

The Leaching Kinetics of Acetone in an Acetone-Polyurethane Adhesive Waste

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Received 14 March 2001; accepted 6 November 2001

ABSTRACT: This work consists of the study of the extraction of solvent (acetone) from a polymeric (polyurethane) substrate during a leaching process. Total organic carbon (T.O.C.) is the main contaminant parameter in the leaching of these systems due to the solution of the acetone which is practically totally extracted from the polymeric system. During the leaching process, the water (polar) diffuses across the holes formed between the chains of polyurethane reacting at the same time with the isocyanate groups at the end of the chains, causing the reticulation or crosslinking of the polymer. On the basis of the experimental results, the amount of acetone diffused versus time in plane sheet systems was studied. A diffusion model based on the Fickian law was developed considering two stages. In the first stage, the water diffuses into the system across the polyurethane chains causing the reticulation of the polymer and dissolving the acetone. In the second stage, the diffusion of acetone in water, which occupies the holes or spaces between the reticulated polymer, takes place. The diffusion kinetics in these kinds of systems are similar to the diffusion kinetics in a rigid solid, considering an effective diffusivity of the acetone through the system. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1945–1955, 2002

Key words: adhesives; waste; polyurethanes; acetone; leaching

INTRODUCTION

Adhesives with an organic solvent base are widely used in the shoe industry, being very frequently polyurethane-acetone adhesives. The adhesive is composed mainly by a polymer (polyurethane) and a solvent (acetone or other solvent), with some amounts of organic load (some additives) and inorganic loads (silica, metal oxides, etc.).

Adhesive wastes contain high or small amounts of the organic solvent depending on the losses by evaporation of the solvent. The hazard of

these wastes depends on the inflammable vapors evolved.

The solvent diffusion in elastomers, such as the polyurethane used, is generally Fickian diffusion.^{1–3} Some references concerning diffusion coefficients can be found in literature: Hung and Autian⁴ for aliphatic alcohols in polyurethane, Storey et al.⁵ for various dialkyl-phthalates in poly(vinyl chloride (PVC), Aithal et al.⁶ and Harogopadd et al.⁷ for some organic solvents in polyurethane, and Waggonner et al.⁸ for several solvents in polystyrene. On the other hand, Mencer and Gomzi⁹ studied the swelling kinetics of poly(ethylene-co-vinyl acetate) in different solvents; Webb and Hall¹⁰ considered the ingress of solvents into vulcanized rubber by nuclear magnetic resonance and observed a good diffusion behavior,

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Contract grant sponsor: Conselleria de Medio Ambiente of the Generalitat Valenciana.

Journal of Applied Polymer Science, Vol. 85, 1945–1955 (2002)
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and Aminabhavi et al.¹¹ studied the molecular migration of organic halocarbons into thermoplastic polymer blend membranes by using a Fickian mechanism of sorption and diffusion.

Adhesives wastes are frequently dumped, inside or outside of tins, causing an organic contamination due to the migration of the solvent to the aqueous phase. Knowledge of the leaching process is therefore useful for the characterization of the behavior of the waste in landing vessels.

One of the characterization methods of a waste is a leaching process:

The extraction procedure in the Spanish legislation¹² is analogous to the extraction procedure (EP) of the USA legislation. The procedure uses deionized water as extractor fluid and the pH is modified by adding acetic acid to bring the pH down to 5 when necessary. Initially, the amount of water added is 16 times the amount of sample for carrying out the extraction for 24 h, but finally the ratio of sample : water + acetic acid solution added must be 1 : 20 prior to the determination of the toxicity with *Photobacterium phosphoreum*. The extraction temperature must be carried out between 20 and 40°C.

The German method DIN-38414-S4,¹³ considered in many proposals of the European Union, considers the extraction procedure that uses a sample which contains at least 100 g in dry basis and is carried out at 25°C. The sample is introduced into a 2-L bottle and 1 L or more of deionized water is added, maintaining the sample : waste ratio equal to 1 : 10. The bottle is closed and placed in a rotator-agitator for 24 h.

The toxicity characteristic leaching procedure (TCLP)¹⁴ method of the Environmental Protection Agency (EPA) uses two different procedures, depending on whether volatile compounds are involved or not, adding acid solutions of acetic acid. The sample and the extraction fluid are put in a bottle and placed in a rotator-agitator for 18 h.

During the leaching process, the solid, paste, or very viscous liquid is put in contact with the water or liquid phase. A proportion of the solvent moves from the solid to the liquid phase. Several factors affect this process: time, stirring velocity, temperature, contact surface between both phases, internal diffusion, and chemical reactions.

The contamination of the extracts from the wastes of polyurethane solvent based adhesives is caused mainly by the organic solvents, most of them nontoxic. Nevertheless, the main contaminant parameter is the total organic carbon (T.O.C.).

The influence of the solvent concentration in the sample and the contact surface are the factors studied in this work. The kinetics of the diffusion process were also studied.

At the end of the polyurethane chains, there are isocyanate groups which react with the water diffused, causing the reticulation or crosslinking of the polymer. This phenomenon must be taken into account in the study of the extraction velocity of solvents during a leaching of acetone-polyurethane adhesives process.¹⁵

No articles were found analyzing the leaching process of an adhesive waste with an organic solvent, in which the polymer reticulates when reacting with the water, forming a semirigid solid.

