THESIS

DIFFUSION AND REACTION OF LOW MOLECULAR WEIGHT
REACTANTS IN MOLTEN POLYMER MEDIUM:
characterization and modelling

Presented at the National Institute of Applied Science (INSA) of Lyon

To obtain the degree of
Doctor of philosophy

(Decree of March 30th, 1992)

Prepared within

ECOLE DOCTORALE MATERIAUX DE LYON

Speciality: Polymer and Composite Materials

By
Redha BELLA

Defence predicted on May 2nd, 2007 before the examination commission:

Jury:

Françoise Fenouillot  Doctor  PhD supervisor
Laurent Falk         Doctor  PhD supervisor
Sandrine Hoppe       Doctor  Referee
René Muller          Professor  Referee
Philippe Cassagnau   Professor  Examiner
Christian Jallut     Professor  Examiner

Redha BELLA, PhD INSA Lyon, 2007
À ma mère
À mon père
PREAMBLE

This work was carried out in the Macromolecular Materials Laboratory (LMM/IMP, UMR CNRS n° 5223) at INSA of Lyon. In addition, this thesis was carried out within the framework of a Contract Program Research (CPR) entitled "reactive extrusion". The PhD was promoted and supervised by Dr. Françoise FENOUILLOT from LMM and Dr. Laurent FALK from LSGC (ENSIC Nancy).

The interdisciplinarity and complementarity of the people involved made possible this project, taking benefits of the experience of LMM in the field of reactive extrusion.

ACKNOWLEDGEMENTS

First of all, I sincerely thank my supervisors to which I return all my gratitude to have guided me during these three years of hard labour. Thank you Françoise to have trusted in me; for your availability and your support especially in difficult moments and how much there was. Thank you, Laurent, for your precious guidance and for your kindness.

I’d like express my thanks to Professor Philippe Cassagnau without whom a great part of this work would never have been born. Large thanks for your assistance, your good mood and your friendship.

I thank also Professor Jérôme Dupuy for his relevant assistance and his councils on the various models developed during this work.

I would also gratefully acknowledge Professor Alain Michel to have made me take part in the reactive extrusion CPR during which the various semi-annual meetings enabled me to meet various industry and academic specialists who will find here my thanks for the interest carried on my work and for their relevant suggestions.

Redha BELLA, PhD INSA Lyon, 2007
I Thank Professor Jean-François Gerard to have accepted me within the laboratory. Thanks to all my colleagues for their good mood and their assistance. Thanks to my office colleagues, Nadir and Elsa, for their kindness. Thank you, Magali, for your support and your friendship.

I do not forget to thank Dr. Sandrine Hoppe, Pr. René Muller and Pr. Christian Jallut who agreed to refer and examine the work presented in this manuscript.

Last but not least, thanks to all those I would have forgotten in spite of me …

To my mother, to my father, to all my family.

Particular thoughts to my died grandmother.
SUMMARY

GENERAL INTRODUCTION

PART A
MIXING / DIFFUSION / REACTION INTERACTIONS WITHIN THE FRAMEWORK OF REACTIVE PROCESSING IN MOLTEN POLYMER

CHAPTER 1. GENERAL BIBLIOGRAPHY

1. REACTIVE PROCESSING OF POLYMERS

2. REACTIVE EXTRUSION AND CHEMICAL ENGINEERING APPROACHES OF THE MIXING, DIFFUSION AND REACTION COUPLING

2.1. APPROACH IN THE FIELD OF CHEMICAL ENGINEERING

2.2. APPROACH IN THE FIELD OF REACTIVE POLYMER PROCESSING

3. OBJECTIVE OF THE STUDY

CHAPTER 2. REACTION AND MORPHOLOGY DEVELOPMENT INFLUENCED BY DIFFUSION IN A THERMOPLASTIC / THERMOSET BLEND

1. INTRODUCTION

2. EXPERIMENTAL SECTION

2.1. MATERIALS AND BLENDS

2.2. DETERMINATION OF THE EPOXY CONVERSION

2.3. OBSERVATION OF THE MORPHOLOGY

2.4. DIFFUSION/REACTION EXPERIMENTS

3. RESULTS AND DISCUSSION

3.1. PHASE SEPARATION IN PS/DGEBA-MDEA THERMOPLASTIC/THERMOSET BLEND

3.2. RHEOLOGICAL BEHAVIOUR

3.3. MORPHOLOGY DEVELOPMENT

4. CONCLUSION

5. PRESENTATION OF THE MODEL SYSTEM

Redha BELLA, PhD INSA Lyon, 2007
CHAPTER 3. DIFFUSION OF LIQUIDS IN MOLten POLYmers: mutual diffusion coefficient dependence on LIQuid mISCIBILITY and polymer molar mass

1. INTRODUCTION
2. DIFFUSION PROCESS
3. DIFFUSION COEFFICIENT
   3.1. Molecular Models for Diffusion
   3.2. Free-Volume Models
4. RHEOLOGY AND MODELLING SCHEME
   4.1. Experimental setup for Diffusion and Rheology
5. EXPERIMENTAL
   5.1. Materials and Samples
   5.2. Viscoelastic Measurements
   5.3. Size Exclusion Chromatography (SEC)
6. RESULTS AND DISCUSSION
   6.1. Diffusion of NEA in EVA Samples
   6.2. Diffusion of EPPE in EVA Samples
7. CONCLUSION

CHAPTER 4. CHARACTERIZATION AND MODELLING OF DIFFUSION AND REACTION OF LOW MOLECULAR WEIGHT REACTANTS IN MOLten POLYmer

1. INTRODUCTION
2. MODELS
   2.1. Mathematical Model
   2.2. Reaction Model
3. EXPERIMENTAL
   3.1. Materials
   3.2. Determination of the Extent of Reaction by Calorimetry
   3.3. Preparation of Homogeneous Samples
   3.4. Preparation of Unpremixed Bi-layer Systems
   3.5. Temperature Homogeneity in the DSC Cell
4. KINETIC AND DIFFUSION DATA
   4.1. Kinetic Model and Constants for the EPPE-DPA Reaction
   4.2. Diffusion Coefficients
5. RESULTS AND DISCUSSIONS
GENERAL
INTRODUCTION
GENERAL INTRODUCTION

During the 30 last years, the industry of polymers reached an enormous growth rate. Because of an accentuated request of the plastics with high added value, the use of extrusion machines as continuous flow reactors for polymers drew a considerable attention. In this context, reactive processing of polymers and more specifically the chemistry of polymers in molten state (such as mass polymerization, polymer modification, reactive blending and compatibilization ...) gains an increasing popularity in the industry and competes with the diluent-free operations with respect to efficiency and economics. However, these reactive processes remain difficult to control because of the number of parameters and the multiple phenomena which can intervene. They present limitations related to the operating conditions in the viscous medium which are often rather drastic and, on the other hand, to the lack of comprehension of these fundamental phenomena.

These restrictions are related to the high viscosity of polymers which must be processed at high temperature in extruders. In this kind of mixers proceeding with continuous flows, the residence times are short and the flow is laminar. The polymer modification requires the introduction of reactive molecules and laminar flow induces a difficulty to mix the reactants at a macroscopic scale (formation of striation, presence of heterogeneous zones...). Also, molecular diffusion on a microscopic scale is slow in molten polymer.

If we examine the fundamental aspects of reactive polymer processing, we note that the basic phenomena implied in the reaction are mixing (mechanical mixing), diffusion and reaction. Furthermore, they are strongly interrelated within the same process. Actually, this feature is valid for any chemical operation in the field of polymers or, more generally, in that of chemical engineering. In the latter case, the coupling of these basic phenomena was largely studied. The objective was to better control the overall process in order to, increase the yield of reaction, avoid undesired products, improve the safety of the operation mode and reduce the cost. This control of the process is approached in chemical engineering by using two different approaches. The first is largely empirical and based on the analysis of a great number of experimental data; from which it is possible to obtain guidelines to optimize and control the process. The second is based on the comprehension of the phenomena and on their modelling and simulation. The ultimate goal of this latter approach could be to obtain a
description of the process realistic enough so that it becomes possible to predict all variables in steady and also in unsteady state.

The same approaches are used in the field of reactive processing but since the history of polymers is much shorter, they are less developed. On the other hand, this field has certain specificities which differentiate it from the field of general chemical engineering because of the high viscosity of the polymeric medium compared with dilute medium. Moreover, the high temperatures used in polymers and the short residence time in extruders, implies a strong reactivity.

The study presented in this manuscript is inspired from the approaches developed in chemical engineering. Our aim is to take an understanding approach to identify the relationships between diffusion and reaction, by using simple model systems in molten viscous medium. The mixing aspects will be simplified considering that the flow field in molten polymers is laminar and produces striations with decreasing thickness.

We have organized the manuscript in two parts. **Part I** is devoted to the background of this study and bibliographic review of reactive processing, chemical engineering approach and a presentation of the complications related to viscous mediums in polymer processing. These difficulties are discussed in a first thermoset/thermoplastic model system. This system has been studied in preceding works ([MEYN 03]; [MEYN 04a]) and the mixing aspect was prospected using a rheological method with a rheomixer device specially developed to study the effect of the mixing in a thermoset/thermoplastic system [CASS 04b]. The same system (which is of complex nature) is used in a complementary step to identify the diffusion and reaction coupling. From this particular example, we illustrate the difficulties related to the definition of a "model" system and the complexity of the interactions between the three phenomena referred above. Key parameters are extracted, as diffusion and reaction prevalence, and discussed in the following of the study.

**Part II** is focused on a simpler model reactive system in which we checked miscibility of small mono-functional molecules with the objective to have a simple reaction in thermoplastic polymers. The ultimate goal of this model system is to decouple the diffusion and the reaction to be able to define *independently* the parameters which govern them (diffusion coefficients, kinetic constants). In fact, we need these parameters to develop a mathematical model and to
simulate the process for our simplified system. Knowing that diffusion coefficients are neither easily measurable nor simply calculable, a specific section of the study is dedicated to determine the diffusion coefficients of our reagents.

After having identified the different parameters and the various coefficients of diffusion which intervene in the mechanism, it appeared interesting to study the coupling between reaction and diffusion in these systems. The experimental follow-up of diffusion/reaction competition was carried out in bi-layer samples designed to take into account the simplified approach of mixing.
PART A

MIXING / DIFFUSION / REACTION INTERACTIONS WITHIN THE FRAMEWORK OF REACTIVE PROCESSING IN MOLTEN POLYMER
CHAPTER 1
GENERAL BIBLIOGRAPHY

SUMMARY

1. REACTIVE PROCESSING OF POLYMERS................................................................. 11

2. REACTIVE EXTRUSION AND CHEMICAL ENGINEERING APPROACHES OF
   THE MIXING, DIFFUSION AND REACTION COUPLING........................................... 13
   2.1. APPROACH IN THE FIELD OF CHEMICAL ENGINEERING ............................... 13
   2.2. APPROACH IN THE FIELD OF REACTIVE POLYMER PROCESSING .................. 15

3. OBJECTIVE OF THE STUDY .................................................................................. 20
CHAPTER 1. GENERAL BIBLIOGRAPHY

1. REACTIVE PROCESSING OF POLYMERS

The reactive processing of polymers grows to be, from few years, an important field of research. Reactive processes technology has, in particular, proven to be one of the most significant new processing of the last two decades. The interest for these processes is traduced by the huge number of applications and the need of new technical materials with new properties which can be generated with reduction of economic costs. These processes are based on a simple idea which is carrying out a modification of the material during the transformation. The industries direct themselves more and more towards this kind of processes because of their facility of use under continuous flow conditions, i.e., chemistry at molten state, and more particularly reactive extrusion. In the same time, it’s a way to avoid the use of solvents/diluents (for environmental considerations). In the same dash, the researchers try to elucidate the phenomena which can intervene in a chemical reactor for polymer processing (such as extruder) for a better control of the process. The reason for this rapid development is captured in one or more of the following points:

- The opportunity to improve and develop new properties to meet specific customer needs;
- The capability to reduce material costs with little sacrifice in properties;
- The ability to improve the processability of materials which are otherwise limited in their ability to be transformed into finished products;
- Permit the much more rapid development of modified polymeric materials to meet emerging needs by passing the polymerization step.

Reactive extrusion has characteristics whose study constitutes an important research orientation in the field of polymers. It is primarily:

1) Transformation temperatures (which can reach 300°C) where the product of the reaction must be stable (no secondary reactions and no unexpected products);
2) The complexity of the rheological behaviour of the involved fluids and strong sensitivity of this behaviour to the thermodynamic parameters (temperature, pressure, shear rate ...);
3) Non-uniform character of temperature and strain fields;
4) Short residence times varying between 0.5 and 5 minutes associated with a reaction that must be fast to reach a maximum yield.

The main objective is to confront with these difficulties and try to establish the relation between the characteristics of used materials (viscosity, crystallinity, solubility...) and the processing conditions. It acts obviously of a strongly interdisciplinary field to the convergence of physics (thermal, physics of polymers...), chemistry (bulk polymerization, grafting, degradation...) and mechanics (rheology, break, tenacity...).

In reactive extrusion, there exist different types of processes depending on the initial properties of used materials (polymer chains, small molecules …) or on the final application of the material (grafting, modification …). We can give as example:

- **Polymerization**: low viscosity small molecules (monomers) with high reactivity and frequently miscible. Then, during the polymerization high evolution of the viscosity (several orders of magnitude) followed, in some cases, by an immiscibility and phase separation of the monomer in the growth chains polymer medium;
- **Grafting and functionalization**: the case of high viscosity media modified using low viscosity reactive molecules. The miscibility is a key parameter;
- **Reactive blending**: case of high viscous multiphase media with high reactivity and molecular weight. In general, the used polymers are immiscible and the reaction intervenes at the interface of the phases. The aim is to target a specified property;
- **Copolymerization**: case of high viscous media in the presence of monomers and catalysts (miscible or not) promoting high reactivity. The reactions operate in heterogeneous media.

Starting these examples, there is still a lack of fundamental understanding of the mechanisms of solubility and diffusion of molecules into polymers at molecular level. Some studies were undertaken to understand the solubility and the transport properties of small molecules in rubbery polymers [ROGE 84]; [CRAN 75]. It is also important to have information on the reaction mechanism and to control it with the objective of optimizing the reactive processes. But that is far from being obvious. It is difficult to quantify the extent of a reaction at various
points along a continuous flow process (in an extruder for example) or at various reaction times in a batch reactor (internal mixer for example). We can add to that, the presence of the several reactive species in separate phases, the difference of mixing modes (laminar or chaotic) and the diffusion limitations which can furthermore complicate the experimental study of this kind of systems.

2. REACTIVE EXTRUSION AND CHEMICAL ENGINEERING APPROACHES OF THE MIXING, DIFFUSION AND REACTION COUPLING

The preoccupations in the field of reactive polymer processing are the same as in other chemical operation from the reactive, diffusive and mixing points of view. It seems interesting to see how chemical engineering researchers are confronted to these problems (although the problem of viscosity is not very important in these processes) and to consider their approaches to resolve these problems.

2.1. Approach in the field of chemical engineering

The objectives in polymer reactive processing are similar to those encountered in chemical processing; the perfect control of the process leading to well defined products and high yield of reaction seems to be the main goal to achieve. Chemical engineering is an “old” research domain where several approaches are implemented to reach this “control of the process”. Two approaches are largely used in chemical engineering to describe the whole phenomena that may take place in reactive medium.

The most elaborate and, in the same time, the most difficult is the global approach in which a modelling of the whole process is implemented. And so flows, mixing, diffusion and chemical reactions are taken into account to acquire a global and complete description as perfect as possible of the process. The main difficulty in the calculation and design of homogeneous chemical reactors lies in the estimation of reactions extents when these reactions are linear or none linear taking into account turbulent flows and fast diffusion processes. Many research works have been developed on this domain and especially for the calculation of reactors efficiency. This efficiency is associated to the process control that is strongly related to mixing process. For this, definitions of characteristic time of mixing, including macromixing, mesomixing and micromixing has been identified and included below the characteristic time.
of the process. As shown in Figure 1.1, the classification of the mixing of miscible fluids is done at three length scales:

**Macromixing** occurs on the scale of the vessel;

**Mesomixing** occurs on the scale of the turbulent eddies;

**Micromixing** occurs on the scale of molecular diffusion in stretching fluid lamellae.

---

![Fluid mixing processes following the cascade of turbulent energy from large to small scales](image)

Examples of sensitive processes initiated by the combination of two fluid streams include precipitation by reaction or anti-solvent addition at high super saturation (Pohorecki and Baldyga, [POHO 83]; Garside and Tavare, [GARS 85]; Marcant and David, [MARC 91]; Mahajan and Kirwan, [MAHA 96]; Baldyga and Bourne, [BALD 99]). In all of these cases, the process kinetics and resulting product quality can be determined by the rate and intimacy of contact between two initially separated fluids.

The second approach, and also at first sight the relatively simplest one, is implementation of test reactions systems like consecutive or parallel competitive reactions. The aim is to experimentally characterize the degree of segregation of the mixture. Actually, these competing reactions act as a tracer revealing the state of segregation of a mixture. Some definitions on consecutive parallel reactions, consecutive competitive reactions systems and the segregation index are given in appendix A. As examples of fast competitive reactions or
competitive and consecutive reactions: Baldyga and Bourne, [BALD 90]; Bourne and al., [BOUR 90], [BOUR 92]; Bourne and Yu, [BOUR 94].

Between these two extremes, there are intermediate approaches whose are more or less experimental or model approaches.

2.2. Approach in the field of reactive polymer processing

In reactive extrusion, we seem less advanced than in chemical engineering. The reason is that this field of research is “young” compared to chemical engineering. Reactive extrusion differs from the traditional processes of the chemical industry on several aspects: difficulties in heat and mass transfer (low thermal conductivity, quasi absence of convection, laminar mixing and low coefficients of diffusion, difficult miscibility). In reactive extrusion, the high viscosity of the reactive medium implies laminar flows and mixing mechanisms of reactants. Some relevant approaches where developed, taking into account the cited difficulties, for practical and comprehensive goals.

A first approach tries to model the process as a whole by calculating flows in the extruder and by superimposing the reaction (in general without diffusion). The modelling of extruders follows different schemes, 1D, 2D or 3D, depending on the global complexity of the process and the geometry of screw elements considering reactive (reactive extrusion) or non reactive (polymer mixing) polymer systems.

