



Equilibrium leaching of selected ultraviolet stabilizers from plastic products

Anh T. Ngoc Do^a, Yeonjeong Ha^a, Hyun-Joong Kang^{a,b}, Ju Min Kim^c, Jung-Hwan Kwon^{a,*},¹

^a Division of Environmental Science and Ecological Engineering, Korea University, 145 Anam-ro, Seongbuk-gu, Seoul 02841, Republic of Korea

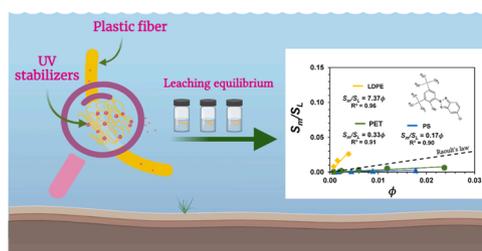
^b Knoell Korea, 37 Gukjegeumyung-ro 2-gil, Yeongdeungpo-gu, Seoul 07327, Republic of Korea

^c Department of Energy Systems Research and Department of Chemical Engineering, Ajou University, 206 Worldcupro, Yeongtong-gu, Suwon 16499, Republic of Korea

HIGHLIGHTS

- Water solubilities and leaching of five UV stabilizers were assessed.
- Flory-Huggins model explains the leaching equilibrium from microplastics.
- Size disparity between solutes and polymer causes the nonideal behavior.
- Polymer material type is also important in determining leaching equilibrium.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Microplastics
Plastic additives
Benzotriazoles
Flory-Huggins model
Passive dosing

ABSTRACT

Despite the importance of (micro)plastics in the release of plastic additives, the leaching mechanism of organic plastic additives from various plastic materials is poorly understood. In this study, the equilibrium leaching of five highly hydrophobic ultraviolet (UV) stabilizers (UV326, UV327, UV328, UV329, and UV531) from three plastics (low-density polyethylene (LDPE), polyethylene terephthalate (PET), and polystyrene (PS)), was investigated employing acetonitrile-water cosolvent systems. Their extrapolated water solubilities were in the 0.15–0.54 $\mu\text{g L}^{-1}$ range, limiting their transport as “dissolved” in water and (micro)plastics are likely those particulate carriers. The equilibrium leaching of UV stabilizers from plastics was better explained by the Flory-Huggins model incorporating the nonideal behavior caused by the size disparity between UV stabilizers and polymer materials and their compatibility. Specifically, leaching of UV stabilizers from LDPE showed a positive deviation from Raoult’s law, whereas slight negative deviations were observed in PET and PS. In addition, the equilibrium concentration of the benzotriazoles in LDPE increased linearly with the volume fraction up to only 0.4%. These observations could be explained by the unfavorable interactions of UV stabilizers with polyethylene, indicating that polymer type should be also important when evaluating the fate of hydrophobic additives. Because equilibrium distribution of additives between (micro)plastics and water is crucial for evaluating the fate

Abbreviations: ϕ , volume fraction; ω , mass fraction; δ , cosolvency power of ACN; ACN, acetonitrile; C_0 , concentration of the plastic phase; f , volume fraction of ACN; LDPE, low-density polyethylene; PDA, photodiode array; PDMS, polydimethylsiloxane; PE, polyethylene; PET, polyethylene terephthalate; PS, polystyrene; PVC, polyvinylchloride; S_L , subcooled liquid solubility; S_m , leaching equilibrium concentration/solubility of the stabilizers in the ACN/water mixture; S_w , solubility of the stabilizers in pure water; UPLC, ultra-performance liquid chromatography; UV, ultraviolet; UV326, 2-(5-chloro-2 H-benzotriazol-2-yl)-4-methyl-6-(2-methyl-2-propanyl)phenol; UV327, 2,4-di-*tert*-butyl-6-(5-chloro-2 H-benzotriazol-2-yl)phenol; UV328, 2-(2 H-benzotriazol-2-yl)-4,6-bis(2-methyl-2butanyl)phenol; UV329, 2-(2 H-benzotriazol-2-yl)-4-(1,1,3,3 tetramethylbutyl)phenol; UV531, (2-hydroxy-4-octoxyphenyl)phenylmethanone; χ , Flory–Huggins interaction parameter.

* Corresponding author.

E-mail address: junghwankwon@korea.ac.kr (J.-H. Kwon).

¹ ORCID: 0000-0002-6341-7562

<https://doi.org/10.1016/j.jhazmat.2021.128144>

Received 26 September 2021; Received in revised form 5 December 2021; Accepted 21 December 2021

Available online 28 December 2021

0304-3894/© 2021 Elsevier B.V. All rights reserved.

and transport of hydrophobic plastic additives, further studies on the leaching equilibrium of various additives from different plastic materials are necessary.

1. Introduction

Owing to the versatility of plastics (durability, flexibility, strength, lightweight, low production cost, and easy manufacture), they are employed in a wide range of applications, including packaging, construction, electronics, agriculture, and households (Andrady, 2011; Thompson et al., 2009). The global production of plastics has increased significantly since the 1950s, and the inappropriate disposal of their wastes remains a serious source of environmental setbacks (Galloway et al., 2017; Geyer et al., 2017; Leal Filho et al., 2019; Ostle et al., 2019). Additives, such as flame retardants, plasticizers, UV stabilizers, and antioxidants, are essential components of plastic products, which are added to enhance their properties (Pfaendner, 2006). They are mostly not covalently bound to the polymer matrix and slowly leached from plastics. This indicates that plastic debris, including microplastics, can act as the mobile sources of those additives (Teuten et al., 2009). Although the leaching of phthalate plasticizers and brominated flame retardants have been extensively studied (Al-Odaini et al., 2015; Cheng et al., 2020; Fries et al., 2013; Jang et al., 2016; Kitahara and Nakata, 2020), there are only a few studies on the other additives such as photostabilizers and antioxidants (Hermabessiere et al., 2017; Kwon et al., 2017; Rani et al., 2017).

Ultraviolet (UV) stabilizers are widely employed as active ingredients in sunscreen products, as well as additives in plastic materials, for many outdoor applications (García-Guerra et al., 2016; Kameda et al., 2011). Among them, benzotriazole and benzophenone UV stabilizers persist significantly in the environment (Billingham et al., 1991; Junglaus et al., 1978). They are highly hydrophobic ($\log K_{ow} > 6.0$) (Wick et al., 2016), and according to reports, they are potential endocrine disruptors (Montesdeoca-Esponda et al., 2013). UV stabilizers have been found in coastal environments (Apel et al., 2018; Kim et al., 2011; Langford et al., 2015; Nakata et al., 2012), as well as house dust, human breast milk, and urine samples (Asimakopoulos et al., 2013; Kim et al., 2019; Lee et al., 2015; Maceira et al., 2019). Plastic products might account for the major sources of UV stabilizers (Rani et al., 2017), although their pathways into organisms and humans are largely unknown. Leaching from plastic products and their environmental fate depends on their physicochemical properties, such as water solubility, diffusion coefficient, and partition constants between the media (Kwon et al., 2017). Thus, obtaining reliable values for these properties would further elucidate the fate and transport of these plastic-derived UV stabilizers into the environment.

Plastic particles could account for the mobile sources of plastic-associated additives; moreover, the driving force of the leaching of these additives could be the partitioning equilibrium between the plastic materials and the environmental media, such as water (Kwon et al., 2017). The equilibrium concentration of plastic additives in the contacting water phase containing plastics, including an additive, might be estimated from their concentrations in the plastic phase (C_0) via Raoult's or Henry's law (Billingham et al., 1981; Little et al., 2012). Recently, the partial pressure (or activity) of phthalate plasticizers in the air was explained employing C_0 via Henry's law (Eichler et al., 2018; Liang and Xu, 2014a, 2014b; Little et al., 2012; Liu and Zhang, 2016; Xu and Little, 2006). Good linear relationships were observed between C_0 , and the partial pressure of the phthalates in polyvinylchloride (PVC) materials was obtained at a weight concentration less than 13% (Liang and Xu, 2014a; Little et al., 2012). Previous findings have indicated that the plasticizers in PVC do not behave as an ideal liquid mixture at low concentrations; thus, Raoult's law cannot be applied for the polymer solutions (Eichler et al., 2018; Liang and Xu, 2014a, 2014b; Little et al., 2012; Liu and Zhang, 2016; Xu and Little, 2006). Notably, previous

studies have focused on the indoor emission of plasticizers that were added into PVC, which is a frequently utilized plastic material. Based on the abundance of (micro)plastics in the aquatic environment (Ostle et al., 2019; Thompson et al., 2009), polyethylene (PE), polyethylene terephthalate (PET), and polystyrene (PS) have been reported as the most frequently found plastics (Andrady, 2011; Geyer et al., 2017). However, the leaching mechanisms of UV stabilizers from these plastics into the aquatic environments are still unclear. Since diverse plastic materials are in use and found as microplastics, it is necessary to investigate the phase equilibrium of UV stabilizers in the different plastic and water systems.

