EFFECT OF VARIOUS ADDITIVES ON THE UV STABILITY OF POLYETHYLENE AND POLYPROPYLENE FILMS

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SYNOPSIS

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The service life of typical plastics is strongly influenced by the ultraviolet (UV) degradation caused by solar radiation. Additives can be used to control the UV stability of polymer products.

This study was initiated to address two problems. In some applications, such as greenhouse films, high UV stability is desirable. In others, for example shopping bags, rapid UV degradation could be desirable to reduce the visual impact of plastic litter. However in such instances it is also of interest to retain the recyclability of the base polymer.

In this study the effect of selected compounds on the UV stability of polyethylene and polypropylene films was investigated. Both UV stabilisers
and UV prodegradants were considered. The compounds included various metal complexes as well as substituted hindered amines.

With respect to the hindered amines, derivatives with higher molecular mass were prepared using esterification reactions. The objectives were two fold: first it is necessary to reduce the inherent volatility of the basic hindered amines (e.g., 2,2,6,6-tetramethyl-4-piperidinol [TAA-OL]) to avoid long-term loss from the polymer matrix. The second objective was to improve the compatibility of the very polar hindered amines with the non-polar polyolefin matrix. Alkyl esters and alkyl polyesters were chosen because of their relatively low polarity and their ease of synthesis.

Keywords: photodegradation, UV stability, polyethylene films.

The metal compounds and complexes investigated included metal stearates, metal 2,4 pentanediol-ones and also nickel dimethyl glyoxime. Masterbatches containing the above additives were prepared by standard plastic compounding techniques. Films were blown on laboratory scale equipment. Accelerated weathering was done using a QUV weatherometer fitted with A 340 lamps using a dry cycle.

Films containing the commercial UV stabiliser Chimasorb 944 were used as reference. The progress of degradation was followed using infrared spectroscopy. The carbonyl index was taken as the absorbance at 1710 cm\(^{-1}\) relative to the absorbance at 729 cm\(^{-1}\) and used as measure of the degree of oxidative degradation in polyethylene. In polypropylene the corresponding absorbances were at 1710 cm\(^{-1}\) and 972 cm\(^{-1}\). Chimasorb 944 outperformed all the UV stabilisers synthesised in this study. However, good UV stability was obtained for films that contained the copolymer of triacetone amino alcohol with caprolactone (TOTA), 1-stearoyloxy-2,2,6,6-tetramethylpiperidine (STETA) and nickel dimethyl glyoxime (Ni-dmg). Interestingly copper stearate also imparted a measure of UV stability to polyethylene film but not to polypropylene.
Most metal complexes were found to accelerate UV degradation. Ferric stearate and titanyl 2,4-pentanedione were found to be the most efficient prodegradants. Poly (1,2-dihydro-2,2,4-trimethyl quinoline) (OTMQ) is a hindered amine with a structure similar to that of 2,2,6,6-tetramethyl-4-piperidinol (TAA-OL). It is used as antioxidant in polyethylene and also in rubber applications. This study confirmed that OTMQ, despite its antioxidant nature, acts as a UV prodegradant in both polyethylene and polypropylene films. Derivatives of this compound could therefore have utility in applications where recyclability is important but where UV degradability is also of interest, e.g. plastic shopping bags.

**Keywords:** photodegradation, UV stability, polyethylene films, polypropylene films, additives, HALS, polyesters, transesterification, QUV weathering, FT-IR.
SINOPSIS

EFFEK VAN VERSKEIE BYMIDDELS OP DIE UV STABILITEIT VAN POLIETILEEN EN POLIPROPILEEN FILMS

deur

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Die diensleeftyd van tipiese plastieke word sterk deur ultraviolet (UV) degradasie, wat deur die son veroorsaak word, beïnvloed. Bymiddels kan gebruik word, om die UV stabiliteit van polimeer produkte te beheer.

Die studie was begin met die doel om twee probleme aan te spreek. In sekere toepassings soos in kweekhuisfilms, word hoë UV stabiliteit benodig. In ander gebruike, soos byvoorbeeld in inkopiesakke, kan vinnige UV degradasie wenslik wees om die visuele impak van afval
plastieksakke te verlaag. Dit is egter wenslik om die herwinbaarheid van
die basis polimeer te behou.

