Plasticiser loss from plastic or rubber products through diffusion and evaporation

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INTRODUCTION

Plasticisers are commonly added to polymers to lower their glass transition temperature and increase their processability, mechanical flexibility, ductility and toughness.¹⁻⁵ They represent a class of usually low-to-medium-high molecular-weight compounds with different polarities that are relatively nonvolatile at ambient conditions. The demand for plasticisers is increasing and is expected to reach approximately 9.75 million tonnes in 2024.⁶ Approximately 90% of these plasticisers are used in plasticised/flexible poly(vinyl chloride) (PVC) products. Other polymer systems that use plasticisers include acrylic polymers, polyamides, polyolefins, polyurethanes, certain fluoroplastics, and elastomers.⁷ Particularly, plasticisers are commonly used in films, cables and plastic tubing applications, which require high material mechanical flexibility.⁶

Plasticisers, when not chemically attached to polymer chains, can in certain conditions leave the polymer through migration, evaporation or extraction by liquids. During service, this loss may be problematic; it leads to (1) unwanted changes in the material properties (e.g., poorer mechanical properties) and (2) eventual contamination of the surrounding medium.⁸ Basically, plasticiser loss will increase the stiffness/modulus and often the strength but decrease the flexibility, extensibility and toughness of the polymer.⁹ For polymers, which are brittle in the unplasticised state, the plasticiser loss can lead to in-service failures, whereas the loss of flexibility limits the range of application of plasticised polymers in films, cables and tubing where high material flexibility is required. Contamination of food, water and air caused by plasticiser migration may affect human health.¹⁰⁻¹²

A detailed understanding of the mechanisms and kinetics of plasticiser loss is essential to evaluate both the short- and long-term performance of plasticised polymers. For instance, with a known correlation between mechanical properties and plasticiser concentration, the kinetics of plasticiser loss can be used to predict the change in mechanical properties associated with a particular service condition, and thus predict the lifetime of the products. Understanding the mechanisms of plasticiser loss and their kinetics is also helpful for developing new methods to eliminate/hinder plasticiser migration.

RESULTS AND DISCUSSION

Two kinetics-dominating migration modes

The migration of plasticiser from polymers to a gas phase is a two-step process that includes diffusion from the polymer bulk to the surface followed by evaporation from the surface to the air/gas phase. The diffusion process can be described by Fick’s second law (given here for a one-to-three-dimensional orthogonal system)¹³ as follows:

\[
\frac{\partial C}{\partial t} = \sum_{i=1}^{3} \frac{\partial}{\partial x_i} \left( D(C) \frac{\partial C}{\partial x_i} \right),
\]

where \( t \), \( x_i \), \( C \) and \( D(C) \) are the diffusion time, distance from the surface in the one-to-three-dimensional case, plasticiser concentration and diffusivity of the plasticiser, respectively. The same equation for cylindrical and spherical geometries is given in ref.¹³. The diffusivity generally increases with the concentration of plasticiser, which can be explained by the increase of the free volume and mobility of the polymer molecules in the presence of plasticisers.¹⁴,¹⁵ This concentration-dependence of the diffusivity

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can be described by the exponential function as follows: \footnote{13,14,16–18}
\[ D(C) = D_0e^{-\alpha C}, \]  
(2)
where \( D_0 \) is the zero-concentration diffusivity and \( \alpha \) is the plasticisation power, which relates to the plasticisation efficiency of the plasticiser. It is here assumed that any plasticiser clustering effects, which may lead to a decreasing diffusivity with increasing plasticiser content, are small or absent. There are also other equations describing the solute concentration-dependent diffusion.\footnote{19–24} The concentration-dependence of the diffusivity can also be expressed as an increase in free-volume (free-volume fraction: \( f \)) of the solute/polymer mixture relative to the neat polymer. Equations 3 and 4 are examples of how \( f \) has been observed to relate to the solute diffusivity.
\[ D = Ae^{-Bf}, \]  
(3)
where \( A \) and \( B \) are constants. \( A \) is considered to depend on the temperature and size/shape of the solute and \( B \) is related to the kinetic diameter of the solute.\footnote{22,23}

The evaporation boundary condition in the \( x \) direction can be described according to\footnote{18,25}
\[ -D(C) \frac{\partial C}{\partial x} = F(C - C_0), \]  
(5)
which equates the mass transfer through a given cross-section of the sample to the surface (flux) evaporation of the same mass from the same surface (right part). The flux to the surface depends on the mobility of the plasticiser molecule \( D(C) \) and the concentration gradient just within the surface. Evaporation takes place as long as the concentration of plasticiser just at the surface is greater than the concentration corresponding to the environment saturated with plasticiser \( (C_0) \) and as long as the evaporation coefficient \( (F) \) is not zero.