MATERIALS

A synthetic mixture made up of 20 wt % polyurethane (Desmocoll 540- Bayer, Leverkusen, Germany) and 80% acetone (MERCK KGaA, Darmstadt, Germany) was initially prepared by mixing and stirring in an Oliver Batlle Dispermix DL-M model with a speed control at 2500 rpm. Some amounts were taken from this initial mixture and introduced inside a bottle in a chamber, where the vaporization of the acetone took place very slowly, to obtain adhesives with less percentage of acetone and with uniform composition inside the sample. Then the content of the bottle was mixed slightly to obtain a uniform composition before taking the sample to introduce it into the holder. In this way, the samples prepared only differentiate in the initial content of the solvent, but the distribution of the polymer chains are similar. The three samples used were the following: PU66/a34, 66 wt % polyurethane and 34 wt % acetone; PU57/a43, 57 wt % polyurethane and 43 wt % acetone; and PU46/a54, 46 wt % polyurethane and 54 wt % acetone.

EXPERIMENTAL

Two procedures were used to carry out the study of the leaching process.

Procedure A

Procedure A consists of a water extraction using a sample : water = 1 : 10 wt ratio, in accordance with the DIN 38414 leaching method,¹³ by turning the vessel at 60 rpm and with variable contact interphase area (sample and water are intro-

duced into a vessel which is turned). Small quantities of extract were extracted with a syringe to carry out the analysis.

Procedure B

Procedure B consists of a water extraction using a sample : water = 1 : 10 ratio. During the test, the contact surface between both stages was constant and the water was agitated with a magnetic stirrer in a vessel. The sample holder is a cylindrical vessel with 1 cm height and 7.8 cm diameter. The area of the contact surface between solid sample and liquid was 47.78 cm².

All the experiments were carried out at 23°C. The analysis of the T.O.C. was carried out by the combustion and infrared method using a T.O.C. Shimadzu model TOC-5050.

The solvent concentration in the extracts was measured by gas chromatography in a Hewlett-Packard 5890 model gas chromatograph. A semi-capillary column Chrompack with 27.5 m length and 0.53 mm diameter, flame ionization detector (FID), and nitrogen as carrier gas was used for analysis.

RESULTS AND DISCUSSION

Procedure A

Logically the amount of extracted solvent at 24 h depends on the initial amount of solvent in the waste due to the high solubility of acetone in water. To deduce the extraction degree, a series of runs with different initial acetone concentrations were carried out following Procedure A (24-h extraction period, 10 : 1 water : sample ratio, water-sample contact surface variable). The values of T.O.C. and the solvent concentration in the extracts versus the initial composition (percentage) of solvent in the initial sample are shown in Figure 1. The values of T.O.C. equivalent to the solvent quantity are also shown in Figure 1. These values are obtained by multiplying the solvent concentration in the extracts by the mass carbon proportion in the solvent molecule: $\text{T.O.C.}_{\text{equivalent}} (\text{mg/L}) = \text{acetone concentration} (\text{mg/L}) \times 36/58$. It can be observed that there is a nearly exact coincidence between the expected values of T.O.C. and the calculated values of T.O.C. due to the acetone analyzed, thus corroborating the experimental values.

Considering that the sample : water ratio was 1 : 10, if the solvent extraction were total, the

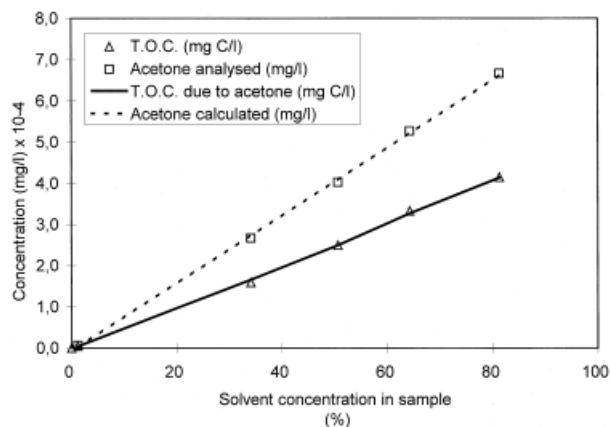


Figure 1 T.O.C., acetone, and T.O.C._{equivalent} concentrations in extracts obtained by procedure A at 24 h versus initial solvent concentration in samples.

ratio between the expected solvent concentration (mg/L)/solvent concentration and the initial sample (wt %) is $1 : 11 \times 10^6 : 10^2$, which equals 909. The calculated slope for the lineal correlations of solvent concentration (mg/L) versus the solvent concentration (wt %) is 881, which is close to that deduced for total extraction, indicating nearly total extraction.

Procedure B: Kinetic Model

The runs for the study of the diffusion kinetics were carried out with slabs by using Procedure B for maintaining the interface area constant. In practice, there are uncontrollable small variations of the interface because of the elasticity of the polymers. The values obtained in the tests and their relationships with the proposed models are described as follows.

The variations of the ratio between the extracted mass of acetone M_t and the maximum mass M_∞ versus the square of time are shown in Figure 2 for the three tests carried out with the three samples PU66/A34, PU57/A43, and PU46/A54, with acetone weight percentages of 34, 43, and 54 wt %, respectively. It can be verified that the kinetics of the extraction in the three tests are similar.