For 1D simulation, in an internal mixer, steady state mixing between a monomer acting as a plasticizer (ε-caprolactone) and a molten polymer (polycarbonate) has been modelled using an analogy between internal mixer and so called Double-Couette flow [ADRA 06]. In this work, the diffusion of small molecules into the molten polymer and also the rotors action in the mixing process have been identified.

In other way, Vergnes [VERG 98] proposed a global computational model (LUDOVIC software) for co-rotating twin-screw extruder. This simulation was successfully developed to reactive systems [VERG 04]. More specifically, crosslinking of a dispersed phase in PP major phase [DELO 96], controlled degradation of PP ([BERZ 00]; [BERZ 06]) and polymerization of ε-caprolactone [POUL 01] in twin-screw extruder were investigated by simulation. In a
same way, Zagal et al [ZAGA 05] developed a mathematical model for the reactive extrusion of methyl methacrylate in a co-rotating twin-screw extruder.

For 2D simulation, the group of Prof. White (Akron, USA) has developed ([WHIT 94]; [WHIT 01]) a global computer software (Akro-Co-Twin Screw) of this model for intermeshing co-rotating twin-screw extruder. These model and software have been successfully applied to reactive extrusion applications. As for example, Kye and White [KYE 96] simulated the anionic polymerization of caprolactam, Kim and White [KIM 97] and Keum and White [KEUM 05] successfully studied the simulations of grafting monomers and associated degradation of polypropylene.

For other considerations, 3D simulations are very accurate but complex and high time consuming. Note that this type of approach is necessarily limited to a small section of the extruder, and to screw elements that are totally filled. As example, Zhu et al [ZHU 05a] introduced a 3D model to predict the polymerization of $\varepsilon$-caprolactone in fully filled screw elements. In a same way [ZHU 05b], they also used a commercial CFD package (FLUENT 6.0).they demonstrated that in 3D considerations, in contrary of 1D models, the non-uniformities in temperature, deformation and conversion are accurately captured in the 3D modeling, whereas they are assumed to be uniform in 1D simulations.

A second approach more empirical and experimental tries to identify trends and gain a certain comprehension by carrying out series of experiments in extruders (considering the whole extruder as black box). The flow and the mixing of reactive systems inside extruders are described with the help of the residence time distribution (RTD) and by identifying significant and relevant parameters of the model estimated from RTD data obtained with tracer. Different basic models inspired from chemical engineering are generally used: the plug flow model, the non-segregated and totally segregated axial dispersion models, cascade of model reactors selected to describe the different sections of the extruder. Modeling of urethane ([SEMS 04]; [PUAU 06]) and styrene [GAO 04] polymerizations and reactive modification of high density polyethylene HDPE [THOM 95] have been investigated from these global models. Nevertheless, they all consider isothermal flow, a strong limitation to reactive processing of high viscous media.
Another approach, also inspired from chemical engineering domain and more global, is based on the use of model reactions in molten and viscous media. The idea is to engage parallel consecutive or competitive reaction with/in the polymer in the presence of mixing and to measure the segregation index.

The competitive reactions need to fulfil various criteria to be valid for mixing characterization:

- The kinetics of the two reactions must be significantly different (from a factor 100);
- The influence of the mixing must be significant;
- The product of reaction must be easy to analyze;
- The experimental procedure must be simple with good repeatability;
- The reactants and products must be soluble in the viscous reactive medium.

Since the concept of competitive reactions for studying mixing was developed for chemical engineering, we find in literature that most parallel reaction systems studied are done in low viscosity homogeneous media, aqueous or organics ([FOUR 96a]; [FOUR 96b]; [GUIC 00a]; [GUIC 00b]). Very few authors apply a micromixing approach using parallel consecutive or competitive reaction in viscous systems ([BOUR 95]; [BALD 98]; [GUIC 97]). However, the maximal viscosity reached in such systems (< 300 mPa.s) is less than we can observe in molten viscous media. Also, most of the time, the polymer is constituted by a polar hydrophilic polymer ([BALD 98]; [GUIC 97]) dissolved in water and mixed at ambient temperature. The studies on apolar polymers at high temperature are even less numerous. The study undertaken by Köster and al. [KOST 01] discussed a reactive extrusion process whereby degraded polypropylene grafted with maleic anhydride PP-g-MAH chains are extended again by chain coupling through a 1,12-diaminododecane diamine. This leads to branched clusters of PP-g-MAH chains. Crosslinking occurs, too, but only on a local level. This system brings closer a system of competitive consecutive reactions where a quality of mixing can be calculated. The principle is that at a given moment t, some molecules of the diamine will have reacted to both end of chain. Thus, Theoretically 70 % of MAH functions should have reacted. But, in experiments, only the 2/3 of 70 % reacted. Therefore, the product roughly has 40 % of functions amide or imide and 60 % of non reacted MAH functions.
Frey and al. [FREY 88], proposed imidization parallel consecutive reactions system for micromixing study in molten polyethylene. The problem with this system is that the reaction is initiated at low temperatures and miscibility was not investigated.

Thus, micromixing studies are applied with success to characterize mixing in chemical engineering but they are rarely reported for polymers, we have attempted to adapt the concept and to develop our own model system based on the amine functionalization of a maleic anhydride-grafted poly(styrene)-block-poly(ethene-co-1-butene)-block-poly(styrene) (SEBS-g-MAH). A large excess of a diamine was added to the molten polymer varying from 0.1 to 0.9 in stoechiometry. The stoechiometric ratio was calculated using equation 1.1.

\[
r = \frac{n_{SEBS}}{n_{diamine}} = \frac{m_{SEBS}}{m_{diamine}} \cdot \frac{M_{diamine}}{M_{SEBS}} \cdot \frac{10.2}{2}
\]  

(1.1)

where \(n_{SEBS}\) and \(n_{diamine}\) are the numbers of moles in reactive functions of SEBS and diamine, \(m_{SEBS}\) and \(m_{diamine}\) masses of SEBS and diamine and \(M_{SEBS}\) and \(M_{diamine}\) the molecular weights of SEBS and diamine. With this system, we carried out many tests not described in the manuscript since not directly profitable, but they were enriching and they directed our following research. The amine was added in the molten SEBS-g-MAH in the chamber of an internal mixer. Depending on the local concentration if diamine in SEBS-g-MAH, that is on the state of segregation, the reaction of the diamine with MAH leads to the functionalization of the polymer chains and to a fraction of crosslinked polymer (figure 1.2.).
Figure 1.2. Anhydride diamine reaction

The proportion of gel (crosslinked polymer) depends on the local concentration of the diamine. More precisely, the zones where the amine is in small excess will crosslink whereas those highly concentrated are functionalized. Here, the idea is that the proportion of gelled SEBS will reflect the state of mixing. We have varied the rotation speed of the rotors of the mixer for a constant mixing time and the gel fraction was measured (see table 1.1.)

Table 1.1: insoluble fraction of SEBS and reacted fraction of MDEA (mixing time: 30 min).

<table>
<thead>
<tr>
<th>Rotation speed (rpm)</th>
<th>Fraction of insoluble (%)</th>
<th>Reacted fraction of amine (%)</th>
<th>Set temperature 200 °C</th>
<th>Temperature of the melt (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>55</td>
<td>65</td>
<td>218</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>40</td>
<td>52</td>
<td>224</td>
<td></td>
</tr>
<tr>
<td>130</td>
<td>33</td>
<td>46</td>
<td>230</td>
<td></td>
</tr>
</tbody>
</table>

Several problems arise to define correctly our model system. It is difficult to find reactants miscible with the polymer. Also, the characterization of the insoluble fraction and of the free diamine appeared to be tricky but these are not the more important points.
In table 1.1, one can note that the actual temperature of the molten SEBS, measured directly in the melt, differs strongly from the set temperature due to the heat dissipation. Also, in high viscosity polymers the temperature shift depends strongly on the shear (that is on the rotor speed). This is obviously a problem since the reaction mechanism may be affected by the temperature change and on the other hand, the viscosity of the melt will change. The critical point here is that objectively we cannot attribute the change of the insoluble fraction to a change in the degree of segregation without having checked that the reaction mechanism doesn’t depend on the temperature.

More generally, this problem will always exist with molten polymers (except with low viscosity) and we believe that it actually makes difficult (almost impossible) to define a real model of competitive reactions adapted to polymers. This approach was not continued.

3. OBJECTIVE OF THE STUDY

Without being able to describe all works, we note that in molten viscous media, the coupling of mixing / diffusion / reaction was approached little or seldom. The mixing mechanisms in extruder are extremely complex. This complexity is due to the coupling of processes by themselves complex (mechanical mixing, molecular diffusion and reaction) and on the other hand to the 3 dimensional velocity field existing in such a machine. Numerical simulation may be very helpful for the understanding and optimisation of mixing/reaction operations. However, the calculation of reactive flows is not easy because the reaction takes place at the molecular scale and it is necessary to represent mathematically the reactive processes at such a scale with a very small scale of resolution.

Experimentally, there is a lake for representative reactive systems (high viscosity, polymer medium), allowing to implement model experiments necessary to better understand the phenomena and confront them to simulations.

The objective of this thesis is to propose such a model system from which we will determine the characteristics and where the decoupling of the fundamental phenomena will be carried out and each phenomenon studied individually. The diffusion will be studied and the relevant parameters will be identified taking into account the polymer/liquid interaction parameters. In a second step, the coupling of the diffusion and reaction will be studied and modelled. We
wish also to highlight that this study was conducted with two complementary approaches: experimental and modelling.

We have seen that numerous situations exist in reactive processing and thus the approach cannot be the same for all cases. There we will focus on the reaction of low molecular weight species, miscible in a viscous molten polymer.
CHAPTER 2
REACTION AND MORPHOLOGY DEVELOPMENT INFLUENCED BY DIFFUSION IN A THERMOPLASTIC / THERMOSET BLEND


SUMMARY

1. INTRODUCTION .............................................................................................................. 26

2. EXPERIMENTAL SECTION .......................................................................................... 27
   2.1. MATERIALS AND BLENDS .................................................................................... 27
   2.2. DETERMINATION OF THE EPOXY CONVERSION .............................................. 27
   2.3. OBSERVATION OF THE MORPHOLOGY .............................................................. 27
   2.4. DIFFUSION/REACTION EXPERIMENTS ............................................................... 28

3. RESULTS AND DISCUSSION ......................................................................................... 29
   3.1. PHASE SEPARATION IN PS/DGEBA-MDEA THERMOPLASTIC/THERMOSET BLEND .......................................................... 29
   3.2. RHEOLOGICAL BEHAVIOUR ................................................................................. 29
   3.3. MORPHOLOGY DEVELOPMENT ............................................................................ 32

4. CONCLUSION ................................................................................................................... 36

5. PRESENTATION OF THE MODEL SYSTEM .................................................................. 36
CHAPTER 2. REACTION AND MORPHOLOGY DEVELOPMENT INFLUENCED BY DIFFUSION IN A THERMOPLASTIC / THERMOSET BLEND

This section presents the work done to analyze the relation between diffusion and reaction. It illustrates the difficulties encountered to define a model system; also the complexity of the interactions between the phenomena is emphasized.

On the basis of what was presented in the bibliographic section, we highlight the interactions between diffusion and reaction of small molecules in a viscous medium. More precisely, in this chapter, we examine the competition of diffusion and reaction with the help of a reactive system that was extensively studied and characterized in our research group. This system is a blend of two monomers (diepoxy and diamine) initially miscible in high viscosity polystyrene. The chemical reactivity, the thermodynamic (phase separation), the morphology and rheological properties evolution of this system have been extensively characterized ([MEYN 03]; [MEYN 04a]; [MEYN 04b]; [MEYN 05]; [RICC 04a]; [RICC 04b]; [TRIB 07]). Here the polymerization of the monomers and their crosslinking is followed by rheology since the reaction induces a drastic increase of the viscosity. The morphology of the blend is characterized. It is controlled by complex dissolution and phase separation phenomena of which a description will be given.

We hope, after this study, identify the key parameters of the phenomena which can intervene in so complex systems.
1. INTRODUCTION

Chemical reactions in molten polymers and blends many often involve the introduction of low molar mass organic molecules. The examples are numerous: the chain extension of polycondensates as polyamide and polyester, the grafting reactions on polyolefines, the polymerization of monomers and copolymers in the molten state, the crosslinking of thermoplastic vulcanizates. Depending on the application, the low molar mass organic molecules may be a chain extender, monomers, an initiator, a catalyst.

The keywords that describe reactive mixing process involving small molecules are: miscibility, mixing, diffusion, reaction. Most often, the miscibility of the components of the reactive system is not characterized in detail since it is not an easy task at high temperature; it is sometimes approached by comparing the solubility parameters of the components. The molecular diffusion is more studied and numerous authors aim to calculate the coefficient of diffusion with the help of diffusion theories such as the free-volume theory [COHE 59]. On the other hand, the diffusion of low molar mass molecules in molten polymers is studied experimentally in the scope of the diffusion of solvent and the plastification of rubbers, but more rarely for the purpose of achieving a chemical reaction ([VREN 77a]; [HONG 95]; [ZIEL 92]; [JOUB 02]). The mechanisms of mixing in molten polymers have focused the attention of the researchers for a long time, in both experimental and theoretical aspects but it is still difficult to predict the evolution of the heterogeneity of a molten mixture ([TADM 79]; [CHEL 85]; [SCOT 96]; [CASS 04a]; [CASS 04b]).

The justification of such studies is that when a low molar mass molecule is involved in a reactive process with molten polymers, the miscibility of the low viscosity reactant, its rate of mixing, diffusion and reaction can play a determinant role for the production of the desired macromolecular structure, especially when the chemical reaction involved is sensitive to the stoichiometry or to heterogeneities of concentration [CASS 99].

The context of the present work is what is generally called reactive processing. The objective is to investigate the complex relations between diffusion and reaction in experimental conditions where no mechanical mixing is imposed. We examine the effect of diffusion on the reaction of small organic molecules miscible in a molten polymer matrix. The polymer is
CHAPTER 2: REACTION AND MORPHOLOGY DEVELOPMENT INFLUENCED BY DIFFUSION IN A THERMOPLASTIC/ THERMOSET BLEND

polystyrene, the reactants are a diepoxy and a diamine. It is a system that we have studied in detail previously in the context of the elaboration of thermoplastic/thermoset blends and that is used here for a different objective ([MEYN 04a]; [RICC 04a]).

2. EXPERIMENTAL SECTION

2.1. Materials and blends

A polystyrene (PS) Lacqrene 1450 N was supplied by Atofina. The epoxy was a diglycidyl ether of bisphenol A (DGEBA) with a degree of polyaddition of n=0.15, supplied by Bakelite. The diamine was 4,4’-methylenebis [2,6-diethylaniline] (MDEA) supplied by Lonza. The global composition of the blend studied was 60 wt % of PS and 40 wt % of epoxy/amine thermoset precursors. Two non reactive mixtures were prepared by extrusion, PS/DGEBA 50/50 wt% and PS/MDEA 73/27 wt%. A PS/DGEBA-MDEA 60/40 blend was also prepared in a batch mixer at low temperature (T=80°C) in order to limit the reaction.

2.2. Determination of the epoxy conversion

The conversion of the epoxy groups of the DGEBA-MDEA mixture, $x_e$, was measured in-situ in the near infra-red spectrometer (equinox 55 from Brucker) thermoregulated cell. The area of the absorption bands at 4530 cm$^{-1}$ (epoxy) and 4623 cm$^{-1}$ (phenyl) were used to calculate the conversion with the following relation:

$$x_e = 1 - \frac{A_{4530}/A_{4623}}{A_{4530}/A_{4623}}_{t=0}$$

2.3. Observation of the morphology

Scanning electron microscopy (SEM) was performed with a Philips XL 20 microscope in order to visualize the morphology. The samples were prepared by cryogenic fracture and gold plated.
2.4. Diffusion/reaction experiments

In order to study the influence of the diffusion of epoxy and amine monomers on the morphology development and rheological behaviour of the reactive blend with PS, two different preparations of the sample test were experienced. The principle of these experiments is shown in figure 2.1.

A) The first one is a unique layer of homogeneous PS/DGEBA-MDEA blend. In the present case we assume a homogeneous initial blend of epoxy and amine monomers in PS; at least we suppose that the concentration in reactants at a micro-scale is at the stoechiometry. The case A is actually the reference corresponding to an homogenous concentration of reactants in molten PS matrix.

B) The second one is a two layers sample constituted of PS/DGEBA layer and PS/MDEA. Each layer is not reactive unless it is mixed or put in contact with the other one. The thickness of the polymer discs was adjusted in order to respect the epoxy-amine stoichiometry and the global composition of the blend. Only the total thickness varied in order to emphasize the diffusion control of the reaction.

From an experimental point of view, the measurements were performed on a Rheometrics Mechanical Spectrometer (RMS 800) at a constant temperature of 177°C and a constant frequency of 1 rad.s\(^{-1}\). The geometry used was parallel plates with a diameter of 25 mm. The strain was adjusted all along the experiment from 400% at the beginning of the experiment to 1% at the end in order to remain in the linear domain of the viscoelasticity while having a good sensitivity of the torque.

![Figure 2.1. Scheme of the experimental set up.](image)

A) Homogeneous reactive medium B) Non homogeneous reactive medium.
3. RESULTS AND DISCUSSION

3.1. Phase separation in PS/DGEBA-MDEA thermoplastic/thermoset blend

Previous work on the same system have shown that initially, before the reaction of the epoxy groups with amino groups, the phase diagram of PS with the monomers is Upper Critical Solution Temperature (UCST). The reactants are soluble in the PS at the experimental temperature of 177°C. Then, the polymerization induces a phase separation of the epoxy-amine oligomers. The morphology evolution is controlled by factors such as initial miscibility, TP concentration, reaction rate, viscosity and interfacial tension. The particles grow during the period from 20 to 55 min. Then, their growth rate decreases leading to a final diameter of 2.8 µm. Their shape remains spherical during all the overall curing process. At the end of the reaction the blend is composed of a pure PS matrix containing micron sized crosslinked epoxy-amine particles in the polystyrene matrix upon curing [MEYN 04a].