Due to the coexistence of diffusion and evaporation, the overall rate of plasticiser loss is determined by the slower process, meaning that the process is either diffusion- or evaporation-controlled. As illustrated in Fig. 1a for the diffusion-controlled case, evaporation is faster than the rate of supply of the plasticiser to the surface, leading to a gradient in the plasticiser concentration in the sample surface region and eventually, also in the bulk. When the system is evaporation-controlled, evaporation is slower than the rate of supply of plasticiser to the surface (Fig. 1b). In this case, depending on the system, a film of plasticiser can form on the surface (Fig. 1b)\footnote{16,26,27}.

To illustrate the effects of different ratios of \( D \), which for simplicity is assumed to be solute concentration-independent here, and \( F \) on the loss kinetics/characteristics, the loss of a “plasticiser” from an \( L = 1 \) mm thick plate of a “polymer” is considered here (the case of \( D \) being concentration-dependent is shown later below). It is assumed that the loss of plasticiser does not lead to a gas phase saturated with plasticiser, hence a case where the surrounding environment is a large/infinite volume of gas/air/vacuum or where there is a gas flow over the surface \( (C_0 = 0) \). A dimensionless ratio can be used to assess which mechanism dominates the loss kinetics: \( F \times L/D \). This also means that the thinner the sample/plate, the lower is the ratio and the more evaporation-controlled is the system. By choosing a high ratio, e.g., 1000 \( (F = 1 \times 10^{-3} \text{ cm s}^{-1} \) and \( D = 1 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1} \), the desorption curve is linear (mass loss relative to the square root of time) and the system is clearly diffusion-controlled (Fig. 2a). If \( F \) is lowered to \( 1 \times 10^{-7} \text{ cm s}^{-1} \) while \( D \) is kept the same, the ratio is 1, and the system is evaporation-controlled. The lower the ratio, the more evaporation-controlled the system is and the more S-shaped the plasticiser loss is (on a square root of time basis, Fig. 2a). In an evaporation-controlled system, the concentration profiles are flatter/more horizontal than those in a diffusion-controlled system (Fig. 2c, d). The evaporation coefficient can be estimated for the evaporation-controlled case by assuming that the initial part of the mass loss is mainly due to evaporation. By fitting the initial mass loss data as a function of time to a polynomial function, and knowing the plate surface area, \( F \) can be estimated.\footnote{28} As the concentration profiles become increasingly flat, a boundary condition such as the one in Eq. 5 can result in an untestable numerical time-integration. Then, a different relationship, where the actual concentration profile is not used in the boundary condition, can be adopted. One example is:
\[ C = C_0e^{-\beta t}. \]  
(6)
where the surface concentration is assumed to decay exponentially from the initial concentration \( (C_0) \) at a rate determined by the \( \beta \) parameter.\footnote{18}

The effects of a plasticiser concentration-dependent diffusivity on the plasticiser migration kinetics are illustrated in Fig. 2a, b, e. The modelling was made with Eq. 2 and input parameters \( (D_{co} = 5 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}, \ a = 8 \) and \( F = 5 \times 10^{-6} \text{ cm s}^{-1} \), chosen to allow for the full loss to occur within the time frame shown in Fig. 2a. The characteristic features are a small initial deviation from a linear loss (on a square root of time basis, hardly observed in the figure), indicative of an evaporation-controlled mode and a slow plasticiser loss at a late stage due to a diffusion-controlled mode. Consequently, the plasticiser concentration profile is initially relatively flat and at later stages shows a stronger concentration profile near the surface.