A mixture of UV stabilizers and a plastic polymer is generally referred to as nonaqueous phase liquids even though these compounds are viscoelastic solids in their pure forms at room temperature (Chiou and Manes, 1986). The water solubility of a UV stabilizer in a plastic-suspended solution is determined by its subcooled liquid solubility (S_L), which is a fundamental parameter for determining the relationship between the plastic and the contacting water phase employing Raoult's law (Schwarzenbach et al., 2016). However, the determination of the concentration of the equilibrium leaching of the UV stabilizers in the water phase from their S_L by assuming the ideal behavior in the plastic phase might not result in an acceptable estimation. According to the Flory–Huggins model, the UV stabilizers in the plastic phase would not behave as an ideal mixture because of the large size difference and incompatibility of the UV stabilizer with the entangled polymer molecules (Chiou and Manes, 1986; Hiemenz and Lodge, 2007; Prausnitz et al., 1998). Therefore, the relationship between UV stabilizers and different plastics must be explored to obtain a plausible explanation for the equilibrium leaching of the plastic additives into the aquatic environment and consequently evaluate their distributions between the plastic and adjacent water phases of the UV stabilizers.

This study is aimed at investigating the equilibrium leaching of five highly hydrophobic UV stabilizers, 2-(5-chloro-2 H-benzotriazol-2-yl)-4-methyl-6-(2-methyl-2-propanyl)phenol (UV326), 2,4-di-*tert*-butyl-6-(5-chloro-2 H-benzotriazol-2-yl)phenol (UV327), 2-(2 H-benzotriazol-2-yl)-4,6-bis(2-methyl-2butanyl)phenol (UV328), 2-(2 H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol (UV329), and (2-hydroxy-4-octoxyphenyl)phenylmethanone (UV531), from microplastic fibers into acetonitrile (ACN)/water cosolvent solutions. The solubilities of the UV stabilizers in the ACN/water mixtures were determined via a series of passive dosing experiments at 25 °C, and the water solubilities were extrapolated employing the log-linear model of the cosolvent systems. The equilibrium relationships between the leaching concentrations of the UV stabilizers in the ACN/water (4:6, v/v) mixture (S_m) and their volume fractions in low-density PE (LDPE), PET, and PS were observed. The theoretical predictions were applied employing Raoult's law, Henry's law, and the Flory–Huggins model to explain the partitioning of the UV stabilizers.

2. Materials and methods

2.1. Chemicals

Four benzotriazoles UV 326 (>98%), UV 327 (>98%), UV 328 (>98%), and UV 329 (>98%), as well as a benzophenone-type photostabilizer, UV 531 (>98%), were obtained from Sigma-Aldrich (St. Louis, MO, USA); their chemical structures, as well as estimated $\log K_{ow}$ values and melting temperatures, are presented in Table S1 (Supplementary Material). A silicone elastomer (Sylgard 184 A) and a curing agent (Sylgard 194B) were purchased from Sewang Hitech (Kimpoo, Korea). All the organic solvents employed in this study were of

analytical grade.

Commercial pristine pellets of LDPE (LUTENE® LB5000, density = 0.918 g cm⁻³) and PS (G20HRE, density = 1.05 g cm⁻³) were purchased from LG Chem Ltd. (Seoul, Republic of Korea), and those of PET (COOL, density = 1.4 g cm⁻³) were purchased from Lotte Chemical Corp. (Seoul, Republic of Korea). To clean the LDPE and PET plastic pellets, they were submerged in *n*-hexane for 24 h. However, methanol was selected to clean the PS pristine pellets via the same procedure. The cleaned pellets were collected, dried at ambient temperature, and stored in an amber glass bottle until use.

2.2. Solubilities of the UV stabilizers in the ACN/water cosolvent solutions

The experimental solubilities of the five UV stabilizers were measured via the passive dosing method employing ACN/water mixtures (the volume fraction of ACN was between 0.2 and 0.9) (Kwon and Kwon, 2012; Li and Yalkowsky, 1998b). A sufficient amount of the crystals of the UV stabilizers was transferred into a 20-mL glass vial, after which 0.2 g of another liquid mixture comprising a polydimethylsiloxane (PDMS) elastomer and the curing agent at a mass ratio of 10:1 was added. The vials were placed in a shaking incubator for 24 h at 25 °C and 80 rpm to achieve the complete solidification of silicone. The surfaces of the solidified silicone were rinsed with 5 mL of methanol, after which they were rinsed three times with 10 mL of deionized water to remove any crystal at the surface of the silicone and the walls of the vial. After washing, the remaining liquids at the surfaces were cleaned with a lint-free tissue, followed by the addition of a solution of ACN/water (10 mL). After gentle agitation in the shaking incubator at 25 °C and 80 rpm, sample aliquots of the solution (100 µL) were acquired at desired time intervals and mixed with 100 µL of ACN to ensure the dissolutions of all the test chemicals in the solution. The concentrations of the solutes were measured directly via ultra-performance liquid chromatography (UPLC) with a photodiode array (PDA) detector system, which is described later. The log-linear cosolvency model (Li and Yalkowsky, 1998a, 1998b; Yalkowsky and Roseman, 1981) was applied to predict the water solubility of the UV stabilizers, as follows:

$$\log S_m = \log S_w + \delta f, \quad (1)$$

where S_m is the solubility of the stabilizers in the ACN/water mixture with a volume fraction of ACN (f), S_w is their solubility in pure water, and δ is the cosolvency power of ACN.

For a crystal UV stabilizer in a polymer solution, the water solubility at equilibrium was determined via the solubilities of the UV stabilizer in the amorphous phase or “liquid-like” form (S_L) (Van Leeuwen and Vermeire, 2007), which can be extrapolated according to Eq. (2):

$$S_L = S_w \exp \left[\frac{\Delta S_f}{R} \left(\frac{T_m}{T} - 1 \right) \right], \quad (2)$$

where T is the temperature (K), T_m is the melting temperature (K) of the UV stabilizers, ΔS_f is the fusion entropy (assumed to be 56.5 J mol⁻¹K⁻¹) (Yalkowsky, 1979) of the UV stabilizers, and R is the universal gas constant (8.3145 J mol⁻¹K⁻¹).

2.3. Production of the plastic fibers containing the UV stabilizers

Plastic fibers containing the desired mass fractions of the UV stabilizers were produced employing a benchtop extruder (LME, Dynisco Inc., Franklin, MA, USA). The cleaned pristine pellets were placed inside the hopper (maintained at 170, 260, and 270 °C for LDPE, PET, and PS, respectively) of the extruder containing the desired mass fractions (ω) of the UV stabilizers (0.1%, 0.2%, 0.5%, 1.0%, and 2.0%, w/w). After the first extrusion, the fibers were crushed and placed inside the extruder two more times to obtain the homogeneous mixing of the additives in the plastic fibers. ω of the additive (i) in the polymer (j) was converted

into the volume fraction (ϕ) by Eq. (3) (Table S2, Supplementary Material):

$$\phi = \frac{(\omega \times m_{fiber})/\rho_i}{(\omega \times m_{fiber})/\rho_i + ((1 - \omega) \times m_{fiber})/\rho_j}, \quad (3)$$

where m_{fiber} (g) is the mass of the plastic fiber containing the UV stabilizers and ρ_i and ρ_j (g/cm³) are the densities of i and j , respectively.

2.4. Leaching of the UV stabilizers from the plastic fibers

Leaching of the UV stabilizers from the semi-crystalline (LDPE and PET) and amorphous (PS) thermoplastic fibers containing 0.1–2% (w/w). The batch equilibrium leaching experiments were conducted to determine the concentrations of the UV stabilizers that leached in the ACN/water mixture (4:6, v/v) due to experimental difficulties in determining precise concentration of them in water. For reliable measurements and proof-of-principle, the ACN/water cosolvent system was chosen despite its limitations. In each 20-mL glass vial, 20–30 mg of the plastic fibers was equilibrated with 10 mL of the ACN/water solution. The vial was gently shaken at 100 rpm and 25 °C in darkness. Sample aliquots (200 µL) were removed at the desired time points (10, 24, 48, 72, 96, and 120 h), and the concentrations of the UV stabilizers were measured with the UPLC–PDA instrument.

