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Kinetics Study of the Migration of Bio-Based Plasticizers in Flexible PVC

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Abstract. The migration of bio-based plasticizers from flexible PVC was investigated by a solid-contact method using sandwiched PS sheets under pressure. A first-order migration kinetic equation was used to model the time-dependent weight gain of the PS sheet. Flexible PVC with acetyl tributyl citrate (ATBC) as plasticizer has serious migration problem, which can be effectively reduced by the addition of epoxidized soybean oil (ESO). It was demonstrated that ESO hinders the migration of plasticizer by reducing the maximum weight gain of PS sheets and the rate constant, as well as by raising the activation energy of migration

Keywords: Flexible PVC, Migration, Bio-based plasticizers

1. Introduction

Flexible polyvinyl chloride (PVC) is made from plastisols, which consist of PVC dispersion resin, plasticizers, and other additives. Due to the excellent processability and flowability of plastisols, flexible PVC finds wide application in toy and stationery consumer products, as well as in the pharmaceutical industry [1]. The main problem of flexible PVC products is the gradual migration of plasticizers when in contact with other objects due to the large contents of plasticizers. The released plasticizers may be harmful to the health or toxic to the environment [2], thus strict limitations have been imposed on the usage of certain petroleum-based plasticizers. The commonly used plasticizers for PVC can be categorized into two groups: petroleum-based plasticizers and non-petroleum-based plasticizers. Petroleum-based plasticizers include phthalate-based plasticizers, adipate-based plasticizers, maleate-based plasticizers, and trimellitate-based plasticizers, etc. Among the non-petroleum-based plasticizers, bio-based plasticizers are the most promising materials for flexible PVC due to its environmental and renewable characteristics, but also its low toxicity and public acceptance. Citrate-based plasticizers and epoxidized soybean oil (ESO) are the most commonly used bio-based plasticizers.

The migration of plasticizers from flexible PVC may occur in different ways [3]: (1) volatilization to the air, (2) extraction to a liquid when in contact with it, (3) migration to a solid when in contact with it. Thus, several approaches have been established based on these routes to assess the migration of plasticizers. The volatilization approach measures the weight loss of samples at high temperatures (373 K) in a container in the presence of activated carbon to absorb gas-phase plasticizers [4]. The extraction approach immerses the sample in hexane [4] or de-ionized water [5] for a period of time and measures its weight loss. Similarly, the solid-contact approach measures the weight loss of samples after in contact with a piece of other materials (polyethylene or polystyrene sheets) [4,6]. Diffusion is the main mechanism of migration in the solid-contact approach.

2. Materials and Methods

2.1. Materials and Sample Preparation

The PVC resin PR-415 (manufactured by emulsion polymerization with a molecular weight of ca. 73.2 kDa) was provided by Formosa Plastics. A combination of zinc stearate and calcium stearate (1:1, reagent grade) was used as a heat stabilizer. Plasticizers di (2-ethylhexyl) phthalate (DEHP), di (2-ethylhexyl) adipate (DEHA), and acetyl tributyl citrate (ATBC) were provided by UPC Technology, while ESO was purchased from Chang Chun Petrochemical.

PVC plastisols were prepared by mixing the PVC resin, the plasticizer and the stabilizer in the following proportions: 100 phr of PVC, 60 phr of plasticizer and 1.25 phr of the mixed stabilizer. After mechanical stirring at 400 rpm for 2 min, the plastisol was vacuumed for 15 min to remove air bubbles. PVC sheets with a thickness of 1 mm were prepared in a hot plate press at 170 ℃ and a pressure of 7.4 MPa for 10 min. The 1-mm-thick polystyrene (PS) sheets used in the solid-contact approach were also prepared in a hot plate press at 190 ℃ and a pressure of 7.4 MPa for 10 min.

2.2. Migration Test

The solid-contact approach was employed to measure the migration of plasticizers from flexible PVC. It was conducted by sandwiching a PS sheet (1 x 1 cm^2) between two PVC sheets (1 x 1 cm^2) under a pressure of 20 kPa using a weight. The sandwiched sheets was then placed on a stainless-steel tray at a fixed temperature. The variation of the weight of each sample was then recorded for a period of 15 d. The migration of plasticizers at different temperatures was also investigated to find the temperature dependence of the migration rate. Some PS sheets after the migration test were further examined by a thermal gravimetric analyzer (Perkin Elmer TGA-7). The TGA experiment was conducted with a heating rate of 10 ℃/min in the presence of air.

3. Results and Discussion

The migration of plasticizers of different flexible PVC samples was examined at 50 ℃ after 1 week. The change of weight for PS and PVC sheets is illustrated in Fig. 1. The weight gain of the PS sheets was somewhat lower than but comparable to the weight loss of the PVC sheets. This was explained by the observation that some of the plasticizer was stuck to the tray or the weight. It is noted that if the PS sheet was replaced by filter paper, the variation of weight was almost undetectable. The migration of plasticizers was serious for the PVC/ATBC and the PVC/DEHA sample, while that for the PVC/DEHP sample was mild, and that for the PVC/ESO sample was insignificant. It seems that ESO is the best choice for flexible PVC; however, it has been shown that the mechanical properties of the PVC/ESO sample were poor [7].