Figure 3 shows a real case where the outer part (jacket) of a plasticised PVC cable displayed a diffusion-controlled mass loss with a near-linear loss (up to 60%) as a function of the square root of time.\footnote{18} The experimental mass loss was modelled with Fick’s second law, with and without considering the plasticiser concentration-dependence of the diffusivity (Eq. 2). Both fits agreed well with the experimental data up to a certain mass loss, where after using a concentration-dependent diffusivity yielded a better fit. It should be noted that with the obtained plasticisation power of 8.6 (unit: 1/volume fraction),\footnote{18} the plasticisation effect was relatively small. In cases where the plasticisation effect is large the difference in the mass loss curve between the two cases will be larger.

Another example where the plasticiser loss displays an essentially linear relationship with the square root of ageing time.
in the diffusion-controlled mode is illustrated in Fig. 4a (120 °C). For the same system, at 90 °C, the system is strongly evaporation-controlled, as observed by the linear loss of plasticiser with time (see Fig. 4b). The data were obtained by simulating the desorption process using a multi-step backwards differentiation procedure (and the Matlab* software) where the diffusion process was described by Eqs. 1 and 2 and the boundary condition was described by Eq. 5.

For a case where the plasticiser has a very high boiling point (e.g., 385 °C for DEHP), and the material is used at low temperature, plasticiser accumulates at the surface and forms a thin film on the surface (Fig. 1b).2,18,25–27 There are several pieces of evidence that indicate the existence of a thin plasticiser layer on the polymer surface. First, there is the case where the plasticiser loss rate is constant, at least over a certain time-period (observed as the linear loss as a function of time at 90 °C in Fig. 4b), meaning that the loss function of time at two temperatures.29 The flat profiles at 110 °C indicate that the system is strongly evaporation-controlled at 110 °C, but diffusion-controlled at 170 °C, where the profiles exhibit clear gradients towards the surface.

Formation of a thin plasticiser surface layer/film in the evaporation-controlled mode
For a case where the plasticiser has a very high boiling point (e.g., 385 °C for DEHP), and the material is used at low temperature, plasticiser accumulates at the surface and forms a thin film on the surface (Fig. 1b).2,18,25–27 There are several pieces of evidence that indicate the existence of a thin plasticiser layer on the polymer surface. First, there is the case where the plasticiser loss rate is constant, at least over a certain time-period (observed as the linear loss as a function of time at 90 °C in Fig. 4b), meaning that the loss
is strongly limited by the evaporation process. The presence of the thin layer implies that the "concentration" of plasticiser on the surface is constant over time.\textsuperscript{18,27,30} If the surface concentration decreases with time, the plasticiser loss is no longer linear with time (refer to the mass loss curve for the evaporation-controlled case in Fig. 2b). Second, the plasticiser evaporation rate from polymer surfaces is similar (on the same order of magnitude) as the rate from their pure liquid state, indicating that the constant plasticiser concentration on the surface is close to that in the pure liquid (100%). Linde and Gedde\textsuperscript{31} reported that the evaporation rate of diisodecyl phthalate (DIDP) from PVC was 0.06 mg h\(^{-1}\) cm\(^{-2}\) at 120 °C, which is slightly higher than the rate for pure DIDP, (0.04 mg h\(^{-1}\) cm\(^{-2}\)). However, Ekelund et al.\textsuperscript{18} determined an evaporation rate of DEHP from a PVC cable surface that was somewhat higher (0.002 mg h\(^{-1}\) cm\(^{-2}\)) than for pure DEHP (0.0006 mg h\(^{-1}\) cm\(^{-2}\)) at 80 °C. Smith et al.\textsuperscript{26} reported that the difference between the evaporation rates of a nitroplasticiser from the pure liquid plasticiser and from a polyurethane surface at 85 °C was within an order of magnitude. Surface blooming (due to crystallisation) and bleeding are effects of the deposition of migrated components on the surface.\textsuperscript{2,3,32} Blooming occurs when the additive crystallises on the surface. The surface of PVC floors tends to become sticky with time, which is caused by the formation of a plasticiser layer on the surface (bleeding).\textsuperscript{33} Shashoua\textsuperscript{34} observed visually that plasticiser droplets formed on the surface of PVC sheets in contact with impenetrable glass during ageing. Figure 1c also clearly shows the formation of a plasticiser layer on the NBR surface in the evaporation-controlled mode. By using sum frequency-generation vibrational spectroscopy, Zhang et al.\textsuperscript{35} observed that the surface of PVC films was covered by a plasticiser layer at higher PVC plasticiser concentrations.