3.2. Rheological behaviour

Considering now the viscosity of the system, the miscibility of the two low molar mass molecules with PS leads to a low viscosity, low glass transition temperature blend before the polymerization (Tg=−20°C). Upon their reaction, the monomers phase separate, diffuse out of the PS-rich matrix and form gelled particles so that the progress of the reaction is accompanied by an increase of the glass transition temperature of the individual phases, and thus an important increase of the viscosity ([MEYN 04a]; [RICC 04a]). Therefore, the evolution of the viscosity permits to follow the global epoxy conversion rate. On other hand, the biphasic structure formed may bring us information about the progress of the reaction at a local scale.

Figure 2.2. represents the increase of viscosity measured for a homogeneous sample (situation A in figure 2.1.), and bi-layer samples with different thicknesses (situation B in figure 2.1.). For the initially homogeneous blend, the polymerization is finished after about 80 minutes as can be deduced from the stabilization of the viscosity. The corresponding average conversion of the epoxy groups was determined in a previous work and found equal to 95 % [MEYN 04a].
The reaction is slower for the bi-layer system as one can observe from the slower rise of the viscosity with time. Moreover, the reaction appears to slow down with time. At the beginning, the evolution of the viscosity in both cases is identical but the reaction in the bi-layer situation is slower and slower. This indicates that the diffusion of the monomers and oligomers is limiting the progress of the polymerization and that diffusion is controlling the reaction. As expected in case of a diffusional limitation, the effect is even more marked when the global thickness of the sample increases.

To verify that, we compare the characteristic times of diffusion of the monomers with the characteristic time of reaction of the DGEBA with MDEA at 177°C, the ideal experiment would have been to measure the rate of diffusion of each monomer in a mixture of PS with the other monomer. For instance measure the diffusion of MDEA in a layer of PS/DGEBA seeing that it is more representative of the actual situation. This is obviously not a realistic experiment since DGEBA and MDEA are reactive and the diffusion process will be perturbed by the reaction. This is the reason why we have simply characterized the diffusion of the
DGEBA and of MDEA at 177°C in neat PS. We have measured the changes in viscosity of a sample constituted of a layer of PS and a layer of monomer. The initial viscosity measured before the diffusion starts reflects the properties of the less viscous layer: the liquid monomer. During the diffusion process, the concentration of small molecule into the polymer increases and a concentration gradient establishes which induces an increase of viscosity until the concentration is constant across the sample and the viscosity stabilizes. The technique is described in the paper of Joubert et al. [JOUB 02]. The thickness of the polymer layer was chosen in the same order of magnitude than the one used for the reactive experiments presented in figure 2.3, since the distance of diffusion determines the time of diffusion.

Figure 2.3. Evolution of the viscosity with time of a sample constituted of a lower layer of PS and an upper layer of monomer (▲: DGEBA, ■: MDEA). The thickness of each layer is 0.8 mm. Temperature = 177°C. Frequency=10 rad s⁻¹.

Actually, we are aware that the rate of diffusion of the monomers is overestimated since the PS is pure, nevertheless it gives orders of magnitude and it allows comparing the behaviour of the two monomers. Also, one important feature is that during the reactive diffusion experiment the monomer are not only diffusing, they are also reacting and their molar mass is increasing. Actually, if we want to account for the overall transport processes, we should
consider the diffusion of all the chemical species, monomers and oligomers. We can imagine that a monomer molecule that is diffusing in the reactive medium is progressively slow down when its molar mass rise at each reaction step of its epoxy and/or amino groups so that the diffusion rate of all the reactive species is much lower than that of the unreacted monomer.

The characteristic time of reaction is determined more easily than the diffusion time, by following the disappearance of the epoxy groups of a mixture of DGEBA with MDEA where the stoichiometry in epoxy and amino groups is respected (figure 2.4.). The polymerization is complete after about 50 minutes.

![Graph showing the conversion of epoxy groups](image)

**Figure 2.4.** Evolution of the conversion of the epoxy groups of a stoichiometric mixture of DGEBA with MDEA polymerized at 177°C.

The conclusion is that for our blend and for the dimensions of our reactive samples the reaction process is faster than the diffusion process and then is controlled by the diffusion.

### 3.3. Morphology Development

A picture of the morphology formed after the polymerization of the epoxy in sample A (homogeneous) is shown in figure 2.5. The final structure is a dispersion of spherical
crosslinked epoxy particles with an average diameter around 3 µm.

Before analyzing the morphology more in details, we have checked that the measurement in oscillatory mode was not influencing the structure of the blend. In other words, the dynamic deformation should not perturb the mechanisms of relaxation. We have compared the morphology obtained after the rheological experiment to that obtained in a oven in the absence of any shear and they were identical, with epoxy-amine particles of 3 microns average diameter (compare picture a and b in figure 2.5.). Therefore, no break up or coalescence was produced under linear deformation in dynamic shear test. Actually, this result was expected in the domain of linear viscoelasticity.

![Morphology obtained after the polymerization of the epoxy in the PS/DGEBA-MDEA 60/40 blend at 177°C. a) homogeneous sample polymerized in the rheometer and submitted to oscillatory shear at 1 rad s⁻¹ and a deformation ranging from 400 to 1 %, b) homogeneous sample polymerized in a oven.](image)

The pictures taken across the sample of 1.6 mm thickness are grouped in figure 2.6. We observe a gradient of morphology across the sample. The larger diameter particles are present in the middle of the PS/DGEBA layer (picture d). At the interface between the two layers (picture c), where the concentration of monomers is rapidly established, it is not surprising that the morphology is similar to that obtained for the homogeneous sample. Besides, on the amine-rich side, near the rheometer upper plate, a low amount of very small particles is formed (picture a). On the epoxy-rich side, near the rheometer lower plate, the particles are bigger (2 to 5 µm) with a stronger interface; the particles were not pulled out the PS matrix (picture e). This was observed previously and is representative of a sample with an intermediate epoxy conversion around 50-60% [MEYN 04a].

Redha BELLA, PhD INSA Lyon, 2007
The morphology observed near the plates (figure 2.6. a and e) is typical of a regions where the conversion in monomer is low. These two regions are far from the interface and the monomers and oligomers did not have sufficient time to diffuse. Thus, the existence of a gradient of morphology starting at the interface and going to the external sides of the sample is easily explained by the necessity of the diffusion of the monomers in order to react and consequently phase separate.
A second interesting point is that the micrographs of the middle of the PS/amine and PS/epoxy layers are different from each other: smaller particles (< 2 µm) are present in the PS/amine layer, compared to 5-8 µm in the PS/epoxy side (pictures b and d). As a matter of fact, an asymmetric gradient of morphology is observed with larger diameter particles in the PS/epoxy side. The asymmetry of the gradient is not so easily interpreted since several reasons may be proposed to account for this asymmetry. First of all, a faster diffusion of the amine in the PS/epoxy than the diffusion of the epoxy in the PS/amine side would lead to such an asymmetry. The data presented previously in figure 2.3 demonstrate that DGEBA is diffusing slower than MDEA in pure PS. However, it is important to remind that in the conditions of diffusion described in figure 2.1., the DGEBA is not diffusing in pure PS but in a mixture of PS/MDEA 73/27, and MDEA is diffusing in a mixture of PS/DGEBA 50/50. Thus the MDEA, actually diffuses in a more "diluted" mixture than the DGEBA and we may hypothesize that the differences in diffusion rate between DGEBA and MDEA will be even greater for the actual experimental conditions, the epoxy diffusing much slower.

A second explanation for the asymmetric gradient is linked to the miscibility of the monomers. The MDEA is miscible with PS at 177°C and also at room temperature while DGEBA is only miscible above 120°C [RICC 04a]. The more favourable thermodynamic interaction in the amine side may lead to a phase separation at a higher monomer conversion and thus smaller particle.

The third explanation may be the lower viscosity of the PS/DGEBA mixture compared to the PS/MDEA. The modulus of the complex viscosity at 177°C has been measured. At 1 rad. s\(^{-1}\), it is equal to 30 Pa.s for the PS/DGEBA mixture and 200 Pa.s for the PS/MDEA mixture. The viscosity of the medium where a phase separation develops has a great influence on the size of the particles formed. The lower the viscosity is, the bigger the separated domains are.

It is tricky to establish what factor is responsible for the asymmetric gradient of particle size since the effect of the three reasons presented above would produce the same qualitative effect that is bigger epoxy particles in the epoxy side of the sample.
4. CONCLUSION

We have examined how the diffusion process of miscible thermoset precursors in a thermoplastic polymer may influence their apparent polymerization rate and the development of the morphology of the resulting thermoplastic/thermoset blend. The relation between the reaction rate and the diffusion rate of two monomers in polystyrene matrix was emphasized by comparing their characteristic times of reaction and diffusion. Actually, depending on the dimension of the sample studied, the reaction rate may be limited by the diffusion process of the monomers and oligomers. As a consequence of the diffusional limitation, a gradient of morphology is obtained across the by-layer samples. However the asymmetricity of the gradient is difficult to attribute with certainty to one of the three determinant parameters that we have identified: a higher rate of diffusion of the MDEA in the PS/DGEBA side compared to the diffusion of the DGEBA in the PS/MDEA side, a phase separation occurring at lower conversion in the PS/DGEBA due to the less favourable interactions between PS and DGEBA and a lower viscosity of the PS/DGEBA side.

This part of the work illustrates very well the complications that we can meet in such complex systems. The definition of a simpler reactive system (without phase separation) and also the decoupling of the diffusion and reaction processes from any other phenomenon appear to be a necessity.

5. PRESENTATION OF THE MODEL SYSTEM

After having seen the difficulties to find a system from which we can deduce reliable interpretations of the phenomena, we can identify and list the important criteria for the choice of such system:

- The reactants must be miscible in the polymer;
- The reaction mechanism must be simple and unique (no secondary reactions, no alternative mechanism);
- Only one product must be formed and the product must be miscible in the polymer;
- The kinetic of the reaction must be easy to follow and characterize.
We have decided to use a simple reaction epoxy amine system with monofunctional molecules. The condition is that these molecules must be miscible in the used polymer in the range of used temperatures. This reaction will be implemented in different grades of poly(ethylene-co-vinyl acetate) polymers (EVA). The choice of such polymer is justified by the large range of molecular weight grades and the capacity the see the influence of chain lengths on the diffusion coefficients. Also, EVA can solubilize a variety of small reactants.

In the first section of this part, we will determine diffusion coefficients using free volume theory and rheological experiments. This method requires data on materials properties such as the density or viscosity according to the temperature, the thermal expansion coefficients above and below $T_g$ and the constants of the Williams-Landel-Ferry (WLF) equation. Other parameters can be estimated from free volumes at equilibrium which must be calculated from the groups’ theory.

In the second section, the reaction parameters will be calculated and a model of coupled diffusion reaction model will be developed. The effect of the mixing action is usually analyzed in the two different categories of distributive and dispersive mixing (appendix C). We will take into account the mixing effect by a multi-layers geometry ([BOUQ 05]; [SERR 05]; [ORR 01]; [TADM 79]). This geometry has been chosen because of the analogy with the laminar flow that can occur in extruders. In what follows, we’ll try to give some elements to describe mixing mechanism in viscous fluids.
PART B

CHARACTERIZATION AND MODELLING OF THE DIFFUSION / REACTION COMPETITION ON A MODEL REACTIVE SYSTEM

Redha BELLA, PhD INSA Lyon, 2007
CHAPTER 3
DIFFUSION OF LIQUIDS IN MOLTEN POLYMERS: MUTUAL DIFFUSION COEFFICIENT DEPENDENCE ON LIQUID MISCIBILITY AND POLYMER MOLAR MASS


SUMMARY

1. INTRODUCTION.............................................................................................................. 44

2. DIFFUSION PROCESS .................................................................................................... 45

3. DIFFUSION COEFFICIENT ........................................................................................... 46

3.1. MOLECULAR MODELS FOR DIFFUSION ................................................................. 46

3.2. FREE-VOLUME MODELS ............................................................................................ 48

4. RHEOLOGY AND MODELLING SCHEME ................................................................ 52

4.1. EXPERIMENTAL SETUP FOR DIFFUSION AND RHEOLOGY ............................................. 52

4.1.1. Diffusion process ..................................................................................................... 53

4.1.2. Inverse calculation .................................................................................................. 54

5. EXPERIMENTAL ............................................................................................................. 58

5.1. MATERIALS AND SAMPLES ....................................................................................... 58

5.2. VISCOELASTIC MEASUREMENTS .............................................................................. 58

5.3. SIZE EXCLUSION CHROMATOGRAPHY (SEC) ........................................................... 59

6. RESULTS AND DISCUSSION......................................................................................... 59

6.1. DIFFUSION OF NEA IN EVA SAMPLES...................................................................... 62

6.2. DIFFUSION OF EPPE IN EVA SAMPLES...................................................................... 65

7. CONCLUSION.................................................................................................................. 71
This part of the study addresses two important features of the diffusion of liquids into a molten polymer matrix: the dependence of the mutual diffusion coefficient on the liquid miscibility and molar mass of polymers, i.e. molten viscosity. In addition, a rheological approach is chosen for its capacity to support relatively simple modeling, and the mutual diffusion coefficient expressed with the free-volume theory, is calculated by an inverse method. For that purpose, the diffusion process of 2,3-epoxypropyl-phenylether (EPPE) and the N-ethylaniline (NEA) in three molten poly(ethylene-co-vinyl acetate) elastomers (EVA) having different molar masses is examined. The NEA is fully miscible with EVA and its diffusion process is not dependent on the molar mass of the polymer. On the other hand, the diffusion process of EPPE, that is partially miscible with EVA, is strongly influenced by the molar mass of the EVA. Furthermore, the evolution of the concentration gradient during the diffusion process of EPPE is driven by the necessity for the mixture to form a two-phase system with an EVA-rich phase and an EPPE-rich phase. In this case, the concentration gradient through the sample is not continuous at a macroscopic scale. Consequently, the calculation procedure is only applied during the early stages of the diffusion. For EPPE, the variation of the mutual diffusion coefficient with the molar mass of EVA is taken into account through the variation of the interaction parameter. Actually, our experimental observations and rheological inverse calculation of the diffusion process are in agreement with the findings of the free volume theory of the diffusion.
1. INTRODUCTION

The transport behaviour of low molecular weight substances in polymeric materials is a topic of broad interest. The importance of such behaviour has become more apparent in recent years with the growing development of reactive processes for the production of materials for specific applications (packaging, membranes for gas separations …), and more general, the increase in the use of polymers for diverse applications.

The diffusion of low molar mass organic molecules in molten polymers is involved in many operations such as mass polymerization processes, polymer modification, devolatilization, rubber formulation, plastification of thermoplastic polymers. More specifically in the field of reactive processing, the desired reaction is obtained provided that the reactants are able to diffuse at a molecular level to the reactive sites during the short period of time allowed for the process. Fortunately, the reactive processing equipments like twin-screw extruders are reactors that provide an intense mechanical mixing so that, most often, the distances of diffusion are considerably reduced by the mixing step. However, when large concentrations of a low viscosity liquid are mixed with high viscosity polymers, there may be some difficulties to achieve an efficient reduction of the characteristic size of the phases. In this particular case, it is essential to be able to characterize diffusion rates to understand the overall reactive process. Self-diffusion coefficients can be determined by NMR such as the pulsed-gradient spin echo technique [PICK 89] but such techniques require nuclei solvents and it is not easy to determine diffusion coefficients in all samples at high temperatures characteristic of most polymer reactive processes. As experiments often have temperature and concentrations limitations, a solution is to calculate the mutual diffusion coefficient over a wide range of temperatures and concentrations from the free volume theory introduced first by Cohen and Turnbull [COHE 59]. In recent papers, several authors [ZIEL 92] ; [VREN 98] ; [TONG 01] have explained how to predict most of the parameters of the free volume theory so that it should be possible to calculate the diffusion coefficient of small molecules in rubbery or glassy polymers. However, important assumptions must be made and consequently, the parameters are generally determined within one order of magnitude. On the other hand, we demonstrated in a previous work that we were able to determine the mutual diffusion coefficient from rheological measurements [JOUB 02]. By comparing the experimental rheological data to the values calculated from the rheological model we have adjusted the
values of three parameters of the free volume expression of the diffusion coefficient. Here, we also wish to examine the influence of the miscibility of the species and of the molar mass of the polymer on the mutual diffusion coefficient. For that purpose, we have studied experimentally and modeled the diffusion behaviour of 2,3-epoxypropyl-phenylether (EPPE) and of N-ethylaniline (NEA), two low molar mass molecules, in copolymers of ethylene and vinyl acetate (EVA) having different molar masses. The system EVA with EPPE and NEA is a model mixture that we have selected to analyze the relationships between mixing, diffusion and reaction in the context of reactive processing in polymer melts.

2. DIFFUSION PROCESS

The approaches to model the diffusion process are generally based on a dimensionless group called the diffusion Deborah number \( (D_b) \), which is defined as the ratio of the characteristic time of the fluid, \( \lambda_m \), to the characteristic time of the diffusion process, \( \theta_D \) [VREN 77c]:

\[
D_b = \frac{\lambda_m}{\theta_D}
\]  

The introduction of \( D_b \) attempts to compare the rate of diffusion with the rate of conformational rearrangement of the macromolecules. If the Deborah number is large, the mass transport is called elastic diffusion. If the Deborah number is small, both the polymer and solvent behave like purely viscous fluid. When the Deborah number approaches one, the molecular relaxation and mass transport processes occur in comparable time scales. The diffusion transport is then denoted as viscoelastic diffusion and diffusion does not follow a Fickian law.

The Deborah number is small when a solvent is diffusing in a polymer at high temperature (above the glass transition temperature) or when the polymer contains a non negligible fraction of solvent. In that case, mass transport can be described by the classical law of diffusion expressing the time evolution of the concentration profile by the following equation commonly referred as Fick’s second law of diffusion:

\[
\frac{\partial C}{\partial t} = \nabla . D_{12} \nabla C
\]
C is the concentration of the diffusing molecule and $\nabla$ is the del operator. $D_{12}$ is the mutual diffusion coefficient that depends strongly on the concentration of the diffusing molecule.

3. DIFFUSION COEFFICIENT

The existing diffusion models aiming to determine the diffusion coefficient mainly refer to rubbery polymers and are either molecular or free-volume in nature. The following list does not intend to be comprehensive in any way of the vast literature available on diffusion models in polymers, but rather aims to spot the features of diffusion processes relevant to this study, for a better rationalization of the model proposed.