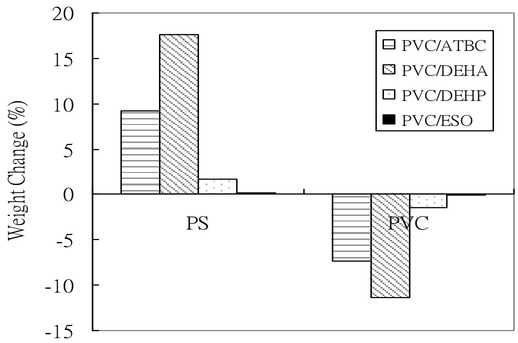

Fig. 1: Migration test at 50 ℃ for flexible PVC

The difference in the migration behaviour can be partially explained by the difference between the solubility parameters of PVC and plasticizers. Table 1 lists the Hansen solubility parameters of PVC and these plasticizers. It can be seen that except for ESO, the amount of migration increases with increasing interaction radius *R*, implying that the compatibility between PVC and plasticizers is the determining factor in plasticizer migration. This trend is broken by the anomalous behaviour of ESO, which has the worst compatibility with PVC, as shown in Table 1. The anomaly can be explained by that ESO tends to combine with PVC through a grafting reaction [8], thus reducing the migration to a trivial level.

Since ATBC is an extensively used bio-based plasticizer for PVC, we further examined the migrated ATBC in the PS sheet using a TGA analyzer. Figure 2 shows the thermogram of the PS sheet after the migration test for the PVC/ATBC sample. The derivative of the TGA curve indicates that there are three peaks in the temperature range of 160–230, 290–350, and 350–450 ℃. The first and the third peaks correspond to the evaporation of ATBC (the boiling point of ATBC: 172 ℃) and the degradation of PS (the degradation temperature of PS: 370 ℃), respectively. The position of the second peak is much higher than the boiling point of ATBC but lower than the degradation temperature of PS, and thus is speculated to be strongly adsorbed ATBC. The combination of the first two intervals of weight loss is approximately 12 %, which is comparable to the value measured by directly weighing the sheet.

The migration test demonstrates that it is difficult to attain flexible PVC with low migration rate when using ATBC. Thus, a combination of ATBC and ESO is proposed to overcome this problem. Fig. 3 compares the migration kinetics of the PVC/ATBC and the mixed system PVC /ATBC+ESO(9:1). The purpose of using a low-ESO content sample is to demonstrate the effectiveness of adding ESO in reducing migration. The weight of the PS sheet increases with time for both samples. The time-dependent mass gain can be simply modeled by a first-order migration kinetic equation:

$$\frac{dm}{dt} = k(m_\infty - m) \tag{1}$$

where k and m_∞ are the parameters representing the rate constant and the maximum weight gain, respectively. An integration of Eq (1) becomes

$$\ln \frac{m_\infty}{m_\infty - m} = kt \tag{2}$$

The two parameters can be obtained by fitting the experimental data using Eq (2) via a non-linear regression method. The resulting model curves, as shown in Fig. 3, agree with the experimental data very well. The model parameters at three different temperatures were also extracted from the kinetics data. Figs. 4 and 5 show that the m_∞ and k values increase with increasing temperature, indicating that the migration becomes severe and the migration rate becomes faster at high temperatures. It can be seen that the addition of ESO effectively reduces both parameters. The Arrhenius plot of the k values at different temperatures for both samples was used to estimate the activation energy of migration, E_a. The resulting E_a values are 21.55 and 42.09 kJ/mol for the PVC/ATBC and the PVC /ATBC+ESO(9:1) samples, respectively. With the addition of ESO in the plasticizer by 10%, the activation energy of migration is almost doubled, indicating that the migration of plasticizers in flexible PVC is hindered in the presence of ESO. In our recent study, it was found that the migration almost disappeared with an addition of 50% ESO.

Table 1: The Hansen solubility parameters of PVC and plasticizers

Materials	δ_d (J/ml)$^{1/2}$	δ_p (J/ml)$^{1/2}$	δ_h (J/ml)$^{1/2}$	R (J/ml)$^{1/2}$
PVC[9]	16.8	8.9	6.1	-
ATBC[9]	16.7	2.7	7.4	6.3
ESO[10]	16.5	1.6	5.1	7.4
DEHP[9]	16.6	7.0	3.1	3.6
DEHA[9]	16.7	2.0	5.1	7.0

Note: δ_d, δ_p, and δ_h represent the dispersion, polar attraction, and hydrogen bonding solubility parameters, separately.