During the leaching process, two phenomena are produced in the polyurethane-acetone (PU/A) system: the water in the system moves into the sample through acetone by diffusion and the water also reacts with the polymeric chains of the polyurethane, causing the reticulation or cross-linking of the polymer and forming a semirigid solid.

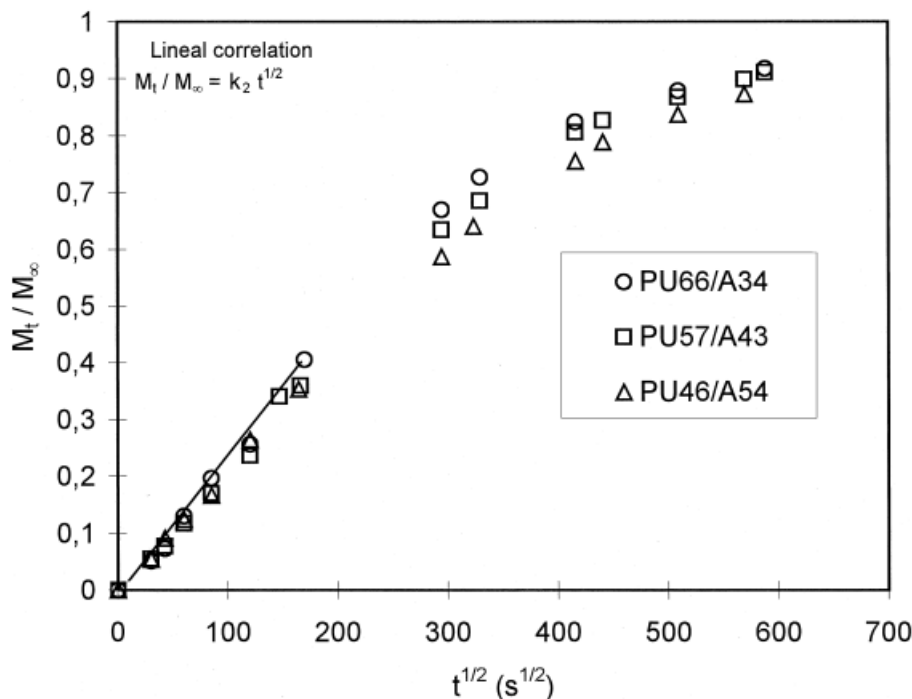


Figure 2 Relationship of M_t/M_∞ extracted solvent versus $t^{1/2}$ for the three samples PU66/A34, PU57/A43, and PU46/A54. Leaching procedure B (surface S constant).

In the present work a diffusion model was proposed, which explains the process considering two stages.

In the first stage, the water moves into the sample by reacting and forming a reaction front and separating the nonreticulated polymer from the reticulated polymer front. The water is totally soluble in acetone, so the movement of the reaction front controls the exit of the water from the polymer.

In the second stage, the reaction front has arrived at the end of the slab, and the process of diffusion of water and acetone goes on until the concentration inside the holes of the sample equals the exterior concentration. The duration of the first stage will be from time zero to critical time t_c and the second stage from critical time to time infinity.

The holes formed can be observed and had a wide distribution size, the biggest ones with a diameter around several millimeters.

Kinetic Model in the First Stage of the Diffusion Process

The mass transfer process can be represented by the Fick law, taking into account that the effective diffusivity can be related to the ordinary diffusivity D_{AW} , the internal porosity ε , and the tor-

tuosity factor τ , in the same way that occurs in the solid catalysts¹⁶:

$$n_A = -\rho D_{AW} \frac{\varepsilon}{\tau} \frac{\partial \omega_A}{\partial x} + \omega_A(n_A + n_W) \quad (1)$$

$$n_W = -\rho D_{WA} \frac{\varepsilon}{\tau} \frac{\partial \omega_W}{\partial x} + \omega_W(n_A + n_W) \quad (2)$$

To simplify and considering that n_A and n_W have opposite signs, it will be assumed that the diffusion process is the controlling process. The total transport of mass is considered negligible and a simplified law can be considered, so

$$n_A = -D_{eA} \frac{\partial \rho_A}{\partial x} \quad (3)$$

$$n_W = -D_{eW} \frac{\partial \rho_W}{\partial x} \quad (4)$$

where D_{eW} is the effective diffusivity of water, $D_{eW} = \varepsilon(D_{WA}/\tau)$ (m^2/s), similar to the diffusivity defined in heterogeneous catalysis; and ρ_A is the acetone concentration in the system that equals ρ_{WA} (kg acetone/ m^3 acetone + water).

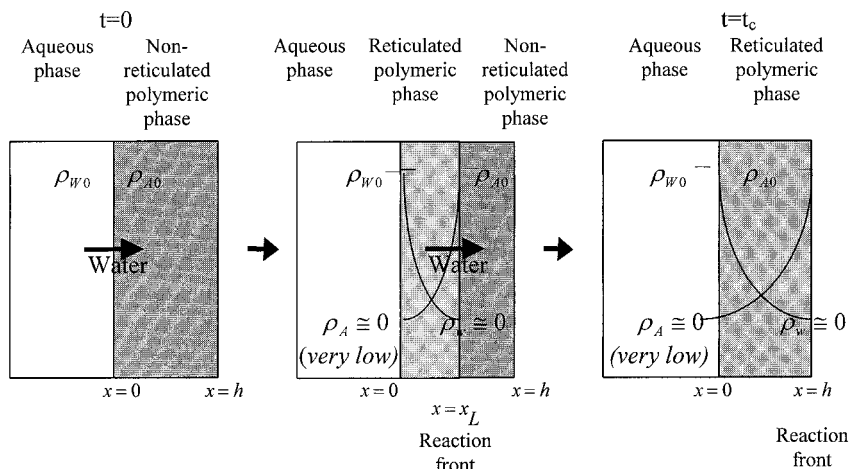


Figure 3 Concentration profile during the diffusion process in the first stage.