3.1. Molecular Models for diffusion

Molecular models analyze specific penetrant (the diffusing specie) and chain motions and offer a detailed description of the molecular interactions. Random motion of the polymer chains, due to energy fluctuations of the whole system, continuously generates and destroys regions of empty space in the matrix. The motion of the diffusing molecule occurs because it acquires thermal energy, enough for a jump into a neighbouring hole which becomes available. All molecular models characterize diffusion as an energy activated process. The calculated energy is then related to the diffusion coefficient via an Arrhenius-type expression.

Meares [MEAR 54] was the first one to propose a molecular model for diffusion in polymers. He found that the activation energy for diffusion was linearly dependent on the square of the diffusant diameter, and not on its cube. Therefore, suggested that the elementary diffusion jump is a function of the energy required to separate the polymer chains to form a cylindrical space of sufficient diameter for the penetrant to move from one equilibrium position to another one. He calculated jump lengths for different gases in poly(vinyl acetate) at 299 K, ranging from 2.6 Å for He to 29 Å for Ar.

In his molecular model, Brandt [BRAN 58] accounted for the molecular structure of the polymer to estimate the activation energy for diffusion. He assumed that the energy was spent by the diffusant to bend the surrounding molecular chains, and to overcome the attractive forces between them. He tested his model on fluorocarbon polymers and found that the
activation energy did not correlate linearly with the square of the penetrant collision diameter, as proposed by Meares, but that it showed a downward concavity. According to this model, sufficiently small penetrants do not require activation energy to pass through existing free spaces. Brandt’s calculated values of the activation energy were found to be up to 70% lower than experimental values.

Di Benedetto [DIBE 63] envisioned a diffusant dissolved in a polymer as a three dimensional harmonic oscillator within a cell or void formed by a bundle of 4 parallel segments. A diffusion jump occurs when the four polymer segments around the diffusant separate sufficiently to create a cylindrical cavity where the penetrant can move. The activation energy was calculated as the potential difference between the normal and the activated state, and the intermolecular forces were described by a Lennard-Jones potential. DiBenedetto’s formulation requires the use of an adjustable parameter, namely the number of backbone carbon atoms which participate in a single diffusion step.

Masaro and Zhu [MASA 99] gave an interesting classification of the different models developed for diffusion based on obstruction effect for molecular models (table 3.1.)

<table>
<thead>
<tr>
<th>Author(s)</th>
<th>Reference(s)</th>
<th>Application(s)</th>
<th>Limitation(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maxwell–Fricke</td>
<td>[FRIC 24]</td>
<td>Solvents and small-sized diffusants</td>
<td>Large diffusants</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Semi-dilute and concentrated polymer solutions</td>
</tr>
<tr>
<td>Mackie and Meares</td>
<td>[MACK 55]</td>
<td>Solvents and small-sized diffusants</td>
<td>Large diffusants</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Semi-dilute polymer solutions</td>
<td>Concentrated polymer solutions</td>
</tr>
<tr>
<td>Ogston et al.</td>
<td>[OGST 73]</td>
<td>Solvents and small-sized diffusants</td>
<td>Large diffusants</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Semi-dilute polymer solutions</td>
<td>Concentrated polymer solutions</td>
</tr>
<tr>
<td>Hard sphere theory</td>
<td>[JOHA 91]</td>
<td>Solvents and small-sized diffusants</td>
<td>Diffusants with $R_t &gt; 20$ Å</td>
</tr>
<tr>
<td></td>
<td>[LÖFR 91]</td>
<td>Semi-dilute polymer solutions</td>
<td>Concentrated polymer solutions</td>
</tr>
</tbody>
</table>
3.2. Free-Volume Models

All free-volume models are based on Cohen and Turnbull’s theory for diffusion in a hard-sphere liquid [COHE 59]. Diffusion results from the redistribution of the free-volume within the liquid, due to random fluctuations in the local density.

In 1961 a relationship between the fractional free-volume and the thermodynamic diffusion coefficient was proposed by Fujita [FUJI 61]. In order to estimate the free volume, Fujita used the concept of Cohen and Turnbull [COHE 59] which defines the probability $P(V^*)$, to find holes of size $V^*$ in a liquid of identical molecules:

$$P(V^*) = A \cdot \exp \left( -\frac{\gamma \cdot V^*}{V_{FH}} \right)$$  \hspace{1cm} (3.3)

where $A$ is constant, $\gamma$ a numerical factor of the order of unity and $V_{FH}$ is the average free volume per molecule. The product $\gamma V^*$ is interpreted as the measure of the minimum hole size required for diffusant displacement $\gamma$. The diffusion model is based on several assumptions:

1. The diffusion process occurs because of the redistribution of the free volume within the matrix;
2. The redistribution of the free volume does not require energy change;
3. The diffusion process is enabled when the free volume exceeds holes of size $V^*$;
4. The diffusion is directly proportional to the probability $P(V^*)$ of finding a hole of volume $V^*$ or larger adjacent to the diffusant molecule [COHE 59].

Fujita tested his model successfully to describe penetrant polymer systems with diffusion coefficients strongly dependent on the penetrant concentration. He thought his theory was inappropriate for small penetrant molecules, but he showed it predicted correctly the absorption of small alkanes in polyethylene. Many researchers later extended Fujita’s model to even lighter penetrants and gas mixtures [STER 72]. Particular Vrentas and Duda ([VREN 77a]; [VREN 77b]; [VREN 77c]; [VREN 78]) formulated a method of predicting mutual diffusion coefficients and their temperature and concentration dependence for a number of
systems. Their approach also requires values for many physical parameters, like the thermal expansion coefficient for the polymer so that there is little predictive capability in the model of Vrentas and Duda. It is, nevertheless, an excellent phenomenological approach. Masaro and Zhu [MASA 99] gave an interesting classification of the different models developed for diffusion using free volume theory (table 3.2.).

**Table 3.2. Summary of the diffusion models based on the free volume theories [MASA 99]**

<table>
<thead>
<tr>
<th>Author(s)</th>
<th>Reference(s)</th>
<th>Application(s)</th>
<th>Limitation(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fujita</td>
<td>[FUJI 61]</td>
<td>Solvents and small-sized diffusants</td>
<td>Large diffusants</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Semi-dilute polymer solutions</td>
<td>Concentrated polymer solutions</td>
</tr>
<tr>
<td>Yasuda et al.</td>
<td>[YASU 68]</td>
<td>Solvents and small-sized diffusants</td>
<td>Large diffusants</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Semi-dilute polymer solutions</td>
<td>Concentrated polymer solutions</td>
</tr>
<tr>
<td>Vrentas and Duda</td>
<td>[VREN 77a, 77b, 77c, 84, 85a, 85b]</td>
<td>Various solutes and solvents</td>
<td>Determination of the numerous parameters</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Both semi-dilute and concentrated polymer solutions</td>
<td>Dilute polymer solutions</td>
</tr>
<tr>
<td>Peppas and Reinhart</td>
<td>[PEPP 83]</td>
<td>Various solutes and solvents</td>
<td>Diffusants with size closer to or greater than the mesh size of the network</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Chemically cross-linked gels and hydrogels</td>
<td>Diffusion in non-cross-linked polymers</td>
</tr>
</tbody>
</table>

The model initiated by Cohen and Turnbull has been extended by Vrentas and Duda [VREN 77a]; [VREN 77b]; [VREN 77c]. The model establishes a relationship between the self-diffusion coefficient of a molecule and the free-volume of a one component liquid. It has been extended to calculate the self-diffusion coefficient, \(D_I\), of specie in a binary system.

\[
D_I = A \cdot \exp \left( - \frac{\gamma V^*}{V_{FH}} \right) \quad (3.4)
\]
$V^*$ is the critical hole free volume into which a molecule of solvent can jump, $\gamma$ is a numerical factor between 0.5 and 1 introduced to account for the overlap between free volume elements, $V_{FH}$ is the average specific free volume, $A$ is a constant related to the gas kinetic theory.

To describe the motion in binary solutions, Vrentas and Duda ([VREN 77a]; [VREN 77b]; [VREN 77c]) derived the following expression:

$$D_1 = D_0 \cdot \exp \left( -\frac{E}{RT} \right) \cdot \exp \left( -\frac{\omega_1 V_1^* + \xi \omega_2 V_2^*}{V_{FH}} \frac{1}{\gamma} \right)$$ (3.5)

$D_0$ is a constant, $E$ is the critical energy necessary for a molecule to overcome attractive forces, $\omega_1$ and $\omega_2$ are the weight fractions of the solvent and the polymer, respectively, $V_1^*$ and $V_2^*$ the specific volumes at 0 K, $\xi$ is the molar volume ratio for the solvent and polymer jumping units.

The free volume parameters are in fact related to the Williams-Landel-Ferry (WLF) equation. Nevertheless, the fractional free volume, $f_i \approx V_{FH} / V_i^*$ cannot be calculated rigorously from thermal variation of the viscosity because the shift factors for modulus master curves, $a_T$, are measured in a narrow range of temperature, especially for semi-crystalline polymers. Furthermore, the method taking into account the universal constant of the WLF law would be a rough approximation only. Thus, as assumed in a previous work [GIME 00a] we can focus directly on the flow activation energies, $E_i$, in the range of temperatures investigated. From equation 3.5 we finally derived the following expression of the diffusion coefficient [PONS 05], where $V_i^T$ is the specific volume at $T$ of the species $i$.

$$D_1 = D_0 \cdot \exp \left( -\frac{E}{RT} \right) \exp \left[ -\frac{\omega_1}{I + \frac{RT}{E_1}} \frac{V_i^T}{1 + \frac{RT}{E_1}} + \frac{\omega_2}{I + \frac{RT}{E_2}} \frac{V_2^T}{1 + \frac{RT}{E_2}} \right]$$ (3.6)
It must be noted that the $\gamma$ parameter is assumed to be 1 for the small molecule and for the polymer and therefore does not appear in this equation.

Finally, the Flory-Huggins theory enables to derive the mutual binary diffusion coefficient, $D_{12}$, from the self diffusion coefficient $D_1$. The expression of $D_{12}$ is then:

\[
D_{12} = D_1 \cdot (1 - \Phi_1)^2 (1 - 2\chi\Phi_1)
\]  \hspace{1cm} (3.7)

with $\Phi_1$ the volume fraction of the solvent in the polymer and $\chi$ the Flory-Huggins interaction parameter.

The dependence of the coefficient diffusion on polymer molar mass, i.e. melt viscosity, is rarely studied experimentally at high temperature. However, it is important to point out that the free volume theory predicts that the self diffusion coefficient is only dependent on the fractional free volume, i.e. on the temperature gap between the experimental temperature and $T_g$ for a liquid/polymer system. For entangled polymers, the $T_g$ does not depend on the molar mass. Consequently, a molar mass dependence of the self diffusion coefficient could be found only for non entangled polymer systems for which the $T_g$ increases with increasing the molar mass. On the other hand, equation 3.7 shows that the mutual coefficient depends on the Flory-Huggins interaction parameter, which represents the interactions between the solvent and the polymer. Since the solubility parameters are generally assumed to be independent on the molar mass for polymers, the mutual diffusion coefficient should be constant regarding the molar mass, i.e the melt viscosity. However, Petri and Wolf [PETR 95] reported that the Flory-Huggins parameters depend on molecular weight even at high polymer concentrations, in contrast to the general belief according to which the individuality of macromolecules should already vanish in the region of moderate polymer concentrations.
4. RHEOLOGY AND MODELLING SCHEME

4.1. Experimental setup for diffusion and rheology

The principle of the rheological experiment for diffusion was described in detail by Joubert [JOUB 02] and its principle is presented in figure 3.1. A layer of liquid is placed on the top of a layer of molten polymer and the complex shear modulus \( G^*(\omega) = G'(\omega) + j \, G''(\omega) \) of the sample at a constant frequency \( \omega = 10 \text{ rad s}^{-1} \) is measured as a function of time. In the present paper we will consider the variation of the absolute complex viscosity, named for a convenient purpose viscosity.

\[
|\eta^*(\omega)| = \sqrt{\frac{G'^2}{\omega^2} + \frac{G''^2}{\omega^2}} \quad (3.8)
\]

![Figure 3.1](image_url)  

Figure 3.1. Illustration of the evolution of the viscosity with the progress of the diffusion. The range of deformation used, \( \gamma \), is indicated.
At the early stages of diffusion, the viscosity of the bi-layer is low since it is dominated the fluid of lower viscosity. In the intermediate stages, the diffusion of the low molar mass molecule across the polymer layer creates a gradient of concentration that induces viscosity variations. The global viscosity of the sample rises and finally, at the end of the diffusion process, the sample homogenizes and the viscosity reaches a stable value. The viscosity varies considerably from the viscosity of the liquid at the beginning of the diffusion process to the viscosity of the polymer-liquid homogeneous medium at the end of the diffusion process. Therefore the evolution of the viscosity can be related to the transport behaviour of the polymer/liquid system.

4.1.1. Diffusion process

The diffusion is supposed to occur in one direction perpendicular to the layer surface. The evolution of the concentration of the bi-layer specimen is calculated with Fick's law.

\[
\frac{\partial C(t,x)}{\partial t} = \frac{\partial C(t,x)}{\partial x} \left( D_{12} \frac{\partial C(t,x)}{\partial x} \right)
\]  

This requires to check that the process is Fickian by estimating the Deborah number, \( Db = \frac{\lambda_m}{\theta_D} \). The relaxation time is equivalent to the reptation time of the EVA chains. Regarding the most unfavorable data for our calculation (longest relaxation time for the highest mass molar), for EVA 2803 at \( T=110^\circ C \), \( \lambda_m \sim 10 \) s. \( \lambda_m \) is expressed here as the longest average relaxation time of the distribution, \( \lambda_m = \frac{\eta_0 J_e^0}{D} \). Note that the shortest time considered here according to data of table 3.3, is \( \lambda_m = \frac{\eta_0 G_N^0}{D} \) for EVA28800, so that \( \lambda_m = 1.5 \times 10^{-4} \) s. \( \eta_0 \) is the zero shear viscosity, \( J_e^0 \) is the steady state compliance, \( G_N^0 \) is the rubbery modulus.

<table>
<thead>
<tr>
<th>Penetrant liquids</th>
<th>Molar mass ( (g. \text{ mol}^{-1}) )</th>
<th>( \eta_0^a ) ( \text{(Pa.s)} )</th>
<th>( E_1^b ) ( \text{(kJ. mol}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,3-epoxypropyl-phenylether (EPPE)</td>
<td>150</td>
<td>( 1.5 \times 10^{-4} )</td>
<td>30</td>
</tr>
<tr>
<td>N-ethylaniline (NEA)</td>
<td>121</td>
<td>( 7 \times 10^{-4} )</td>
<td>30</td>
</tr>
</tbody>
</table>

\( a) T = 110^\circ C \)

\( b) \) Calculated from EVA/amine blend according to ref. [GIME 00a].
The characteristic time of the diffusion, $\theta_D$, is more difficult to estimate, Peppas et al. [PEPP 94] proposed the following expression:

$$\theta_D \sim L^2/D_{12}$$  \hfill (3.10)

where $L$ is the thickness of the polymer layer. According to our experimental conditions, $L \sim 10^{-3} \text{ m}$ and according to our next calculation $D_{12} \sim 10^{-8} \text{ m}^2 \text{ s}^{-1}$ for a polymer volume fraction of 0.1, we find $\theta_D \sim 10^2 \text{ s}$. The Deborah number is therefore: $Db \sim 10^{-1}$, which indicates that the process is fickian even for the most unfavourable case of calculation.

Those estimates show that the molecular relaxation is faster than the diffusive transport so that changes in the polymer conformations are not limiting the process and we have a viscous or liquid-liquid diffusion.

### 4.1.2. Inverse calculation

The difficulty for calculating the self-diffusion and mutual diffusion coefficients is that the expressions in equations 3.6 and 3.7 require the determination of a number of parameters. Some of them are directly accessible: $\omega_1$ and $\omega_2$ are the weight fractions of the small molecules and the EVA, respectively. The specific volumes $V_1^T$ and $V_2^T$ at the temperature $T$ were calculated from the experimental determination of the volume of the NEA and of the EPPE at 90, 110, 130 and 150°C. The following relations were established:

$$V_1^T = 0.93104 \exp (2.203 \times 10^{-5} \ T^{3/2}) \text{ cm}^3 \text{ g}^{-1} \text{ for the NEA}$$  \hfill (3.11)

$$V_1^T = 0.80344 \exp (2.218 \times 10^{-5} \ T^{3/2}) \text{ cm}^3 \text{ g}^{-1} \text{ for the EPPE}$$  \hfill (3.12)

The specific volume of the EVA28 was measured by Rodgers [RODG 93], it is equal to:

$$V_2^T = 1.00832 \exp (2.241 \times 10^{-5} \ T^{3/2}) \text{ cm}^3 \text{ g}^{-1}$$  \hfill (3.13)
$E$ is generally considered to be zero. $E_1$ and $E_2$ are the flow activation energies of the low molar mass molecule and the EVA respectively, their determination is based [GIME 00a] on the measurement of the viscoelastic properties of the EVA alone and of the binary mixtures of EVA with NEA and with EPPE (table 3.3 and table 3.4). In first approximation, the Flory-Huggins parameter, $\chi$, can be estimated according to the following equation:

\[
\chi = 0.34 + \frac{V}{RT} \left( \delta_1 - \delta_2 \right)^2
\]  

(3.14)

where $V$ is the molar volume of the penetrant liquid, $\delta_1$ and $\delta_2$ are the solubility parameters of the liquid and the polymer respectively. According to the Van Krevelen method [BART 91] we find $\chi \approx 0.40$ for the EVA/NEA and $\chi \approx 0.50$ for EVA/EPPE systems. It must be pointed out that higher values of $\chi$ are obtained from Hoy method [BART 91]. In the present work we use Van Krevelen reference ($\chi_{NEA/EVA} \approx 0.40$). Regarding EPPE/EVA system, the value of the Flory-Huggins parameter will be discussed later from the procedure modelling point of view.

