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Characterization and modelling of diffusion and reaction of low molecular weight reactants in molten polymer

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Abstract

A model reactive system was defined for studying experimentally and by simulation the competition between reaction and diffusion of two low molecular weight reactants, 2,3-epoxypropyl-phenylether (EPPE) and dipentylamine (DPA). Both reactants are miscible in a high-viscous molten polymer, poly(ethylene-*co*-vinyl acetate) (EVA). The comparison of the experimental rates of reaction for initially homogeneous samples and bi-layer unpremixed samples proved that the reaction was diffusion controlled. A kinetic model of the epoxy–amine reaction was coupled to mutual diffusion coefficients of reacting species in a transport model and the simulations were compared with experimental results. The diffusion/reaction process was finally related to typical mixing conditions encountered in reactive polymer processes. For the model reactive system, the simulations have established that actual mixing conditions with shear rate values encountered in polymer processing machines, were able to homogenize the system in less than 10 s. In other words, the reaction should no longer be controlled by molecular diffusion as soon as a relatively low intensity mixing is applied (shear rate $> 10\ s^{-1}$).

Keywords: Diffusion; Reaction; Mixing

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1. Introduction

Mixing, diffusion and reaction are the mechanisms involved in the content of chemical engineering. In some cases, the interaction between these fundamental processes can affect the yield of the reaction and its selectivity since the local concentration of the species depends on the relative rate of convection (fluid mechanics), mass transfer and chemical reaction. In other words, the apparent rate of a chemical reaction may appear much slower than the intrinsic chemical kinetics when convective and diffusive mixing are the limiting steps. This is the case when the rates of the involved processes are of the same order of magnitude and such situation is encountered in reactive polymer processing (reactive extrusion) where the residence time is very short (<2 min). Reactive processing is one solution for obtaining new polymer materials with research cost substantially lower than that needed to develop a new polymer and several industrial materials are produced in this way. Thus, the research on this topic is very active with two main purposes: finding new materials, producing basic understanding and the related physical description of the process leading to prediction. As a practical example, an adequate description of the process allows to implement process control of the extruder considered as a chemical reactor [1,2].

The barrier which remains to be crossed in this kind of process is the understanding and control of the mixing phenomena which occur during the transformation. In order to ensure perfect control of the reactive process and thus predict and fix the yield of the reaction and product distribution, the

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ideal situation would be to measure the concentration of reactants at every location in the reactor throughout the duration of the process. Indeed this is unrealistic. A more realistic and practical objective, although less ambitious, is to get quantitative information on the efficiency of micromixing. The approach developed in the domain of chemical engineering concerns mainly low viscosity fluids. Its principle is to add chemical species that will act as tracers for the state of segregation of the medium since they react upon mixing. Generally one uses a set of two competitive reactions, the first one being very fast and the rate of the second being of the same order as the mixing process. The concentrations of the chemical species are selected such that the selectivity of the second reaction is a function of the mixing conditions (use of a stoichiometric defect of one of the reagents). If mixing is very fast, only the first reaction takes place as it consumes the totality of involved species. On the contrary, in imperfect mixing conditions there is a local overconcentration which allows the second reaction to take place. The quantity of the products formed by the secondary reaction is thus a measure of the bad mixing quality. Very few authors have attempted to adapt this concept to viscous fluids like molten polymers. The redox reaction of iodide and iodate ions in glycerine has been tested experimentally and compared to simulation but even the highest viscosity attained, $\eta = 0.3$ Pa s, was not comparable to that of molten polymers [3]. Other authors have used the imidization reaction between phthalic anhydride and *p*-phenylene diamine in molten polyethylene ($\eta = 100$ Pa s at 150 °C) and have shown that this reaction is mixing-sensitive [4]. However, their system was reacting in quiescent conditions, in the absence of flow. Micromixing studies by competitive reactions are widely used to characterize chemical reactors but do not develop in the context of reactive extrusion. The reason lies probably in the fact that difficulties are encountered in defining a tracer system respecting the numerous criteria essential to obtain reliable information. It should be pointed out that polymers being high molecular weight species, thermodynamics tells that it is difficult to ensure a perfect miscibility of the tracers and that this miscibility is very difficult to characterize in polymers. Also, the high viscosity of the polymer submitted to an intense velocity field produces heat dissipation so that the temperature is not controllable and even impossible to measure with accuracy in the extruder.

If we come back to the basic objective that is to know the concentration of reactants and products at each time and in every location of the extruder (reactor), in theory mathematical modelling and simulation of the global process may provide such detailed information. However it requires deriving equations for the convective mixing, for mass transfer by diffusion and for reaction kinetics, all these equations being strongly coupled. For some reactors and for simple geometry extruders it is possible to compute flow patterns. However, the ultimate size of the concentration scale being of the order of several microns, the resolution on the whole concentration spectrum requires extremely important mesh for which actual calculation power is insufficient to directly compute the concentration field in a complex industrial device [5,6].

Based on the above comments and in light of disappointing attempts to apply competitive reaction to polymer processed in machines with complex geometries (mixers or extruders), one possibility is to define simple model reactive systems on which it is possible to analyse in detail the coupled phenomena. Therefore, in this paper we consider a model for the reaction of two initially separated low molecular weight species miscible in a high viscosity molten polymer. The originality of the work lies in the fact that we not only model concurrent diffusion and reaction, but also compare the predictions to actual experimental data collected on a carefully selected and well-characterized model reactive system. Moreover, the complex mechanical mixing is taken into account by using simple bi-layered sample geometry.

2. Models

On top of the short residence time, the specificity of reactive extrusion is the high viscosity of the reactive medium where mixing is laminar and produces spatially organized striations (lamellar structure) with characteristic thicknesses that decrease with time at a rate that depends essentially on the intensity of mixing imposed by the rotation of the screws [7–9]. This picture of the mixing mechanism in viscous flow is valid when the entities to be mixed are miscible. In the case of immiscible entities, lamellae are formed during the early stage of the process but then mixing proceeds by break-up and coalescence of the dispersed droplets [10,11]. The purpose was to focus on diffusion and reaction in a bi-layer sample (Fig. 1). The thickness of the layers can be varied to figure the evolution of the striation thickness in mixtures evolving in a laminar flow. The higher is the time of mixing or the intensity of agitation and the lower is the striation thickness and so the thickness of our sample.

The sample is constituted by two layers of the same polymer, containing a proportion of low molecular weight organic molecule, named A and B. These species are totally miscible in the polymer and may react chemically. The product of their reaction is denoted as C. The initial separation of these reactants and their diffusion from one layer to the other lead to the formation of a mobile reaction front. The concentration profiles will develop differently depending on the kinetics of diffusion compared to reaction. If diffusion is slower than reaction, the reaction may become diffusion controlled and its apparent kinetics may be lower than that expected for the corresponding homogeneous reactive medium.

