



Application Note No. 151/2014

High molecular weight HALS in LDPE

SpeedExtractor E-916:

Quantification of high molecular weight HALS (hindered amine light stabilizer) in LDPE (Low density polyethylene) comparing Soxhlet extraction and pressurized solvent extraction using the SpeedExtractor E-916



1. Introduction

Polymeric materials such as plastics and rubbers are easily degraded by heat, sunlight, etc. during manufacturing or usage. Therefore, in general to ensure the required product lifetime a polymeric material has small amounts of stabilizers added to it. High molecular weight hindered amine light stabilizer (HALS) is one of the stabilizers used in polymeric materials. High molecular weight HALS improves the heat resistance and the light resistance of polymeric materials, and it has low volatility and extractability from the materials. High molecular weight HALS is widely added to polyethylene (PE) or polypropylene (PP) film.

In order to analyze the amount of stabilizer in the polymeric materials, typically, the solvent extracted stabilizer is quantified using general purpose equipment, i.e. gas chromatography. However, the quantification of high molecular weight HALS is limited due to its low extraction efficiency [1]. For example, the precipitation method with toluene under high temperature conditions has been published [1], but this method was cumbersome and dangerous. Therefore, a method to easily extract high molecular weight HALS from polymers is desired.

Pressurized solvent extraction (PSE) methods differ from common extraction methods, such as Soxhlet extraction, as it uses solvent at high temperatures and pressures. The PSE method is easily performed using the SpeedExtractor E-916. Using PSE is expected to improve the extraction efficiency for the materials that are difficult to extract by other methods.

This application note describes the extraction and determination of high molecular weight HALS in a low density polyethylene (LDPE) sample, including the method development. The results of PSE were compared with the results obtained using a Soxhlet method.

2. Equipment

- SpeedExtractor E-916 with 20 mL cells (BUCHI 11516024)
- 2 mL Expansion element (BUCHI 053708)
- Extraction thimble 10 x 110 (Munktell)
- Soxhlet extractor (not automated)
- Rotavapor[®] R-114 (BUCHI) with Controller and Chiller. The evaporation can be done on all BUCHI Rotavapors[®]
- GC/MS 6890A 5973N (Agilent Technologies)
- Cryogenic mill (for example Retsch CryoMill)

3. Chemicals and Materials

Chemicals:

- Methanol, for HPLC > 99.8 %, (GC), Kanto Chemical Co., Inc. (25183-1B)
- Dichloromethane, for HPLC > 99.5 % (GC), Kanto Chemical Co., Inc. (10158-1B)
- Heptane, for HPLC > 99.0 % (GC), Kanto Chemical Co., Inc (18005-1B)
- Tetramethylammonium hydroxide (TMAH) (10 % in methanol), Tokyo Chemical Industry Co., Ltd (T1201)

Samples:

Two high molecular weight HALS were used (chemical structures are shown in Section 8)

- LA62: 1,2,3-tris(1,2,2,6,6-pentamethyl-4-piperidyl) 4-tridecyl butane-1,2,3,4-tetracarboxylate, ADEKA corporation (ADK STAB LA62)
- LA63: Mixed esterification product of 1,2,3,4-butanetetracarboxylic acid and 1,2,2,6,6-pentamethyl-4- piperidinol and 3,9-bis(2-hydroxy-1,1-dimethyl)-2,4,8,10-tetraoxaspiro[5.5]undecane, ADEKA corporation (ADK STAB LA63p)
- LDPE: Novatec[®] LD, Japan Polychem Corporation

4. Procedure

The determination of high molecular weight HALS includes the following steps:

- Sample preparation
- Preparation of the extraction cells
- Extraction with the SpeedExtractor E-916
- Concentration of the extracts
- Quantification by GC/MS

4.1. Sample preparation

- Removal of additives from LDPE sample using Soxhlet extraction
- Addition of HALS 0.1 wt % to the sample
- Blend kneading (hot rolling)
- Cryogenic crushing to a homogeneous powder

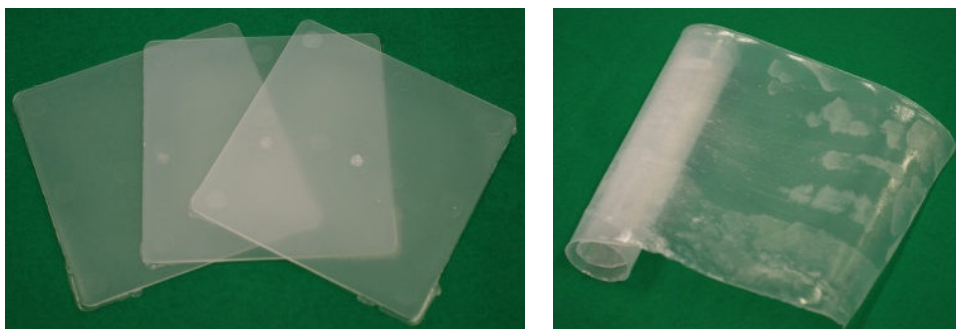


Fig 1: LDPE sample before and after blend kneading

4.2. Preparation of the extraction cells

- Place a glass fiber filter (BUCHI 11055932) and a metal frit (BUCHI 049568) at the bottom of the extraction cell and close with a plug (BUCHI 053209)
- Turn the extraction cell and insert a 2 mL expansion element (BUCHI 053708) to reduce the solvent consumption
- Load 1.0 g samples into a cellulose extraction thimble 10 x 110 mm. Cover the open thimble to ensure that the sample will not be flushed out.