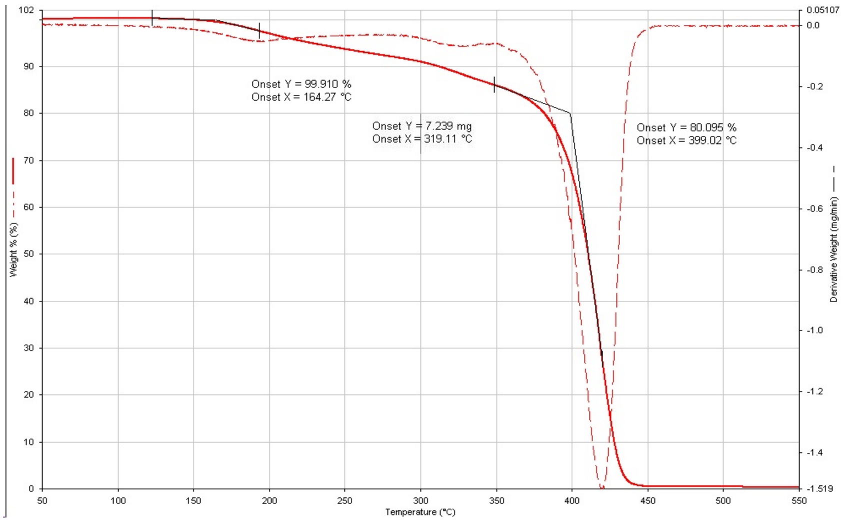

Fig. 2: Thermogram of the PS sheet after the migration test at 50 ℃ for PVC /ATBC

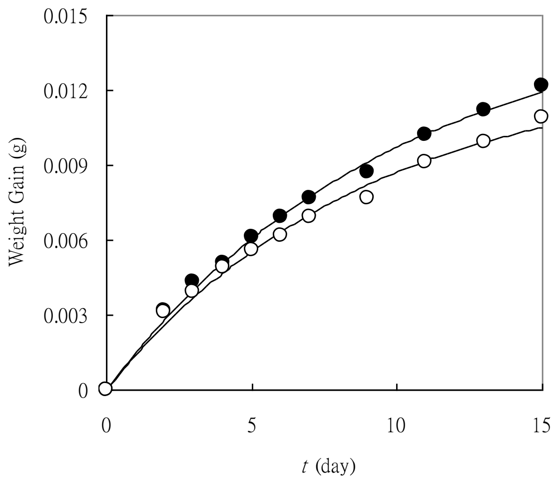

Fig. 3: The weight gain of the PS sheet during the migration test at 50 ℃ (●: PVC /ATBC, ○: PVC /ATBC+ESO(9:1); the solid curves are generated by Eq (2))

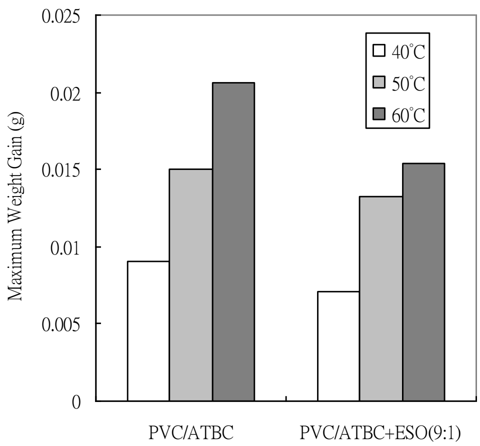

Fig. 4: The variation of the maximum weight gain with temperature

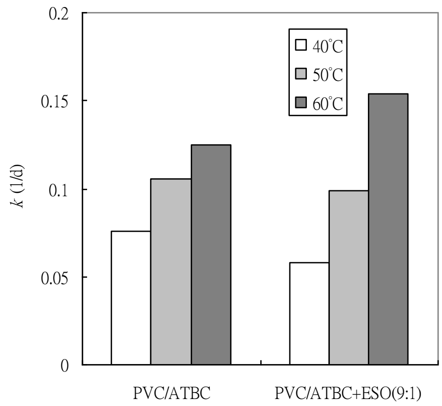

Fig. 5: The variation of the rate constant with temperature

4. Conclusions

In this study, we utilized the solid-contact approach using sandwiched PS sheets under pressure to investigate the migration of plasticizers from flexible PVC. The migration test demonstrated that the migration becomes severe as the compatibility between PVC and plasticizers is poor, which can be readily assessed by the Hansen solubility parameters. ESO, though poor in compatibility with PVC, has a negligible amount of migration due to that it can be bonded to PVC via a grating reaction.

The time-dependent migration data was successfully modelled by a first-order migration kinetic equation. The fitting results demonstrated that the migration of plasticizer for the PVC/ATBC can be significantly reduced with an addition of 10% ESO by decreasing both of the maximum weight gain and the rate constant. The Arrhenius analysis of the rate constant further showed that the activation energy of migration is almost doubled in the presence of 10% ESO.

5. Acknowledgements

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