2.5. Theoretical equilibrium-leaching relationship

The relationship between C_0 and S_m could be explained via Raoult’s or Henry’s law. The relationship can be explained by Raoult’s law if the UV stabilizers and polymer form an ideal mixture (Schwarzenbach et al., 2016). Since it is challenging to define the mole fractions (x) of the additives in plastics (Eichler et al., 2018; Robeson, 2007), the volume, which they occupy, is generally used to evaluate their thermodynamic behaviors (i.e., entropy effects) in the plastic phase (Chiou and Manes, 1986; Hiemenz and Lodge, 2007; Prausnitz et al., 1998).

$$S_m = S_L \gamma x \approx S_L \phi, \quad (4)$$

where S_m is the solubility of the UV stabilizers in the ACN/water mixture (4:6, v/v) and γ is the activity coefficient (assumed to be unity). Raoult’s law for ideal solutions predicts that the slope of S_m/S_L and ϕ is constantly unity.

The partitioning of the UV stabilizers between the plastic phase and solution can also be described by Henry’s law employing the partition constant for a dilute solution (Schwarzenbach et al., 2016):

$$S_m = K \phi, \quad (5)$$

where K is the partition constant of the UV stabilizer between the solvent mixture and plastic phase.

The Flory–Huggins model, which is described in detail in the Supplementary Material, can better explain the behavior of the selected UV stabilizers in the polymer (Billingham et al., 1981; Hiemenz and Lodge, 2007; Prausnitz et al., 1998). Briefly, the solubility of the solid additives in the polymer is predicted by assuming that the negative free energy (ΔG_m) of the mixing of the subcooled liquid additive with the polymer is equal to the positive free energy (ΔG_f) of the fusion of the additive at the same temperature (Billingham et al., 1981). The free energy of fusion, ΔG_f , of a crystalline solid can be expressed, as follows:

$$\Delta G_f = \Delta H_f - T \Delta S_f, \quad (6)$$

where ΔH_f and ΔS_f are the enthalpy and entropy of the fusion, respectively, and T is the absolute temperature. Here, $\Delta S_f = \Delta H_f/T_m$ (T_m is the melting temperature of the crystalline additive).

Considering that the molar volume of the polymer (V_2) is much higher than that of the additive (V_1) ($V_2 \gg V_1$), the Flory–Huggins

theory can be employed to calculate the solubility of the solid additive at T in the polymer solution, as follows:

$$-\ln\phi_1 = \frac{\Delta H_f}{RT} \left(1 - \frac{T}{T_m}\right) + \left(1 - \frac{V_1}{V_2}\right)\phi_2 + \chi\phi_2^2, \quad (7)$$

where V_1 , ϕ_1 and V_2 , ϕ_2 are the molar volumes and volume fraction of the additive and polymer, respectively, and χ is the Flory–Huggins interaction parameter. The first term on the right-hand side of Eq. (7) shows the temperature dependence of the solubility of the additive in the polymer matrix. The second term reflects the geometric entropy of mixing, and the third term represents the nonideality of the solution due to the compatibility of the combination of the additive and polymer (Billingham et al., 1981).

2.6. Instrumental analyses

The concentrations of the UV stabilizers were analyzed using a Water Acquity™ UPLC system that was coupled with a PDA detector. The UV stabilizers were separated on a C18 column (2.1 mm × 50 mm, 1.7 μm, Water) at 35 °C. The mobile phase comprised 95% ACN and 5% water in an isocratic mode (flow rate = 0.20 mL min⁻¹). The optimal wavelengths for the detections were 221 (UV326), 204 (UV327 and UV328), 218 (UV329), and 287 nm (UV531).

2.7. Quality assurance and quality control

A procedural blank was included in each batch experiment. The blank analyses were conducted via the same procedure as that for the actual samples. Detection limits in the μg L⁻¹ range were obtained for UV326 (20 μg L⁻¹), UV327 (10 μg L⁻¹), UV328 (10 μg L⁻¹), UV329 (50 μg L⁻¹), and UV531 (50 μg L⁻¹) at a signal-to-noise ratio of 3:1 (Waters, 2016), respectively. No analyte was detected above the MDLs in each blank. To ensure that the plastic fibers contained the desired ω of the UV stabilizers, the LDPE fibers were serially extracted with ACN.

This preliminary experiment revealed that ≥ 80% of the extractable additives was extracted in the first extraction, and almost negligible amounts were extracted during the third extraction (Table S3, Supplementary Material). Thus, three serial extractions were considered sufficient to extract all the additives from the plastic fibers.

3. Results and discussion

3.1. Solubilities of the UV stabilizers in the ACN/water cosolvent solutions and extrapolation to aqueous solubility

Fig. 1 shows the relationship between the logarithmic concentration of the UV stabilizers in the cosolvent solution ($\log S_m$) and the f of ACN. Since the concentration was lower than the detection limits, $\log S_m$ was measured at $f \geq 0.2$. The solubility of the UV stabilizers increased with the increasing f . The time-course changes in the concentration of the UV stabilizers at different f values of the ACN/water mixture are shown in Fig. S1. The logarithmic solubilities of all the UV stabilizers in the ACN/water mixture generally increased linearly in the $0.2 \leq f \leq 0.5$ range but deviated from the linear relationship between $\log S_m$ and f at higher ACN values of f (Fig. 1). The coefficients of determination (R^2) ranged from 0.969 to 0.998 with the standard errors of 0.066 – 0.336. The significance F values of the regression and the p values for slopes and intercepts were all less than 0.05, showing good linearity. The details of the linear regression are presented in Table S4 (Supplementary Material). The deviation from the log-linear relationship at a higher cosolvent f has also been reported in the literature, and the decreased hydrogen-bonding capability of the water molecules could account for the phenomena (Rubino and Obeng, 1991). Interestingly, UV326 and UV327 containing substituted chlorine, which acted as a hydrogen-bonding acceptor, on the benzene ring exhibited a more distinct tendency than those without chlorine substitution (UV328 and UV329).

The water solubilities of the UV stabilizers, which were obtained by extrapolation using Eq. (1), are listed in Table 1. Assuming that the