Fig 2: Thimbles containing the sample

- Load the sample into the extraction cell
- Close the cell with a top cellulose filter paper (BUCHI 049572) by pressing down with the plunger (BUCHI 053037)

4.3. Extraction with the SpeedExtractor E-916

To carry out the extraction use the parameters in Table 1.

Table 1: Extraction method for SpeedExtractor E-916

Parameter	Value
Temperature	110 °C
Pressure	150 bar
Solvent	Methanol 100 %
Cells	20 mL
Vials	240 mL
Cycles	10
Heat-up	1 min
Hold	10 min
Discharge	1 min
Flush with solvent	1 min
Flush with gas	3 min
Total extraction time	2 h 55 min

4.4. Concentration of the extracts

The extracts were concentrated to 1 mL using the Rotavapor® R-114 with the parameters shown in Table 2.

Table 2: Evaporation parameters for Rotavapor® R-114

Parameter	Value
Temperature	45 °C
Pressure	300 mbar
Water bath temperature	40 °C
Time	15 - 20 min

4.5. Quantification with GC/MS

The concentrated extract was diluted with 10 mL dichloromethane. 20 µL of tetramethyl ammonium hydroxide (TMAH) 10% methanol solution was added to 1 mL of the sample solution. The solution was mixed and then analyzed by GC/MS using the parameters shown in Table 3.

Table 3: GC/MS parameter

Type of GC/MS	Agilent 6890 A 5973 N
Column	DB-5 MS (Agilent J&W); 30 m x 0.25 mm x 0.25 µm
Carrier gas	He, 1 mL/min
Oven program	60 °C (hold 2 min) – (10 °C/min) – 280 °C (30 min)
Injection temperature	280 °C
Injection method	Pulsed splitless
Injection volume	1 µL
Transfer line temperature	280 °C
Measurement mode	Selected Ion Monitoring (SIM)
Measurement mass number	1,2,2,6,6-Pentamethyl-4-piperidinol (HPMP) 156

5. Result

GC/MS chromatograms, SCAN measurement are shown in Fig. 3 and 4.

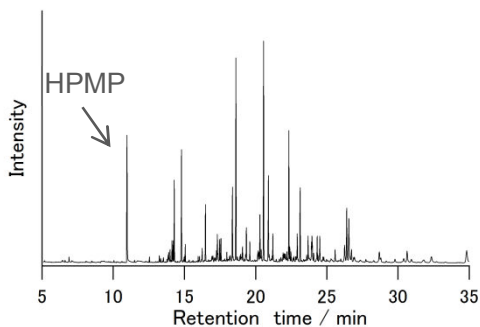


Fig. 3: GC/MS chromatogram of LA62 in LDPE

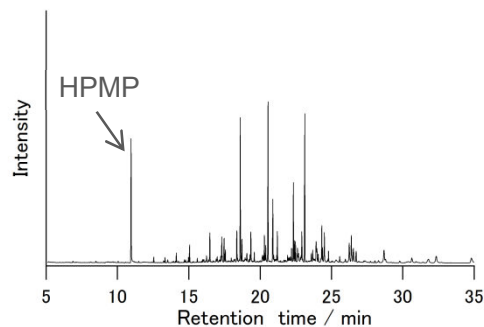


Fig. 4: GC/MS chromatogram of LA63 in LDPE

Pentamethylpiperidine in the base structure of LA62 and LA63 was hydrolyzed to 1,2,2,6,6-Pentamethyl-4-piperidinol (HPMP) by TMAH, HPMP was detected at a retention time of 11min and this was used for quantification.

For comparison the sample was also extracted using a Soxhlet method (extraction time: 16 h). The results of the PSE and the Soxhlet extraction are shown in Table 4.

Table 4: Recoveries of LA62 and LA63 in LDPE using the SpeedExtractor E-916 (extraction time: approx.3 h) and a Soxhlet extraction method (extraction time: 16 h)

HALS	Recovery of PSE	Recovery of Soxhlet
LA62	98 %	44 %
LA63	57 %	16 %

6. Method development

6.1. Procedure for PSE and Soxhlet extraction

For method development the LDPE sample was also extracted with the SpeedExtractor E-916 using dichloromethane and heptane. The parameters are shown in Table 5.