The rate of evaporation (\(v_o\) (g cm\(^{-1}\) s\(^{-1}\))) of a pure substance (plasticiser), from a strip of width \(l\) over which gas flows at velocity \(\mu\) (cm s\(^{-1}\)), can be calculated\textsuperscript{36,37} by the application of the mass transfer theory of evaporation from a stationary liquid into a stirred gas, as

\[
v_o = 0.33 \left( \frac{\rho l}{\mu} \right)^{1/3} S_0 D_0 \rho \mu^{1/6},
\]

where \(S_0\) (g cm\(^{-3}\)) is the concentration of the substance in the gas phase and \(D_0\) (cm\(^2\) s\(^{-1}\)) is its diffusion coefficient in the gas phase. \(\rho\) is the density (g cm\(^{-3}\)), and \(\mu\) is the viscosity (g cm\(^{-1}\) s\(^{-1}\)) of the gas into which evaporation takes place. Bellobono et al.\textsuperscript{37} have calculated \(v_o\) of several types of plasticisers by using Eq. 7 and the results obtained agreed with the experimental data.

The formation of the plasticiser film results in a 100% plasticiser concentration on the surface, hampering the diffusion process, as it is gradient driven.\textsuperscript{2} A full understanding of the mechanisms of the formation of a plasticiser film and its effect on plasticiser diffusion and loss kinetics remains to be developed.\textsuperscript{2} The thin plasticiser film can change the surface properties of polymers significantly. Ljungberg et al.\textsuperscript{38} showed that the migration of triacetin and tributyl citrate plasticisers increased the hydrophilicity of a poly (lactic acid) (PLA) surface, as indicated by a decrease in the water contact angle during ageing.

Main factors

Due to the formation of the plasticiser film, the kinetics of plasticiser loss for a strongly evaporation-controlled process is essentially independent of the polymer—plasticiser interactions, plasticiser concentration and gradient within the material and is essentially only influenced by the temperature, plasticiser features (size, shape, polarity, vapour pressure), flow rate of the gas above the surface and the size of the volume of gas surrounding the material. The plasticiser loss rate in stagnant air is approximately 1/3 of that in ventilated ageing conditions.\textsuperscript{33} Ekelund et al.\textsuperscript{25} reported that the DEHP evaporation rate from PVC and pure DEHP increased with the air flow rate for 20–75 mL min\(^{-1}\) and was independent at higher flow rates (75–130 mL min\(^{-1}\)). They also reported that the DEHP evaporation rate was the same in dry and moist (50% relative humidity) nitrogen. Using a Field and Laboratory Emission Cell, Clausen et al.\textsuperscript{39} determined that the evaporation/emission rate of DEHP from PVC flooring was not influenced by the relative humidity.

As shown in Table 1, evaporation is, in general, the rate-limiting process for plasticiser migration at lower temperatures, whereas diffusion is the limiting process at higher temperatures. Hence, the

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Table 1. The reported occurrence of the two migration modes for different polymer—plasticiser systems (The division into the two migration modes is based on the main features at each temperature as reported. Any eventual switch between the two modes at each temperature due to a strong concentration-dependent diffusivity is not explicitly reported.)

| Polymer—plasticiser         | Evaporation-controlled | Diffusion-controlled |
|-----------------------------|------------------------|---------------------|
| PVC-DEHP                    | 80 °C\textsuperscript{18,27,29}, 90 °C\textsuperscript{27,29}, 100 °C\textsuperscript{18,25,27,75}, 110 °C\textsuperscript{27} | 120 °C\textsuperscript{18,155 °C}\textsuperscript{18} |
| PVC-(DIDP + DEHP coplasticiser) | 110 °C, 120 °C\textsuperscript{31} |                     |
| PVC-ELATUR CH               | 100 °C\textsuperscript{50} |                     |
| NBR-DEHP                    | 90 °C\textsuperscript{43} | 120 °C, 140 °C\textsuperscript{43} |
| EPDM-undefined plasticiser  | 110 °C\textsuperscript{29} | 170 °C\textsuperscript{29,76} |
| Polyamide 12-n-butyl-benzesulphonamide | 125 °C\textsuperscript{41} |                     |
| PLA-acetyl triethyl citrate | 100 °C, 135 °C\textsuperscript{49} |                     |
| Polyurethane-nitroplasticiser | 73 °C\textsuperscript{26} |                     |
temperature-dependence is stronger for the evaporation process than for the diffusion process. It is possible to define a "transition" temperature ($T_c$) at which there is a switch from evaporation being the rate-limiting factor to diffusion being the rate-limiting factor for the loss of plasticiser (Fig. 6). As shown in Table 1, $T_c$ is between 110 and 120 °C for the PVC-DEHP system and between 90 and 120 °C for the NBR-DEHP system. For other common polymer–plasticiser systems, $T_c$ remains to be determined.