Table 3.4. Viscoelastic parameters of EVA samples determined from the master curve (Time-temperature superposition) of the complex shear modulus at the reference temperature $T_0=110^\circ$C. The plateau modulus $G_N^0$ was taken equal to $5.10^5$ Pa according to ref. [CASS 93].

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Melt Flow Index</th>
<th>$M_w$ (g mol$^{-1}$)</th>
<th>$J_e^0$ (Pa$^{-1}$)</th>
<th>$\eta_0$ (Pa.s)</th>
<th>$E_2$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EVA 2803</td>
<td>3</td>
<td>53500$^{a)}$</td>
<td>$2.0 \times 10^{-4}$</td>
<td>$5.0 \times 10^4$</td>
<td>44.5</td>
</tr>
<tr>
<td>EVA 2840</td>
<td>40</td>
<td>27500$^{b)}$</td>
<td>$0.9 \times 10^{-4}$</td>
<td>$5.2 \times 10^3$</td>
<td>45.8</td>
</tr>
<tr>
<td>EVA 28800</td>
<td>800</td>
<td>7900$^{b)}$</td>
<td>$1.1 \times 10^{-4}$</td>
<td>75</td>
<td>38.0</td>
</tr>
</tbody>
</table>

$^{a)}$ From ref. [CASS 93].

$^{b)}$ From rheological calculation assuming $M_w \propto \eta_0^{1/3.4}$ for entangled polymers.

Eventually, only $D_0$ and $\xi$, need to be fitted with the help of the diffusion and rheological model to express the mutual coefficient of diffusion. At the beginning of the calculation, we assume values for the parameters $D_0$ and $\xi$ of the diffusion model in order to calculate $D_{12}$. $D_{12}$ is needed to calculate the evolution of the concentration through the sample. The
knowledge of the concentration allows to deduce the viscosity profile and to derive the viscosity of the overall sample at each time, referring to a theoretical framework of the dilution effect ([GIME 00b], [MARI 80]). The next step is to compare the calculated viscosity evolution to the experimental one and subsequently modify $D_0$ and $\xi$ to obtain the best adjustment of the variation of the viscosity. The method can be assimilated to a rheological inverse calculation method since the parameters of the free volume expression of the diffusion coefficient are calculated by comparing the experimental viscosity versus time curve to the values calculated from the rheological model. This method was described in details by Joubert et al [JOUB 02] and we use the software developed by these authors. However, the numerical method is based on a fundamental assumption of liquid-polymer diffusion between the gap of the rheometer plates. This assumption must be actually checked in the present work. As shown in figure 3.2., the thickness of the solid is initially divided into $(n-1)$ equal slices and the liquid fills the last $n^{th}$ slice completely.

![Diagram](image)

**Figure 3.2.** Schematic description of the diffusion process for numerical purpose. The upper layer $(i=n)$ is considered to be composed of pure liquid until it is reduced to 0.01% of the gap, it is then suppressed.

According to the additivity of the volumes of the solid and of the liquid, the polymer swells as the liquid gets into a slice. Thus, the thickness of each “solid” slice increases over diffusion time whereas the liquid one decreases. The assumption considered that, when the abscissa of the last slide (upper slide $i=n-1$) of the “solid” reaches 99.99% of the gap, the swelled polymer occupies the entire gap and there is no more free liquid above it. In computation, the last slice corresponding to liquid $i=n$ is then suppressed and the diffusion of liquid continues inside the polymer until the equilibrium is achieved.
Actually, this assumption means that the penetrant liquid diffuses in the polymer which swells and the polymer chains does not diffuse in the pure liquid slice. In other words, there is no dissolution effect of polymer in the upper n\textsuperscript{th} slice. This assumption can be discussed from the comparison between the diffusion coefficient of the liquid $D_{12}$ and the diffusion coefficient of the polymer $D_p$. We can then define a diffusion Deborah number as:

$$D_b = \frac{D_p}{D_{12}}$$  \hspace{1cm} (3.15)$$

If $D_b$ is lower than 1, the solvent penetration rate is faster the polymer dissolution rate. $D_{12}$ is calculated a posteriori in the present work. According to the reptation theory $D_p$ can be expressed for bulk conditions as following:

$$D_p = \frac{\langle R^2 \rangle_0}{\pi^2 T_d}$$  \hspace{1cm} (3.16)$$

where $\langle R^2 \rangle_0$ is the unperturbed mean-square end-to-end distance of the polymer chain. $T_d$ is the reptation time and can be assimilated to $\lambda_m$. For semi-diluted and concentrated solutions $T_d$ is expressed as:

$$T_d (\Phi_2) = a_\Phi \cdot \Phi_2^{1.75} \cdot T_{d_{bulk}}$$  \hspace{1cm} (3.17)$$

Where $\Phi_2$ is the volume concentration of polymer in the penetrant liquid, $a_\Phi$ is the free volume correction that takes into account the change of the glass temperature with dilution $\Phi_2$, $T_{d_{bulk}}$ is the reptation time of the bulk polymer at the temperature considered.

$\langle R^2 \rangle_0$ was calculated according to Fetters et al [FETT 94] who proposed a direct and simple relation between the various viscoelastic parameters and chain packing length. We used data on polyethylene so that $\langle R^2 \rangle_0 / M = 1.25 \text{ (Å}^2\text{ mol g}^{-1})$. Using the most unfavourable conditions (EVA28800) in concentrated conditions at $T = 110°C$ ($\Phi_2 \rightarrow l$, $a_\Phi \approx l$, $T_d=1.5 \times 10^{-4} \text{s}$) we find $D_p \approx 7 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$ and $D_{12} \approx 7 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$ (see figure 3.9., $\omega_1 \rightarrow 0$) so that $D_b \approx 1$. Actually the most unfavourable condition for polymer diffusion at $T = 110°C$ should be at $\Phi_2=0.5$ (EVA28800, $T_d (\Phi_2=0.5) \approx 1 \times 10^{-5} \text{ s}$ according to equation 3.17 with $a_\Phi=0.25$),
consequently $D_p \approx 5 \times 10^{-13} \text{ m}^2 \text{s}^{-1}$. However $D_{12} \approx 10^{-9} \text{m}^2 \text{s}^{-1}$ (see figure 3.9.) so that $D_b \approx 5 \times 10^{-4}$. Therefore, due to the fact that $D_{12}$ is more sensitive to the variation of polymer concentration than $D_p$, the most unfavourable case is obtained with $\Phi_2 \rightarrow 1$. The most favourable conditions (EVA2803, $T_d = 1 \times 10^{-1} \text{s}$) with $D_p \approx 7 \times 10^{-16} \text{ m}^2 \text{s}^{-1}$ and $D_{12} \approx 7 \times 10^{-14} \text{ m}^2 \text{s}^{-1}$ leads to $D_b \approx 10^{-2}$. This simple calculation shows that $10^{-2} < D_b < 10^0$ for EVA samples investigated in the present work so that the dilution effect of the polymer can be neglected. Indeed, the diffusion Deborah number shows that the solvent penetration rate is much higher than the dissolution rate. According to this result, the hypothesis of the upper n slice containing pure liquid and decreasing with diffusion time is correct.

5. EXPERIMENTAL

5.1. Materials and samples

The polymers used are three poly(ethylene-co-vinyle acetate) (EVA) with different molar masses, i.e. melt viscosity (see table 3.3). The samples were kindly supplied by Arkema. The amount of acetate groups contained in these copolymers is 28 wt%. The organic molecules are the 2,3-epoxypropyl-phenylether (EPPE) and the N-ethylaniline (NEA) purchased from Aldrich and used without further purification.

5.2. Viscoelastic measurements

The zero shear viscosities of the liquids, NEA and EPPE, have been measured on a stress rheometer from TA Instruments (AR 1000) on shear steady regime at 90, 110, 130 and 150°C.

For the viscoelastic characterization of the pure polymers, frequency sweep test were run from $10^{-1}$ to $10^2 \text{ rad s}^{-1}$ at different temperatures, 90, 110, 130, 150, 170 et 190°C on a Rheometrics Mechanical Spectrometer (RMS800). The terminal viscoelastic parameters (see table 3.4) of the three EVA grades were deduced from the time-temperature superposition of the viscosity curves at the reference temperature of 110°C.

For the diffusion experiments, parallel plate geometry with a diameter of 50 mm was mounted on the RMS800. The tests were run in dynamic conditions at 10 rad.s$^{-1}$, and four temperatures
were experimented: 90, 110, 130 and 150 °C. A disc of EVA was prepared by compression molding and its thickness was precisely measured. It was brought into contact with the lower plate heated at 110°C. The liquid additive was deposited over the polymer layer. The upper plate was then lowered in order to respect a gap of 2 mm between the plates. The thickness of the EVA was equal to 0.9 mm and the thickness of the liquid was equal to 1.1 mm. The strain amplitude was manually adjusted from 400% at the beginning of the test to 1% at the end of the experiment to obtain a measurable torque and to remain within the domain of linear viscoelasticity.

5.3 Size Exclusion Chromatography (SEC)

The composition of EVA/EPPE mixture phases was determined by SEC after reaching the thermodynamic equilibrium of the mixture placed in a glass tube at controlled temperature. A sample of the two distinct phases was taken from the upper and lower sections of the tube and analyzed. The apparatus was a VISCOTEK SEC for low molecular weight polymers with two ViscoGEL® HR High Resolution Columns (pores diameter ~100-500 nm). The elution solvent was tetrahydrofurane (THF). The refractive index peaks, measured using a VISCOTEK VE 3580 RI Detector, were integrated and the EPPE concentration deduced thanks to a calibration curve prepared with (EPPE/THF) solutions of known concentration with taking into account that the calibration of the apparatus was made with polystyrene standards.

6. RESULTS AND DISCUSSION

Prior to the results, it is interesting to examine the sensitivity of the model to variations of its parameters, \( D_0 \), \( \xi \), and \( \chi \). The viscosity evolutions for different sets of parameters varying independently one from each other have been calculated for NEA and EPPE diffusing in EVA at 110, 130 and 150°C. In figure 3.3. and 3.4., we have selected several representative examples of the variations of the model calculations. In all cases, the viscosity evolution of the EPPE/EVA systems was more sensitive to variations of the parameters than that of NEA/EVA.
Chapter 3. Diffusion of Liquids in Molten Polymers: Mutual Diffusion Coefficient Dependence on Liquid Miscibility and Polymer Molar Mass

Figure 3.3. Sensitivity of the calculated viscosity to the variations of the $D_0$, $\xi$, and $\chi$ parameters for NEA/EVA2840 bi-layer at 130°C.
Figure 3.4. Sensitivity of the calculated viscosity to the variations of the $D_0$, $\xi$ and $\chi$ parameters for EPPE/EVA2840 bi-layer at 130°C.
6.1. Diffusion of NEA in EVA samples

Before going further, it must be pointed out that the NEA was found to be miscible in all proportions with the different grades of EVA at 110°C. The evolution of the viscosity at different temperatures of the NEA/EVA2840 bi-layer is shown in figure 3.5. The absolute viscosity varies considerably from absolute viscosity of NEA liquid at the beginning of the diffusion process compared to the absolute viscosity of EVA2840-NEA homogeneous medium at the end of the diffusion process. Furthermore, the rate of diffusion is obviously activated by an increase of temperature.

\[ D_0, \text{ and } \xi \text{ have been optimized by inverse calculation with the experimental data at 110°C for EVA2840 only. Then their values (} D_0=0.2 \text{ m}^2/\text{s and } \xi=2 \text{) were integrated in the model to simulate all the other experiments with variable temperature and variable molar mass of the EVA (Figure 3.6.).} \]

![Figure 3.5. Evolution of the viscosity of the NEA/EVA2840 bi-layer at different temperatures, T=90, 110, 130 and 150 °C. Symbols: experimental data, Continuous line: prediction of the diffusion model.](image)
The diffusion process of the amine is finished after 2500 s at 90°C whereas it is finished after 100s at 150°C. Actually, the influence of temperature is clearly illustrated on the initial slope of the viscosity plot. The diffusion rate is enhanced by increasing temperature as predicted by equation 3.6. On the other hand, figure 3.6. shows the evolution of the absolute viscosity for EVA samples having different mass molar at T=110°C. Interestingly, the evolution of the viscosity before reaching the final plateau is similar for all samples. In other words, the slopes of the viscosity versus time curves are the same regardless of the molar mass of the EVA. This feature indicates that the kinetics of NEA diffusion does not depend on EVA molar mass. Moreover, the time necessary to attain a stabilized value of the viscosity is equivalent for the three samples. Only the value of the final viscosity varies, as a consequence of the difference in molar masses.

---

**Figure 3.6.** Evolution of the viscosity of the NEA/EVA bi-layer at 110°C for different molar masses of the EVA. Symbols: experimental data. Continuous line: prediction of the diffusion model. See comments in legend of Figure 3.5.
We have applied the model in order to determine the parameters of the diffusion coefficient expression. The parameters $D_0$ and $\xi$ have been optimized with the experimental data collected at 110°C only. Their values ($D_0=0.2$ m²/s and $\xi=2$) were integrated in the model to simulate all the other experiments with variable temperature and variable molar mass of the EVA. Examples of calculated viscosities are shown in figures 3.5. and 3.6. It can be seen that the model mainly captures the initial and final features of the experimental plots, whereas the actual global kinetics of diffusion is slower than modelled. Some assumptions can be revisited for this. First some limits of the free volume diffusion models can be put forward, as it was done recently [ZIEL 92], [TONG 01]. For example, the critical energy $E$ is presently set equal to zero, whereas the model was shown to be very sensitive to its value [TONG 01]. The experimental and computed plots are in better agreement at 150°C than 90°C (see figure 3.5.). This is consistent with the fact that energy effects are all the more dominant over free volume effects as temperature increases [ZIEL 92]. On the other hand, the original framework of the free volume theory assumes the additivity of free volumes; this hypothesis is generally a rough approximation [FERR 80]. However this assumption is always assumed in all literature devoted to the free volume theory for diffusion. The poor agreement between the calculated and experimental viscosities at the intermediate stage of diffusion might be due to the amine dissolving the EVA so that the model of an upper layer being pure liquid is not representing adequately the actual process. This possible aspect was discussed in term of the diffusion Deborah number (equation 3.15). Our previous discussion showed that the polymer disentanglement from bulk phase to the liquid upper layer is not the dominant mode. Indeed, our experimental results (figure 3.6.) confirm our hypothesis since the viscosity variation at the earlier stage of diffusion is not molecular weight dependent. Assuming a disentanglement process would lead to a molecular weight dependence of the viscosity due to the fact that a short chain disentangles faster than a longer.

In spite of these reservations, the physical significance of the calculated $D_0$ and $\xi$ is demonstrated here by the fact that equally satisfactory, or even better prediction can be achieved (equation 3.6) at different temperatures while keeping the values of these parameters constant, as expected.
The parameters of equations 3.6 and 3.7 being known, it is finally possible to calculate in one hand the self diffusion coefficient $D_1$ (equation 3.6) and on the other hand the mutual diffusion coefficient $D_{12}$ (equation 3.7) versus the volume fraction of the polymer at any temperature (figure 3.7.).

![Graph showing variation of $D_1$ and $D_{12}$ vs solvent volume fraction at different temperatures for NEA/EVA2840 system.]

**Figure 3.7.** Calculated variation of the self diffusion coefficient $D_1$ and mutual coefficient $D_{12}$ versus solvent volume fraction at different temperature for NEA/EVA2840 system.

6.2. Diffusion of EPPE in EVA samples

The evolution of the viscosity at different temperatures of the EPPE/EVA2840 bi-layer is shown in figure 3.8. As previously reported, the absolute viscosity varies considerably from absolute viscosity of the EPPE liquid at the beginning of the diffusion process to the absolute viscosity of EPPE/EVA2840 equilibrium medium at the end of the diffusion process. Qualitatively, the apparent rate of diffusion of EPPE in EVA is two to five times slower than that of the NEA in EVA. Nevertheless, the trend of the diffusion curve is quite different compared with NEA/EVA system and especially at low temperature ($T=90^\circ$C). The diffusion curve is separated in two distinct behaviours. The first part of the curve shows a slow
variation of the viscosity with diffusion time whereas the second part of the curve shows a strong increase of the viscosity towards the final equilibrium plateau. Also, the apparent rate of diffusion is more strongly activated by the temperature compared with NEA/EVA system. Moreover, figure 3.9 shows by contrast with figure 3.6 that the diffusion rate of the EPPE depends strongly on the molar mass of the polymer. The explanation for such different behaviours is linked to differences in the solubility of the two small molecules in EVA. Actually, EPPE is only partially miscible with the EVAs, with an Upper Critical Solution Temperature (UCST). At 110°C, a mixture of EVA with EPPE forms a two phase system with one phase rich in EVA and the other rich in EPPE. The equilibrium compositions at 110°C (with EVA 28800) of the EPPE-rich phase and of the EVA-rich phase are respectively 66 wt% and 26 wt% of EPPE as determined by SEC.

![Figure 3.8](image-url)

**Figure 3.8.** Evolution of the viscosity of the EPPE/EVA2840 bi-layer at different temperatures, T = 90, 110, 130 and 150 °C. Symbols: experimental data, Continuous line: prediction of the diffusion model.

Prediction of the diffusion model for EPPE/EVA system. \( \chi, D_0, \) and \( \xi \) have been optimized by inverse calculation with the experimental data at 110°C for EVA2840. Then the values \( D_0=0.1 \text{ m}^2/\text{s} \) and \( \xi=2 \) were kept constant and integrated in the model to simulate all the other experiments by fitting \( \chi \).
Figure 3.9. Evolution of the viscosity of the EPPE/EVA bi-layer for different molar masses of the EVA. Symbols: experimental data, Continuous lines: prediction of the diffusion model.

Prediction of the diffusion model for EPPE/EVA system. $\chi$, $D_0$, and $\xi$ have been optimized by inverse calculation with the experimental data at 110°C for EVA2840. Then the values $D_0=0.1$ m²/s and $\xi=2$ were kept constant and integrated in the model to simulate all the other experiments by fitting $\chi$.