By mixing the polyurethane + acetone with water, it was observed that the reaction of the water with the isocyanate groups at the end of the chains of the polyurethane is very fast, producing the reticulation of the polyurethane. In the model considered, the front of reaction separates the nonreticulated solid with the reticulated solid and the water diffuses from the interface slab-solution through the holes of the reticulated polymer to the boundary between the reticulated solid and the nonreticulated solid where the water reacts with the isocyanate groups, as occurs in the non-reacted core model. On the other hand, the acetone diffuses in the opposite direction. Figure 3 shows a scheme of the diffusion process in this stage.

Considering an element of thickness volume Δx , the mass balance of water can be deduced as:

$$\varepsilon \frac{\partial \rho_W}{\partial t} + \frac{\partial n_W}{\partial x} = 0 \quad (5)$$

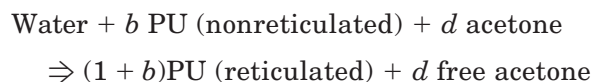
and taking into account the velocity law, the result is

$$\varepsilon \frac{\partial \rho_W}{\partial t} - D_{eW} \frac{\partial^2 \rho_W}{\partial x^2} = 0 \quad (6)$$

Considering that in the previous equations ρ_W represents the concentration of water in the spaces or holes between the chains of reticulated polymer (kg of water/m³ fluid) and n_W is the flux density through the total area, the general equation of the second Fick law is obtained:

$$\frac{\partial \rho_W}{\partial t} = \frac{D_{eW}}{\varepsilon} \frac{\partial^2 \rho_W}{\partial x^2} \quad (7)$$

The process of the reaction of water with the polyurethane molecule (in the presence of acetone) is equivalent to the following reaction scheme:¹⁵



where b and d are the yield factors: b is the mass of polyurethane/mass of water reacted and d is the mass of free acetone between the polymeric chains/mass of water reacted.

The reacted mass water by volume of reticulated polymeric phase is equal to $((1 - \varepsilon)/(1 + b))\rho_{PU}$ (mass of reacted water/volume reticulated polymeric phase), where ρ_{PU} is the reticulated polyurethane density (reticulated polyurethane mass/reticulated polyurethane volume); $(1 - \varepsilon)$ is the volumetric fraction of reticulated polyurethane in the reticulated polymeric phase; and $(1 + b)$ is the mass unit of the reticulated polyurethane by reacted mass unit of water.

The profile of solvent concentration during the diffusion process in the first stage is also shown in Figure 3 at $t = 0$ (at beginning of the run), at an intermediate time t , and at $t = t_c$ (critical time) when the reaction front or interface arrives at the end of the slab.

It was observed that a small contraction and contact surface deformation in the solid phase is

produced during the process, but this fact has not been considered in the model.

Taking into account the concentration profile, the boundary conditions are

At the outside extreme ($x = 0$)

$$w_A \approx 0 \tag{8}$$

$$w_W \approx 1 \tag{9}$$

$$\rho_W = \rho_{W0} \tag{10}$$

At the reaction front ($x = x_L$)

$$w_A = 1 \tag{11}$$

$$w_W = 0 \tag{12}$$

$$\rho_W = 0 \tag{13}$$

$$n_A|_{x=L} = -n_W d \tag{14}$$

$$n_W|_{x=L} = -D_{eW} \left. \frac{\partial \rho_W}{\partial x} \right|_{x=L} \quad (\text{considering diffusion}) \tag{15}$$

$$n_W|_{x=L} = \frac{1 - \varepsilon}{1 + b} \rho_{PU} \frac{\partial x_L}{\partial t} \quad (\text{considering reaction}) \tag{16}$$

So, the solution of eq. (7) is

$$\rho_W = A + B \operatorname{erf} \frac{x_L}{2 \sqrt{\frac{D_{eW}}{\varepsilon} t}} \tag{17}$$

Applying the boundary conditions to the general solution eq. (17), the following equations are obtained:

At the outside extreme ($x = 0$)

$$\rho_W = A = \rho_{W0} \tag{18}$$

At the reaction front ($x = x_L$)

$$0 = A + B \operatorname{erf} \frac{x_L}{2 \sqrt{\frac{D_{eW}}{\varepsilon} t}} \tag{19}$$

$$B = - \frac{\rho_{W0}}{\operatorname{erf} \frac{x_L}{2 \sqrt{\frac{D_{eW}}{\varepsilon} t}}} \tag{20}$$

From eqs. (17), (18), and (20):

$$\rho_W = \rho_{W0} \left(1 - \operatorname{erf} \frac{x}{2 \sqrt{\frac{D_{eW}}{\varepsilon} t}} / \operatorname{erf} \frac{x_L}{2 \sqrt{\frac{D_{eW}}{\varepsilon} t}} \right) \tag{21}$$