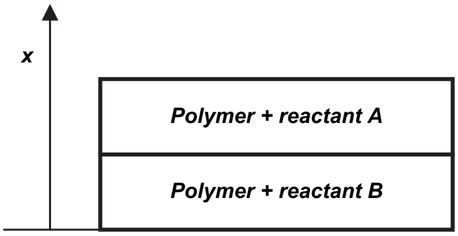


Fig. 1. Representation of the sample. Two layers of the same polymer containing a proportion of reactants A and B initially separated.

2.1. Mathematical model

Theoretical studies on the modelling of diffusion and reaction with initially separated reactants are numerous [8,12–15]. The model presented here is based on similar considerations. The chemical reaction is of the type:

$$A + B \rightarrow C \tag{1}$$

The geometry of the bi-layer sample refers to a one dimensional diffusion model in cartesian coordinates. Accordingly, the modelling of Fickian diffusion and reaction is based on differential equation system (Eq. (2)) to describe the relation between molecular diffusion, chemical reaction and the instantaneous concentration field of each species j:

$$\frac{\partial C_j}{\partial t} = D_{12}\frac{\partial^2 C_j}{\partial x^2} + r_j \tag{2}$$

r_j (x,t) is the rate of production (or consumption) of j entities ($j =$ A, B, C). D_{12} is the mutual diffusion coefficient, C_j is the molar concentration of the entities. Here, it will be admitted that the mutual diffusion coefficient of the two species depends only on the initial concentration of reactants. In our experimental case, the reaction between A and B leads to the formation of the product C. The volume fraction of C in the polymer is close to that of the two reactants A and B. Thus, the glass temperature of the polymer mixture does not vary much with the extent of the chemical reaction since the global volume concentration of small molecules in the viscous medium is almost constant during the experiment. According to the free volume theory of diffusion, we can then admit that the mutual diffusion coefficient of the species depends only on the initial concentration of molecules A and B [16]. A system of differential equations must be solved in order to express the extent of the reaction (or the concentration of reactants A, B and product C) in the case of these non-homogeneous conditions. This resolution is reported in Appendix A.

2.2. Reaction model

The difficulties in selecting an experimental model reactive system are numerous and are related first and foremost to the properties and specificities of the reactive medium that is a high molecular weight polymer. Small reactive molecules A and B must be miscible in the polymer in the range of proportions and operating temperatures studied. These molecules should have high evaporation and degradation temperatures and it is necessary to avoid undesired reactions at the high temperature of operation. Also, the yield of reaction must be easily measurable during the course of the reaction. The characteristic time of the implemented reaction must be smaller or of the same order as the characteristic time of the mixing process. Indeed if the reaction is limited by convective and diffusive mixing, the apparent consumption of the reactants is slower than that foreseen by the true chemical kinetics. This delay is a signature of the mixing time in the system. In order to perform mixing studies in a device, it is necessary that this delay is not too weak. If the reaction is too slow with regard to mixing, the competition does not take place and the system seems to be ideally mixed. After having tested several inadequate systems, we have selected a monofunctional epoxy, 2,3-epoxypropyl-phenylether (EPPE), and a secondary amine, dipentylamine (DPA) as reactants A and B. The polymer was poly(ethylene-*co*-vinyl acetate) (EVA) because of its low melting point that allows to run the reaction at moderate temperature and avoid degradation and undesired reactions. Also a variety of low molecular weight entities are miscible in EVA.

3. Experimental

3.1. Materials

The polymer used is poly(ethylene-*co*-vinyl acetate) (EVA) EVATANE® with 28 wt% of vinyl acetate and a melt index flow of 800 g/10 min (190 °C–2.16 kg). The zero shear viscosity of this copolymer at $T = 110$ °C is 75 Pa s. The samples were kindly supplied by Arkema. 2,3-Epoxypropyl-phenylether (EPPE) (99% purity) and dipentylamine (DPA) (98% purity) are from Aldrich Chemical Co. Both reagents were used as received (Table 1).

3.2. Determination of the extent of reaction by calorimetry

The main objective is to establish the reaction mechanism, derive the appropriate kinetic model and determine the kinetic constants. Differential scanning calorimetry (DSC) is widely used in this field [17,18], it is simple and less time consuming than indirect analysis methods like high pressure liquid chromatography. The reaction enthalpy is proportional to the consumption of the reactive groups. Thus, the conversion (x) of epoxy groups can be directly calculated from the heat flow signal (Eq. (3)), and the conversion rate (Eq. (4)) dx/dt, can be calculated as follows:

$$x(t) = \frac{\Delta H_t}{\Delta H_{\text{tot}}} = \frac{C_0 - C}{C_0} \tag{3}$$

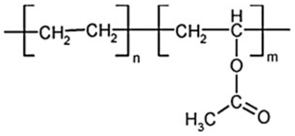
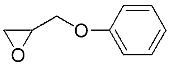
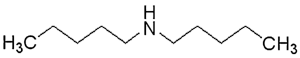
and

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{1}{\Delta H_{\text{tot}}}\frac{\mathrm{d}H_t}{\mathrm{d}t} \tag{4}$$

ΔH_t is the heat released by reaction up to time t and ΔH_{tot} is the total enthalpy of the reaction (total conversion, $x = 1$).

Calorimetric measurements were performed in a Perkin Elmer DSC Pyris Diamond into O-ring sealed large volume capsules from Perkin Elmer. The enthalpy and temperature measurements are calibrated using indium as a standard. The atmosphere was made inert using nitrogen gas with a flow rate of 20 mL min^{-1}. The use of this calorimeter enabled us to determine isothermal and non-isothermal reaction kinetics [19].

Table 1
Structures of polymer and liquids

Materials	Structure	M_n (g mol^{-1})	Glass transition temperature (°C)	Melting temperature (°C)	Boiling point (°C)
Poly(ethylene-*co*-vinyl acetate) (EVA)		4000[a]	−30[b]	64[b]	–
2,3-Epoxypropyl-phenylether (EPPE)		150[c]	–	3.5[c]	245[c]
Dipentylamine (DPA)		157[c]	–	–	202–203[c]

[a] From inverse rheological calculation assuming $M_w \propto \eta_0^{3.4}$ for entangled polymers.
[b] Calorimetric measurements.
[c] Supplier data.

3.3. Preparation of homogeneous samples

Two types of homogeneous samples have been prepared.

First, a liquid mixture of EPPE and DPA in stoichiometric ratio (EPPE–DPA) was prepared. The samples' weights range from 5 to 10 mg. The total reaction enthalpy ΔH_{tot} for the pure EPPE–DPA system was measured in non-isothermal conditions from room temperature to 300 °C at different heating rates (5, 10, 15 and 20 °C min^{-1}) and was evaluated to be 400 J g^{-1}, that is, 120 kJ per mole of epoxy groups.

