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Stabiliser distribution and efficiency examined by depth profiling polypropylene using a positron beam

Steven J. Pas [a,b], Filip Tuomisto [c], Kimmo Saarinen [c,✠], Anne Ammala [a],
Terence W. Turney [a,d], Anita J. Hill [a,d,*]

[a] CSIRO Manufacturing and Materials Technology, Private Bag 33, Clayton MDC, Victoria 3169, Australia
[b] Department of Materials Engineering, Monash University, Clayton, 3800 Victoria, Australia
[c] Laboratory of Physics, Helsinki University of Technology, P.O. Box 1100, FIN-02015 HUT, Finland
[d] School of Chemistry and ARC Special Centre for Green Chemistry, Monash University, Clayton, 3800 Victoria, Australia

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Abstract

The effectiveness of stabilisers, organic (hindered amine light stabilisers), inorganic (nanoparticulate zinc oxide), and combinations thereof, in preventing the signatures of degradation in polypropylene subjected to accelerated weathering is studied. Not only the type of stabiliser but also its distribution is important for stabiliser efficiency. The spatial effects of stabilization are studied using positron spectroscopy depth profiling.

Keywords: Polypropylene; Degradation; UV stabiliser; Positron; Doppler broadening; Nanoparticulate ZnO; HALS

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1. Introduction

The effect of stabiliser distribution and efficiency on the properties of both traditional and environmentally friendly polymers is taking on increasing importance as consumers demand more sustainable use of polymers with control over both durability and degradability. Polymeric materials are an increasingly important class of material for outdoor load-bearing and cladding applications. Exposure to the UV portion of solar radiation, however, causes photochemical degradation of the polymers, resulting in discoloration, crazing, cracking and embrittlement that are not only detrimental to aesthetic properties, but may also lead to mechanical failure. Absorption of UV light (above 290 nm) by chromophores in polymers leads to the release of enough energy to cause bond scission resulting in the formation of radicals (photolysis), which in the presence of oxygen/water leads to the formation of more chromophores (carbonyl groups) and/or free radicals [1]. In order to mitigate the harmful effects of the sun, efficient and cost effective methods of stabilizing polymers against UV degradation, as well as the rapid evaluation of their performance, are required, especially when a long period of outdoor exposure is anticipated. Depending on the intended use, product service lifetimes up to 30 years may be required.

In the past, commercially available organic UV absorbers, which provide protection by either absorbing UV light and dissipating it harmlessly as heat or deactivating the products of photolysis, *e.g.* hindered amine light stabilisers (HALS), have been widely employed. HALS help retain gloss and flexibility by scavenging peroxyl radicals. However, these stabilisers decompose in intercepting photolysis events and although deactivating the products of photolysis that result from chain scission, polymer degradation still occurs. HALS are also able to migrate and replenish their concentrations at depletion zones near to the exposed surface. Ultimately, the bulk of the polymer becomes depleted

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[*] Corresponding author. Tel.: +61 3 9545 2665; fax: +61 3 9544 1128. *E-mail address:* anita.hill@csiro.au (A.J. Hill).

[✠] Deceased.

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of HALS (at the typically used loading levels of 0.1–1.0 wt%) limiting the overall useful lifetime of the polymer [2]. In contrast, inorganic stabilisers (*e.g.* ZnO) do not decompose, and they are not able to migrate to the surface to protect it against bond scission. ZnO is an effective stabiliser as it exhibits a steep transmission cut-off at 385 nm, which extends well into the far-IR. Typical loadings for ZnO stabilisers in polymers are around 1.0–2.0 wt%.

We have previously reported the use of nanoparticulate ZnO for UV stabilization of polyolefins [3]. It was shown that nanoparticulate ZnO gives superior resistance to degradation compared to organic HALS at their appropriate loading levels. This result was achieved as the UV absorbing efficiency of nanoparticulate ZnO is increased with reduced particle size (Fig. 1), thus allowing a reduction in loading when compared to a larger particle size. As particles with dimensions well below the wavelength of light and above the level of appreciable quantum confinement have negligible loss from scattering [4], it has been shown that 20–50 nm unagglomerated ZnO, even at very high loading levels (up to 60 wt%), effectively absorbs UV radiation but remains transparent in the visible region [5]. Therefore, the incorporation of nanoparticulate ZnO should result in a marked reduction in HALS stabiliser loading, which in turn reduces the cost of the end product and also reduces any adverse effects of the stabiliser on the aesthetic properties of the material. This is particularly important as colour and transparency have become the major factors in the choice of UV stabilisers for use in the marketplace.