The length x_L of the reaction front can be related with the time t considering a constant α :

$$\alpha = \frac{x_L}{2 \sqrt{\frac{D_{eW}}{\varepsilon} t}} \tag{22}$$

and

$$\frac{\partial x_L}{\partial t} = \alpha \left[\frac{D_{eW}}{\varepsilon} \right]^{1/2} t^{-(1/2)} \tag{23}$$

On the other hand, from eq. (21)

$$\left. \frac{\partial \rho_W}{\partial x} \right|_{x=L} = - \frac{\rho_{W0} \frac{2}{\sqrt{\pi}} e^{[x_L / (2 \sqrt{\frac{D_{eW}}{\varepsilon} t})]^2} \left[1 / \left(2 \sqrt{\frac{D_{eW}}{\varepsilon} t} \right) \right]}{- \operatorname{erf} \left[x_L / \left(2 \sqrt{\frac{D_{eW}}{\varepsilon} t} \right) \right]} \tag{24}$$

$$\left. \frac{\partial \rho_W}{\partial x} \right|_{x=L} = - \frac{\rho_{W0} \frac{2}{\sqrt{\pi}} e^{-\alpha^2} \left[1 / \left(2 \sqrt{\frac{D_{eW}}{\varepsilon} t} \right) \right]}{\operatorname{erf} \alpha} \tag{25}$$

The water flux density across the reaction front, considering eq. (23), is described by the equation:

$$n_W = -D_{eW} \left. \frac{\partial \rho_W}{\partial x} \right|_{x=L} = - \frac{\rho_{W0} \varepsilon}{\sqrt{\pi} e^{\alpha^2} \operatorname{erf} \alpha} \left(\frac{D_{eW}}{\varepsilon} \right)^{1/2} t^{-(1/2)} = \frac{1 - \varepsilon}{1 + b} \rho_{PU} \frac{\partial x_L}{\partial t} = \frac{1 - \varepsilon}{1 + b} \rho_{PU} \alpha \left(\frac{D_{eW}}{\varepsilon} \right)^{1/2} t^{-(1/2)} \tag{26}$$

Considering $g(\alpha) = \sqrt{\pi} \alpha \operatorname{erf} \alpha e^{\alpha^2}$ in the above equation, the expression obtained is

$$g(\alpha) = \frac{1 + b}{1 - \varepsilon} \frac{\rho_{W0}}{\rho_{PU}} \varepsilon \quad (27)$$

On the other hand,

$$\begin{aligned} n_W|_{x=0} &= -D_{eW} \frac{\partial \rho_W}{\partial x} \Big|_{x=0} \\ &= -\frac{D_{eW} \rho_{W0}}{\sqrt{\pi}} e^{-0} \left[\frac{1}{\left(2 \sqrt{\frac{D_{eW}}{\varepsilon} t} \right)} \right] \\ &= \frac{D_{eW} \rho_{W0}}{\text{erf} \left[\frac{x_L}{\left(2 \sqrt{\frac{D_{eW}}{\varepsilon} t} \right)} \right]} \\ &= \frac{\rho_{W0} \varepsilon}{(\text{erf} \alpha) \sqrt{\pi}} \left(\frac{D_{eW}}{\varepsilon} \right)^{1/2} t^{-1/2} \quad (28) \end{aligned}$$

The equation that can be deduced with respect to the acetone is

$$n_A|_{x=L} = -dn_W|_{x=L} = -d \frac{\varepsilon \rho_{W0}}{g(\alpha)} \left(\frac{D_{eW}}{\varepsilon} \right)^{1/2} t^{-(1/2)} \quad (29)$$

The equation deduced by applying a mass balance to the reticulated polymer is

$$n_W|_{x=L} + n_A|_{x=L} - n_W|_{x=0} + n_A|_{x=0} + \varepsilon \rho \frac{dx_L}{dt} = 0 \quad (30)$$

where ρ is the average density that can be considered as not very different to ρ_{W0} . So,

$$\begin{aligned} -n_A|_{x=0} &= -\frac{\varepsilon \rho_{W0}}{g(\alpha)} \left(\frac{D_{eW}}{\varepsilon} \right)^{1/2} t^{-(1/2)} (1 - d) \\ &+ \frac{\rho_{WA} \varepsilon}{(\text{erf} \alpha) \sqrt{\pi}} \left(\frac{D_{eW}}{\varepsilon} \right)^{1/2} t^{-1/2} - \varepsilon \rho_{W0} \alpha \left(\frac{D_{eW}}{\varepsilon} \right)^{1/2} t^{-(1/2)} \\ &= \varepsilon \rho_{W0} \left(\frac{D_{eW}}{\varepsilon} \right)^{1/2} t^{-(1/2)} \left(-\frac{1 - d}{g(\alpha)} + \frac{1}{(\text{erf} \alpha) \sqrt{\pi}} - \alpha \right) \\ &= C \varepsilon \rho_{W0} \left(\frac{D_{eW}}{\varepsilon} \right)^{1/2} t^{-(1/2)} \quad (31) \end{aligned}$$

where, considering also eq. (27), the following expression can be obtained:

$$\begin{aligned} C &= \frac{1}{(\text{erf} \alpha) \sqrt{\pi}} - \alpha - \frac{1 - d}{g(\alpha)} \approx \frac{d - 1}{g(\alpha)} \\ &= \frac{d - 1}{1 + b} \frac{1 - \varepsilon}{\varepsilon} \frac{\rho_{PU}}{\rho_{W0}} \quad (32) \end{aligned}$$

In the previous equation, it has been considered that for high values of d , as occurs in the reticulation process considered, the approximation carried out can be done (this was tested considering different values of b , d , densities of reticulated polymer, and porosity).