The second type of sample was a homogeneous mixture of EVA with EPPE and DPA (EVA/EPPE–DPA). A liquid premix of EPPE and DPA was prepared in stoichiometric ratio and then laid out with the polymeric layer during 24 h in sealed capsules to permit the diffusion of the reagents in the polymer. All these steps were performed at room temperature. The thicknesses of EVA/EPPE–DPA samples were 0.5 and 1 mm and the EPPE–DPA concentration in EVA was 20 wt%.

3.4. Preparation of unpremixed bi-layer systems

The two layers were prepared by letting EPPE and DPA diffuse at room temperature into EVA to form separate layers. The EVA/DPA layer is prepared directly in the DSC capsule and the EVA/EPPE layer is then put in contact on top of the first layer containing DPA. Finally the capsule is sealed. The thicknesses of EVA/EPPE and EVA/DPA layers were 0.5 and 1 mm and the reactants' concentration in EVA was 20 wt% (Fig. 2). The reaction kinetics was studied in isothermal conditions at $T = 150$ °C.

In both homogeneous and bi-layer systems, the reaction kinetics was studied in isothermal conditions at $T = 150$ °C.

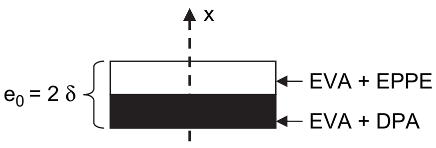


Fig. 2. The reactive bi-layer system. $\delta = 0.5$ or 1 mm.

3.5. Temperature homogeneity in the DSC cell

Before going further in the study, it was necessary to confirm that our samples are homogeneous from a thermal point of view. In other words, the temperature gradient across the sample should be limited. For that purpose, we must check that the reaction rate is slow compared to heat diffusion and that the adiabatic increase in temperature is not too high.

The adiabatic increase in temperature is calculated with the following expression:

$$\Delta T_{adiab} = \frac{\Delta H_{tot} C_0}{\rho C_P} \tag{5}$$

ΔH_{tot} is the reaction enthalpy (120 kJ mol^{-1}) and C_0 is the initial molar concentration of reactive species in homogeneous EVA/EPPE–DPA (80/20 wt%) system and is equal to 532 mol m^{-3} (Table 3). Using these values, the adiabatic increase of temperature is $\Delta T_{adiab} = 28$ °C.

The local increase of temperature is estimated by the relation:

$$\Delta T = \Delta T_{adiab} \frac{t_{Dth}}{t_R} \tag{6}$$

The characteristic time of thermal diffusion in the sample, t_{Dth}, is estimated as follows:

$$t_{Dth} = \frac{e_0^2}{\alpha} \tag{7}$$

e_0 is the thickness of the layer and α is the thermal diffusivity of EVA calculated with Eq. (8).

$$\alpha = \frac{\lambda}{\rho C_P} \tag{8}$$

λ is the thermal conductivity of EVA (1.7×10^{-1} W m^{-1} K^{-1}), ρ is the density of EVA at 150 °C (816 kg m^{-3} calculated from Eq. (17)) and C_P is the heat capacity of EVA (2.75 kJ kg^{-1} K^{-1}).

The calculation of α gives a value of 7.5×10^{-8} m^2 s^{-1}. The calculation of the characteristic time of thermal diffusion for each sample thickness gives $t_{\mathrm{Dth}} = 53$ s for the thicker one ($e_0 = 2$ mm), and $t_{\mathrm{Dth}} = 3$ s for the thinner ($e_0 = 0.5$ mm).

The characteristic time of reaction, t_{R}, is estimated by calculating the inverse of the slope of the extent of reaction versus time curve at $t = 0$.

$$t_{\mathrm{R}} = \frac{1}{\left(\frac{\mathrm{d}x}{\mathrm{d}t}\right)_{x=0}} \tag{9}$$

From our experiments presented further in Fig. 4, we find $t_{\mathrm{R}} = 2700$ s (EVA/EPPE–DPA 80/20).

First, we note that thermal diffusivity being much higher than molecular diffusion (diffusion coefficient $= 10^{-10}$–$10^{-12}\ \mathrm{m^2\,s^{-1}}$), heat transfer will be much faster than mass transfer. Therefore, the samples should attain homogeneity in temperature rather quickly during the heating stage in the DSC. Moreover, $\Delta T_{\mathrm{adiab}}$ is not too high and $t_{\mathrm{R}} >> t_{\mathrm{Dth}}$; thus, the calculated local temperature increase is 0.55 s. This low value can be considered as negligible during the course of the reaction.

4. Kinetic and diffusion data

The resolution of Eq. (2) implies to determine the diffusion coefficients of the reactants in EVA at $T = 150$ °C. A kinetic model and the related constants are also needed to express r_j. The following sections detail these aspects.

4.1. Kinetic model and constants for the EPPE–DPA reaction

Numerous studies were carried out on the reaction of EPPE with aliphatic or aromatic amines [20–22] to elucidate mechanisms of reaction and identify the intermediate steps. This reaction occurs through the formation of an amine, epoxy and hydroxyl intermediate termolecule due to the existence of intramolecular hydrogen bonds (Fig. 3b). The explanation of this stage lies in the fact that the amine presents both the nucleophilic and electrophilic aspects at the same time and that the acidity of the hydroxyl group which is more important than that of the amine in this termolecule, reduced the capacity of the amine to attack the α-carbon of epoxy oxirane.

Secondary reactions like epoxy–epoxy reaction or the etherification (reaction of the hydroxy with epoxy) become significant when the reaction is carried out at higher temperatures (>170 °C) or in the presence of catalysts [23].

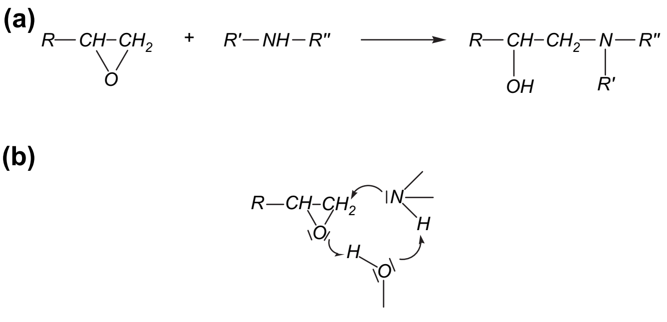


Fig. 3. (a) Reaction of epoxy with a secondary amine and (b) termolecular intermediate.

From kinetic point of view, semi-empirical models were developed taking into account parameters which intervene in the majority of epoxy–amine systems and which distinguish steps of the epoxy reaction with the primary and the secondary amines [22]. Kinetic measurements are commonly performed in low viscosity solvents and for stoichiometric mixtures. Kinetically, a second-order reaction following two parallel mechanisms can be assumed in our case: a non-catalytic mechanism and a self-catalyzed mechanism by hydroxyl groups formed after the opening of the oxiranes. Eq. (10) illustrates the mathematical representation used for the calculation of the kinetic constants of our reaction [24].