With the exception of temperature, other factors can affect the actual migration mode, especially when the ageing temperature is close to $T_c$. Royaux et al. reported that at 80 °C, the plasticiser migration from PVC transitioned from a diffusion-controlled mode in an open air environment to an evaporation-controlled mode in a space-limited environment (closed Petri dishes). Both the limited space, building up a plasticiser vapour pressure, and the stagnant/non-circulating air contributed to this. This switch led to a large difference in the mass loss, which was 25% after 20 weeks in the open environment, but less than 5% in the closed environment. This type of mode-transition was also reported by Shashoua for DEHP-plasticised PVC in closed and open environments at 70 °C. Audouin and Verdu observed that both the initial plasticiser concentration and the plasticiser size play important roles in determining the dominant mode. They observed that the evaporation-controlled mode dominates for large plasticisers and low initial plasticiser concentrations. The authors also showed that the migration kinetics of both didecyl phthalate and dinonyl phthalate from PVC were controlled by evaporation when the concentration was higher than 20 wt.% but were controlled by diffusion at lower concentrations. This agrees with the fact that the diffusivity is plasticiser concentration-dependent and decreases with the concentration (Eq. 2). In addition, a smaller concentration gradient at low plasticiser concentrations also contributes to the dominance of the diffusion-controlled mode.

Their results indicate that in some cases, such as for the migration of plasticiser from samples with a high initial concentration of plasticiser, it is possible to observe both modes during ageing where the migration is at first controlled by diffusion and then switches to become controlled by evaporation when the concentration of plasticiser decreases beyond a critical level.

In addition, inorganic fillers (e.g., fibres, carbon black and nanoparticles) can affect the diffusion of plasticiser in polymers but there are only a few reported studies on this topic. The probable reason is that the plasticiser is mainly used to soften the polymer, but the inorganic filler basically acts in the opposite way, reinforcing/stiffening the polymer. As a result, the incorporation of fillers into commercial products of plasticised plastics is not so common or the filler is used in a small concentration. As an example, the outer layer of a fuel pipe made of plasticised polyamide 12 only contains 0.5 wt.% carbon black, which is added as a UV stabiliser and pigment. Nevertheless, Wang et al. reported that the diffusivity of the plasticiser in PLA decreased significantly with increasing carbon black content. They explained that this was caused by a strong interaction between the plasticiser and carbon black. The situation is different in rubbers where a large amount of carbon black is often used in combination with plasticiser. However, the effects of carbon black on the plasticiser diffusion have not been investigated separately. In essence, however, the inorganic fillers can act as geometrical obstacles (they are impermeable to at least larger penetrants) and may also interact strongly with the plasticiser, leading to a decrease of the plasticiser diffusion in the polymer.

Ways to determine the type of migration mode

The type of plasticiser migration mode is traditionally determined by analysing the shape of the plasticiser desorption curve or the concentration profile within the sample. The curves of the mass loss versus ageing time or the square root of ageing time are commonly obtained by intermittently measuring the mass loss as a function of time using an analytical balance or by measuring the remaining plasticiser concentration inside the sample. The plasticiser concentration in polymers can be measured by thermogravimetry and infrared spectroscopy (IR) directly, or by extracting plasticiser with solvents, followed by measuring the plasticiser concentration in the extracted solution with chromatography. Whenever there is a reason to believe that there is a non-uniform distribution of plasticiser inside the sample, techniques that capture the total or average plasticiser content should always be used when evaluating any plasticiser-dependent properties. For example, an IR measurement on the surface, which typically involves the outer 1–5 µm of the sample, overestimates the average concentration in the evaporation-controlled mode when there is a plasticiser film on the surface. However, in the diffusion-controlled mode, the same measurement underestimates the average sample plasticiser concentration due to the existence of a concentration gradient towards the surface.