The interdiffusion at the interface between partially miscible binary liquid-liquid systems has been studied for a long time in the case of low molar mass species [PERE 73], [AGUI 85]. In the case of polymers, the behaviour of interfaces in non equilibrium conditions, that is when a macroscopic mass transfer exists at long distance, is not perfectly understood. When two fluid layers are put into contact and heated at a temperature below their critical temperature, the initially sharp interface broadens in the early stage of the interdiffusion. For polymer/polymer systems, the thickness of the interface, $w$, stabilizes around 100 nm [BRUD 89], [PURI 91], a value that is probably higher for a polymer/solvent system. Then, the interface is being crossed by a macroscopic mass flow until the equilibrium concentrations, $C_{1eq}$ and $C_{2eq}$, are attained in the phases (figure 3.10.). The concentration of the phases has to reach its equilibrium value by means of a diffusion process. In other words, compared to a fully miscible system, the molecular transport is not only driven by the necessity to homogenize the
mixture, but also by the necessity to create two distinct phases. The sample may be viewed as two macroscopic layers where a classical Fickian transport occurs, separated by a thin interface where the concentration profile is very sharp. Note also that when one of the species diffuses faster than the other, or if the global concentration of the species is different from the critical composition, the interface shifts toward the side of the faster diffusion component or toward the minor component. To summarize, for our particular system, the partial immiscibility of EPPE in EVA influences deeply the profile of concentration produced. We can no longer consider a continuous variation of concentration.

Figure 3.10. Schematic description of the concentration profiles of the partially miscible system. The coordinate $z$ is the axis perpendicular to the bi-layer specimen. The initial condition consists of pure liquid upper layer separated from the pure polymer layer by a sharp interface ($t=0, w=0$). For late times ($t \rightarrow \infty$) the equilibrium concentration profile is established with a liquid-rich layer of concentration $C_{2eq}$ and a polymer-rich layer of concentration $C_{1eq}$. The thickness of the interface, $w$, has increased ($w > 0$). The non-equilibrium profiles are represented at two intermediate stages (dashed curves). Since the liquid diffuses much faster than the polymer chains, the concentration gradient in the polymer establishes faster than in the liquid layer.

Although the mass transfer on both sides of the interface region is classical, it is difficult to say whether the existence of this interface between the phases, has an impact on the global rate of the diffusion process, and the literature does not indicate whether the molecular flow having to cross the interface is slowed down. In our case this is of importance since the
diffusion process takes longer time for the EPPE than for the NEA. But this feature might be linked to other parameters like the hydrodynamic volume of the molecules and their interactions with EVA as it will be discussed further.

Despite the partial miscibility of EPPE, the evolution of the viscosity of the bi-layer is able to represent the rate of the diffusion process. The reason is that the liquid EPPE layer thickness is decreasing consequently to the mass transfer and this decrease dominates the measured viscosity as explained in the section presenting the inverse calculation method.

**Table 3.5. Parameters of the diffusion model**

<table>
<thead>
<tr>
<th>System</th>
<th>Parameters for all temperatures and EVAs</th>
<th>Parameters depending on the molar mass</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>NEA/EVA system</strong></td>
<td>( D_0 = 0.2 \text{ m}^2 \text{s}^{-1}, \ \xi = 2, \ \chi = 0.4 )</td>
<td></td>
</tr>
<tr>
<td><strong>EPPE/EVA system</strong></td>
<td>( D_0 = 0.1 \text{ m}^2 \text{s}^{-1}, \ \xi = 2 )</td>
<td></td>
</tr>
<tr>
<td><strong>Parameters for all temperatures and EVAs</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EVA 2840</td>
<td></td>
<td>EVA 2803</td>
</tr>
<tr>
<td>EVA 28800</td>
<td>( T=90^\circ\text{C}, \ \chi = 0.58 )</td>
<td>( T=110^\circ\text{C}, \ \chi = 0.58 )</td>
</tr>
<tr>
<td>( T=110^\circ\text{C}, \ \chi = 0.34 )</td>
<td>( T=110^\circ\text{C}, \ \chi = 0.55 )</td>
<td></td>
</tr>
<tr>
<td>( T=130^\circ\text{C}, \ \chi = 0.5 )</td>
<td>( T=130^\circ\text{C}, \ \chi = 0.5 )</td>
<td></td>
</tr>
<tr>
<td>( T=150^\circ\text{C}, \ \chi = 0.46 )</td>
<td>( T=150^\circ\text{C}, \ \chi = 0.46 )</td>
<td></td>
</tr>
</tbody>
</table>

Therefore, the rheological model that decomposes the sample disk in layers with the upper layer being pure liquid is valid as long as the interface between the EPPE-rich phase and the EPPE does not reach the upper boundary of the specimen, which is the upper plate. Therefore, the model was applied to EPPE/EVA systems and the evolution of the experimental and calculated viscosities is depicted in figures 3.8. and 3.9., with different operating temperatures, and different molar masses of the EVA respectively. It is interesting to note that a correct agreement of the calculated viscosity with the experiment was obtained only if the interaction parameter, \( \chi \), depended on the molar mass of the polymer (table 3.5). Actually, the variations of \( \chi \) reflects well the behaviour of EPPE/EVA binary mixtures, that have an upper critical solution temperature and which miscibility window is enlarged for a lower molar mass.
of the polymer. The other parameters of the model were found to be: $D_0=0.1 \text{ m}^2 \text{s}^{-1}$ and $\xi=2$. The variations of $D_1$ and $D_{12}$ at $T=110^\circ\text{C}$ are plotted in figure 3.11.

**Figure 3.11.** Calculated variation of the self diffusion $D_1$ and mutual $D_{12}$ coefficients versus solvent volume fraction at $T=110^\circ\text{C}$ for EPPE/EVA systems with EVAs of different molar masses (EVA2803, EVA2840 and EVA28800).
7. CONCLUSION

In this part, we investigated from original rheological experiments the diffusion of organic molecules in molten EVA of different molar mass. As demonstrated, fitting a model of Fickian diffusion to our rheological measurements enabled us to determine the mutual diffusion coefficient of the polymer/liquid system. This calculation was developed from a rheological inversion method based on the free volume theory. Furthermore, two different organic molecules were chosen in order to study the dependence of the mutual diffusion coefficient on the Flory-Huggins interaction parameter. The diffusion process of the amine (N-ethylaniline, NEA), which is miscible with the polymer, was not depending on the molar mass of the EVA. Indeed, the mutual diffusion coefficient of the amine in EVA samples was calculated to be constant regardless EVA mass molar and only dependent on temperature. This finding is in agreement with the general framework of the free volume theory and leads to the conclusion that the Flory-Huggins parameter does not depend neither on EVA mass molar and neither on temperature for the amine/EVA system. By contrast with the amine, the diffusion process of the epoxy (2,3-epoxypropyl-phenylether, EPPE), that is only partially miscible with the EVA, depended strongly on the molar mass of the EVA. However the self diffusion coefficient, $D_1$, was found to depend only on the liquid volume fraction and on temperature. Actually, only the mutual coefficient diffusion, $D_{12}$, depends on the mass molar of EVA through the dependence of the Flory-Huggins interaction parameter. It is to be noticed that the diffusion process for this latter molecule is complex. In non equilibrium conditions, the epoxy/EVA sample formed a two-phase system with a concentration profile that was not continuous at a macroscopic level. Despite that, the hypothesis of the late persistence of a layer of pure epoxy in contact with the upper plate allowed to simulate the viscosity evolution until the EVA diffusion front reaches the boundary of the sample. In conclusion, our experimental observations and rheological inverse calculation of the diffusion process are in agreement with the general finding of the free volume theory of the diffusion. On the other hand, it is the first time that such experimental investigations on molten polymer aimed to verify the free volume theory of diffusion of liquid in molten polymers. This is a key issue in further prospects of predicting the balance between reaction and diffusion in reactive systems involving molten polymers. Apart the dependence of the mutual coefficient diffusion on molar mass for partially miscible system, our study shows that the mutual coefficient diffusion depends strongly on the volume fraction of diffusing molecules.
The results of the above study are essential for the last part of our work where we will simulate the diffusion together with the reaction. We now have an experimental way for measuring the diffusion coefficient. Note that the technique is easy to implement experimentally but necessitates several hypothesis and calculation steps to have access to the diffusion coefficient.
CHAPTER 4
CHARACTERIZATION AND MODELLING OF DIFFUSION AND REACTION OF LOW MOLECULAR WEIGHT REACTANTS IN MOLTEN POLYMER

Submitted to Polymer

SUMMARY

1. INTRODUCTION .............................................................................................................. 76

2. MODELS ............................................................................................................................. 78
   2.1. MATHEMATICAL MODEL .......................................................................................... 79
   2.2. REACTION MODEL ..................................................................................................... 80

3. EXPERIMENTAL ............................................................................................................. 80
   3.1. MATERIALS ................................................................................................................. 80
   3.2. DETERMINATION OF THE EXTENT OF REACTION BY CALORIMETRY .................. 81
   3.3. PREPARATION OF HOMOGENEOUS SAMPLES ....................................................... 82
   3.4. PREPARATION OF UNPREMIXED BI-LAYER SYSTEMS ........................................... 82
   3.5. TEMPERATURE HOMOGENEITY IN THE DSC CELL .............................................. 83

4. KINETIC AND DIFFUSION DATA ................................................................................ 85
   4.1. KINETIC MODEL AND CONSTANTS FOR THE EPPE-DPA REACTION ................. 85
   4.2. DIFFUSION COEFFICIENTS ...................................................................................... 90

5. RESULTS AND DISCUSSIONS ..................................................................................... 90
   5.1. APPLICATION TO MIXING .......................................................................................... 95

6. CONCLUSION ................................................................................................................... 99
In this part, a mathematical model has been developed for studying the competition between reaction and diffusion of two low molecular weight reactants, 2,3-epoxypropyl-phenylether (EPPE) and dipentylamine (DPA), miscible in a high viscous molten polymer, poly(ethylene-co-vinyl acetate) (EVA). Differential scanning calorimetry measurements of homogenous and bi-layer reagents polymer mixed systems have been made. Comparison between epoxy amine bulk reaction and homogenous polymer system reaction shows a deviation of about 10 times in autocatalytic part due to the interaction with the viscous media and proved that the reaction was diffusion controlled. Kinetic model of epoxy amine reaction was coupled to mutual diffusion coefficients of reacting species in function of there concentrations in a transport model. This has been resolved by a finite volume method. Model predictions were compared with experimental results. The determination of the diffusion coefficients of the reactants and the kinetic constants allowed simulating the diffusion/reaction process and relating it 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, typically encountered in polymer processing equipments, were able to homogenize the system in less than 10 seconds. In other words, the reaction should no longer be controlled by molecular diffusion as soon that a relatively low intensity mixing is applied (shear rate > 10 s\(^{-1}\)).
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 minutes). 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 seen as a chemical reactor ([GIME 00b], [CHOU 04]).

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 products distribution, the 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 so that the selectivity of the second reaction is a function of the mixing conditions (use of a stoichiometric defect of one of the reagent). If mixing is very fast, only the first reaction takes place as it consumes the totality of involved species. On the opposite, 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 higher viscosity attained, $\eta=0.3$ Pa.s, was not comparable to that of molten polymers [GUIC 97]. 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 [FREY 88]. 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 binds probably in the difficulties encountered to define 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 step 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 are insufficient to directly compute the concentration field in a complex industrial device ([VERG 98]; [VERG 04]).

Based on the above comments and in light of disappointing attempts to apply competitive reaction to polymer processed in complex geometries machines (mixers or extruders), one possibility is to define simple model reactive systems on which it is possible to analyse in detail 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 ([MOHR 57]; [OTTI 79]; [OTTI 83]). 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 ([JANS 97]; [TADM 79]). The purpose was to focus on diffusion and reaction in a bilayer sample (figure 4.1.). 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.

![Figure 4.1. Representation of the sample. Two layers of the same polymer containing respectively a proportion of reactants A and B initially separated.](image)

The sample is constituted by two layers of the same polymer, containing respectively 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 C. The initial separation of these reactants and their diffusion from one layer to the other leads to the formation of a mobile reaction front. The concentration profiles will develop differently depending on the kinetic of diffusion compared to reaction. If diffusion is
slower than reaction, the reaction may become diffusion controlled and its apparent kinetic be lower than that expected for the corresponding homogeneous reactive medium.

2.1. Mathematical model

Theoretical studies on the modelling of diffusion and reaction with initially separated reactants are numerous ([OTTI 79]; [FIEL 87a]; [FIEL 87b]; [LARR 92]; [TAIT 92]). The model presented here is based on similar considerations. The chemical reaction is of the type:

$$A + B \rightarrow C$$  \hspace{1cm} (4.1)

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 equations system (equation 4.2) to describe the relation between molecular diffusion, chemical reaction and the instantaneous concentration field of each specie j:

$$\frac{\partial C_j}{\partial t} = D_{12} \frac{\partial^2 C_j}{\partial x^2} + r_j$$  \hspace{1cm} (4.2)

$r_j (x,t)$ is the rate of production (or consumption) of $j$ entities ($j=A, B, C$). $D_{12}$ is the mutual diffusion coefficient. Here, it will be admitted that the mutual diffusion coefficient of the two species depends only on the initial concentration in monomers. In our experimental case, the reaction between monomer A and B leads to the formation of the product C. Then the glass temperature of the polymer mixture does not vary much with the extent of the chemical reaction since the global volume concentration of monomers in the viscous media is 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 [VREN 84]. This 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 homogenous conditions. This resolution is reported in appendix B.
2.2. Reaction model

The difficulties to select 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. A and B small reactive molecules 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 lower or of the same order of 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) (EVATANE®) with 28wt % of vinyl acetate and a melt index flow of 800 g/10min (190°C-2.16 kg). The samples were kindly supplied by Arkema. 2,3-epoxypropyl-phenylether (EPPE), (99% purity) and dipentyamine (DPA), (98% purity) are from Aldrich Chemical Co. Both reagents were used as received (table 4.1)
Table 4.1. Structures of polymer and liquids

<table>
<thead>
<tr>
<th>Materials</th>
<th>Structure</th>
<th>$M_n$ (g/mol)</th>
<th>Glass transition temperature ($^\circ$C)</th>
<th>Melting temperature ($^\circ$C)</th>
<th>Boiling point ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>poly (ethylene-co-vinyl acetate) (EVA)</td>
<td><img src="image" alt="Structure" /></td>
<td>4000$^a$</td>
<td>-30$^b$</td>
<td>64$^b$</td>
<td>-</td>
</tr>
<tr>
<td>2,3-epoxypropyl-phenylether (EPPE)</td>
<td><img src="image" alt="Structure" /></td>
<td>150$^c$</td>
<td>-</td>
<td>3.5$^c$</td>
<td>245$^c$</td>
</tr>
<tr>
<td>Dipentylamine (DPA)</td>
<td><img src="image" alt="Structure" /></td>
<td>157$^c$</td>
<td>-</td>
<td>-</td>
<td>202-203$^c$</td>
</tr>
</tbody>
</table>

$a)$ From rheological calculation assuming $M_w \propto \eta_0^{1/3.4}$ for entangled polymers.

$b)$ Calorimetric measurements.

c) Supplier data.

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 ([ASSC 02]; [LERO 01]), 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 (equation 4.3) and the conversion rate (equation 4.4), $dx/dt$, can be calculated as follows:

$$x(t) = \frac{\Delta H_t}{\Delta H_{tot}} = \frac{C_0 - C}{C_0} \quad (4.3)$$

and

$$\frac{dx}{dt} = \frac{1}{\Delta H_{tot}} \frac{dH_t}{dt} \quad (4.4)$$

$\Delta H_t$ is the heat released by reaction up to time $t$ and $\Delta H_{tot}$ 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 inerted using nitrogen gas with a flow rate of 20 ml/min. The use of this calorimeter enabled us to determine isothermal and non-isothermal reaction kinetics [SWIE 04].

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 $\Delta H_{tot}$ for the pure EPPE/DPA system was measured in non-isothermal conditions from room temperature to 300°C at different heating rate (5, 10, 15 and 20°C/min) and was evaluated to be 400 J/g, that is 120 kJ per mole of epoxy groups.

The second type of sample was an homogenous mixture of EVA with EPPE and DPA (EVA/EPPE-DPA). A liquid premix of EPPE and DPA was prepared in stoichiometric ratio then laid out with the polymeric layer during 24 hours in sealed capsules to permit the diffusion of the reagents in the polymer. All these steps were made 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 the EPPE and DPA diffuse at room temperature into EVA 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% (figure 4.2.). The reaction kinetics was studied in isothermal conditions at $T=150^\circ C$. 

Redha BELLA, PhD INSA Lyon, 2007
In both homogeneous and bilayer systems, the reaction kinetics was studied in isothermal conditions at T=150°C.

### 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:

\[
\Delta T_{\text{adiab}} = \frac{\Delta H_{\text{tot}} \cdot C_0}{\rho \cdot C_p}
\]  

(4.5)

\(\Delta H_{\text{tot}}\) is the reaction enthalpy (120 kJ/mole) 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 mole/m\(^3\) (table 4.3). Using these values, the adiabatic increase of temperature is \(\Delta T_{\text{adiab}} = 28\) °C.

The local increase of temperature is estimated by the relation:

\[
\Delta T = \Delta T_{\text{adiab}} \cdot \frac{t_{\text{diff}}}{t_R}
\]  

(4.6)

Where the characteristic times of thermal diffusion and reaction are defined hereafter.

The characteristic time of thermal diffusion in the sample, \(t_{\text{Diff}}\), is estimated as follows:
\[ t_{Dh} = \frac{e_0^2}{\alpha} \]  
(4.7)

\( e_0 \) is thickness of the layer and \( \alpha \) the thermal diffusivity of EVA calculated with equation 4.8.

\[ \alpha = \frac{\lambda}{\rho \cdot C_P} \]  
(4.8)

\( \lambda \) is the thermal conductivity of EVA (0.17 W/m.K), \( \rho \) the density of EVA at 150°C (816 kg/m\(^3\)) calculated from equation 4.17 and \( C_P \) is the heat capacity of EVA (2750 J/kg.K) [BADE 02].

The calculation of \( \alpha \) gives a value of 7.5x10\(^{-8}\) m\(^2\)/s. The calculation of the characteristic time of thermal diffusion for each sample thickness gives \( t_{Dh} = 53 \) s for the thicker one (\( e_0 = 2 \) mm), and \( t_{Dh} = 3 \) 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 to time curve at \( t=0 \).

\[ t_x = \left( \frac{1}{\left( \frac{dx}{dt} \right)_{t=0}} \right) \]  
(4.9)

From our experiments presented further in figure 4.4., we find \( t_R = 2700 \) s. (EVA/EPPE-DPA 80/20).