The used rate expression for this reaction is the following:

$$r_{\mathrm{A}} = -\frac{\mathrm{d}C_{\mathrm{A}}}{\mathrm{d}t} = (k + k'C_{\mathrm{C}})C_{\mathrm{A}}C_{\mathrm{B}} \tag{10}$$

C_{A}, C_{B}, C_{C} are the molar concentrations of the epoxy, the amine and the product, respectively, at time t. Kinetic constants are denoted by k for non-catalytic mechanism and k' for auto-catalytic mechanism in Eq. (10).

In homogeneous case, the concentration of product C can be calculated, thanks to the mass balance, by:

$$C_{\mathrm{C}} = C_{0\mathrm{A}} - C_{\mathrm{A}} \tag{11}$$

By introducing Eq. (11) in Eq. (10), we obtain:

$$r_{\mathrm{A}} = -\frac{\mathrm{d}C_{\mathrm{A}}}{\mathrm{d}t} = (k + k'(C_{0\mathrm{A}} - C_{\mathrm{A}}))C_{\mathrm{A}}C_{\mathrm{B}} \tag{12}$$

$C_{\mathrm{A}} = C_{\mathrm{B}}$ since EPPE and DPA are in stoichiometric ratio (so at $t = 0$, $C_0 = C_{0\mathrm{A}} = C_{0\mathrm{B}}$) (Eq. (12)):

$$r_{\mathrm{A}} = -\frac{\mathrm{d}C_{\mathrm{A}}}{\mathrm{d}t} = (k + k'(C_{0\mathrm{A}} - C_{\mathrm{A}}))C_{\mathrm{A}}^2 \tag{13}$$

The integration of Eq. (13) leads to the following expression (Eq. (14)):

$$t = -\left(\frac{k'}{(k + k'C_{0\mathrm{A}})^2}\right)\ln\frac{C_{\mathrm{A}}}{C_{0\mathrm{A}}} + \frac{C_{\mathrm{A}} - C_{0\mathrm{A}}}{2(k + k'C_{0\mathrm{A}})} + \frac{k'}{(k + k'C_{0\mathrm{A}})^2}\ln\frac{[(k + k'(C_{0\mathrm{A}} - C_{\mathrm{A}}))]}{k} \tag{14}$$

where the concentration C_{A} of the epoxy (and thus that of the amine and that of the product of the reaction) from Eq. (14) can be calculated at each time t for the pure EPPE–DPA or the viscous EVA/EPPE–DPA homogeneous system.

Note that the concentrations of the reactive species were calculated (Table 2) using specific volumes $V_1{}^T$ and $V_2{}^T$ at 150 °C determined experimentally from the measurement of the volume of DPA and EPPE at 90, 110, 130 and 150 °C. The following relations were established (Eqs. (15)–(17)):

$$V_1^T = 0.80344\exp\left(2.218\times10^{-5}T^{3/2}\right)\ \mathrm{cm^3\,g^{-1}}\ \ \text{for EPPE} \tag{15}$$

Table 2
DPA and EPPE concentrations in the different studied systems

	Pure system	20% Epoxy + amine; 80% EVA			10% Epoxy + amine; 90% EVA	
		Homogeneous	0.5/0.5 mm	1/1 mm	0.5/0.5 mm	1/1 mm
C_0 (mol L^{-1})	2.698	0.532	0.532	0.532	0.266	0.266

$$V_1^T = 1.15303 \exp\left(2.442 \times 10^{-5} T^{3/2}\right) \mathrm{cm}^3\,\mathrm{g}^{-1} \text{ for DPA} \qquad (16)$$

The specific volume of the EVA was measured by Rodgers [25], it is equal to:

$$V_2^T = 1.00832 \exp\left(2.241 \times 10^{-5} T^{3/2}\right) \mathrm{cm}^3\,\mathrm{g}^{-1} \qquad (17)$$

- *Pure EPPE–DPA*

  The calorimetric isothermal measurement at 110, 130, and 150 °C on the pure EPPE–DPA allowed measuring the conversion in epoxy groups as a function of time. k and k' were adjusted by comparing the data to the conversion calculated with Eq. (12). The result for $T = 150$ °C is presented in Fig. 4 after optimization of the kinetic constants by least square method.
- *Diluted EPPE–DPA*

  If the solvent had no effect on the reaction mechanism and kinetics, the dilution of the reactants in EVA should be taken into account simply by modifying the reactants concentration in Eq. (12). To investigate that effect, 20 wt% of EPPE–DPA was homogeneously diluted in dodecane and then reacted at 150 °C. The model predicts correctly the epoxy conversion variation with time. However, in EVA at the same concentrations and temperature, the reaction is clearly accelerated (Fig. 4) and, indeed, the model established on the basis of Eq. (12) with the kinetic constants determined previously predicted slower kinetics. Since EVA modifies the reaction kinetics, it was necessary to determine k and k' specifically in EVA. The optimization of the new kinetic constants in the presence of EVA was done and the calculated curve is presented in Fig. 4. The values of kinetic constants are summarized in Table 3.

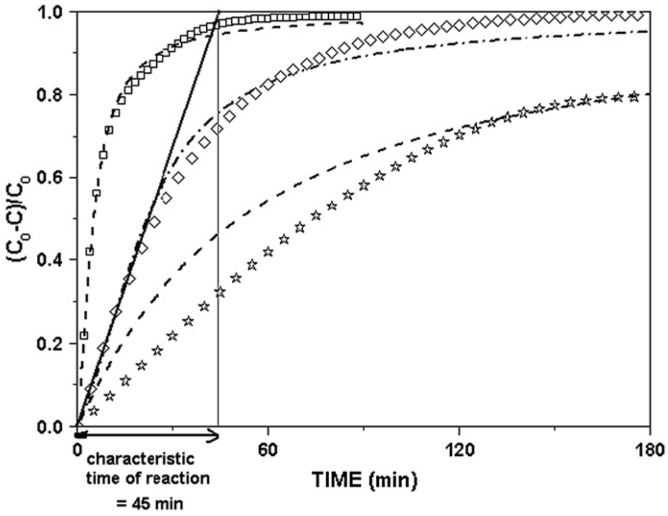


Fig. 4. Experimental and calculated extents of reaction as a function of time at $T = 150$ °C. (□) Pure EPPE–DPA, (◇) homogeneous EVA/EPPE–DPA 80/20, (☆) homogeneous dodecane/EPPE–DPA 80/20. Symbols represent experimental data and solid curves represent the extent of reaction calculated with Eq. (12). Optimized kinetic constants are given in Table 3.

A good agreement between the experimental and the calculated conversion is obtained.

