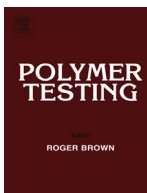




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Analysis method

Determination of stabilisers in polymeric materials used as encapsulants in photovoltaic modules



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ABSTRACT

Synthetic polymers are used as encapsulants or front and back sheets in photovoltaic modules. Since the concentrations of (intact) stabilisers are crucial for the durability of the polymeric material, the current study provides methods for the determination of stabilisers in commercially relevant encapsulants for photovoltaic modules: ethylene vinyl acetate (EVA), polyvinyl butyral (PVB) and thermoplastic silicone elastomer (TPSE). For identification of the stabilisers present in EVA, direct analysis in real time coupled with mass spectrometry (DART-MS) is employed as a rapid method applicable to the polymeric film without sample preparation. For qualitative analysis of PVB and TPSE, but also for the subsequent quantification of the identified stabilisers in all investigated encapsulants, gas chromatography (GC) coupled with MS as well as high performance liquid chromatography (HPLC) coupled with UV and MS detectors are applied. Optimised protocols for the preparation of stabiliser extracts needed for these methods are presented for all three materials.

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1. Introduction

Polymeric materials are used in more and more fields of application due to advantages such as lighter weight, easier processing and handling combined with lower prices in comparison with many inorganic materials. However, a main drawback is that polymers are prone to degradation if they are exposed to heat, humidity or UV-radiation, which leads to deterioration of the material's mechanical properties. Degradation of the polymeric backbone can be prevented or at least slowed down by the addition of stabilisers [1]. A broad range of possible additives for

polymeric materials is available on the market. In order to obtain materials for specific purposes, the selection of suitable additives is crucial.

In recent decades, synthetic polymers have become increasingly important as encapsulation materials in photovoltaic (PV) modules [2]. For PV modules, the desired lifespan is about 20 to 30 years [3–5]. Degradation of the encapsulation can cause discolouration and lead to light transmission losses and delamination, which might significantly reduce the durability of the module [5]. In order to prevent or at least slow down degradation of polymeric materials, the addition of appropriate stabilisers is necessary [6].

As the concentration of the stabilisers strongly influences the durability of the material, stabiliser determination is of major analytical concern [6]. In the literature, two different approaches for additive analysis have been reported. The first is based on separation of the stabilisers from the matrix. This can be performed either by

Abbreviations: DART, direct analysis in real time; EI, electron ionisation; EVA, ethylene vinyl acetate; GC, gas chromatography; HPLC, high performance liquid chromatography; MS, mass spectrometry; PV, photovoltaic; PVB, polyvinyl butyral; TPSE, thermoplastic silicone elastomer.

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dissolution of the polymer or liquid-solid-extraction [7]. The other method is to analyse the polymeric sample directly without performing any extensive sample preparation [8]. Both methods have strengths and weaknesses and there is not an ideal method [6,7,9].

For polyolefins, there are already some methods available for sample preparation as well as stabiliser qualification and quantification [6,8,10,11]. However, for PV module encapsulants a variety of different polymers is used, as for instance ethylene vinyl acetate (EVA), ionomers, polyvinyl butyral (PVB) or thermoplastic silicone elastomer (TPSE) [5]. New methods are essential in order to analyse stabilisers in these materials.

This work presents methods for the qualitative and quantitative determination of stabilising agents in three different synthetic polymers employed as encapsulants in photovoltaic modules: EVA, PVB and TPSE. For identification of stabilisers present in these materials, different methods were investigated: direct analysis in real time (DART) with a time-of-flight mass spectrometer, high performance liquid chromatography coupled with mass spectrometry (HPLC/MS), and gas chromatography coupled with mass spectrometry (GC/MS). For DART-MS measurements, no sample preparation was necessary; for the other qualification methods, as well as for the subsequent quantification of the identified stabilisers by HPLC with a UV detector (HPLC/UV) and GC/MS, extracts of the polymers were required. Hence, comprehensive sample preparation protocols were developed for each material investigated.