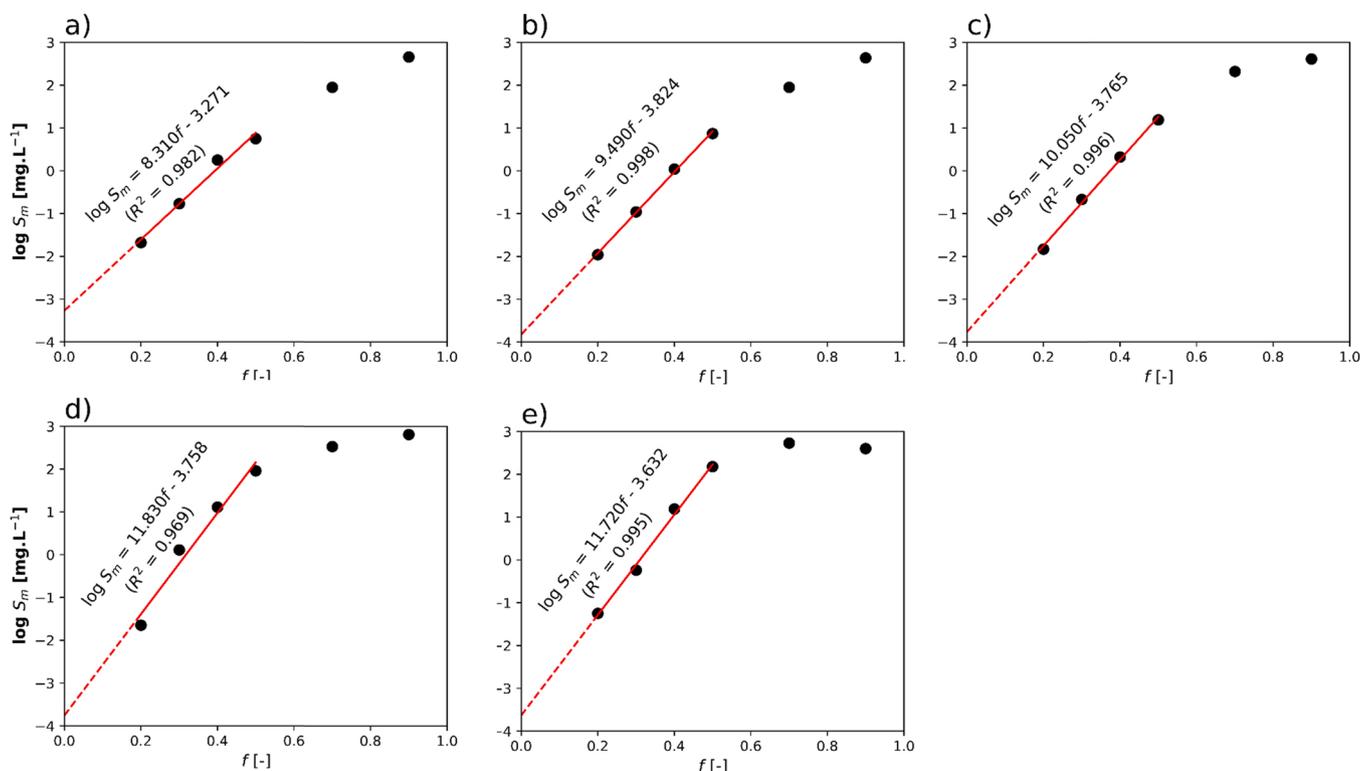


Fig. 1. Relationships between $\log S_m$ in the ACN/water mixture and f of (a) UV326, (b) UV327, (c) UV328, (d) UV329, and (e) UV531. The solid lines represent the interpolation within the ϕ range of 0.2–0.5 using Eq. (1); the dashed lines are employed to estimate S_w via the extrapolation to $\sigma = 0$.

Table 1
Measured and estimated S_w and S_L values of the five UV stabilizers.

Chemicals	Water Solubility S_w ($\mu\text{g L}^{-1}$)			Subcooled liquid solubility S_L ($\mu\text{g L}^{-1}$) ^e		
	In water			In the ACN/water mixture (4:6, v/v) ^d (S_m)		
	Experimental data		Estimated data	In this study		
	In this study ^a	Column elution method ^b	EPISuite ^c	In water	In the ACN/water mixture (4:6, v/v)	
UV326	0.54 (\pm 0.36)	4	683	1770 (\pm 50)	8.3	27,300
UV327	0.15 (\pm 0.04)	–	26.3	1090 (\pm 60)	3.0	21,700
UV328	0.17 (\pm 0.07)	< 1	14.8	2070 (\pm 140)	0.65	7900
UV329	0.17 (\pm 0.22)	2	168	12,700 (\pm 300)	1.1	78,600
UV531	0.23 (\pm 0.12)	< 1	36.9	18,700 (\pm 1900)	0.39	31,600

^a Values are extrapolated from Eq. (1). Errors were calculated from the regression errors of the intercept.

^b Values from the experimental data that were submitted to the European Chemical Agency in the REACH registration dossiers (ECHA, 2017).

^c Estimated values from the EPISuite version 4.11 (EPA, 2012).

^d Mean \pm standard deviation. After reaching equilibrium, all samples were employed to calculate the mean and standard deviation values. The mean values were calculated from the experimental values at designated time points (from the starting equilibrium time) with triplicate measurements for each experiment.

^e Values were extrapolated from Eq. (2).

solvent composition at the solute–solvent interface was the same as that of the bulk solution, the log-linear model might cause uncertainties in the estimation of the water solubility when the experimental data were obtained at $f >> 0$. Nonetheless, the extrapolation still availed a reasonable estimation for the highly hydrophobic chemicals, such as the UV stabilizers, whose concentrations in pure water were below the measurement limit, as in this study.

Uncertainties in the extrapolated S_w values were obtained from the standard error of the intercept in Fig. 1. Relatively large errors were resulted after the antilogarithmic conversion of the mantissa of the intercept derived from the log-linear model. Despite the large deviation of the extrapolated values, the experimental S_w values in this study were slightly lower than those reported by the European Chemical Agency for the registration of the substances employing the generator column method; they were much lower than those estimated employing the

EPISuite software (Table 1). Similar observations were also reported previously (de Maagd et al., 1998; Kwon and Kwon, 2012). As reported in the literature, the high initial concentration in water, as measured by the generator column, could be attributed to the detachment of the coated crystals at the surface of an inert support material, e.g., glass beads. However, the concentration decreased via the recirculation of water through the column, where the detached crystals were most likely stored. However, the passive dosing in which an excess amount of the solid chemicals is loaded onto silicone, induced an initial increase in the aqueous concentration, followed by a plateau. Therefore, this method reduces the risk of crystal detachment from the column by avoiding the direct contact of the crystals with water and by forming microemulsions. Additionally, owing to the low accuracy of predicting the S_w of highly hydrophobic chemicals, experimental data are highly recommended (Hanson et al., 2019; Mannhold et al., 2009). To evaluate the solubility

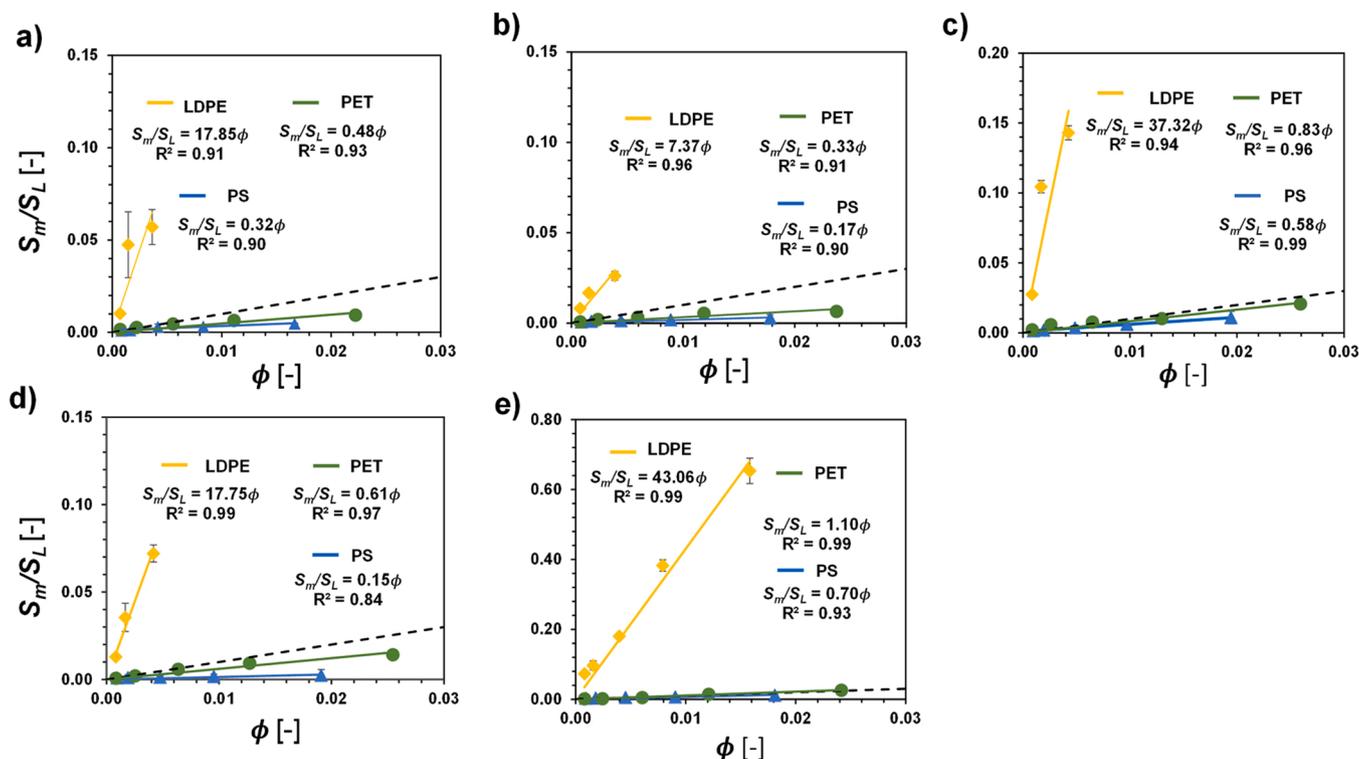


Fig. 2. Partitioning between the normalized concentration of the contacting ACN/water mixture (S_m/S_L) and ϕ of (a) UV326, (b) UV327, (c) UV328, (d) UV329, and (e) UV531 in the plastic fibers. The dashed line represents the ideal solution obeying Raoult's law. The yellow, green, and blue solid lines exhibit the linear relationship between the concentration of the UV stabilizers in LDPE, PET, and PS and the adjacent ACN/water mixture (4:6, v/v), respectively.

of the UV stabilizers in the plastic phase, the S_L of the UV stabilizers were also obtained from Eq. (2) and listed in Table 1.