This part of the study illustrates well the importance of progressing step by step to characterize the behaviour of the model reactive system correctly.

Table 3
k and k' calculated for pure EPPE–DPA and for 20 wt% of EPPE–DPA dissolved in EVA ($T = 150$ °C)

Reactive system	k (L mol^{-1} s^{-1})	k' (L^2 mol^{-2} s^{-1})
EPPE–DPA and dodecane/ EPPE–DPA 80/20	5.55×10^{-4}	6.43×10^{-4}
EVA/EPPE–DPA 80/20	5.55×10^{-4}	6.57×10^{-3}

4.2. Diffusion coefficients

The diffusion coefficients are not easily measured experimentally in polymer melts. They are also difficult to calculate reliably because of the number of parameters involved in the diffusion models. In preceding work we studied the diffusion of methylaniline (NEA) and EPPE in EVAs with different molecular weights [26]. The mutual diffusion coefficient, D_{12}, was determined by an inverse rheological method developed by Ponsard-Filette et al. [27]. As predicted by the free volume theory, D_{12} depended strongly on the concentration of the two molecules in the polymeric medium and for the same concentration the amine diffuses faster than the epoxy. In addition, we demonstrated that the diffusion coefficient of the amine does not depend on the molecular weight while that of the epoxy depended on the molecular weight of the polymer.

In the current study, we use DPA and we observed that this amine behaves qualitatively like NEA but with diffusion rates twice higher. The calculated mutual diffusion coefficients D_{12} of the three diffusing entities (EPPE, DPA and product) in EVA at $T = 150$ °C are presented in Table 4.

Table 4
Diffusion coefficients of DPA, EPPE and product in EVA at $T = 150$ °C calculated according to Ref. [26]

Reactants' mass fraction in EVA (wt%)	Calculated D_{12} (m^2 s^{-1})		
	DPA	EPPE	Product
20	1.2×10^{-10}	1.8×10^{-11}	1.25×10^{-11}

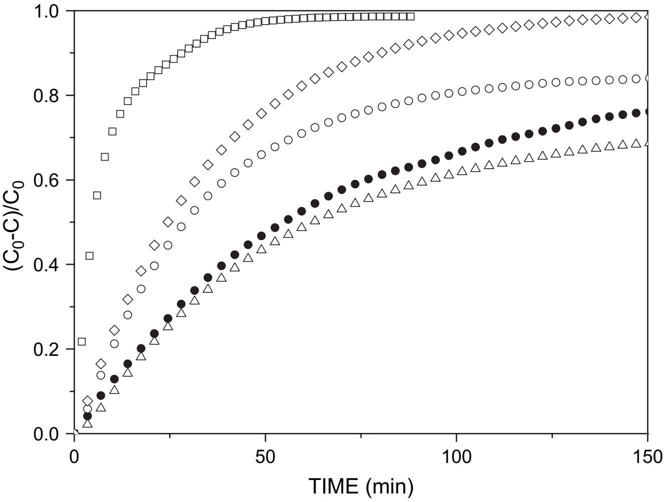


Fig. 5. Extent of reaction measured as a function of time for different concentrations and bi-layer thicknesses. ($T = 150$ °C). (□) Pure EPPE–DPA, (◇) homogeneous EVA/EPPE–DPA 80/20, (○) 0.5/0.5 mm bi-layer system with 20 wt% EPPE and DPA, (●) 0.5/0.5 mm bi-layer system with 10 wt% EPPE and DPA, (△) 1/1 mm bi-layer system with 20 wt% EPPE and DPA.

5. Results and discussions

The objective of the study is to characterize the competition between diffusion and reaction of the two low molecular weight reactants in EVA. For this purpose, we compared the kinetics of the reaction when EPPE and DPA are homogeneously diluted in EVA or when they are initially separated in the bi-layer samples presented in Section 4.1.

From the modelling point of view, the determination of the kinetic constants allowed to calculate the evolution of the conversion versus time for the homogeneous samples (Fig. 4). Now, the mutual diffusion coefficients are also known and thus we have all the parameters necessary to calculate the evolution of the reaction in the bi-layer sample according to the calculation described in Appendix A.

In bi-layer experiments, the reaction and diffusion are concurrent so that the following can be concluded.

1. If the characteristic time of diffusion is very small compared to the reaction time then the concentration profile of the two reagents is rapidly homogenized and the apparent reaction kinetics is the same as that observed in the initially homogeneous sample.
2. If the characteristic time of diffusion is large compared to the reaction time then the reaction will be controlled by diffusion and the apparent kinetics should be slower.

Conversion curves of all the systems studied are depicted in Fig. 5. For the homogeneous system, total conversion is reached in 160 min. But for bi-layer systems, the conversion is 60% to 80% after 240 min of reaction, which shows that the reaction in bi-layer systems is controlled by diffusion.

The evolution of the extent of reaction calculated with the model is satisfactory but not perfect (Fig. 6). Some discrepancies are observed between simulation and experimental