First, we note that thermal diffusivity being much higher than molecular diffusion (diffusion coefficient = 10\(^{-10}\) to 10\(^{-12}\) m\(^2\).s\(^{-1}\)), heat transfer will be much faster than mass transfer. Therefore, the samples should be homogeneous in temperature rather quickly during the heating stage in the DSC. Moreover, \( \Delta T_{ad} \) is not too high and \( t_R >> t_{Dh} \) thus, the calculated local temperature increase is \( \Delta T = 28 \cdot \frac{53}{2700} = 0.55 \cdot C'_{m.ax} \). This low value can be considered as negligible during the course of the reaction.
4. KINETIC AND DIFFUSION DATA

The resolution of equation 4.2 implies to determine the diffusion coefficients of the reactants in EVA at $T=150^\circ C$. 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 ([LIU 04]; [MARS 00]; [XU 94]) to elucidate mechanisms of reaction and identify the intermediate steps. This reaction occurs with the formation of an amine, epoxy and hydroxyl group intermediate termolecule due to the existence of intramolecular hydrogen bonds (figure 4.3. b). The explanation of this stage lies in the fact that the amine presents both the nucleophilic and electrophilic aspects in the same time and that the acidity of the hydroxyl group which is more important than that of the amine in this termolecule, reduced capacity of the amine to attack the $\alpha$-carbon of epoxy oxirane.

$$R-CH-CH_2 + R'-NH-R'' \rightarrow R-CH-CH_2N-R''$$

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 [PASC 02].

Figure 4.3. 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 amine [XU 94].

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-catalysed mechanism by hydroxyl groups formed after the opening of the oxiranes. Equation 4.10 illustrates the mathematical representation used for the calculation of the kinetic constants of our reaction [KAMA 74].

The used rate expression for this reaction is the following:

$$r_s = -\frac{dC_A}{dt} = \left( k + k' \cdot C_c \right) C_A \cdot C_B \quad (4.10)$$

$C_A$ is the concentration at time $t$ of the epoxy, $C_B$ concentration at time $t$ of the amine and $C_C$ concentration at time $t$ of the product. Kinetic constants are denoted $k$ for non-catalytic mechanism and $k'$ for auto-catalytic mechanism in equation 4.10.

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

$$C_C = C_{0A} - C_A \quad (4.11)$$

By introducing (4.11) in (4.10), we obtain:

$$r_s = -\frac{dC_A}{dt} = \left( k + k' \cdot \left(C_{0A} - C_A\right) \right) C_A \cdot C_B \quad (4.12)$$

$C_A = C_B$ since EPPE and DPA are in stoichiometric ratio (so at $t=0$: $C_0 = C_{0A} = C_{0B}$) (equation 4.12):
\[ r_A = -\frac{dC_A}{dt} = \left( k + k' \left( C_{A_0} - C_A \right) \right) C_A' \]  

(4.13)

The integration of equation 4.13 leads to the following expression (equation 4.14):

\[
t = \left( \frac{k'}{k + k' C_{A_0}} \right)^2 \ln \left( \frac{C_A}{C_{A_0}} \right) + \frac{k'}{2 \left( k + k' C_{A_0} \right)^{3/2}} \ln \left( \frac{k + k' \left( C_{A_0} - C_A \right)}{k} \right) \]  

(4.14)

where the concentration \( C_A \) of the epoxy (and thus that of the amine and that of the product of the reaction from equation 4.14) 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 4.2) using specific volumes \( V_{1T} \) and \( V_{2T} \) at 150°C determined from the measurement of the volume of DPA and EPPE at 90, 110, 130 and 150°C. The following relations were established (equations 4.15, 4.16 and 4.17):

\[
V_{1T} = 0.80344 \exp \left( 2.218 \times 10^{-5} \ T^{3/2} \right) \text{cm}^3 \text{g}^{-1} \text{ for the EPPE} \]  

(4.15)

\[
V_{2T} = 1.15303 \exp \left( 2.442 \times 10^{-5} \ T^{3/2} \right) \text{cm}^3 \text{g}^{-1} \text{ for the DPA} \]  

(4.16)

The specific volume of the EVA28 was measured by Rodgers [RODG 93], it is equal to:

\[
V_{2T} = 1.00832 \exp \left( 2.241 \times 10^{-5} \ T^{3/2} \right) \text{cm}^3 \text{g}^{-1} \]  

(4.17)

| Table 4.2. DPA and EPPE concentrations in the different studied systems |
|---|---|---|---|---|---|---|
| | Pure system | 20% epoxyde+amine ; 80% EVA 28800 | 10% epoxyde+amine ; 90% EVA 28800 |
| | homogeneous | 0,5mm/0,5mm | 1mm/1mm | 0,5mm/0,5mm | 1mm/1mm |
| \( C_0 \) (mol/l) | 2,698 | 0,532 | 0,532 | 0,532 | 0,266 | 0,266 |
• **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 equation 4.12. The result for \( T = 150°C \) is presented in figure 4.4. after optimization of the kinetic constants by a least square method.

• **Diluted EPPE-DPA**

If the solvent has 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 equation 4.12. 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 (figure 4.4.) and indeed, the model established on the basis of equation 4.12 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 presence of EVA was done and the calculated curve is presented in figure 4.4. The kinetic constants values are summarized in table 4.3.
Figure 4.4. Experimental and calculated extent of reaction as a function of time at $T=150^\circ$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 equation 4.12. Optimized kinetic constants are given in table 4.3.

Table 4.3. $k$ and $k'$ calculated for pure EPPE-DPA and for 20 wt% of EPPE-DPA dissolved in EVA ($T=150^\circ$C).

<table>
<thead>
<tr>
<th>Reactive system</th>
<th>$k$ (L.mol$^{-1}$.s$^{-1}$)</th>
<th>$k'$ (L$^2$.mol$^{-2}$.s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPPE/DPA and dodecane/EPPE-DPA 80/20</td>
<td>$5.55 \times 10^4$</td>
<td>$6.43 \times 10^4$</td>
</tr>
<tr>
<td>EVA/EPPE-DPA 80/20</td>
<td>$5.55 \times 10^4$</td>
<td>$6.57 \times 10^3$</td>
</tr>
</tbody>
</table>

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 correctly the behaviour of the model reactive system.
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 [BELL 06]. The mutual diffusion coefficient, $D_{12}$, was determined by an inverse rheological method developed by Ponsard [PONS 05]. 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 4.4.

<table>
<thead>
<tr>
<th>Reactants mass fraction in EVA (wt %)</th>
<th>Calculated $D_{12}$ (m$^2$.s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DPA</td>
</tr>
<tr>
<td>20</td>
<td>$1.2x10^{-10}$</td>
</tr>
</tbody>
</table>

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 kinetic of the reaction when EPPE and DPA are homogeneously diluted in EVA or when they are initially separated in the bilayer 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 (figure 4.4.). 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 bilayer sample according to the procedure described in appendix B.

In bilayer experiments, the reaction and diffusion are concurrent so that:

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 homogenised and the apparent reaction kinetics is the same than 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 figure 4.5. 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 the diffusion.
Figure 4.5. Extent of reaction measured as a function of time for different concentrations and bilayer thicknesses ($T=150^\circ C$)

- $\square$ pure EPPE-DPA,
- $\bigtriangleup$ homogeneous EVA/EPPE-DPA 80/20,
- $\bigcirc$ 0.5/0.5 mm bi-layer system with 20 wt % EPPE and DPA,
- $\bullet$ 0.5/0.5 mm bi-layer system with 10 wt % EPPE and DPA,
- $\triangle$ 1/1 mm bi-layer system with 20 wt % EPPE and DPA.

The evolution of the extent of reaction calculated with the model is satisfactory but not perfect (figure 4.6.). Some discrepancies are observed between simulation and experimental 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-catalysed 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 was 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.
Concentrations profile of EPPE, DPA and their product of reaction can be computed at every time across the sample. An example of the concentration profile obtained is shown in figure 4.7. Because of the faster diffusion of the amine compared to epoxy, one observes that the reaction zone, characterized by the peak of concentration in 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.

**Figure 4.6.** Comparison between experimental and calculated extent 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.
At this stage it is interesting to examine the sensitivity of the simulations to variations of the diffusion coefficient (figure 4.8.). For that purpose, we divided and multiplied the values of epoxy, amine and product diffusion coefficients simultaneously by a factor 5 and 10 compared to optimized values. The results presented in figure 4.8. They illustrate well the high 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.

Figure 4.7. Product concentration profile for 1/1 mm bilayer (20wt% reactants)
Figure 4.8. Influence of the diffusion coefficient value on the simulation of conversion for 1/1 mm bi-layer system with 20wt% of EPPE and DPA. The diffusion coefficient is multiplied and divided by a factor 5 and 10 (indication on the curves). (Δ) Experimental data.

5.1. Application to mixing

Remind that 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 \(\dot{\gamma}\) (figure 4.9.). For more details, see appendix C.

Figure 4.9. Simplified vision of laminar mixing with decrease of the striation thickness, \(\delta = e_0/2\) in simple shear flow.
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, $\delta$, is equal or smaller than 0.25 mm (figure 4.10.).

**Figure 4.10.** Simulation of homogenous and bi-layer systems with different thicknesses. The concentration of EPPE and DPA is 20wt%.

(1/1 - 0.75/0.75 - 0.5/0.5 and 0.25/0.25 mm)

In table 4.5, we calculated for every bi-layer thickness the ratio of the characteristic time of diffusion by the characteristic time of reaction (taken here equal to 45 minutes for a 20wt% concentration of EPPE and DPA). We identify clearly that for a 250 microns thickness, the characteristic times ratio 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. This shows that for the used concentrations set, the limit of detection of the striation thicknesses is of the order of 250 microns in a pure diffusion case.

Table 4.5. Comparison of characteristic times of diffusion and reaction as a function of the bilayer thickness. The concentration of EPPE and DPA is 20wt%.

<table>
<thead>
<tr>
<th>Bilayer thickness</th>
<th>Diffusion time (min)</th>
<th>Diffusion time/reaction time</th>
<th>Delay with regard to the homogeneous system (min) (60 % conversion)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25/0.25 mm</td>
<td>17</td>
<td>0.38</td>
<td>0</td>
</tr>
<tr>
<td>0.50/0.50 mm</td>
<td>70</td>
<td>1.15</td>
<td>12</td>
</tr>
<tr>
<td>0.75/0.75 mm</td>
<td>156</td>
<td>3.47</td>
<td>35</td>
</tr>
<tr>
<td>1/1 mm</td>
<td>278</td>
<td>6.2</td>
<td>67</td>
</tr>
</tbody>
</table>

In the geometry depicted in figure 4.9., 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 proportional with time and the shear rate [TADM 79]:

$$e(t) = \frac{2 \cdot \rho_0}{t \cdot \dot{\gamma}}$$  \hspace{1cm} (4.18)

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

$$t_B = \frac{\rho^2(t)}{2 \cdot D \dot{\gamma}}$$  \hspace{1cm} (4.19)

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

$$t_M = \sqrt[3]{\frac{2 \cdot \rho_0^2}{D \dot{\gamma}}}$$  \hspace{1cm} (4.20)
Note that when the striation thickness decreases the diffusion time subsequently decreases. It is proportional to $\gamma^{-2/3}$. This time is the request time to smooth 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 figure 4.9. By considering the respective diffusion coefficients the reactants at this concentration and a shear rate of 10 s$^{-1}$, we should reach the homogeneous state in 10 seconds which is very 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 for 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 necessary to adapt the reaction kinetic constants since EVA accelerated the reaction compared to 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 in homogenous 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 only 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. This is obviously what is required in actual reactive processing of polymers where mixing must occur at the earliest stage to optimize and control the yield of the reaction at the die exit.

However, the used reaction is too slow for the characterization of mixing in such mixers regarded the fact that the viscosity of the used polymer (EVA 28800) is low which implies high coefficients of diffusion of the reactive species (EPPE and DPA). For a better characterization of mixing, it would be necessary to increase the viscosity of the medium by...
using higher molecular weight EVA (EVA 2840 or EVA 2803) to slow down the diffusion of EPPE. The use of high reactivity species is also a solution provided that we are still able to measure easily and reliably the conversion as a function of time.
CONCLUSION

AND

PERSPECTIVES
During the three last decades, the industry of polymers draws the attention in fundamental research and the access to innovative products with original applications passes by a good understanding of the fundamental phenomena that can occur during polymer reactive processing (mixing, diffusion and reaction). Nevertheless, having a comprehensive approach in reactive extrusion still difficult to develop since the difficulties that can be met during the process, like high viscosity, nonuniform temperature and flow profiles, are difficult to predict.

This work aimed to open a way in this comprehension by developing new tools (rheology) and experimental models to understand the coupling of diffusion and reaction within simple laminar flow geometry.

The implementation of competitive reactions being largely used in chemical engineering to assess micromixing efficiency, we first attempted to apply it to viscous reactive medium. We have used a system of maleic anhydride-grafted poly(styrene)-block-poly(ethene-co-1-butene)-block-poly(styrene) (SEBS-g-MA) polymer with 4,4’-methylenebis [2,6-diethylaniline] (MDEA) diamine in internal mixer where intervened competitive consecutive reactions between anhydride of the polymer and the diamine. The fraction of gelled SEBS was reflecting the state of mixing. Apart to several experimental difficulties encountered this attempt leads us to the conclusion that the concept of competitive reactions is hardly applicable to molten polymer mainly because of the lack of temperature control. The viscous nature of the reactive medium induces temperature increase directly linked to the intensity of mixing. Thus we cannot be affirmative on whether the degree of segregation or the temperature variation is responsible for the modification of the equilibrium between the competitive reactions. In fact, these limitations can be encountered in any molten viscous medium and especially in formulations for reactive extrusion and in this context we believe that this feature may compromise the use of competitive reactions to characterize mixing in polymers.

Starting from these observations, the choice of a simplified approach was imposed to identify the interactions between mixing, diffusion and reaction. The used system was diglycidyl ether of bisphenol A (DGEBA) and 4,4’-methylenebis [2,6- diethylaniline] (MDEA) which are
miscible in polystyrene at setting temperature. We have studied how their diffusion rate in a molten polystyrene matrix influences their polymerization rate and the morphology of the thermoset particles formed at the end of the reaction. The diffusional control of the reaction was evidenced by comparing the time of reaction of an initially homogeneous mixture with that of different bi-layer samples. The reaction was controlled by the diffusion for relatively thick layers (>0.3 mm). A gradient of morphology was obtained due to the diffusional control of the reaction. The asymmetry of this gradient may be explained by three factors: differences in diffusion coefficients, in thermodynamic interactions and in viscosity. Thus with this system the complexity of the interaction between the different phenomena is clearly pointed out but the interpretations are multiple and difficult to discriminate.

The solution was to decouple these phenomena, to study them separately in a well defined model system, then to identify the interactions. The first step was to select the model system. In light of the above previous studies, we laid down condition for the choice of our reactive systems enumerated below:

- The initial miscibility of the reagents and the product of the reaction is essential;
- The choice of reactive system where we will prevent, if it is possible, secondary reactions and the parasite reactions;
- The temperature must be perfectly controlled;
- The experimental procedure and the characterization of the system must be easy.

The molten polymer medium was poly(ethylene-co-vinyl acetate) and the reactants were 2,3-epoxypropyl-phenylether (EPPE) and N-ethylaniline (NEA).

The second step was the calculation of diffusion coefficients of each reactant in the viscous medium. We have seen that, theoretically, the diffusion can be described, by the free volume theory. However, few works treat experimental measurement of the diffusion coefficient of small molecules in molten polymers. The diffusion process of two liquids, 2,3-epoxypropyl-phenylether (EPPE) and the N-ethylaniline (NEA) in three poly(ethylene-co-vinyle acetate) elastomers (EVA) having different molar masses has been studied thanks to a rheological technique. The mutual diffusion coefficient expressed with the free-volume theory has been estimated by an inverse method. The diffusion rate of the NEA, that is fully miscible with EVA, was not dependent on the molar mass of the polymer. On the other hand, the EPPE is
only partially miscible with EVA. Therefore, the evolution of the concentration gradient during the diffusion process is driven by the necessity for the mixture to form a two-phase system with an EVA-rich phase and a EPPE-rich phase. In this case, the concentration gradient through the sample is not continuous at a macroscopic scale. Nevertheless, we have applied the calculation model in the early stages of the diffusion in order to estimate the diffusion coefficient. The diffusion rate was found to be twice slower than that of the NEA. A correct prediction of the viscosity was obtained when the interaction parameter varies as a function of the molar mass of the polymer.

After having collected the different diffusion parameters and understood the diffusional behaviour of these molecules, the next step was the coupling of diffusion and reaction by using multilayer geometry to take mixing into account. A mathematical model for the multi-component diffusion of reacting species into the polymer has been developed. In this case the reactants were 2,3-epoxypropyl-phenylether (EPPE) and dipentylamine (DPA) in poly(ethylene-co-vinyle acetate) (EVA). The amine was substituted to increase the rate of reaction. The results based on this approach have been used to answer some relevant questions concerning the coupling of diffusion and reaction mechanisms in homogeneous system and initially separated reactants in molten polymer. It was possible to identify the strong influence of the layer thickness and the initial reactants concentrations on the reaction extent in the context of layered system assuming that in polymer systems we are in laminar mixing. In this case, it was possible to answer if the system is reaction or diffusion controlled. Lastly, we were able to predict the thickness from which bi-layer system is assimilated to a homogeneous system and the time necessary to be homogeneous in dynamic conditions.