3.2. Equilibrium leaching of the UV stabilizers between the plastic fibers and ACN/water mixture

The equilibrium leaching concentration (S_m) of the five UV stabilizers from LDPE, PET, and PS into the ACN/water mixture (4:6, v/v) was measured via the batch equilibrium experiments. Generally, S_m increased with the increasing ϕ , and the experimental equilibrium leaching concentrations of the five UV stabilizers were achieved after 24 (for LDPE) and 72 h (for PET and PS (Figs. S2–S4, Supplementary Material)).

The solubilities of the five UV stabilizers from the LDPE, PET, and PS fibers in the ACN/water (4:6, v/v) mixture at different ϕ were observed (Fig. 2, S5, and S6, Supplementary Material). The changes in the solubilities were observed with the increasing ϕ . The difference between the ω and ϕ results was small, as reported in the literature (Eichler et al., 2018). The dashed lines in Fig. 2 denote the ideal solubility of the UV stabilizers in the ACN/water (4:6) solution according to Raoult's law (Eq. (4)), and the solid lines represent the linear increase in the activity (S_m/S_L) with the increasing ϕ according to Henry's law. The experimental results show that the slopes in Fig. 2, i.e., the activity coefficients of the UV stabilizers in the plastics, were far from unity, indicating that Raoult's law could not be applied to the quantitative estimations of their leaching from the plastics. The linear relationship between S_m/S_L and ϕ allowed us to obtain the activity coefficients or partition constants between the plastic phase and the contacting ACN/water mixture.

Raoult's law accounts for the behaviors of small molecules with similar sizes and not for the polymer with a long chain, which generally exhibits an accepted molecular weight in the 10^3 – 10^7 gmol⁻¹ range that is much higher than those of the UV stabilizers (Cowie and Arrighi, 2007). Therefore, the degree of polymerization, r ($=V_2/V_1$), of a monomer is generally a large number, and the entropy of the mixing from the polymer, as shown in the second term on the right-hand side of Eq. (7), is small even in the athermal solution (Hiemenz and Lodge, 2007). The nonideal entropy of the mixing caused the deviation from the ideal line, as shown in Fig. 2.

A significantly positive deviation from Raoult's law could be observed in LDPE, whereas a slightly negative deviation from the ideal solution was observed in PET and PS (except for UV531 in PET) (Fig. 2 and S6, Supplementary Material). In the ideal solution obeying Raoult's law, the sizes of the components are comparable, and the intermolecular interactions between the similar and dissimilar molecules are expectedly equal (Chiou and Manes, 1986). The latter implies that there was no change in the total enthalpy of the system ($\Delta H_{mix} = 0$). However, the enthalpy of the mixing in real polymeric systems cannot be ignored (Eq. (7)) (Hiemenz and Lodge, 2007). The Flory–Huggins interaction parameter (χ) between the UV stabilizers and polymer molecules representing the enthalpy of mixing could explain the differences (Prausnitz et al., 1998). A quantitative expression of χ (Table 2) is directly related to the difference between the solubility parameters, δ , of the UV

stabilizers (δ_{UV}) and polymers (δ_P) [$\chi \sim (\delta_{UV} - \delta_P)^2$] (Fried, 2014), which is presented in detail in the Supplementary Material. At ambient temperature, the mixing is generally not favorable in the plastic phase owing to the net repulsive intermolecular forces between the additives and LDPE (except UV 531 containing long linear alkyl chain, and thus having the lowest δ), and the χ_1 values are large, indicating the low solubilities of the UV stabilizers in LDPE (Table 2). The linear increase in S_m up to the highest ϕ was investigated, and only slightly negative deviation from Raoult's law was observed for the UV stabilizers in PET and PS because the stabilizers were much more compatible with PET and PS than LDPE, resulting in smaller χ_2 and χ_3 values (Table 2 and Fig. 2). Specific π - π interactions and H-bondings between the UV stabilizers and PET or PS could explain the higher compatibility. Similar tendencies were observed in previous studies (Billingham et al., 1991; Földes, 1998; Lazare and Billingham, 2001). The deviation from the ideal behavior also depends on the differences in the molecular weights (Holcik et al., 1976; Prausnitz et al., 1998). Although the molar masses of the five UV stabilizers were only slightly different, a trend therein could be observed (Fig. S7, Supplementary Material). For example, larger S_m values were observed for the small-molecular-weight UV stabilizers in LDPE, PET, and PS.

The solubility increased linearly with the increasing ϕ in the lower range (up to $\sim 0.5\%$), whereas the linear relationship was terminated at higher ϕ ($>0.5\%$) for the four benzotriazoles in the LDPE polymer solutions (Fig. 2). This trend was also observed in previous studies (Durmis et al., 1975; Spatafore and Pearson, 1991). One possible explanation is that the UV stabilizers could form a glassy state at high ϕ before PE is completely cooled at room temperature during the manufacturing processes (Spatafore and Pearson, 1991). Blooming may occur with the precipitation of benzotriazoles on the surface of the polymer, and the formation of crystals is a common phenomenon involving moderately high-molecular-weight additives. The solubility of the UV stabilizers in a polymer depends on the concentration of the additives, which is relative to their saturation solubility. Thus, the solubility of the UV stabilizers in LDPE might be much lesser than the actual mass of the additives in the polymer, indicating that the estimation of the release kinetics of these hydrophobic additives via their water solubilities could overestimate their leaching from (micro)plastics. The loss of the additives from LDPE depends on the contacting solution and the phase separation at the surface of the polymer (Billingham, 1989). The UV stabilizers ($<1\%$ (w/w)) must be added into polyolefin as the LDPE during the manufacture of LDPE products with them (Billingham et al., 1981; Malik et al., 1995; Spatafore and Pearson, 1991).

Regarding the benzophenone compound (UV531), a linear relationship was observed between S_m/S_L and ϕ in the entire ϕ range of all the three types of plastic fibers (Fig. 2(e)). This can be explained by the effect of the structure of the additives on the solubility of the polymer. UV531 contains a benzophenone group, and the long alkyl chain especially increases the compatibility between the UV531 molecules and the LDPE, PET, and PS polymer molecules, as reflected by the lower value of χ (Table 2) (Billingham et al., 1981; Holcik et al., 1976).

Notably, the solubilities of the UV stabilizers were restricted in the

Table 2
Solubility parameters of the UV stabilizers and plastics, and the interaction parameter between the additives and plastic polymers.

	Additives					Plastic		
	UV326	UV327	UV328	UV329	UV531	LDPE	PET	PS
$\delta(Jcm^{-3})^{1/2}$	26.46 ^a	24.72 ^a	22.77 ^a	23.24 ^a	21.31 ^a	16.2 ^b	21.9 ^b	18.4 ^b
χ_1^c	11.62	9.69	6.19	6.42	3.51	–	–	–
χ_2^d	2.30	1.06	0.11	0.23	0.048	–	–	–
χ_3^e	7.17	5.33	2.74	3.03	1.14	–	–	–

^aThe solubility parameters of the UV stabilizers were calculated via the group contribution method employing Fedor's data (Fedor, 1974)

^bThe data from Prausnitz et al. (1998)

^{c,d,e}The Flory–Huggins interaction parameters between the UV stabilizers and LDPE, PET, and PS, respectively, were calculated by Eq. (S14) (Supplementary Material)

amorphous phase of the polymer because the UV stabilizers were generally excluded from the crystalline phase (Prausnitz et al., 1998). Therefore, the solubilities of the additives were affected by the degree of crystallinity of the polymer. Below the melting temperature, LDPE and PET are in the semicrystalline phase, whereas PS is in the amorphous phase; the glass transition temperature of LDPE ($-125\text{ }^{\circ}\text{C}$) is significantly lower than those of PET ($69\text{ }^{\circ}\text{C}$) and PS ($100\text{ }^{\circ}\text{C}$) (Fried, 2014). Accordingly, the amorphous region of LDPE, which exhibits a large free volume at ambient temperature, is rubbery state, while the amorphous regions of PET and PS with small free volumes are glassy-states (Stevens, 1990; Young and Lovell, 2011). Therefore, the leaching of the additives from LDPE at room temperature would reach equilibrium faster than in PET and PS employing the UV stabilizers because of the fast diffusion of the additive molecules through the large free volume; however, the kinetics of the leaching process should be further studied.