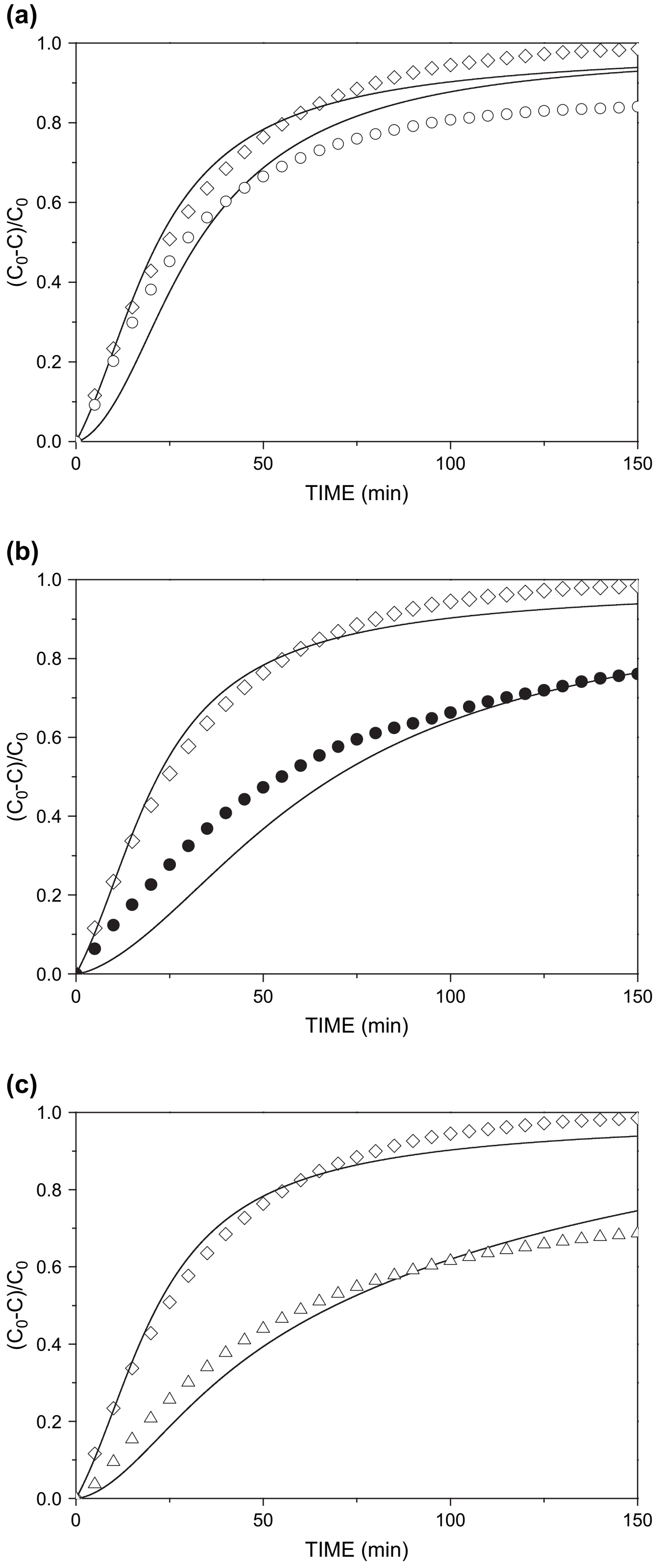


Fig. 6. Comparison between experimental and calculated extents of reaction as a function of time. (◇) Homogeneous EVA/EPPE–DPA 80/20. (a) (○) 0.5/0.5 mm bi-layer system with 20 wt% EPPE and DPA, (b) (●) 0.5/0.5 mm bi-layer system with 10 wt% EPPE and DPA, (c) (△) 1/1 mm bi-layer system with 20 wt% EPPE and DPA. Solid curves represent the calculated extent of reaction.

data, especially at the initial stage of the reaction and also at high conversion. We notice that at the beginning of reaction, the effect of the heating stage in the calorimeter masks the self-catalyzed aspect of the reaction that is clearly visible on the model. Also, for long reaction times, the experimental conversion is lower than the predicted one. This can be attributed to the mode of determination of the extent of reaction by integration of the enthalpy peak that becomes very inaccurate since the reaction is so slow that we attain the limit of sensitivity of the calorimeter. Also, the volume of the layers was considered constant although it may slightly vary since EPPE and DPA are progressively replaced by the product of reaction, C, with a different molar volume.

Concentration profiles of EPPE, DPA and their product of reaction can be computed at different times across the sample. An example of the concentration profile obtained is shown in Fig. 7. Because of the faster diffusion of the amine compared to epoxy, one observes that the reaction zone, characterized by the peak of concentration in the formed product, is deported preferentially in the epoxy-rich zone. This reaction zone evolves towards the right-hand side (epoxy-rich zone) during time. Moreover, because of the catalytic effect of the product, the reaction is accelerated in the epoxy side and the concentration of the product of reaction remains weak in the amine side even after relatively advanced times.

At this stage it is interesting to examine the sensitivity of the simulations to variations of the diffusion coefficient. For that purpose, we divided and multiplied the values of epoxy, amine and product diffusion coefficients simultaneously by a factor 5 and a factor 10 compared to optimized values. The results are presented in Fig. 8. They illustrate well the great influence of the diffusion coefficient and we point out again that this parameter is very difficult to determine accurately. Finally, the values determined in this work seem to describe well the reaction/diffusion behaviour.

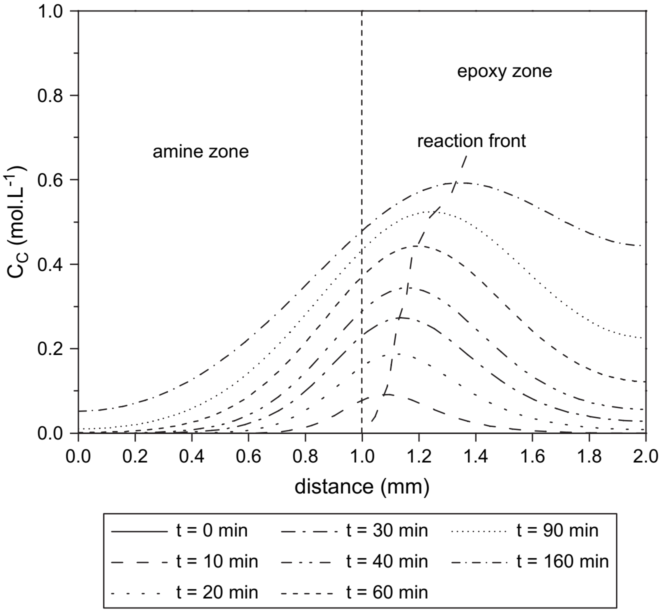


Fig. 7. Local concentration profile of the product of reaction in 1/1 mm bi-layer (20 wt% reactants).

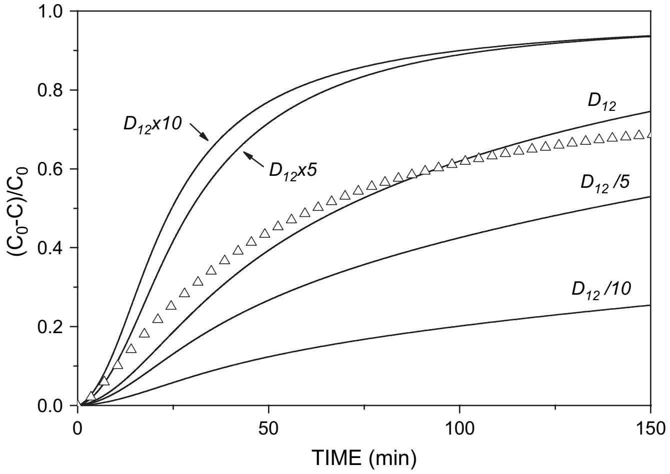


Fig. 8. Influence of the diffusion coefficient value on the simulation of conversion for 1/1 mm bi-layer system with 20 wt% of EPPE and DPA. The diffusion coefficient is multiplied and divided by a factor 5 and a factor 10 (indicated on the curves). (△) Experimental data.

5.1. Application to mixing

In this study a chemical reaction is studied with molecular diffusion being the only mass transfer mechanism involved to put the reactants in contact. In reactive polymer processes, convective mixing in laminar flow is to be considered, especially in the early stages of the process. It is actually possible to relate bi-layer geometry to a simplified vision of the mixing process where two fluids with thickness $e_0/2$, initially separated, are submitted to a shear rate $\dot{\gamma}$ (Fig. 9).