In cases where it is not possible to monitor the plasticiser loss over time, the shape of the plasticiser concentration profile at a single ageing time can be used to reveal the migration mode. Slicing is the most common method used to profile the plasticiser concentration. Two-dimensional mapping technologies, such as IR imaging, have been employed to obtain spatial distributions of concentrations of plasticiser. Confocal techniques, such as Raman micro-spectroscopy, can be used to obtain concentration profiles within the sample without any need for slicing. Additionally, in a recent study conducted by Adams et al., it was shown that single-sided nuclear magnetic resonance spectroscopy could be used to determine the plasticiser concentration profile in PVC in a direct and non-destructive way.
Prediction of plasticiser loss

The expected lifetime of polymer products can be as long as several decades and for prediction purposes, the migration process needs to be accelerated by ageing samples at high temperatures. The plasticiser loss can then be predicted by extrapolating the obtained data at high temperatures to service temperatures. Studies have shown that both the plasticiser evaporation and diffusion processes obey the Arrhenius law, which indicates that the Arrhenius law is valid for the extrapolation.\textsuperscript{25,27,43,49} However, the diffusion activation energy is concentration-dependent, and it is also, as is the case for the evaporation activation energy, temperature-dependent. Hence, when considering large plasticiser concentrations and temperature intervals, this should not be ignored. Due to the existence of the two rate-dominating modes, accelerated ageing needs to follow the same migration mode as the actual service conditions. For instance, the highest accelerating temperature should be lower than \( T_c \) for the actual case controlled by evaporation. This requires the determination of the temperature regions for these two modes before selection of the accelerating temperatures. Overlooking the existence of these two modes can lead to a false prediction. As shown in Fig. 6, the extrapolation of the plasticiser loss rate in the diffusion-controlled mode temperature region (data points in region A) to a temperature in the evaporation-controlled region leads to an overestimation of the plasticiser loss rate and an underestimation of the lifetime.

The plasticiser loss is typically controlled by the evaporation process at low temperatures, i.e., at the service temperature for most cases (implying a plasticiser film on the sample surface). This makes the prediction easier since the evaporation process is independent of the glass transition temperature of the polymer and the plasticiser concentration within the polymer product, but it depends on the evaporation characteristics of the plasticiser. For this case, a database of the evaporation rates of common plasticisers at different temperatures and their activation energies is useful for prediction purposes. However, this type of database covering various common plasticisers is currently not available.

As mentioned above, the evaporation rate of a plasticiser from the polymer is similar (within an order of magnitude) to that from its liquid state when a plasticiser film forms on the surface. The evaporation rate should be possible to estimate by using the evaporation rate data for the pure plasticiser directly. In this approach, the temperatures for accelerated testing can be greater than \( T_c \), as illustrated by the extrapolation of the data points in region C in Fig. 6.

However, it is important that the high temperatures chosen for accelerated ageing should not cause any degradation of the plasticiser. Ekelund et al.\textsuperscript{25} observed that degraded DEHP evaporated faster than undegraded DEHP because of the higher volatility of the degradation products, which have a lower molar mass than the undegraded compound. The degradation of DEHP resulted in a lower evaporation activation energy (55 kJ mol\(^{-1}\), compared to 91 kJ mol\(^{-1}\) for pristine DEHP). In addition, other ageing processes, such as the oxidation and annealing of polymers, are also accelerated at high temperature.\textsuperscript{60} Any effects of these processes on the plasticiser migration process should be determined to yield a correct prediction.

In some cases, a plasticised-polymer product, such as a polyamide-based fuel pipe in a car, may experience high temperatures during service and diffusion-controlled migration.\textsuperscript{41} The extrapolation of diffusivity is more complex, since the diffusivity is concentration-dependent and the desorption process at a certain temperature needs to be described by at least two factors, e.g., \( \alpha \) and \( D_{co} \) (Eq. 2). In this case, the activation energies of both \( \alpha \) and \( D_{co} \), which are obtained from extrapolation, are needed for the prediction. There are, however, currently no studies with data available on the extrapolation of both \( \alpha \) and \( D_{co} \).