Die effek van geselekteerde verbindings op die UV stabiliteit van poliëetyleen
en polipropyleen films is tydens die studie ondersoek. Beide UV
stabiliseerders en UV prodegradante is beskou. Die verbindings het
verskeie metaalkomplekse, sowel as gesubstitueerde verhinderde amiene
ingesluit.

Daar is gevind dat najaar van die metaal polimeer UV degradasie
verhinder.

In die geval van die verhinderde amiene is hoër molekulêre massa derivate
deur middel van verestering berei. Die doel hiervan was tweevoudig. Dit
is eerstens nodig om die inherente vlugtigheid van die basiese verhinderde
amien (byvoorbeeld 2,2,6,6-tetrametiet-4-piperidinol [TAA-OL]) te verlaag,
on die lang termyn verliese uit die polimeer matriks te voorkom.

Tweedens moes die versoenbaarheid van die hoog polère verhinderde
amien met die nie-polère poliólefien matriks verhoog word. Akiel esters
en akiel poliësters is weens hulle relatiewe lae polariteit en maklike
sintese verkies.

Die metaalverbindings en metal komplekse wat ondersoek was het metaal
stearate, metaal 2,4 pentaandioon en nikkel dimetielgloksiem ingesluit.

Standaard plastiekkvermenging en film-blaas procedures met
laboratoriumskaaltoerusting is gebruik om die films – met lae hoeveelhede
van die bogenoemde bymiddels – voor te berei. ’n QUV verweringsmeter,
toeerus met A 340 lampe, is gebruik om die versnelde verwerkingstoets
e uit te voer, deur van die droë siklus gebruik te maak.

Films wat die kommersiële Chimasorb 944 UV stabiliseerder bevat, is as
verwysing gebruik. Die proses van degradasie is deur middel van infrarooi
(IR) spektroskopie gevolg. ’n Karbonielindeks is gedefinieer as die
absorbsie by 1710 cm⁻¹ relatief tot die absorbansie by 729 cm⁻¹. Dit was
gebruik as maatstaf vir die oksiedatiewe degradasie van poliëetyleen. In die
geval van polipropyleen was die ooreenstemmende absorbansies vir die
karbonielindeks 1710 cm\(^{-1}\) en 972 cm\(^{-1}\). Chimasorb 944 was meer effektief as enige van die gesintetiseerde UV stabiliseerders. Goeie UV stabilitéit is nogtans verkry vir films wat bymiddels van kopolimere van triasetoon amino alkohol met kaprolaktoon (TOTA), 1-stearoëblokse-2,2,6,6-tetrametielpiperidië (STETA) en nikkel dimetiêlglioksiëm (Ni-dmg) bevat het. Interessant genoeg het koper stearaat ook ‘n mate van UV stabilitéit aan poliëtileenfilm verleen, maar nie aan polipropileenfilm nie.

Daar is gevind dat meeste van die metaal kolmekse UV degradasie versnel. Yster (III) stearaat en titaniël 2,4-pentaandioon is as die mees effektiewe prodegradante geïdentifiseer. Poli(1,2-dihidro-2,2,4-trimetiêlkinolin) (OTMQ) is ‘n verhinderde amien met ‘n struktuur soortgelyk aan die van 2,2,6,6-tetrametiël-4-piperidinol (TAA-OL). Dit word kommersieel as antioksidant in poliëtileen gebruik asook in rubbertoeapplings. In die studie is bevestig dat OTMQ as ‘n UV prodegradant optree in beide poliëtileen- en polipropileenfilms, ten spyte van sy antioksidasie eienskappe. Dit is dus moontlik dat derivate van die verbinding gebruik mag vind in toepassings waar herwinbaarheid, maar ook UV degradasie van belang is, soos byvoorbeeld plastiek inkopiesakke.