UV stabilisers are usually evaluated in accelerated weathering tests resulting in a much reduced time required to predict the life of the product. Thus, a polymer sample can be exposed to the equivalent of several years of ambient UV radiation over a period of weeks. After exposure, the degree of degradation can be quantified by change in yellowness (reflectance), the presence of oxidation products that can be defined as a ‘carbonyl index’ (infrared) and other macroscopic (*e.g.* gloss) and microscopic (*e.g.* imaging) techniques. Most techniques monitor a surface property because degradation is most evident at the surface. Recent work in polypropylene and other polymers [6,7], however, has highlighted the importance of the degradation profile as a function of depth from the surface. This profile is caused by the diffusion rate of oxygen, which limits the degradation and results in a gradient of oxidation products from the surface, and by the penetration depth of UV radiation. As such, techniques that give an indication of damage state as a function of depth from the surface can give important information on stabiliser efficiency. In addition, knowledge of these spatial effects can be used to tailor the stabiliser spatial distribution for product life extension.

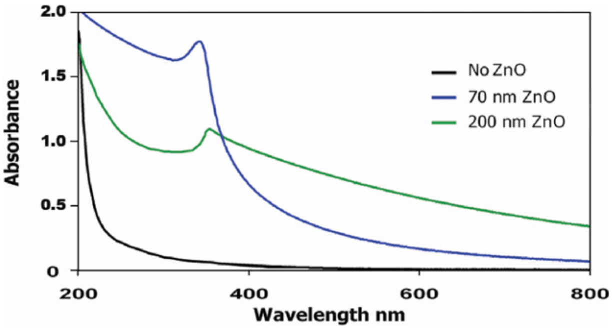

Fig. 1. UV absorbance of 70 nm and 200 nm unagglomerated ZnO showing increased absorption above 385 nm (UV) and decreased absorption below 400 nm (visible) for 70 nm ZnO compared to 200 nm ZnO.

Hulett et al. [8] first reported the use of positron depth profiling to study the degradation of paint films. The authors not only showed that positrons are useful measures of degradation as a function of depth but also that the molecular level sensitivity of positrons provides an “early warning” of degradation, making them useful for rapid screening of paint formulations. It can be noted that even without depth profiling, positron annihilation lifetime spectroscopy (PALS) has been shown to be sensitive to degradation in polymers [9], and by comparison at a much earlier time than is observable by other techniques [3,10,11].

Positron annihilation methods use the positron (e^+) or positronium (e^+e^-) as a probe. Positrons (e^+) are the antiparticles of electrons (e^-), having the same mass as an electron but opposite charge. A positron may bind with an electron of parallel spin forming a semi-stable species called *ortho*-positronium (*o*-Ps). *o*-Ps has a lifetime of approximately 142 ns in vacuo, but, when formed in polymers the high electron density makes it most probable that the *o*-Ps will annihilate with an electron of the polymer with opposite spin (pick-off annihilation), which reduces the *o*-Ps lifetime to approximately 0.8–10 ns. The *o*-Ps lifetime depends on the probability of the overlap of the *o*-Ps wavefunction with the wavefunction of the surrounding electrons; therefore, the *o*-Ps lifetime is a function of the local electron density of the material. The *o*-Ps intensity (or statistical weight of the *o*-Ps component in the timing histogram) reflects the Ps formation probability. Ps formation occurs in competition with electron-ion recombination (from inelastic collisions during the thermalisation process), electron scavenging and positron scavenging [12]. The PALS technique relies on the measurement of positron and positronium lifetimes and intensities and the ability to relate these parameters to the local electron density of materials.

Information on the electron momentum distribution in the material can be obtained by Doppler broadening energy spectroscopy (DBES). Electron–positron annihilation results in the mass to energy conversion of particle–antiparticle while conserving the momentum of the annihilating pair. The annihilation radiation is typically two 511 keV photons that contain information of the electron momentum distribution. In the DBES experiment the momentum component in the photon propagation direction leads to a small