The amount of acetone extracted from $t = 0$, considering also eq. (32) is

$$\begin{aligned} M_t &= \int_0^t (-n_A)_{x=0} S dt = 2SC\varepsilon\rho_{W0} \left(\frac{D_{eW}}{\varepsilon} \right)^{1/2} t^{1/2} \\ &= 2S \frac{d - 1}{1 + b} (1 - \varepsilon) \rho_{PU} \left(\frac{D_{eW}}{\varepsilon} \right)^{1/2} t^{1/2} \quad (33) \end{aligned}$$

Equation (33) can be simplified as follows: The term $(1 - \varepsilon) \rho_{PU}$ represents the kg reticulated polyurethane per unit of total volume in the slab that equals the product between the ratio $(1 + b)/d$ (reticulated polymer/acetone) and the acetone concentration (M_∞/Sh). So, introducing this equality in eq. (33), it is deduced that

$$\begin{aligned} M_t &= 2S \frac{d - 1}{1 + b} \frac{1 + b}{d} \frac{M_\infty}{Sh} \left(\frac{D_{eW}}{\varepsilon} \right)^{1/2} t^{1/2} \\ &= 2 \frac{d - 1}{d} \frac{M_\infty}{h} \left(\frac{D_{eW}}{\varepsilon} \right)^{1/2} t^{1/2} \quad (34) \end{aligned}$$

and

$$\frac{M_t}{M_\infty} = \frac{2}{h} \frac{d - 1}{d} \left(\frac{D_{eW}}{\varepsilon} \right)^{1/2} t^{1/2} \approx \frac{2}{h} \left(\frac{D_{eW}}{\varepsilon} \right)^{1/2} t^{1/2} \quad (35)$$

In this system, the extraction of acetone kinetics follows Fick's law so that $M_t = k_1 t^{1/2}$, where k_1 is a constant which depends on several parameters: water diffusivity (D_{WA}) in the system, porosity of the system ε , tortuosity factor τ , and the efficiency of the reticulating reaction. In the previous equations, the parameter (D_{eW}/ε) equals (D_{AB}/τ) , and consequently, it is possible that the variation of M_t/M_∞ versus $t^{1/2}$ for samples with the same value of h and with different initial acetone percentages was similar. Figure 2 shows the evolution of the ratio M_t/M_∞ versus $t^{1/2}$ for the three samples tested with different initial acetone concentrations. The evolution of the rate, at small time values, is similar for the three systems to a critical time t_c , in accordance with the reasons explained previously. The slopes obtained are shown in Table I.

Table I Slope and Lineal Correlation Parameter Values Obtained by Lineal $M_t/M_\infty = k_1 t^{1/2}$ Correlation of the Experimental Dates at Short Periods of Time (until $t = t_c$)

Sample	$k_1 \times 10^3$ (s ^{-1/2})	r ²
PU66/A34	2.25	0.995
PU57/A43	2.16	0.994
PU46/A54	2.20	0.998

The slopes k_1 were calculated by using the data obtained as follows: from $t = 0$ s to $t_c = 1.08 \times 10^5$ s for the system PU66/A34; from $t = 0$ s to $t_c = 8.64 \times 10^4$ s for the system PU57/A43; and from $t = 0$ s to $t_c = 2.70 \times 10^4$ s for the system PU46/A54, in accordance with the limit of linearity observed.

From Table I and Figure 2, it can be observed that the constants k_1 are similar, around a mean value of 2.2×10^{-3} s^{-1/2}.

Considering the reaction between the polyurethane and the water, the estimated value of b is around 40, so the values of $(d - 1)/d$ are close to unity (between 0.95 and 0.98). The estimated values for (D_{eW}/ε) that equals (D_{AB}/τ) is around 1.4×10^{-10} m²/s, which is an acceptable value taking into account that the acetone–water diffusion coefficients¹⁷ are around $2\text{--}4 \times 10^{-9}$ m²/s and the tortuosity factor is greater than 1 (it can be greater than 10, considering that the reticulation is not uniform and small channels connecting bags can be formed). Although values of the porosity are not necessary for the correlation of the data, the estimated overall value of the porosity was 0.4. Nevertheless, it must be remembered that many simplifications were done and the calculation of the exact values of diffusion coefficients would require many considerations, far from the objective of this work.

Kinetic Model in the Second Stage of the Diffusion Process

The result of the polymer reticulation process by water is a solid with great holes containing acetone and water through these holes. Acetone continues diffusing to the water. D_{AW} is the diffusivity of acetone in the water retained in the holes throughout the reticulated polymer and D_{eA} is the effective diffusivity, defined as

$$D_{eA} = \frac{D_{AW}}{\tau} \varepsilon \quad (36)$$

from the continuity equation and the Fick law, similar to eq. (7) but applied to the acetone, it can be deduced that

$$\frac{\partial \rho_A}{\partial t} = \frac{D_{eA}}{\varepsilon} \frac{\partial^2 \rho_A}{\partial x^2} \quad (37)$$