3.3. Implications for the environmental fate of hydrophobic UV stabilizers

This study estimated the equilibrium leaching of highly hydrophobic UV stabilizers from three representative plastic materials. The obtained results revealed that the water solubilities of these UV stabilizers were very low, indicating that they might not be readily transported as “dissolved” in water. Thus, an understanding of the role of their leaching from plastic products could elucidate the sources of UV stabilizers in environmental samples since UV stabilizers are not only included in liquid coatings, such as cosmetics. Microplastics might contain their additives, and the relatively high concentrations of UV stabilizers in sediment samples might be due to these particulate carriers. Notably, the presence of UV stabilizers in marine sediments far from their production facilities was reported in Japan, China, South Korea and the United States (Cantwell et al., 2015; Jeon et al., 2006; Nakata et al., 2012; Zhang et al., 2011). 1 H-benzotriazole was also found at high concentration in the sediment samples despite its high aqueous solubility (Cantwell et al., 2015). It warrants further studies on the roles of microplastics carrying those additives to the sediment. In addition, it has been proposed that microplastics might be associated with biofilms, thus favoring gravitational settling into sediments (Tarafdar et al., 2021). The potential transport of a hydrophobic additive, hexabromocyclododecane, in expanded polystyrene buoys into the coastal sediment has been proposed (Kim et al., 2021), and the similar transport processes of hydrophobic UV stabilizers into the coastal sediments would explain their high concentrations in the sediment samples (Apel et al., 2018; Langford et al., 2015).

When the tracing of the concentration of plastic additives from plastics in water is challenging, the partition constants or activity coefficients could be applied with known concentrations of the additives in plastic. Furthermore, this study reveals that the equilibrium leaching concentration (S_m) of the UV stabilizers, as obtained via Henry's constants, is smaller than their water solubilities. Therefore, by simply applying their water solubilities, the degree of leaching of UV stabilizers might be overestimated. The equilibrium concentration of the additives in plastic and their adjacent water is crucial to assess their exposure, thereby allowing the prediction of the release of plastic additives into the aquatic environment. Where the information for estimating the leaching mass of plastic additives that are chemically similar to the UV stabilizers (chemical structures in Table S1, Supplementary Material) is lacking, the partition constants in this study could be referenced. However, the solubility of an additive in a polymer depends on its intrinsic properties, as well as the interaction between the additive and the plastic. Therefore, the specific relationship between additives and plastics must be further investigated to gain detailed insights.

It is well-known that environmental factors such as salinity, temperature, and dissolved organic matters influence solubilities of hydrophobic organic chemicals (Schwarzenbach et al., 2016). Further studies on the effects of environmental factors are necessary especially to evaluate the behavior of hydrophobic additives in marine environment

with lower temperature and higher salinity. In addition, the phase equilibrium between (micro)plastics and water is not likely attained under most environmental conditions. Thus, equilibrium relations could be more important to evaluate the leaching kinetics of hydrophobic additives from (micro)plastics rather than predicting equilibrium distribution. Moreover, leaching of these additives into aquatic environment could be affected by other dynamic processes such as photodegradation and biodegradation of microplastics (Gewert et al., 2015). Further studies on effects of those dynamic changes on the equilibrium and leaching kinetics are needed.

4. Conclusions

Leaching of hydrophobic additives from plastic products is driven by the phase equilibrium between plastic materials and water. In this study, water solubilities of five highly hydrophobic UV stabilizers were determined and their equilibrium leaching from three representative plastic materials (i.e., PE, PS, and PET) was evaluated. The phase equilibrium between plastic materials and water was better explained by the Flory–Huggins model incorporating the nonideal behavior caused by the size disparity between UV stabilizers and polymer materials and their compatibility. Furthermore, it was found that the specific interactions between polymer chain and additives are important to explain the deviations from Raoult' law assuming an ideal mixture of plastic and hydrophobic additives. Although only limited combinations of plastic materials and hydrophobic additives were evaluated in this study, the results warrant further investigations on specific interactions between additives and polymer segments to extend our understanding of the fate of hydrophobic additives originated from plastic products.

CRediT authorship contribution statement

Anh Thi Ngoc Do: Conceptualization, Methodology, Data curation, Investigation, Writing – original draft. **Yeonjeong Ha:** Methodology, Investigation, Writing – review & editing. **Hyun-Joong Kang:** Methodology, Data curation. **Ju Min Kim:** Conceptualization, Writing – review & editing. **Jung-Hwan Kwon:** Conceptualization, Supervision, Funding acquisition, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

This research was supported by the National Research Foundation of Korea (NRF) grant funded by the Korean government (MEST) (No. 2020R1A2C2009244) and by the Korea Environment Industry & Technology Institute (KEITI) through the Measurement and Risk Assessment Program for Management of Microplastics, funded by the Korea Ministry of Environment (MOE) (2020003110005). AD was supported by the Global Korea Scholarship (GKS).

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jhazmat.2021.128144](https://doi.org/10.1016/j.jhazmat.2021.128144).

References

- Al-Odaini, N.A., Shim, W.J., Han, G.M., Jang, M., Hong, S.H., 2015. Enrichment of hexabromocyclododecanes in coastal sediments near aquaculture areas and a wastewater treatment plant in a semi-enclosed bay in South Korea. *Sci. Total Environ.* 505, 290–298. <https://doi.org/10.1016/j.scitotenv.2014.10.019>.