It is thus possible to predict the conversion in a bi-layer assimilated to a system subjected to laminar flow characterized by a shear rate $\dot{\gamma}$ and to see from which thickness of striation the bi-layer reactive system will behave like the initially homogeneous one. For this reason, we simulate the conversion in bi-layers with decreasing thicknesses, until the conversion rate obtained tends to that of the homogeneous sample. The model shows that the conversion in bi-layer system is identical to that in homogeneous system when the layer thickness, δ, is equal to or smaller than 0.25 mm (Fig. 10).

In Table 5, we calculated for every bi-layer thickness the ratio of the characteristic time of diffusion to the characteristic time of reaction (taken here equal to 45 min for a 20 wt% concentration of EPPE and DPA). We identify clearly that for 250 μm thickness, the ratio of the characteristic times is lower than 1 and the bi-layer behaves as a homogeneous system.

The delay with regard to a homogeneous system (calculated for a 60% conversion) is a quadratic function of the thickness.

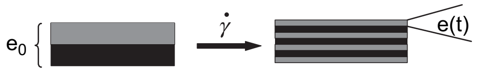


Fig. 9. Simplified vision of laminar mixing with decrease of the striation thickness, $\delta = e_0/2$ in simple shear flow.

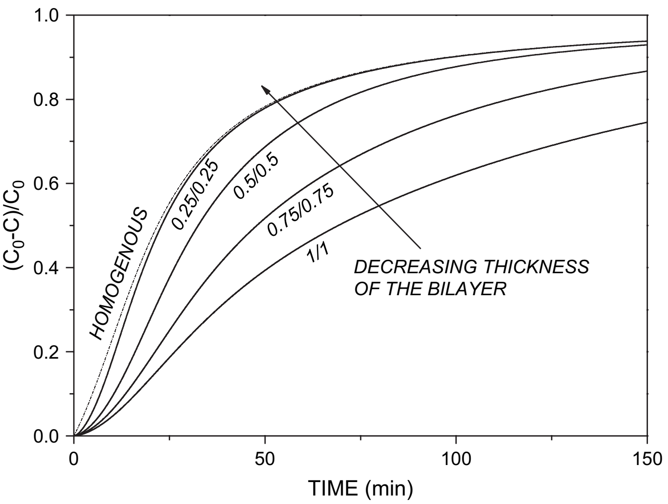


Fig. 10. Simulation of homogeneous and bi-layer systems with different thicknesses. The concentration of EPPE and DPA is 20 wt% (1/1, 0.75/0.75, 0.5/0.5 and 0.25/0.25 mm).

This shows that for the set of used concentrations, the limit of detection of the striation thicknesses is of the order of 250 μm in a pure diffusion case.

In the geometry depicted in Fig. 9, the striation thickness is in fact not constant because the bi-layer is stretched and folded by the shear flow. Besides the coupled diffusion/reaction phenomena presented previously, there is then an advective stretching of the laminae whose thickness $e(t)$ decreases inversely with time and the shear rate [11]:

$$\delta = \frac{2\delta_0}{t\dot{\gamma}} \tag{18}$$

The characteristic time of diffusion in pure diffusion case is given by the following expression:

$$t_\mathrm{D} = \frac{2\delta^2}{D_{12}} \tag{19}$$

In the case of a stretched bi-layer, the characteristic time of diffusion is given by the combination of the two preceding equations:

$$t_\mathrm{M} = \sqrt[3]{\frac{8\delta_0}{D_{12}\dot{\gamma}^2}} \tag{20}$$

Table 5
Comparison of characteristic times of diffusion and reaction as a function of the bi-layer thickness

Bi-layer thickness (mm)	Diffusion time (min)	Diffusion time/ reaction time	Delay with regard to the homogeneous system (min) (at 60% conversion)
0.25/0.25	17	0.38	0
0.50/0.50	70	1.15	12
0.75/0.75	156	3.47	35
1/1	278	6.2	67

The concentration of EPPE and DPA is 20 wt%.

Note that when the striation thickness decreases, the diffusion time subsequently decreases. It is proportional to $\dot{\gamma}^{-2/3}$. This time is that requested to smoothen the concentration profile in the bi-layer and can be considered as a mixing time in a coupled diffusion–convective case. As a practical example, we consider two streams of molten polymer with 1 mm initial characteristic dimension (thickness) containing, respectively, 20 wt% of epoxy and 20 wt% of amine. These molten streams are mixed with the idealized mechanism described in Fig. 9. By considering the respective diffusion coefficients of the reactants at this concentration and a shear rate of $10\ \mathrm{s}^{-1}$, we should reach the homogeneous state in 90–160 s which is short compared to the characteristic reaction time. Nevertheless, this simplified approach cannot be directly extended to the estimation of mixing time in real equipment where the velocity field is very complex.

6. Conclusion

This study leads to several conclusions.

- The difficulties in defining a true model reactive system to characterize micromixing in viscous media were emphasized. Despite the great care taken to select the model system (miscible, absence of secondary reaction, absence of degradation, good temperature control…) it proved to be necessary to adapt the reaction kinetic constants since EVA accelerated the reaction compared to the other solvent (dodecane). Experiments in molten EVA show deviation (acceleration) in auto-catalyzed term compared to bulk epoxy–amine reaction.
- By comparing the rate of reaction measured when the reactants were premixed in a homogeneous sample, or initially separated in bi-layer samples, it was observed that diffusion controls the reaction for the thicknesses tested (1/1 and 0.5/0.5 mm). The conversion of epoxy–amine in bi-layer systems was slower than that in homogeneous system.
- The diffusion/reaction process was modelled and the calculated extent of reaction compared to the experimental data. The apparent rate of reaction being strongly dependent on the diffusion coefficient, a reasonable agreement was found provided that this parameter was determined reliably.
- The model does not integrate mass transport by convective mixing. Nevertheless, with a simplified approach, it has been possible to establish that a relatively low intensity mixing would homogenize the medium so that the reaction is no longer controlled by molecular diffusion. Regarding the fact that this approach underestimates the mixing time compared to real mixers, the used model reaction should be correct for the characterization of mixing especially if we note that the viscosity of the used polymer is quite low, which implies high coefficients of diffusion of the epoxy. Thus we still have the possibility to increase the viscosity of the medium by using higher molecular weight EVA to slow down the diffusion of EPPE. The use of

$$D_{j,\mathrm{n}}\frac{\left(C^t_{j,\mathrm{N}}-C^t_{j,\mathrm{P}}\right)}{\Delta x}-\left(k+k'C^t_{\mathrm{C,P}}\right)C^t_{\mathrm{A,P}}C^t_{\mathrm{B,P}}\Delta x=D_{j,\mathrm{s}}\frac{\left(C^t_{j,\mathrm{P}}-C^t_{j,\mathrm{S}}\right)}{\Delta x}+\frac{\Delta x\left(C^{t+\Delta t}_{j,\mathrm{P}}-C^{t+\Delta t}_{j,\mathrm{S}}\right)}{\Delta t}(\mathrm{A5}) \tag{A5}$$

higher reactivity species is also a solution provided that we are still able to measure the conversion easily and reliably as a function of time.