2. Experimental

2.1. Materials, reagents and standard solutions

Stabilisers Irganox 1135, Tinuvin 328, Tinuvin 571 and Tinuvin 770 were obtained from BASF (Ludwigshafen, Germany), ADK Stab AO 40 from Adeka (Strasbourg, France), Chimassorb 81 and Irgafos 168 from Ciba (Basel, Switzerland) and Cyanox 1790 from Cytec Industries Inc (Garret Mountain Plaza). The internal standard triphenylbenzene was obtained from Merck (Darmstadt, Germany). Helium gas for GC/MS and DART-MS was purchased from Linde (Stadl-Paura, Austria). Acetonitrile, methanol and toluene were obtained from VWR (Vienna, Austria). The stabiliser standard solutions were prepared in toluene (2000 mg/L) and diluted with acetonitrile to obtain concentrations between 0.5 and 50 mg/L.

2.2. Preparation of polymer extracts

In order to prepare a PVB extract, about 20 mg of polymer was dissolved in 1.5 ml of methanol in an oven at a temperature of 130 °C (for 45 minutes). After placing it in a freezer (−19 °C), the sample was centrifuged and 300 µL of supernatant brought to dryness, followed by reconstitution in 300 µL of acetonitrile.

Similar to PVB, the sample preparation of EVA samples was also based on dissolution of the polymer. 20 mg of sample was dissolved in 0.75 mL toluene (130 °C, 45 minutes). The polymer was re-precipitated with 0.75 mL

acetonitrile and centrifuged. Again, 300 µL of supernatant were brought to dryness and reconstituted in 300 µL of acetonitrile.

The preparation of the TPSE extracts was done without dissolution of the polymer. In order to enhance the effectiveness of the extraction, the sample was ground with a cryogenic mill. 1.5 mL of acetonitrile was added to about 20 mg of the powdered sample and the mixture placed into an oven (130 °C, 45 minutes). Unlike EVA and PVB, the extract was analysed directly after separation from the powdered polymer by centrifugation.

For all samples and standards, either triphenylbenzene or Cyanox 1790 was applied as internal standard.

2.3. Instrumentation and parameters

2.3.1. DART-MS

The DART ion source was provided by IonSense, Inc. (Saugus, MA, USA) and was coupled with a JMS T100 (AccuTOF-LC-plus) time-of-flight mass spectrometer (JEOL Ltd, Tokyo, Japan). The measurements were performed in the positive ion mode with the following voltages: capillary voltage: 3000 V, discharge electrode: 100 V, grid electrode: 50 V, peaks voltage: 600 V. The temperature of the gas heater on the ceramic tube temperature was 250 °C and the data acquisition was performed in a range from 100 to 1200 m/z.

The DART was tuned by positioning the ceramic tube (4 mm ID) in such a way that maximum intensities for water-clusters were obtained. After the adjustment of the ceramic tube, the mass calibration of the instrument was performed using a polyethylene glycol solution containing PEG 400, PEG 600 and PEG 800 in methanol.

2.3.2. GC/MS

The experiments with GC/MS were carried out with an Agilent GC 6890N instrument coupled with a 5973Network mass spectrometer (with electron ionisation (EI)), both from Agilent Technologies (Waldbronn, Germany). The GC was equipped with a MPS 2L autosampler from Gerstel (Mülheim, Germany). Separations were achieved on a Rxi-5HT column (15 m, 0.25 mm ID, 0.10 µm film thickness) from Restek (Bad Homburg, Germany). Helium with a constant flow of 1.5 mL/min was used as carrier gas.

The injector was operated in the splitless mode starting at a temperature of 40 °C with an injection volume of 1 µL. The temperature of the injection port was increased by 12 °C/s, ending at a temperature of 275 °C which was held for two minutes. The temperature program of the oven started at 40 °C and went up to 400 °C at a rate of 10 °C/min. The final temperature was held for five minutes.

2.3.3. HPLC/UV

For HPLC/UV quantification experiments, an Agilent 1260 HPLC system equipped with a vacuum degasser, a quaternary pump, an autosampler and a UV/VIS diode array detector was utilised. A Kinetex C18 column (50 × 4.6 mm ID; 2.6 µm particle size) from Phenomenex (Aschaffenburg, Germany) was employed for separation. A gradient elution with acetonitrile (A) and water (B) with a flow rate of 2.1 mL/min and the following elution program was

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