- Andrady, A.L., 2011. Microplastics in the marine environment. *Mar. Pollut. Bull.* 62, 1596–1605. <https://doi.org/10.1016/j.marpolbul.2011.05.030>.
- Apel, C., Tang, J., Ebinghaus, R., 2018. Environmental occurrence and distribution of organic UV stabilizers and UV filters in the sediment of Chinese Bohai and Yellow Seas. *Environ. Pollut.* 235, 85–94. <https://doi.org/10.1016/j.envpol.2017.12.051>.
- Asimakopoulos, A.G., Wang, L., Thomaidis, N.S., Kannan, K., 2013. Benzotriazoles and benzothiazoles in human urine from several countries: a perspective on occurrence, biotransformation, and human exposure. *Environ. Int.* 59, 274–281. <https://doi.org/10.1016/j.envint.2013.06.007>.
- Billingham, N.C., 1989. Designing polymer additives to minimise loss, *Makromolekulare Chemie. Macromolecular Symposia*. Wiley Online Library, pp. 187–205. <https://doi.org/10.1002/masy.19890270110>.
- Billingham, N.C., Calvert, P., Manke, A., 1981. Solubility of phenolic antioxidants in polyolefins. *J. Appl. Polym. Sci.* 26, 3543–3555. <https://doi.org/10.1002/app.1981.070261103>.
- Billingham, N.C., Calvert, P., Okopi, I., Uzuner, A., 1991. The solubility of stabilizing additives in polypropylene. *Polym. Degrad. Stabil.* 31, 23–36. [https://doi.org/10.1016/0141-3910\(91\)90093-7](https://doi.org/10.1016/0141-3910(91)90093-7).
- Cantwell, M.G., Sullivan, J.C., Katz, D.R., Burgess, R.M., Hubeny, J.B., King, J., 2015. Source determination of benzotriazoles in sediment cores from two urban estuaries on the Atlantic Coast of the United States. *Mar. Pollut. Bull.* 101, 208–218. <https://doi.org/10.1016/j.marpolbul.2015.10.075>.
- Cheng, H., Luo, H., Hu, Y., Tao, S., 2020. Release kinetics as a key linkage between the occurrence of flame retardants in microplastics and their risk to the environment and ecosystem: a critical review. *Water Res.* 185, 116253. <https://doi.org/10.1016/j.watres.2020.116253>.
- Chiou, C.T., Manes, M., 1986. Application of the Flory–Huggins theory to the solubility of solids in glyceryl trioleate. *J. Chem. Soc. Faraday Trans. 1* (82), 243–246. <https://doi.org/10.1039/F19868200243>.
- Cowie, J.M.G., Arrighi, V., 2007. *Polymers: Chemistry and Physics of Modern Materials*. CRC Press.
- de Maagd, P.G.J., ten Hulscher, D.T.E., van den Heuvel, H., Opperhuizen, A., Sijm, D.T., 1998. Physicochemical properties of polycyclic aromatic hydrocarbons: aqueous solubilities, n-octanol/water partition coefficients, and Henry's law constants. *Environ. Toxicol. Chem.* 17, 251–257. <https://doi.org/10.1002/etc.5620170216>.
- Durmis, J., Karvaš, M., Holčík, J., 1975. Loss of light stabilizers from polypropylene. *Eur. Polym. J.* 11, 219–222. [https://doi.org/10.1016/0014-3057\(75\)90066-X](https://doi.org/10.1016/0014-3057(75)90066-X).
- European Chemical Agency (ECHA), 2017. Registered substances. Retrieved.
- Eichler, C.M., Wu, Y., Cao, J., Shi, S., Little, J.C., 2018. Equilibrium relationship between SVOCs in PVC products and the air in contact with the product. *Environ. Sci. Technol.* 52, 2918–2925. <https://doi.org/10.1021/acs.est.7b06253>.
- US Environmental Protection Agency (EPA), 2012. Exposure Assessment Tools and Models, Estimation Program Interface (EPI) Suite, V 4.11. US Environmental Protection Agency, Exposure Assessment Branch Washington, DC.
- Fedors, R.F., 1974. A method for estimating both the solubility parameters and molar volumes of liquids. *Poly. Eng. Sci.* 14, 147–154. <https://doi.org/10.1002/pen.760140211>.
- Földes, E., 1998. Study of the effects influencing additive migration in polymers. *Die Angew. Makromol. Chem.* 261, 65–76. [https://doi.org/10.1002/\(SICI\)1522-9505\(19981201\)261:262:1<65::AID-APMC65>3.0.CO;2-S](https://doi.org/10.1002/(SICI)1522-9505(19981201)261:262:1<65::AID-APMC65>3.0.CO;2-S).
- Fried, J.R., 2014. *Polymer Science and Technology, third ed.* Pearson Education.
- Fries, E., Dekiff, J.H., Willmeyer, J., Nuelle, M.-T., Ebert, M., Remy, D., 2013. Identification of polymer types and additives in marine microplastic particles using pyrolysis-GC/MS and scanning electron microscopy. *Environ. Sci. Proc. Impacts* 15, 1949–1956. <https://doi.org/10.1039/C3EM00214D>.
- Galloway, T.S., Cole, M., Lewis, C., 2017. Interactions of microplastic debris throughout the marine ecosystem. *Nat. Ecol. Evol.* 1, 1–8. <https://doi.org/10.1038/s41559-017-0116>.
- García-Guerra, R.B., Montesdeoca-Esponda, S., Sosa-Ferrera, Z., Kabir, A., Furton, K.G., Santana-Rodríguez, J.J., 2016. Rapid monitoring of residual UV-stabilizers in seawater samples from beaches using fabric phase sorptive extraction and UHPLC-MS/MS. *Chemosphere* 164, 201–207. <https://doi.org/10.1016/j.chemosphere.2016.08.102>.
- Gewert, B., Plassmann, M.M., MacLeod, M., 2015. Pathways for degradation of plastic polymers floating in the marine environment. *Environ. Sci. Proc. Impacts* 17, 1513–1521. <https://doi.org/10.1039/C5EM00207A>.
- Geyer, R., Jambeck, J.R., Law, K.L., 2017. Production, use, and fate of all plastics ever made. *Sci. Adv.* 3, e1700782. <https://doi.org/10.1126/sciadv.1700782>.
- Hanson, K.B., Hoff, D.J., Lahren, T.J., Mount, D.R., Squillace, A.J., Burkhard, L.P., 2019. Estimating n-octanol-water partition coefficients for neutral highly hydrophobic chemicals using measured n-butanol-water partition coefficients. *Chemosphere* 218, 616–623. <https://doi.org/10.1016/j.chemosphere.2018.11.141>.
- Hermabessiere, L., Dehaut, A., Paul-Pont, I., Lacroix, C., Jezequel, R., Soudant, P., Duflos, G., 2017. Occurrence and effects of plastic additives on marine environments and organisms: a review. *Chemosphere* 182, 781–793. <https://doi.org/10.1016/j.chemosphere.2017.05.096>.
- Hiemenz, P.C., Lodge, T.P., 2007. *Polymer Chemistry, second ed.* CRC press.
- Holčík, J., Karvas, M., Kassovicova, D., Durmis, J., 1976. Loss of phenolic antioxidants from polypropylene. *Eur. Polym. J.* 12, 173–175. [https://doi.org/10.1016/0014-3057\(76\)90049-5](https://doi.org/10.1016/0014-3057(76)90049-5).
- Jang, M., Shim, W.J., Han, G.M., Rani, M., Song, Y.K., Hong, S.H., 2016. Styrofoam debris as a source of hazardous additives for marine organisms. *Environ. Sci. Technol.* 50, 4951–4960. <https://doi.org/10.1016/j.envpol.2021.117461>.
- Jeon, H.-K., Chung, Y., Ryu, J.-C., 2006. Simultaneous determination of benzophenone-type UV filters in water and soil by gas chromatography–mass spectrometry. *J. Chromatogr. A* 1131, 192–202. <https://doi.org/10.1016/j.chroma.2006.07.036>.
- Jungclaus, G., Avila, V., Hites, R., 1978. Organic compounds in an industrial wastewater: a case study of their environmental impact. *Environ. Sci. Technol.* 12, 88–96.
- Kameda, Y., Kimura, K., Miyazaki, M., 2011. Occurrence and profiles of organic sun-blocking agents in surface waters and sediments in Japanese rivers and lakes. *Environ. Pollut.* 159, 1570–1576. <https://doi.org/10.1016/j.envpol.2011.02.055>.
- Kim, J.-W., Chang, K.-H., Prudente, M., Viet, P.H., Takahashi, S., Tanabe, S., Kunisue, T., Isobe, T., 2019. Occurrence of benzotriazole ultraviolet stabilizers (BUVSs) in human breast milk from three Asian countries. *Sci. Total Environ.* 655, 1081–1088. <https://doi.org/10.1016/j.scitotenv.2018.11.298>.
- Kim, J.-W., Isobe, T., Ramaswamy, B.R., Chang, K.-H., Amano, A., Miller, T.M., Siringan, F.P., Tanabe, S., 2011. Contamination and bioaccumulation of benzotriazole ultraviolet stabilizers in fish from Manila Bay, the Philippines using an ultra-fast liquid chromatography–tandem mass spectrometry. *Chemosphere* 85, 751–758. <https://doi.org/10.1016/j.chemosphere.2011.06.054>.
- Kim, Y., Lee, H., Jang, M., Hong, S.H., Kwon, J.-H., 2021. Evaluating the fate of hexabromocyclododecanes in the coastal environment: fugacity analysis using field data. *Environ. Pollut.* 286, 117461. <https://doi.org/10.1016/j.envpol.2021.117461>.
- Kitahara, K.-I., Nakata, H., 2020. Plastic additives as tracers of microplastic sources in Japanese road dusts. *Sci. Total Environ.* 736, 139694. <https://doi.org/10.1016/j.scitotenv.2020.139694>.
- Kwon, H.-C., Kwon, J.-H., 2012. Measuring aqueous solubility in the presence of small cosolvent volume fractions by passive dosing. *Environ. Sci. Technol.* 46, 12550–12556. <https://doi.org/10.1021/es3035363>.
- Kwon, J.H., Chang, S., Hong, S.H., Shim, W.J., 2017. Microplastics as a vector of hydrophobic contaminants: importance of hydrophobic additives. *Integr. Environ. Assess. Manag.* 13, 494–499. <https://doi.org/10.1002/ieam.1906>.
- Langford, K.H., Reid, M.J., Fjeld, E., Øxnevad, S., Thomas, K.V., 2015. Environmental occurrence and risk of organic UV filters and stabilizers in multiple matrices in Norway. *Environ. Int.* 80, 1–7. <https://doi.org/10.1016/j.envint.2015.03.012>.
- Lazare, L., Billingham, N., 2001. Solubility of a UV-stabiliser in some poly (ester-block-ether) co. *Polymer* 42, 1001–1007. [https://doi.org/10.1016/S0032-3861\(00\)00359-1](https://doi.org/10.1016/S0032-3861(00)00359-1).
- Leal Filho, W., Saari, U., Fedoruk, M., Iital, A., Moora, H., Klöga, M., Voronova, V., 2019. An overview of the problems posed by plastic products and the role of extended producer responsibility in Europe. *J. Clean. Prod.* 214, 550–558. <https://doi.org/10.1016/j.jclepro.2018.12.256>.
- Lee, S., Kim, S., Park, J., Kim, H.J., Lee, J.J., Choi, G., Choi, S., Kim, S., Kim, S.Y., Choi, K., 2015. Synthetic musk compounds and benzotriazole ultraviolet stabilizers in breast milk: occurrence, time-course variation and infant health risk. *Environ. Res.* 140, 466–473. <https://doi.org/10.1016/j.envres.2015.04.017>.
- Li, A., Yalkowsky, S.H., 1998a. Predicting cosolvency. 1. solubility ratio and solute log Kow. *Ind. Eng. Chem. Res.* 37, 4470–4475. <https://doi.org/10.1021/ie980232v>.
- Li, A., Yalkowsky, S.H., 1998b. Predicting cosolvency. 2. correlation with solvent physicochemical properties. *Ind. Eng. Chem. Res.* 37, 4476–4480. <https://doi.org/10.1021/ie980233n>.
- Liang, Y., Xu, Y., 2014a. Emission of phthalates and phthalate alternatives from vinyl flooring and crib mattress covers: the influence of temperature. *Environ. Sci. Technol.* 48, 14228–14237. <https://doi.org/10.1021/es504801x>.
- Liang, Y., Xu, Y., 2014b. Improved method for measuring and characterizing phthalate emissions from building materials and its application to exposure assessment. *Environ. Sci. Technol.* 48, 4475–4484. <https://doi.org/10.1021/es405809r>.
- Little, J.C., Weschler, C.J., Nazaroff, W.W., Liu, Z., Cohen Hubal, E.A., 2012. Rapid methods to estimate potential exposure to semivolatile organic compounds in the indoor environment. *Environ. Sci. Technol.* 46, 11171–11178. <https://doi.org/10.1021/es301088a>.
- Liu, C., Zhang, Y., 2016. Characterizing the equilibrium relationship between DEHP in PVC flooring and air using a closed-chamber SPME method. *Build. Environ.* 95, 283–290. <https://doi.org/10.1016/j.buildenv.2015.09.028>.
- Maceira, A., Borrull, F., Marcé, R.M., 2019. Occurrence of plastic additives in outdoor air particulate matters from two industrial parks of Tarragona, Spain: Human inhalation intake risk assessment. *J. Hazard. Mater.* 373, 649–659. <https://doi.org/10.1016/j.jhazmat.2019.04.014>.
- Malik, J., Tuan, D., Spirk, E., 1995. Lifetime prediction for HALS-stabilized LDPE and PP. *Polym. Deg. Stabil.* 47, 1–8. [https://doi.org/10.1016/0141-3910\(94\)00098-S](https://doi.org/10.1016/0141-3910(94)00098-S).
- Mannhold, R., Poda, G.L., Ostermann, C., Tetko, I.V., 2009. Calculation of molecular lipophilicity: state-of-the-art and comparison of Log P methods on more than 96,000 compounds. *J. Pharm. Sci.* 98, 861–893. <https://doi.org/10.1002/jps.21494>.
- Montesdeoca-Esponda, S., Vega-Morales, T., Sosa-Ferrera, Z., Santana-Rodríguez, J., 2013. Extraction and determination methodologies for benzotriazole UV stabilizers in personal-care products in environmental and biological samples. *TrAC Trends Anal. Chem.* 51, 23–32. <https://doi.org/10.1016/j.trac.2013.05.012>.
- Nakata, H., Shinohara, R.-I., Nakazawa, Y., Isobe, T., Sudaryanto, A., Subramanian, A., Tanabe, S., Zakaria, M.P., Zheng, G.J., Lam, P.K., 2012. Asia–Pacific mussel watch for emerging pollutants: distribution of synthetic musks and benzotriazole UV stabilizers in Asian and US coastal waters. *Mar. Pollut. Bull.* 64, 2211–2218. <https://doi.org/10.1016/j.marpolbul.2012.07.049>.
- Ostle, C., Thompson, R.C., Broughton, D., Gregory, L., Wootton, M., Johns, D.G., 2019. The rise in ocean plastics evidenced from a 60-year time series. *Nat. Comm.* 10, 1–6. <https://doi.org/10.1038/s41467-019-09506-1>.
- Pfaendner, R., 2006. How will additives shape the future of plastics? *Polym. Deg. Stabil.* 91, 2249–2256. <https://doi.org/10.1016/j.polyimdegstab.2005.10.017>.
- Prausnitz, J.M., Lichtenthaler, R.N., De Azevedo, E.G., 1998. *Molecular Thermodynamics of Fluid-Phase Equilibria, third ed.* Pearson Education.
- Rani, M., Shim, W.J., Han, G.M., Jang, M., Song, Y.K., Hong, S.H., 2017. Benzotriazole-type ultraviolet stabilizers and antioxidants in plastic marine debris and their new