There is a profile of acetone concentration at time t_c . At the inner part of the slab, the concentration of acetone is high, whereas at the layer just next to the solution, it is practically nil. In this case, it can be considered that the acetone profile would be similar to that obtained in a system with the same uniform initial concentration as the real one, but from a theoretical time t_h^* instead the critical time t_c at the end of the first stage. So, relating the empirical date of total mass of acetone M_{tc} at the time t_c after the first stage (equivalent to the theoretical t_h^*), where a concentration profile is assumed, and considering that only the first term of the series is important, it can be deduced that

$$\begin{aligned} \frac{M_\infty - M_{tc}}{M_\infty} &= \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \\ &\times \exp \left[- (2n+1)^2 \frac{\frac{D_{eA}}{\varepsilon} \pi^2 t_h^*}{4h^2} \right] \approx \frac{8}{\pi^2} \\ &\times \exp \left[- \frac{\frac{D_{eA}}{\varepsilon} \pi^2 t_h^*}{4h^2} \right] \quad (38) \end{aligned}$$

where h is the thickness of reticulated polymer, M_{tc} is the theoretical mass of acetone extracted at t_h^* , and M_∞ is the total amount of free acetone.

The concentration profiles during the diffusion process in the second stage are shown, in schematic form, in Figure 4. During this stage, the system is made up of two phases: one of reticulated polymer with acetone and water through their holes and the other aqueous phase of water plus dissolved acetone.

The concentration of acetone in water, which occupies the holes between the reticulated polymer, is higher than the concentration of acetone in water, which is on the surface. The acetone diffuses through the holes to the aqueous phase until the concentrations are equal.

On the other hand, at time $t^* > t_h^*$, it occurs that

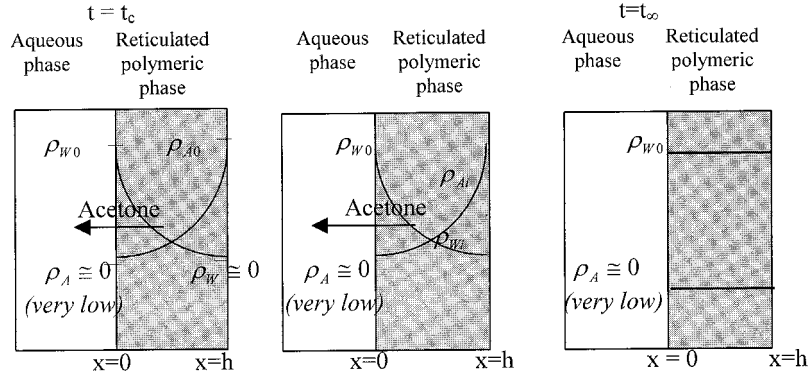


Figure 4 Concentration profiles during the diffusion process in the second stage.

$$\frac{M_\infty - M_t}{M_\infty} = \frac{8}{\pi^2} \exp\left[-\frac{D_{eA}}{\varepsilon} \frac{\pi^2 t^*}{4h^2}\right] \quad (39)$$

$$\ln(M_\infty - M_t) = \ln(M_\infty - M_{t_c}) + \frac{D_{eA}}{\varepsilon} \frac{\pi^2 t_c}{4h^2} - \frac{D_{eA}}{\varepsilon} \frac{\pi^2 t}{4h^2}$$

$$= \ln(M_\infty - M_{t_c}) + k_2 t_c - k_2 t \quad (41)$$

Dividing both equations,

$$\frac{M_\infty - M_t}{M_\infty - M_{t_c}} = \exp\left[\frac{D_{eA}}{\varepsilon} \frac{\pi^2 (t^* - t_h^*)}{4h^2}\right]$$

$$= \exp\left[\frac{D_{eA}}{\varepsilon} \frac{\pi^2 (t - t_c)}{4h^2}\right] \quad (40)$$

in the previous equation, it was considered that the increment $t^* - t_h^*$ in the second stage equals $t - t_c$ logically. Equation (40) can be written as

The values of $\ln(M_\infty - M_t)$ calculated from the experimental dates are shown versus time in Figure 5. The representation is linear at higher time values. Also, the curves $\ln(M_\infty - k_1 t^{1/2})$ versus t are shown, where k_1 is the kinetic constant obtained for the kinetic study in the first stage. The values of the slopes and intersections with the x -axis are shown in Table II, with the values of t_c obtained from the intersection of the corresponding linear correlations and the curve correlations. The t_c value is different for each one of the runs, although it is around $1-1.2 \times 10^5$ s. This fact

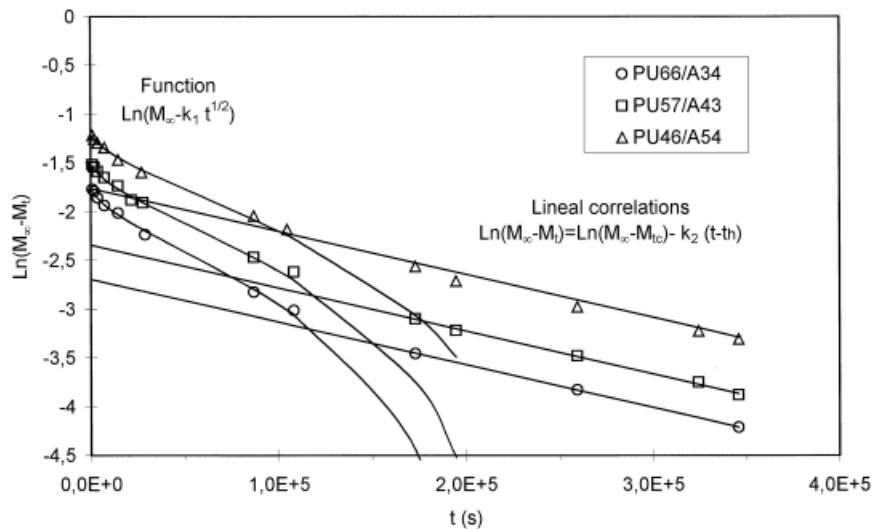


Figure 5 Relationship $\ln(M_\infty - M_t)$ versus t for PU66/A34, PU57/A43, and PU46/A54 samples.

