

Pressurized Solvent Extraction

Efficient extraction of stabilizer in polyethylene

Quantification of high molecular weight HALS in LDPE comparing Soxhlet extraction and pressurized solvent extraction with SpeedExtractor E-916

Abstract

The BUCHI SpeedExtractor E-916 (Figure 1) is used for the fast extraction of high molecular weight hindered amine light stabilizer (HALS) in polyethylene film. In comparison to the Soxhlet method the SpeedExtractor can extract HALS in 3 h instead of 16 h to 48 h leading to even higher recoveries. Up to six samples are processed in parallel using the SpeedExtractor E-916 at elevated temperatures and pressures.

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 HALS improves the heat resistance and the light resistance of polymeric materials, e.g. polyethylene (PE) or polypropylene (PP) films, and it has low volatility and extractability from the materials.

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 the polymer is desired.

The SpeedExtractor E-916 (Figure 1) is an automated instrument for parallel extraction of primarily organic compounds from a variety of solid or semi-solid samples. Conventional methodologies are accelerated by using a solvent at elevated temperatures. In order to maintain the solvent in a liquid state during the extraction process, the solvent inside the extraction cell is put under pressure. To achieve high recoveries multiple extraction cycles are applied. Once the extraction step is finished, the extracts are cooled down in a cooling unit and flushed into collection vials.



Figure 1: SpeedExtractor E-916

The amount of high molecular weight HALS in low density polyethylene (LDPE) was determined using

two extraction methods: Soxhlet extraction and pressurized solvent extraction (PSE) using the SpeedExtractor E-916. The recoveries of high molecular weight HALS obtained by these two methods were compared.

2. Samples

(1) High molecular weight HALS

The following two high molecular weight HALS compounds were used for testing:

- 1,2,3-tris(1,2,2,6,6-pentamethyl-4-piperidyl) 4-tridecyl butane-1,2,3,4-tetracarboxylate (Made by ADEKA corporation, ADK STAB LA62, abbreviation : LA62)

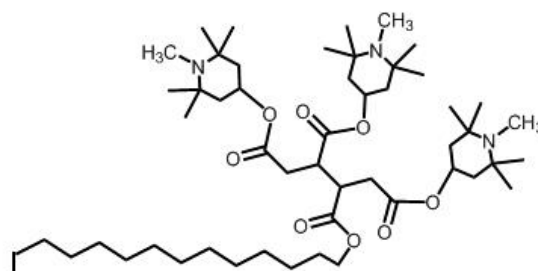


Figure 2: Chemical structure of LA62

- 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 (Made by ADEKA corporation, ADK STAB LA63p, abbreviation : LA63)

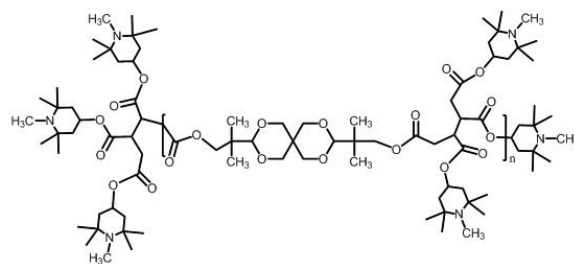


Figure 3: Chemical structure of LA63

(2) Preparation of the test piece

High molecular weight HALS 0.1 wt% was kneaded into LDPE (Novatec[®] LD provided by Japan Polychem Corporation) using a high temperature roll. The test piece was cryogenically crushed to a homogeneous powder to use in the extraction.

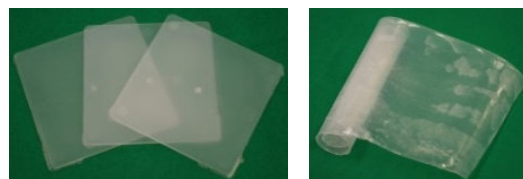


Figure 4: LDPE sample before and after blend kneading

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3. Methods

(1) Extraction

PSE was performed at 110 °C, 150 bar with 10 cycles of 10 minutes each. Soxhlet extractions were performed for 16 h to 48 h.

The extract obtained was concentrated by evaporation (Rotavapor®, BUCHI) and reconstituted to 1 mL with dichloromethane. Tetramethyl ammonium hydroxide (TMAH) 10% methanol solution was added into the 1 mL sample solution. The mixed solution was analyzed by GC/MS (Agilent Technologies).

(2) Quantitative analysis of HALS

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 11 min and this was used for quantification. GC/MS chromatograms of LDPE samples by SCAN measurement are shown in Figures 5 and 6.

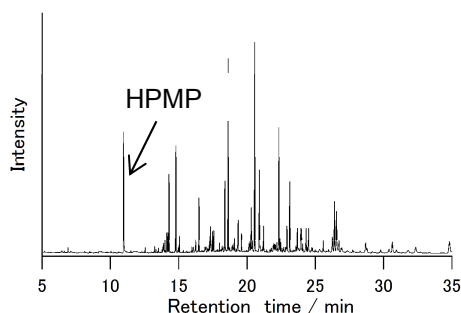


Figure 5: GC/MS chromatogram of extract of LA62 in LDPE

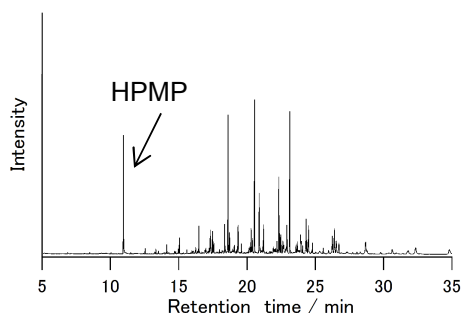


Figure 6: GC/MS chromatogram of extract of LA63 in LDPE

4. Results

Recovery rates of LA62 and LA63 in LDPE are shown in Tables 1 and 2.

Table 1. Recovery rates by PSE using the SpeedExtractor E-916

Extraction solvent	Methanol	Dichloromethane	Heptane
Extraction time	3 h	3 h	3 h
LA62	98	< 20	< 20
LA63	57	< 20	< 20

Table 2. Recovery rates using Soxhlet extraction

Extraction solvent	Methanol	Dichloromethane	
Extraction time	16 h	16 h	48 h
LA62	44	49	51
LA63	16	31	48

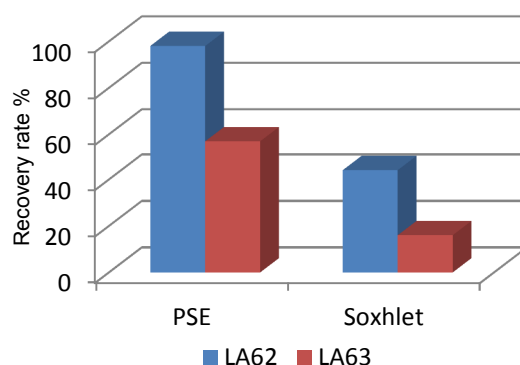


Figure 7: Recovery rates of PSE and Soxhlet extraction using methanol

5. Conclusion

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.

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 2, the recoveries of LA62 and LA63 were dependent on the type of solvent used. The recoveries using dichloromethane were higher than those 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 %.

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.

6. Acknowledgement

We gratefully acknowledge Mr. Yoshito Otake and Mr. Tatsuya Horimai from the Chemicals Evaluation and Research Institute, Japan.

7. References

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

For further information see:
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