Table 5: Extraction parameters for method development using the SpeedExtractor E-916

Parameter	Value
Temperature	110 °C
Pressure	150 bar
Solvent	Dichloromethane 100 % resp. Heptane 100 %
Cells	20 mL
Vials	240 mL
Cycles	10
Heat-up	1 min
Hold	10 min
Discharge	1 min
Flush with solvent	1 min
Flush with gas	3 min
Total extraction time	2 h 55 min

The LDPE sample was extracted using dichloromethane with different Soxhlet methods. The parameters are shown in Table 6.

Table 6: Extraction parameters for method development using the Soxhlet extraction

Solvent	Extraction time in h
Dichloromethane	16
Dichloromethane	48

6.2. Results of method development

Table 7: Recoveries of HALS for method development for PSE using the SpeedExtractor E-916

Extraction Solvent	Methanol	Dichloromethane	Heptane
LA62	98 %	< 20 %	< 20 %
LA63	57 %	< 20 %	< 20 %

Table 8: Recoveries of HALS for method development using Soxhlet extraction

Extraction Solvent	Methanol	Dichloromethane	Heptane
Extraction time	16 h	16 h	48 h
LA62	44 %	49 %	51 %
LA63	16 %	31 %	48 %

7. Conclusion

For method development the Soxhlet extractions were carried out for 16 hours. 16 hours is the typical time for Soxhlet extractions for this type of sample. As shown in Table 8, the recoveries of LA62 and LA63 were dependent on the type of solvent used. The recoveries using dichloromethane were higher than those received using methanol. Therefore the Soxhlet extraction time using dichloromethane was extended to 48 h. However, the recoveries of LA62 and LA63 were only increased to approx. 50 %.

The PSE method with methanol using the SpeedExtractor E-916 increased the recoveries for LA62 and LA63. LA62 showed a recovery of 98 % after an extraction time of only 3 h compared to minimum of 16 h with Soxhlet.

In conclusion, the PSE method using the SpeedExtractor E-916 obtained higher recovery rates of high molecular weight HALS in polymeric materials in a faster time than the Soxhlet extraction.

8. Supporting information

Chemical structures:

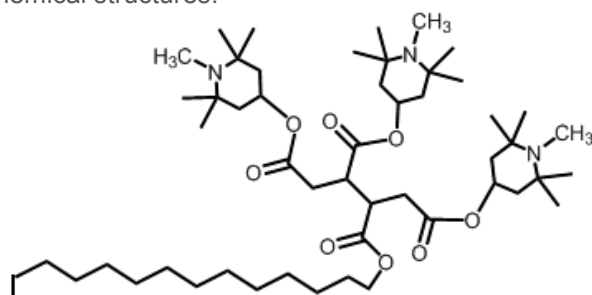


Fig. 5: LA62

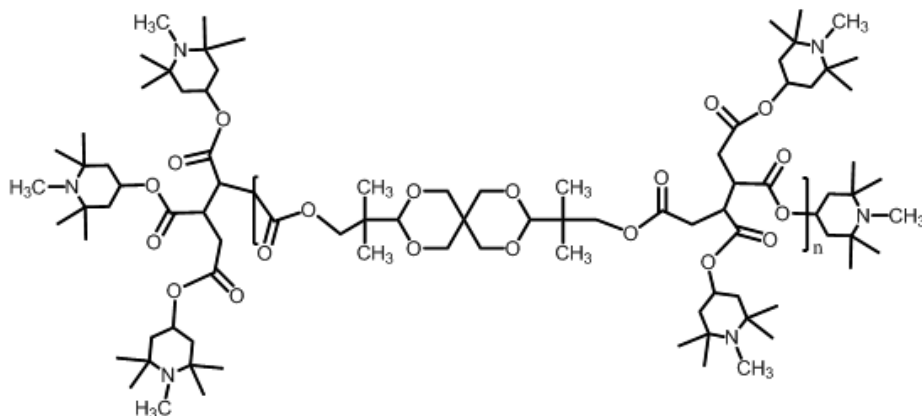


Fig. 6: LA63

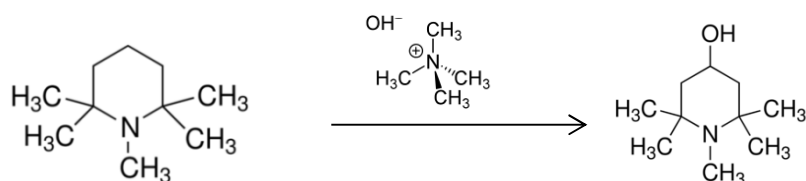


Fig. 7: Hydrolysis of 1,2,2,6,6-Pentamethylpiperidine to 1,2,2,6,6,-Pentamethyl-4-piperidinol using tetramethylammonium hydroxide

9. Acknowledgements

We gratefully acknowledge Mr. Yoshito Otake (Director of the Institute) and Mr. Tatsuya Horimai from the Chemicals Evaluation and Research Institute, Japan who developed this Application Note.

10. References

- [1] L. Coulier, E.R. Kaal, M. Tienstra, T. Hankemeier *J. Chromatogr. A*, 1062, 227-238, (2005)

Operation Manual of SpeedExtractor E-916 / E-914