DEVELOPMENT OF EXTRACTION AND ANALYSIS METHOD FOR HIGH MOLECULAR WEIGHT HINDERED AMIN LIGHT STABILIZER (HALS) IN SYNTHETIC POLYMERS

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INTRODUCTION

HALS are additives which are used widely in recent years due to their resistance against weather, and further, when used in combination with other stabilizers, it is possible to further improve the light stabilizing function and to improve other details depending on polymer and application. However, it is difficult to extract high molecular weight HALS from polymer materials because of its high hydrophobicity and this hydrophobicity has strong interaction with reverse phase columns making it difficult to elute even with C4 column. Therefore, it is a compound with few quantitative analysis methods.

Soxhlet extraction, dissolution reprecipitation, Accelerated Solvent Extraction (ASE), etc. are commonly used for extracting additives in polymer materials, however since it is difficult to extract high molecular weight (MW) HALS in materials with these technologies, we investigated the Supercritical Fluid Extraction (SFE) method for high MW HALS extraction. As LC analysis requires mobile phase conditions with a high elution power that can elute high MW HALS, it is indispensable to select an analytical system and column that have durability against mobile phase with higher elution power and can be used universally. In addition, as the elution power of the mobile phase increases, similar HALS compounds with similar hydrophobicity are expected to co-elute, so the selectivity of the detector should also be considered. In this report, we introduce the effectiveness of selective extraction of high MW HALS using SFE and chromatographic method using column with high durability to high elution power solvent.

A polybutylene terephthalate resin containing low and high molecular weight HALS at known concentrations was applied to verify the developed extraction and analysis conditions

In general, compared to the Soxhlet extraction method, dissolution reprecipitation method, accelerated solvent extraction (ASE) method, there are few examples using SFE for extraction of additives from synthetic polymers, however there are advantages as follows

1. **Faster elution speed**
2. **Less oxidation**
3. **Selective extraction**
4.

METHODS

Sample

Sample was prepared by adding 500 ppm (w / w) each of HALS manufactured by BASF shown in FIG. 1 to polybutylene terephthalate resin.

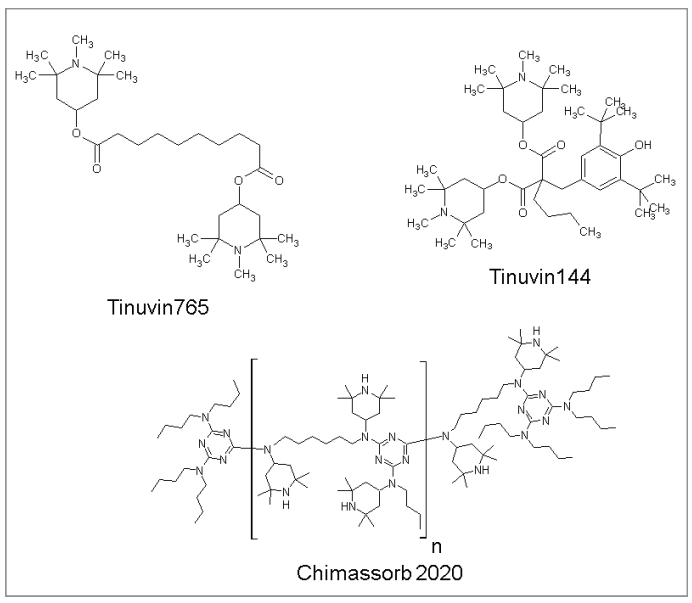


Figure 1. Structures of HALS

Extraction condition

Extraction was performed by using Waters MV-10 ASFE system (FIG. 2). Common extraction condition in poster are described below.