Table II Slope, Intersections with x -Axis and Lineal Correlation Parameter Obtained by Lineal Correlation of the Experimental Data at High Time Values and t_c Estimated Value by Intersection of the Corresponding Lines Plotted in Figure 5

Sample	r^2	Slope $k_2 = D_{eA}\pi^2/\varepsilon 4h^2$ (s^{-1}) $\times 10^6$	Axe Intersection $\ln(M_\infty - M_{t_c}) + k_2 t_h$	$t_c \times 10^{-5}$ (s)
PU66/A34	0.999	4.39	-1.76	1.17
PU57/A43	0.998	4.41	-2.34	1.20
PU46/A54	0.993	4.41	-2.69	1.00

confirms that the lineal correlation of the experimental data in the first stage is accepted for the different ranges of time for each system.

As the lineal relation is performed from different times t_c in each run, the $\ln(M_\infty - M_t) = \ln(M_\infty - M_{t_c}) - k_2 t$ lineal correlations were obtained by using values from $t = 10.44 \times 10^2$ s to $t = 34.56 \times 10^2$ s for the PU66/A34 system, values from $t = 17.28 \times 10^2$ s to $t = 34.56 \times 10^2$ s for the PU57/A43 system and values from $t = 17.28 \times 10^2$ s to $t = 34.56 \times 10^2$ s for the PU46/A54 system.

Note also that the values of k_2 are similar for the three runs, because the ratio D_{eA}/ε is the diffusivity divided by the tortuosity factor that can be approximately constant and h is the thickness that has approximately the same value for the three runs. Considering that the thickness is 0.01 m, the estimated values of D_{eA}/ε that equals D_{AB}/τ are around 1.8×10^{-10} m²/s, which are close to the corresponding values obtained in the first stage (1.4×10^{-10} m²/s). The differences between the values of D_{AB}/τ can be due to the different range of concentration, the simplifications assumed in each stage, and perhaps also to the change of the tortuosity that can be different when the polymer is reticulating than after a period of time.

Extrapolation to Other Conditions

In view of the assumptions considered previously, it would be possible to deduce the extraction process of a waste with different thickness and similar concentration to those shown in this article (30–70% acetone) when the concentration of acetone in the aqueous phase is low and the external diffusion is fast, as follows:

In the first stage, the kinetic constant k_1 is directly proportional to the surface S and does not depend on the thickness, as indicated by eq. (35), but as the value of M_∞ is directly proportional to the product of the surface and the thickness, it can be written that

$$\frac{M_1}{M_\infty} = k_1 \frac{0.01}{h(m)} t^{1/2} \quad (42)$$

where k_1 is around 2.25×10^{-3} s^{1/2}.

The critical time t_c (at the end of the first stage) is directly proportional to the square of the thickness h , in accordance with eq. (22), so it can be deduced that

$$t_c(s) \approx 1.1 \times 10^{-5} \frac{h(m)^2}{(0.01)^2} \quad (43)$$

the mass M_{t_c} at the critical time tc can be calculated by using eq. (42) with the value of tc calculated from eq. (43).

For the second stage, the following expression can be used:

$$\frac{M_\infty - M_t}{M_\infty - M_{t_c}} = \exp\left(-\frac{k_2(0.01)^2(t - t_c)}{h(m)^2}\right) \quad (44)$$

where k_2 equals 4.4×10^{-6} s⁻¹.

If the surface S is not constant and/or the geometry of the waste is not a slab and/or there is a considerable increase of acetone in the extracts, the numerical integration using the basic parameters cited in this article should be used for obtaining the solution.

CONCLUSION

The main contaminant in the extracts of solvent-based adhesive wastes is the organic mater, analyzed by the parameter T.O.C., due to the solvent extraction. The main comments on the process of leaching of the systems made up of acetone and polyurethane are as follows: The acetone is practically completely extracted by the water. During the leaching process, the water (polar) passes through the polyurethane chains reacting, at the same time, with the isocyanate groups at the ends

of the chains producing the reticulation or crosslinking of the polymer chains.

The experimental leaching data can be satisfactorily correlated by a diffusion model considering two stages:

1. During the first stage, the water penetrates into the system producing the reticulation of the polymer chains and mixing with the acetone. The acetone extraction kinetics can be represented by an equation where the extracted acetone mass is directly proportional to the square of the time.
2. During the second stage, the acetone diffuses through the water, which is occupying the holes between the reticulated polymer. The diffusion kinetics are similar to the diffusion in a rigid porous solid, but using an effective diffusivity of the acetone through the retained water in the holes.

In any case, the diffusion rate is directly proportioned to the surface exposed to the extraction solution.

The authors are grateful for the financial support of the Consellería de Medio Ambiente of the Generalitat Valenciana (Spain).

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