- products. *Sci. Total Environ.* 579, 745–754. <https://doi.org/10.1016/j.scitotenv.2016.11.033>.
- Robeson, L.M., 2007. Polymer Blends. A Comprehensive Review.
- Rubino, J.T., Obeng, E.K., 1991. Influence of solute structure on deviations from the log-linear solubility equation in propylene glycol: Water mixtures. *J. Pharm. Sci.* 80, 479–483. <https://doi.org/10.1002/jps.2600800516>.
- Schwarzenbach, R.P., Gschwend, P.M., Imboden, D.M., 2016. *Environmental Organic Chemistry*, third ed. John Wiley & Sons.
- Spatafore, R., Pearson, L.T., 1991. Migration and blooming of stabilizing antioxidants in polypropylene. *Polym. Eng. Sci.* 31, 1610–1617. <https://doi.org/10.1002/pen.760312209>.
- Stevens, M.P., 1990. *Polymer Chemistry*. Oxford Univ. Press, New York.
- Tarafdar, A., Lee, J.-U., Jeong, J.-E., Lee, H., Jung, Y., Oh, H.B., Woo, H.Y., Kwon, J.-H., 2021. Biofilm development of *Bacillus siamensis* ATKU1 on pristine short chain low-density polyethylene: a case study on microbe-microplastics interaction. *J. Hazard. Mater.* 409, 124516 <https://doi.org/10.1016/j.jhazmat.2020.124516>.
- Teuten, E.L., Saquing, J.M., Knappe, D.R., Barlaz, M.A., Jonsson, S., Björn, A., Rowland, S.J., Thompson, R.C., Galloway, T.S., Yamashita, R., 2009. Transport and release of chemicals from plastics to the environment and to wildlife. *Philos. Trans. R. Soc. B* 364, 2027–2045. <https://doi.org/10.1098/rstb.2008.0284>.
- Thompson, R.C., Swan, S.H., Moore, C.J., Vom Saal, F.S., 2009. *Our Plastic Age*. The Royal Society Publishing.
- Van Leeuwen, C.J., Vermeire, T.G., 2007. *Risk Assessment of Chemicals: An introduction*, second ed. Springer Science & Business Media.
- Waters Corp, 2016. TECN134884650: Signal-to-Noise Values in Empower 3 (Technical Notes).
- Wick, A., Jacobs, B., Kunkel, U., Heininger, P., Ternes, T.A., 2016. Benzotriazole UV stabilizers in sediments, suspended particulate matter and fish of German rivers: new insights into occurrence, time trends and persistency. *Environ. Pollut.* 212, 401–412. <https://doi.org/10.1016/j.envpol.2016.01.024>.
- Xu, Y., Little, J.C., 2006. Predicting emissions of SVOCs from polymeric materials and their interaction with airborne particles. *Environ. Sci. Technol.* 40, 456–461. <https://doi.org/10.1021/es051517j>.
- Yalkowsky, S.H., 1979. Estimation of entropies of fusion of organic compounds. *Ind. Eng. Chem. Fundam.* 18 (2), 108–111.
- Yalkowsky, S.H., Roseman, T., 1981. *Techniques of Solubilization of Drugs*. M. Dekker New York (NY).
- Young, R.J., Lovell, P.A., 2011. *Introduction to Polymers*, third ed. CRC press.
- Zhang, Z., Ren, N., Li, Y.-F., Kunisue, T., Gao, D., Kannan, K., 2011. Determination of benzotriazole and benzophenone UV filters in sediment and sewage sludge. *Environ. Sci. Technol.* 45, 3909–3916. <https://doi.org/10.1021/es2004057>.