- Sample Weight : 50mg
- Extraction Vessel : 5 mL
- Flow rate : 10 mL/min

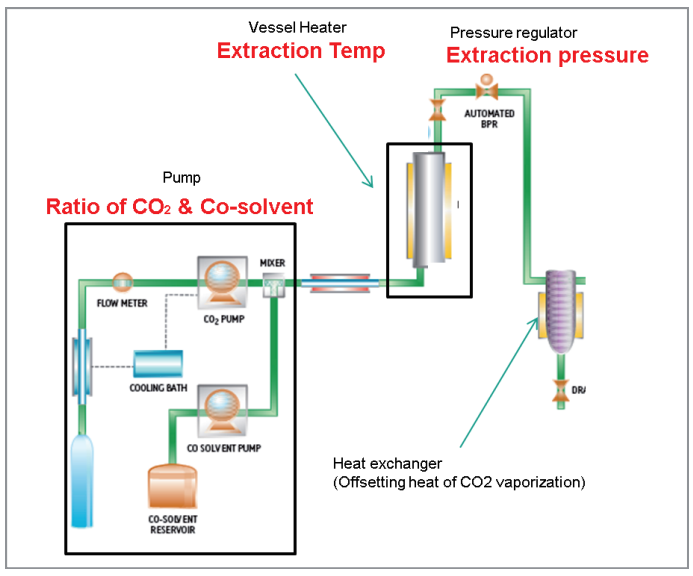


Figure 2. Schematic of MV-10 ASFE system

LC/MS analytical condition

- LC system : ACQUITY UPLC H-Class with PDA
- MS system : ACQUTY QDa mass detector
- Mobile phase : Water
  Acetonitrile
  Tetrahyrdofuran
  Ammonium bicarbonate aq
- Column : ACQUITY UPLC BEH C8 1.7 um, 2.1x50 mm
- Column Temperature : 40 C
- Injection Volume : 2 uL
- Ionization mode : ESI positive
- Monitor ion : 509.6 (Tinuvin 765 M+H)
  685.7 (Tinuvin 144 M+H)
  872.8 (Chimasorb 2020 (M+2H)

RESULTS

Effect of modifier on extraction

-Low molecular weight HALS

Tinuvin 765 was used as the compound. The extraction time was fixed at 20 minutes, and the extraction efficiency when evaluating modifiers was evaluated. When the modifier is not added, a high recovery rate could not be obtained. By adding the modifier, an improvement of about 10 times was observed, and the recovery rate in methanol was particularly high. This was adopted as a modifier for extraction of low molecular weight HALS.

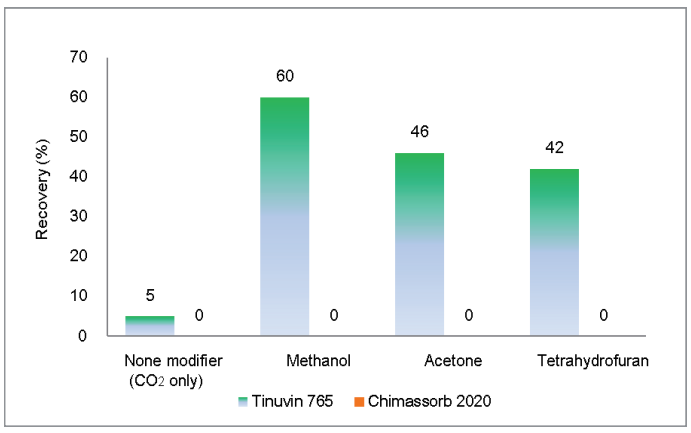


Figure 3. Effect of modifier on extraction of Low molecular weight HALS (Tinuvin 765)

-High molecular weight HALS

Fig. 4 shows the extraction recovery of Chimassorb 2020. When the same modifier as previous was used, HALS was not extracted under all conditions.

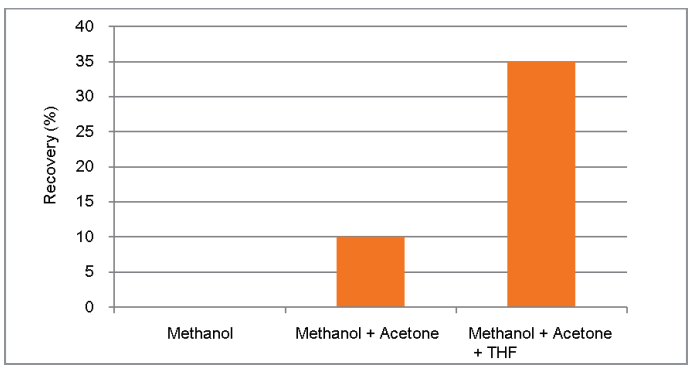


Figure 4. Effect of modifier on extraction of High molecular weight HALS (Chimassorb 2020)

High molecular HALS is known to have high solubility in solvents such as acetone, tetrahydrofuran, and dimethylformamide, but its dissolution rate is not so large due to the influence of hydrogen bonds and ionic interactions in the hindered amine structure. For reducing these interaction, basic solvent was tested as modifier. With adding ammonia into modifier, recovery of Chimassorb 2020 was improved.