Appendix. Diffusion/reaction model development

$$\begin{cases}\dfrac{\partial C_\mathrm{A}}{\partial t}=D^\mathrm{A}_{12}\dfrac{\partial^2 C_\mathrm{A}}{\partial x^2}+r_\mathrm{A}\\[2mm]\dfrac{\partial C_\mathrm{B}}{\partial t}=D^\mathrm{B}_{12}\dfrac{\partial^2 C_\mathrm{B}}{\partial x^2}+r_\mathrm{B}\\[2mm]\dfrac{\partial C_\mathrm{C}}{\partial t}=D^\mathrm{C}_{12}\dfrac{\partial^2 C_\mathrm{C}}{\partial x^2}+r_\mathrm{C}\end{cases} \tag{A1}$$

$$r_j(x,t)=\upsilon_j r_\mathrm{c}(x,t),\quad \text{so}\quad \upsilon_\mathrm{A}=\upsilon_\mathrm{B}=-1;\ \upsilon_\mathrm{C}=1 \tag{A2}$$

υ_j is the stoichiometric parameter for species j. We consider $C_\mathrm{A}=C_\mathrm{A}(x,t)$, $C_\mathrm{B}=C_\mathrm{B}(x,t)$ and $C_\mathrm{C}=C_\mathrm{C}(x,t)$ as the molar concentrations of monomers A, B and product C at position x and time t. We assume that C_{j0} is the initial concentration. D^A_{12}, D^B_{12} and D^C_{12} are the mutual diffusion coefficients of A, B and their product C of reaction, respectively.

According to Eq. (A1), an easy numerical solution with explicit finite differences is given for the time dependence of the concentration of each species A, B and C.

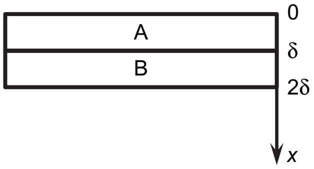


Fig. A1. Bi-layer schematic representation of initially separated A and B reactants considering the one dimensional x orientation of the diffusion. The thickness of each layer is δ.

Thus, there are three initial conditions and two boundary conditions:

$$\begin{array}{ll}C_\mathrm{A}=C_{0\mathrm{A}} & \text{in } [0,\delta]\\ C_\mathrm{B}=C_{0\mathrm{B}} & \text{in } [\delta,2\delta]\\ C_\mathrm{C}=0 & \text{in } [0,2\delta]\end{array} \tag{A3}$$

$$\left(\frac{\partial C_j}{\partial x}\right)_{x=0}=0;\quad \left(\frac{\partial C_j}{\partial x}\right)_{x=2\delta}=0 \tag{A4}$$

The resolution is made in terms of finite volume and in Fig. A2 we present a schematic representation of the integrated volume:

We put

$$a_k=\frac{D_{j,k}\Delta t}{\Delta x^2} \tag{A6}$$

where the diffusion coefficient is calculated at the n or s face of the considered volume (Fig. A2). The mass balance is the following:

$$a_\mathrm{n}\left(C^t_{j,\mathrm{N}}-C^t_{j,\mathrm{P}}\right)+r_j\Delta t=a_\mathrm{s}\left(C^t_{j,\mathrm{P}}-C^t_{j,\mathrm{S}}\right)+\left(C^{t+\Delta t}_{j,\mathrm{P}}-C^t_{j,\mathrm{P}}\right) \tag{A7}$$

with

$$C^{t+\Delta t}_{j,\mathrm{P}}=C^t_{j,\mathrm{N}}(a_\mathrm{n})+C^t_{j,\mathrm{S}}(a_\mathrm{s})+C^t_{j,\mathrm{P}}(1-a_\mathrm{n}-a_\mathrm{s})+r_j\Delta t \tag{A8}$$

To develop an equation system out of the differential equation system (Eq. (A1)), the following linearization is made:

$$r_j\Delta t=\left(k+k'C^t_{\mathrm{C,P}}\right)C^t_{\mathrm{B,P}}C^t_{\mathrm{A,P}} \tag{A9}$$

We make the linearization for each species A, B and C. Conditions at the limits:

- at $x=0$ half a volume
  Assessment:

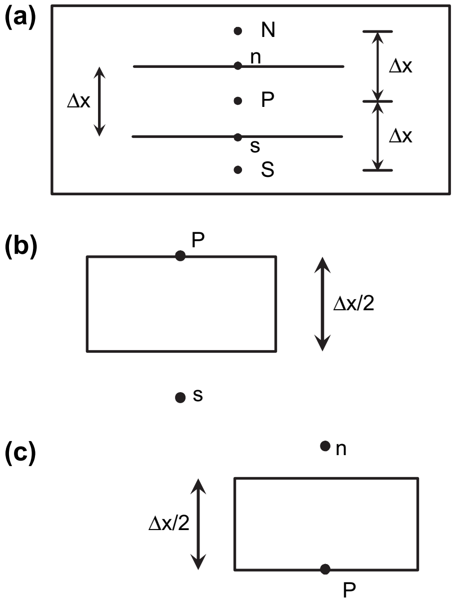


Fig. A2. Schematic representation of (a) integration volume, (b) upper half volume, (c) lower half volume.

$$r_j \frac{\Delta x}{2} = D_{j,\mathrm{s}} \frac{\left(C_{j,\mathrm{P}}^{t} - C_{j,\mathrm{S}}^{t}\right)}{\Delta x} + \frac{\Delta x/2\left(C_{j,\mathrm{P}}^{t+\Delta t} - C_{j,\mathrm{P}}^{t}\right)}{\Delta t} \tag{A10}$$

Eq. (A10) is written like Eq. (A6) but with

$$a_\mathrm{n} = 0; \quad a_\mathrm{s} = \frac{2D_{j,\mathrm{s}}\Delta t}{\Delta x^2} \tag{A11}$$

- at $x = \delta$ half a volume
  Assessment:

$$r_j \frac{\Delta x}{2} + D_{j,\mathrm{n}} \frac{\left(C_{j,\mathrm{N}}^{t} - C_{j,\mathrm{P}}^{t}\right)}{\Delta x} = \frac{\Delta x/2\left(C_{j,\mathrm{P}}^{t+\Delta t} - C_{j,\mathrm{P}}^{t}\right)}{\Delta t} \tag{A12}$$

Eq. (A12) is written like Eq. (A6) but with

$$a_\mathrm{S} = 0; \quad a_\mathrm{N} = \frac{2D_{j,\mathrm{n}}\Delta t}{\Delta x^2} \tag{A13}$$

Eqs. (A10) and (A12) are solved using finite volume method and numerical solution is calculated using Matlab software.

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