improves the retention of aesthetic attributes and long-term durability of polymers [1–4]. The chemical mechanisms of HALS action have been a contentious area of research over the past 30 years [5–13]. However, a recent computational study by Coote and co-workers [14] has dismissed the vast majority of previously reported mechanisms based on kinetic or thermodynamic calculations. Within this report, Coote and co-workers proposed new mechanisms for amine/aminoxyl radical cycling of HALS during stabilisation of polymers that are energetically feasible and consistent with previous experimental observations. Within these schemes however, the persistent aminoxyl radical remains central to the mode of action of HALS where it acts as a free radical scavenging intermediate and is thought to be involved in converting harmful free radical polymer fragments to less harmful even-electron species [14–17].

Robust methods for the quantitation of HALS within polymers have been developed that utilise electron spin resonance (ESR) spectroscopy to detect the total amount of aminoxyl radical forming material present. This method requires solvent-based extraction of the HALS from the polymeric substrate followed by peracid oxidation to convert them to aminoxyl radicals [18,19]. Although quantitative and highly selective, the ESR technique is unable to provide detailed structural information for HALS, most notably, changes of the substituent at the piperidinyl nitrogen prior to oxidation. This is because the method relies on total conversion of all *N*-substituted piperidines to aminoxyl radicals. Unfortunately, it is precisely the chemistry at the piperidinyl nitrogen that is central to understanding both the action and loss of action of HALS in polymer systems. As our previous work has demonstrated, under degradative conditions changes to the piperidinyl *N*-substituent can occur within the polymer that alter both the physical and chemical properties of the HALS and consequently its efficacy as an antioxidant [20,21]. Specifically, modification to TINUVIN® 123 (*bis*-(1-octyloxy-2,2,6,6-tetramethyl-4-piperidyl) sebacate) present within a cross-linked polyester was observed where one *N*-ether piperidine moiety (*N*-OC_8H_{17}) was converted to a secondary piperidine (*N*-H) due to high curing temperatures (292 °C) and simulated weathering conditions. These findings were supported by the recently proposed mechanisms of Coote and co-workers that included the formation of secondary amines as a major pathway involved in aminoxyl radical activation/regeneration [14]. Another example where activation of the HALS molecule employed is heavily influenced by the functional group present at the piperidinyl nitrogen is TINUVIN® 292 (TIN292; *bis*-(1,2,2,6,6-pentamethylpiperidine) sebacate). Many commercial HALS compounds such as TIN292 have been designed for specific applications with their chemical properties altered by different substitutions at the piperidinyl nitrogen. It is this substitution that dictates the mechanism of and propensity for conversion to the active aminoxyl radical. Therefore, the motivation of our study was to characterise the activation/degradation products of HALS generated *in situ* and understand how the formation of these products are influenced by: (i) the initial fuctionalisation (*N*-R) of the piperidinyl nitrogen; (ii) the polymer within which they are incorporated; and (iii) exposure to simulated in-service conditions.

Recently, we have reported the application of the LESA-MS to the direct analysis of polymer additives [22]. Although this approach does not readily allow absolute quantitation, with its highly reproducible sampling through an automated sampling probe LESA-MS can provide relative quantitation across multiple samples by monitoring relative changes in additive speciation. Importantly, LESA-MS does not require time-consuming chromatographic separations and/or sample preparation steps. Therefore, LESA-MS offers the distinct advantage of being a much faster, simpler technique than conventional quantitative techniques such as gas (GC) [15,16] and liquid (LC) [17–20] chromatography. Herein, we report the successful application of LESA-MS to the analysis of two commercial HALS compounds (TIN123 and TIN292; Fig. 1) formulated in either a polyacrylate or cross-linked polyester surface coating. Tandem mass spectra obtained on the ions observed by LESA-MS from these substrates clearly identify structurally modified HALS derivatives that are formed as a result of exposure of samples to heat or UV light. Highly selective tandem mass spectrometry using a triple quadrupole mass spectrometer was shown to elucidate changes in abundance of modified HALS during simulated curing and weathering events.

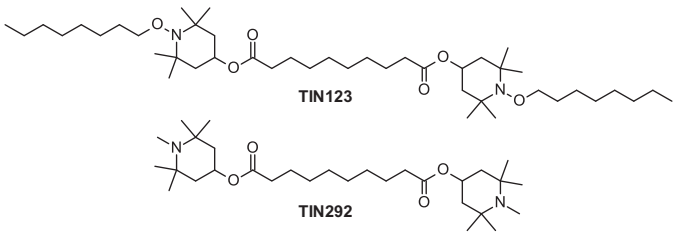

Fig. 1. The chemical structures of two commercially available HALS investigated in this study; TIN123 (*bis*-(1-octyloxy-2,2,6,6-tetramethyl-4-piperidinyl) sebacate), and TIN292 (*bis*-(1,2,2,6,6-pentamethyl-4-piperidinyl) sebacate).

2. Methods

2.1. Reagents

Methanol and formic acid were HPLC grade (Crown Scientific, Minto, NSW, Australia). Chloroform was analytical reagent (AR) grade (Crown Scientific, Minto, NSW, Australia). TINUVIN® 123 (TIN123, *bis*-(1-octyloxy-2,2,6,6-tetramethyl-4-piperidinyl) sebacate) and TINUVIN® 292 (TIN292, *bis*-(1,2,2,6,6-pentamethyl-4-piperidinyl) sebacate) were supplied by Ciba Specialty Chemicals (Basel, Switzerland) and were used without further purification.

2.2. Preparation of samples

Samples of TIN123 were deposited directly on to a glass substrate (representing an authentic TIN123 sample) and heated in an oven at 90 °C for 2 h, 292 °C for 35 s, or left at room temperature (control). TIN123 was also formulated within a solvent-borne, polyester resin incorporating an acid catalysed melamine-formaldehyde cross-linker and cured at in an oven at 292 °C for 35 s. The solvent-based formulation was found to be 40% (w/w) resin solids by thermogravimetry (Perkin-Elmer TGA 7) with TIN123 added at *ca.* 2% (w/w) (based upon total resin solids).

A thin polyacrylate film containing the HALS TIN292 was cured onto a sheet of aluminium and cut into 15 sub-samples. Seven of these sub-samples were aged in an oven at 70 °C for either 5, 10, or 60 min, 48, 96, 192, or 392 h in the absence of UV light. Another seven sub-samples were exposed to UV light using a Q-Sun xenon test chamber (Q-Lab Corporation, Westlake, OH, USA) that utilises a xenon arc lamp to mimic the full solar spectrum and were exposed for 5, 10, or 60 min, 48, 96, 192, or 392 h. The 15th sub-sample was left untreated and constituted a control sample. All sub-samples were analysed in series on the same day to minimise experimental