As a result of optimizing extraction condition, by using methanol first for extraction of low molecular HALS and using 4-solvent mixture containing ammonia as following extraction, selective extraction of low and high molecular HALS could be achieved.

Recovery (%)	Tinuvin 765	Tinuvin 144	Chimassorb 2020
N=1	83	85	84
N=2	83	82	83
N=3	84	83	86
Means	83	83	84
S.D.	0.53	1.42	1.60
%RSD	0.64	1.70	1.90

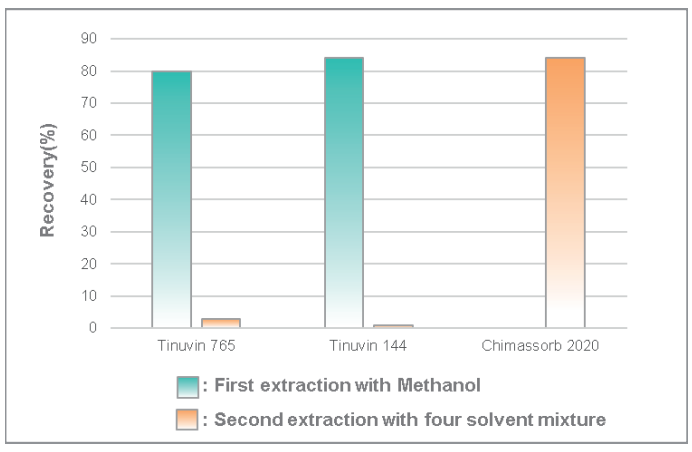
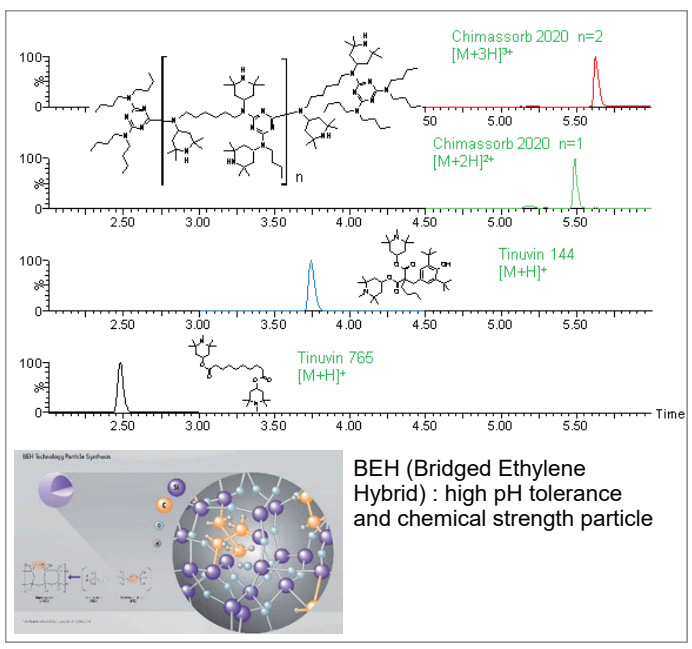


Figure 5. Selective extraction of low and high molecular weight HALS

- LC/MS analysis

Due to its high hydrophobicity, it is difficult to elute high molecular weight HALS from reverse phase column, even shorter carbon chain column such as C4. For making elution power stronger, although occasionally basic solution (high pH solution) is used, most of commercialized particle in reverse phase column do not have enough tolerance. However BEH column particle which is not silica based, and it is ethylene hybrid based, can provide tolerance and stability in high pH mobile phase.



BEH (Bridged Ethylene Hybrid) : high pH tolerance and chemical strength particle

Figure 6. Elution of HALS additives with THF and basic mobile phase on UPLC H-Class/QDa with BEH C8

CONCLUSION

A selective extraction method of HALS from polymer materials with SFE and quantitative analysis method with LC / MS could be developed. It is implied that this method can be adapted to extract additives in diverse polymer materials.

References

1. Calculation of Solubility of Organic Compounds in Supercritical CO2 by Quantitative Structure-Activity Relationships ", Daisuke Tomita et al. (Tohoku University), Netsu Bussei 21 [3] (2007) 137-142

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