Plasticisers in biopolymers and bio-based plasticisers

Plasticisers are increasingly used in a wide range of biopolymers to mainly improve their poor processability and make them more ductile and tough.\textsuperscript{3,5,51–53} For more or less brittle biopolymers, such as PLA, starch and proteins, it is important to understand the full plasticiser migration process and limit plasticiser losses, as this will cause the materials to revert to their inherent brittle state and service failures. Studies have shown that the migration behaviour of plasticiser in biopolymers is often complex. This is caused by: (i) cold crystallisation during service/ageing, (ii) phase separation between the plasticiser and the polymer, and (iii) hydrolysis and interactions with water. The cold crystallisation of biopolymers, such as PLA\textsuperscript{50,54–56} and starch\textsuperscript{57,58}, is accelerated in the presence of plasticisers,\textsuperscript{59} which increases the crystallinity and then the plasticiser concentration in the amorphous region. This, in turn, affects the plasticiser diffusion properties during ageing. In some cases, phase separation between the biopolymer and the plasticiser occurs during ageing/long-term storage, even at room temperature.\textsuperscript{55} This is a consequence of cold crystallisation and/or limited miscibility between the biopolymer and plasticiser.\textsuperscript{54,60} In addition, moisture can have a complex effect on the plasticisation and migration of hygroscopic plasticisers in hygroscopic biopolymers.\textsuperscript{51}

There is an increasing interest in the development of bio-based (green) plasticisers from agricultural industry co-by-products and waste to replace petroleum-based plasticisers.\textsuperscript{5,62} Glycerol and epoxidised triglyceride vegetable oils are examples of common bio-based plasticisers,\textsuperscript{2} and the use of these leads to products where both the matrix polymer and the plasticiser are bio-based.\textsuperscript{63} In most studies related to bio-based plasticisers and their applications, an investigation of the full migration mechanisms is missing and needs to be developed in this fast-growing field.

Ways to hinder plasticiser loss

To avoid the deterioration of polymer materials caused by plasticiser loss, several approaches have been used to hinder plasticiser migration. The most common way is to increase the molecular size of the plasticiser, which can be achieved by using polymeric plasticisers and oligomers,\textsuperscript{64,65} and branched and star-shape plasticisers.\textsuperscript{66} The diffusivity of these plasticisers in polymers is low due to their large size, leading to slow plasticiser losses. However, plasticisers with a larger molecular size have a lower plasticising efficiency than most traditional plasticisers.\textsuperscript{4} Another common approach is to graft the plasticisers onto the polymer chains.\textsuperscript{69–71} Due to the chemical bonds, the grafted plasticisers do not migrate. In addition, surface modifications, such as surface coatings and crosslinking, are commonly employed to suppress plasticiser migration.\textsuperscript{1,72,73} The modified surface layer acts as a barrier to the plasticiser and isolates the plasticiser from the exposed medium, preventing its migration.\textsuperscript{1,74}

In this paper, we discuss plasticiser losses from plastics and rubbers, losses which lead to inferior product properties, bleeding and eventual pollution of the surrounding environment. The loss to the surrounding gas phase occurs through diffusion inside the material to the surface and through evaporation from the surface. The loss is either diffusion- or evaporation-controlled, where the former usually occurs at high temperatures and the latter at low temperatures. In the evaporation-controlled mode, a film of plasticiser is often formed at the surface, which is indicated by a linear loss with time, at least over a certain time period. In addition to the temperature, the actual mode that dominates depends on several factors, including the plasticiser and polymer characteristics, product geometry and specific environment. The fact that the plasticiser diffusivity is plasticiser concentration-dependent can lead to a shift in the loss-mode (from diffusion to evaporation control) at otherwise constant conditions. It is also shown here
how it is possible to determine which mode limits the loss and the ways to extrapolate accelerated migration tests to service conditions. Warnings are also given that meaningful extrapolation and prediction of plasticiser migration requires consideration of several important factors. We also highlight issues with new emerging systems with bio-based plasticisers in biopolymers.

DATA AVAILABILITY

The data that support the findings (modelling results) of this study are available from the corresponding author upon reasonable request.

AUTHOR CONTRIBUTIONS

All authors contributed to the development and discussion of the ideas presented within this paper. X.-F.W. wrote the manuscript with the help of the other authors.

ADDITIONAL INFORMATION

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