**Sleutelwoorde:** fotodegradasie, UV stabilitéit, poliëtileen films, polipropileen films, bymiddels, HALS, poliësters, transverestering, QUV verwering, FT-IR.
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TABLE OF CONTENTS

Synopsis .................................................................................................................................................. i
Acknowledgements ............................................................................................................................ vii

CHAPTER 1. INTRODUCTION ............................................................................................................. 1
CHAPTER 2. BACKGROUND INFORMATION .................................................................................. 3
  2.1 POLYOLEFINS STRUCTURE ...................................................................................................... 3
     2.1.1 Polyolefins. ......................................................................................................................... 3
     2.1.2 Polyolefins in the environment ......................................................................................... 4
  2.2 DEGRADATION OF POLYMERS ............................................................................................... 5
     2.2.1 Overview of polymer degradation ....................................................................................... 5
     2.2.2 General types of polymer degradation processes ............................................................. 7
     2.2.3 Degradation reactions ........................................................................................................ 8
     2.2.4 Thermal oxidative reactions of polymers: ....................................................................... 10
  2.3 DETAILED PHOTOOXIDATION AND PHOTODEGRADATION MECHANISM 
     FOR POLYETHYLENE AND POLYPROPYLENE ........................................................................ 13
     2.3.1 Introduction...................................................................................................................... 13
     2.3.2 Light absorption processes ............................................................................................... 13
     2.3.3 The general features of polyethylene and polypropylene oxidation: 
          qualitative characterisation of process ................................................................................. 14
     2.3.4 Mechanism of polyethylene and polypropylene oxidation ............................................ 15
     2.3.5 Photodegradation mechanisms of polyethylene and polypropylene............................. 22
     2.3.6 Effects of ultraviolet irradiation ....................................................................................... 31
     2.3.7 Quantifying degradation: the Carbonyl Index................................................................. 34
  2.4 PHOTOSTABILISATION OF POLYETHYLENE AND POLYPROPYLENE ................................ 35
     2.4.1 Mechanism of photostabilisation ...................................................................................... 35
     2.4.2 Photostabilisation by excited-state quenching. ............................................................... 38
  2.5 FUNCTIONAL ADDITIVES FOR POLYMERS ........................................................................ 41
     2.5.1 Introduction..................................................................................................................... 41
     2.5.2 Physical properties of additives ....................................................................................... 43
     2.5.3 Ultraviolet stable antioxidants ........................................................................................ 44
     2.5.4 Light stabilisers ................................................................................................................ 47
     2.5.5 Synergism and antagonism ............................................................................................... 53
     2.5.6 Factors controlling the choice of stabiliser ....................................................................... 55
  2.6 PHOTODEGRADABLE POLYMERS ......................................................................................... 56
     2.6.1 Introduction..................................................................................................................... 56
     2.6.2 Photosensitive plastics .................................................................................................... 57
APPENDICES

APPENDIX A: DSC spectra for reagents and additives synthesised
APPENDIX B: UV spectra for additives synthesised
APPENDIX C: DSC/TGA traces for additives synthesised
APPENDIX D: DSC/OIT scans
APPENDIX E: Table E1: Measured carbonyl indices for weathered polyethylene (LDPE) films samples

Table E2: Measured carbonyl indices for weathered polypropylene films samples

Polyethylene (PE) and polypropylene (PP) are synthetic polymers with large annual sales volumes. The typical life cycle of PE and PP as synthetic polymers is [2]: synthesis, compounding, conversion to petrochemical processing, usage, disposal or recovery and re-use. Because of their relatively low cost, polyethylenes (PEs) and polypropylenes (PPs) are widely used in a variety of applications, e.g. green house films [3, 4]. In fact, both polymers are especially susceptible to ultraviolet radiation in the 300-380 nm region. UV energy causes the chemical bond to break and initiate oxidation processes. This in turn results in embrittlement, surface scorching, discoloration and loss of impact and tensile strength. The intensity and nature of light-absorbing groups in a polymeric system are important factors in photo-degradation in polymers that have an ultraviolet absorber. Impurities induce degradation [5].

Plastic shopping bags have become an integral part of the South African lifestyle. Most retailers supply them free of charge to their customers. Unfortunately, progress in film-blowing and resin technology have made it possible to produce bags that are so thin that post-consumer recycling becomes impractical. Furthermore, the public is not yet sensitised with respect to environmental issues. Littering is therefore a major problem. A possible solution can be that degradation under UV but good heat stability so that they can still be recycled.