In spite of these results, the door opens to several perspectives:

- It will be interesting to investigate the influence of the polymer on the reaction of small reactants (presence of hydrogen bonds, polymer-reactant interaction);
- Introduce, the mixing aspect on the global model;
- Use tools to investigate the inter-relation between mixing, diffusion and reaction in-line (ultrasound, NIR, RAMAN, mapping …)
This field of research remains at its beginnings and the combinations of products are innumerable in reactive extrusion. We hope that this work will give new ideas to other researchers to multiply the steps forwards in the comprehension of viscous reactive systems.
APPENDIX

SUMMARY

APPENDIX A: MICROMIXING, MACROMIXING AND SEGREGATION CONCEPTS .................................................................................................................................................................................. 109

APPENDIX B: DIFFUSION/REACTION MODEL DEVELOPMENT ........................................ 113

APPENDIX C: MIXING IN VISCOUS MEDIA .................................................................................. 116
**APPENDIX A: micromixing, macromixing and segregation concepts**

### A.1. Choice of a reactive system

We can display that three types of reactions can be used:

1. Simple reactions;
2. Competitive consecutive reactions;

- **Simple reactions**

\[ A + B \rightarrow R \quad (A1) \]

These reactions are quasi-instantaneous whose kinetics are known and characterized by a reaction time \( t_r \).

When characteristic time of micromixing \( t_m \) is of the same order or higher than \( t_r \), conversion is influenced by the micromixing. The disadvantage of these systems is that the reaction continues even after the micromixing time is exceeded, and the final influence on the conversion is experimentally unimportant.

It is interesting to have a certain idea on what occurs during \( t_m \) that can be reached by coupling two reactions.

- **Competitive consecutive reactions**

\[ A + B \rightarrow R \quad \text{quasi-instantaneous: } k_1 \text{ very high} \quad (A2) \]
\[ R + B \rightarrow S \quad \text{fast } k_2 \ll k_1 \quad (A3) \]

Reaction (A2) is quasi-instantaneous and reaction (A3) is fast having a reaction time of the same order as the micromixing time.

Let’s consider a reactor filled with A. By adding a small quantity of B under good conditions of mixture \( (t_m \ll t_r) \), the product of reaction R will be immediately dissolved in the mixture and will not be able to react with the remainder of B. On the other hand, if the mixture is bad
(t_m \geq t_r2), R remains in contact with B and will have the product S resulting from the second reaction.

Therefore, the ratio of the products R and S represent a measure of the efficiency of the mixing, which has been detailed before.

- **Competitive parallel reactions**

  \[ A + B \rightarrow R \quad \text{quasi-instantaneous } k_1 \text{ very high } \]  
  \[ C + B \rightarrow S \quad \text{fast } k_2 \ll k_1 \]  

  (A4) 
  (A5)

As for the preceding case, reaction (A4) is definitely faster than the second (A5). When a small quantity of B is added to an excess of A and C, the proportion of R and S will depend on the quality of the mixing and thus of the micromixing.

In the case of a perfectly micromixed system, there will be only the formation of R, on the other hand, the formation of S will indicate a partial segregation of the mixture.

**A.2. Concept of macromixing and micromixing**

In the case of a chemical reaction, the transformation of the reagents takes place on a molecular scale and, consequently, is conditioned by the contact of molecules. One foresees here the idea of a scale of the mixture, this one being able to be completed on the scale of the reactor (homogeneous concentration) without being realized at the molecular scale. This distinction brought to define two concepts:

- **Macromixing**: the whole of the phenomena which ensure a homogenization of compositions in reactional mixture on a macroscopic scale. This is translated in continuous reactors by the existence of a distribution of the residence times (RTD).
- **Micromixing**: processes which ensure the homogeneity on a microscopic and molecular scale, and which characterize the fine texture of the mixture (direct influence on the quality of the products, selectivity and output of polymerization reactions, crystallization and organic synthesis).
A real fluid can be considered as a combination of the two phenomena:

\[ \text{macromixing} > \text{real fluid} > \text{micromixing} \]

### A.2. Concept of segregation

The scale of segregation measures the size of the domains of segregation (those in which the concentration of species differs). In a high viscous medium, it is the thickness of the striations corresponding to the lattices of badly mixed fluid, in a turbulent medium; it is for example the dimension of the small swirls where the matter does only penetrate by diffusion.

For the measure of the segregation state, we take, for example, the case of competitive consecutive or parallel reactions, the quality of mixing can be determined by the definition of the segregation index \( X_S \) who has as a characteristic to be representative of the local micromixing as following:

\[
X_S = \frac{2C_S}{2C_S + C_R} = \frac{2C_S}{C_B^0 + C_S}
\]  

where \( C_R \) and \( C_S \) are concentrations of R and S products respectively, and \( C_B^0 \) the initial concentration of B reactive.

The reactional fluid, macroscopically homogeneous, can have a variable microscopic structure:

- we speak about *macrofluid* or fluid in total segregation \( (X_S= 0) \) when the fluid is mixed on a macroscopic scale and the molecules remains grouped in small aggregates and are free to mix and enter in collision only to the interior of their own aggregate;

- while the term of *microfluid* or fluid in maximum mixture \( (X_S= 1) \) is reserved for the fluid in which each molecule is free to mix and to enter in collision with any other molecule of the fluid, or, the molecules remain grouped by packages whose dimension is very small on a macroscopic scale, but which keeps a certain coherence. These packages are called fields of segregation (Danckwerts).
In a real reactor, for the same Residence Time Distribution (RTD), the state of micromixing does not correspond systematically to one of the two cited limiting states. It can vary between those according to the properties of the fluid (viscosity, polydispersity), to the reaction (simple or complex) and to the mixing mode. The fluid can then be considered as a mixture of *microfluid* and *macrofluid*. In general, a real fluid presents a partial segregation.

**A.3. Micromixing and characteristic times**

For a mixed reactional system, we can identify three characteristic times on which the evolution of the reaction strongly depends. *Macromixing time* \( t_M \) corresponds to the mixing time on macroscopic scale; *micromixing time* \( t_m \) corresponds to mixing time on microscopic scale which is the characteristic time of the decrease of the segregation under the influence of the diffusion, turbulence or mechanical agitation; and *characteristic time for chemical reaction* \( t_r \) which correspond to the scale of time over which proceeds the kinetic process which controls the reaction.

The reaction is limited by the phenomenon of segregation when characteristic time of reaction \( t_r \) is shorter than the micromixing time \( t_m \). It is thus seen that, from the point of view of chemistry, the concept of segregation considered is quite relative. If there is \( t_m \ll t_r \), the medium seems as a microfluid, on the contrary if there is \( t_m \gg t_r \), the medium seems strongly segregated. In fact, we note empirically that the quantities:

\[
\frac{1 - X_s}{X_s} = \text{\%microfluid} \quad \text{and} \quad \frac{t_r}{t_m}
\]

vary in the same direction and are often of the same order of magnitude. From a practical point of view, to know if the segregation (the imperfect micromixing) risk to disturb the reaction, it is thus enough to estimate \( t_r \) and \( t_m \) and to evaluate their ratio. If \( t_r / t_m \gg 1 \), we will be able to consider the fluid as well micromixed.
**APPENDIX B: diffusion/reaction model development**

\[
\begin{align*}
\frac{\partial C_A}{\partial t} &= D_{12}^A \frac{\partial^2 C_A}{\partial x^2} + r_A \\
\frac{\partial C_B}{\partial t} &= D_{12}^B \frac{\partial^2 C_B}{\partial x^2} + r_B \\
\frac{\partial C_C}{\partial t} &= D_{12}^C \frac{\partial^2 C_C}{\partial x^2} + r_C
\end{align*}
\]

\( r_j(x,t) = \nu_j \cdot r_c(x,t) \quad \text{so:} \quad \nu_A = \nu_B = -1 \quad ; \quad \nu_C = 1 \)

\( \nu_j \) is the stoichiometric parameter for \( j \) specie. We consider \( C_A = C_A(x,t) \), \( C_B = C_B(x,t) \) and \( C_C = C_C(x,t) \) the concentrations of monomers A, B and product C at position \( x \) and time \( t \). We assume that \( C_{j0} \) is initial concentration. \( D_{12}^A \), \( D_{12}^B \) and \( D_{12}^C \) are the mutual diffusion coefficients of A, B and their product C of reaction respectively.

According to equations B1, an easy numerical solution with explicit finite differences is given for the time dependence of the concentration of each specie A, B and C.

\[ \text{Figure B1. Bi-layer schematic representation of initially separated A and B reactants considering the one dimensional x orientation of the diffusion. The thickness of each layer is } \delta. \]
Thus, there are three initial conditions and two boundary conditions:

\[ \begin{align*}
C_A - C_{0A} & \quad \text{in} \quad [0, \delta] \\
C_B - C_{0B} & \quad \text{in} \quad [\delta, 2\delta] \\
C_C - 0 & \quad \text{in} \quad [0, 2\delta] 
\end{align*} \]  

\[ (B3) \]

\[ \begin{align*}
\left( \frac{\partial C_j}{\partial x} \right)_{x=\delta} = \theta ; \quad \left( \frac{\partial C_j}{\partial x} \right)_{x=2\delta} = \theta
\end{align*} \]  

\[ (B4) \]

The resolution is made in term of finite volume and in figure B2 we present a schematic representation of the integrated volume:

\[ D_{j,t} \cdot \left( \frac{C_{j,N}^t - C_{j,P}^t}{\Delta x} \right) - \left( k + k' \cdot C_{c,P}^t \right) \cdot C_{A,P}^t \cdot C_{S,P}^t \cdot \Delta x = D_{j,t} \cdot \left( \frac{C_{j,P}^t - C_{j,S}^t}{\Delta x} \right) + \frac{\Delta x \left( C_{j,P}^{n+1} - C_{j,S}^{n+1} \right)}{\Delta t} \]  

\[ (B5) \]

We put:

\[ a_h = \frac{D_{j,k} \cdot \Delta t}{\Delta x^2} \]  

\[ (B6) \]

where the diffusion coefficient is calculated at the n or s face of the considered volume (figure B2). The mass balance is the following:

\[ a_s \cdot \left( C_{j,N}^{t+1} - C_{j,P}^{t+1} \right) + r_j \cdot \Delta t = a_s \cdot \left( C_{j,P}^{t+1} - C_{j,S}^{t+1} \right) + \left( C_{j,P}^{n+1} - C_{j,F}^{n+1} \right) \]  

\[ (B7) \]

with:

\[ C_{j,P}^{n+1} = C_{j,N}^{n+1} \cdot (a_h) + C_{j,S}^{n+1} \cdot (a_s) + C_{j,P}^{n} \cdot (1 - a_h - a_s) + r_j \cdot \Delta t \]  

\[ (B8) \]
To develop an equation system out of the differential equations system (equations B1), the following linearization is made:

\[ r_j \cdot \Delta t = \left( k + k' \cdot C_{C,P}^{\varepsilon} \right) \cdot C_{B,P}^{\varepsilon} \cdot C_{A,P}^{\varepsilon} \]  \hspace{1cm} (B9)

We make the linearization for each species A, B and C.

Conditions at the limits:

- at \( x=0 \) half a volume

Assessment:

\[ r_j \cdot \frac{\Delta x}{2} = \frac{D_{j,s}}{\Delta x^2} \cdot \frac{\Delta x}{\Delta x} \cdot \left( C_{j,P}^{\varepsilon} - C_{j,P}^{\varepsilon} \right) + \frac{D_{j,s}}{\Delta x^2} \cdot \frac{\Delta x}{\Delta x} \cdot \left( C_{j,P}^{\varepsilon} - C_{j,P}^{\varepsilon} \right) \]  \hspace{1cm} (B10)

The equation B10 is written like the equation B6 but with:

\[ a_x = 0 \quad ; \quad a_z = \frac{2 \cdot D_{j,s} \cdot \Delta t}{\Delta x^2} \]  \hspace{1cm} (B11)

- at \( x=\delta \) half a volume

Assessment:

\[ r_j \cdot \frac{\Delta x}{2} + D_{j,s} \cdot \frac{\Delta x}{\Delta x} \cdot \left( C_{j,P}^{\varepsilon} - C_{j,P}^{\varepsilon} \right) = \frac{D_{j,s}}{\Delta x^2} \cdot \frac{\Delta x}{\Delta x} \cdot \left( C_{j,P}^{\varepsilon} - C_{j,P}^{\varepsilon} \right) \]  \hspace{1cm} (B12)

The equation B12 is written like the equation B6 but with:

\[ a_z = 0 \quad ; \quad a_n = \frac{2 \cdot D_{j,s} \cdot \Delta t}{\Delta x^2} \]  \hspace{1cm} (B13)

Equations B10 and B12 are solved using finite volume method and numerical solution is calculated using Matlab software.
**APPENDIX C: mixing in viscous media**

*C.1. Distributive and Dispersive Mixing*

In polymer mixing, we usually distinguish between *distributive* and *dispersive* mixing (figure C1). Distributive mixing aims to improve the spatial distribution of the components without cohesive resistance playing a role; it is also called simple or extensive mixing. In dispersive mixing cohesive resistances have to be overcome to achieve finer levels of dispersion; dispersive mixing is also called intensive mixing.

![Schematic illustration of dispersive and distributive mixing mechanisms](figure C1)

The cohesive component can consist of agglomerates where a certain minimum stress level is necessary to break the agglomerate. It can also be droplets where minimum stresses are required to overcome the interfacial stresses and deform the droplet to cause break-up. Dispersive mixing is usually more difficult to achieve than distributive mixing. Single screw extruders are generally considered to be poor dispersive mixers while twin screw compounding extruders have much better dispersive mixing capability. Mixing devices that
split and reorient the fluid while generating strong elongational flow can achieve both efficient distributive and dispersive mixing.

**C.2. Laminar mixing**

The traditional solution for many mixing problems has been to increase the energy input and to let the turbulence produce effective mixing. With the high viscosities associated with polymers, turbulent flow is not achievable and laminar flow is the only possible mechanism for polymer mixing. Another reason why mixing processes are often laminar is when excessive stresses should be avoided.

As already observed by Reynolds [REYN 1894], effective laminar mixing of fluids arises due to repeated stretching and folding. This repetitive operation, often referred to as the *bakers’ transformation*, is illustrated in figure C2. The bakers’ transformation results in doubling the number of material layers on every step and in a corresponding decrease of the striation thickness. The time-periodic Stokes flow in the gap between two eccentric cylinders is a good example of stretching and folding operations. Unlike the simplified scheme as shown in figure C2, in real flows stretching and folding effects are normally not separated in time and happen simultaneously. A close companion of the stretching and folding operation is a “stretch, cut and stake”. This operation principle is typical for static mixers.

![Figure C.2: Example of “stretching and folding” operation in a Stokes flow of viscous fluid in the gap between eccentric cylinders](image)

**C.3. Diffusion and reaction in laminar mixing**

Mixing of molten polymers cannot be assisted by either diffusion or turbulence and the absence of diffusion makes the two components engaged in extrusion process and their interface easily identifiable and organized in striations (figure C3). The striation thickness concept was first introduced by Mohr and al. [MOHR 57] and analyzed extensively by Ottino and al. ([OTTI 79]; [OTTI 81]; [OTTI 83]).
The striation thickness, $\delta$, is defined as one-half of the thickness of the repeating unit (i.e., one-half of the sum of the thickness of two adjacent layers of components A and B).

The case of our study involves the diffusion and reaction of two small molecules in a medium of high viscosity. The two reactants are initially separated in each layer of a unique polymer. This implies that A and B layers are similar. We observe diffusion, reaction and mixing simultaneously and the coupling of these phenomena induces the progressive disappearance of the interface.

**C.4. Mixing time under shearing effect**

We can calculate the expected influence of shear rate on reaction. Consider first a static layer of polymer A of thickness $2\delta$ in a sea of polymer B. If B goes into A with diffusion coefficient $D_{BA}$, then Ficks law predicts the time for concentration difference in the A layer to fall to < 1% is [ORR 01]; [TADM 79]:

$$t_D = \frac{2 \cdot \delta(i)}{D_{BA}} \quad (C1)$$

Considering just diffusion to homogenize the sample, it will take a very long time. However in simple shear flow, $\delta$ continually decreases [TADM 79]:

$$\delta(i) = \frac{2 \cdot \delta_0}{t \cdot \gamma} \quad (C2)$$
Combining equation C1 and C2 gives the mixing time:

\[ \begin{align*}
\xi_H &= \sqrt[3]{\frac{8 \cdot \delta^2}{D_{LA} \cdot r^2}} \\
\end{align*} \]  
(C3)
EXTENDED ABSTRACT IN FRENCH

SUMMARY

INTRODUCTION GENERALE ........................................................................................................... 123

1. ETUDE PRELIMINAIRE........................................................................................................... 125

2. REACTION ET DEVELOPPEMENT DE MORPHOLOGIE INFLUENCE PAR LA DIFFUSION DANS UN MELANGE THERMOPLASTIQUE / THERMODURCISSABLE .......................................................... 126

2.1. MATERIAUX....................................................................................................................... 126

2.2. PARTIE EXPERIMENTALE ET DISCUSSIONS .................................................................. 127

2.3. CONCLUSION..................................................................................................................... 129

3. DIFFUSION DE LIQUIDES DANS DES POLYMERES FONDUS : DEPENDANCE DU COEFFICIENT MUTUELLE DE DIFFUSION AVEC LA MISCEBILITE DE LA MASSE MOLAIRE DU POLYMERE ...................................................................................... 130

3.1. LA DIFFUSION................................................................................................................... 130

3.2. LES MATERIAUX............................................................................................................... 131

3.3. PROCEDURE EXPERIMENTALE ....................................................................................... 132

3.4. MODELE DE DIFFUSION .................................................................................................. 132

3.5. RESULTATS ET DISCUSSION............................................................................................. 133

3.6. CONCLUSION..................................................................................................................... 137

4. CARACTERISATION ET MODELISATION DE LA DIFFUSION ET DE LA REACTION DE REACTIFS A FAIBLE POIDS MOLECULAIRE DANS UN POLYMERE FONDU......................................................................................................................... 137

4.1. MODELE ............................................................................................................................ 138

4.2. EXPERIMENTAL ............................................................................................................... 139

4.2.1. Matériaux .................................................................................................................... 139

4.2.2. La réaction époxyde/amine ....................................................................................... 139

5. CONCLUSION......................................................................................................................... 142

CONCLUSION ET PERSPECTIVE ................................................................................................ 143
DIFFUSION ET REACTION DE PETITES MOLECULES DANS DES MILIEUX POLYMERES FONDUS:

caractérisation et modélisation

INTRODUCTION GENERALE

Durant les 30 dernières années, l'industrie des polymères a atteint un énorme taux de croissance. En raison d'une demande accentuée des matières plastiques à forte valeur ajoutée, l'utilisation d'extrudeuses en tant que réacteurs continus pour les polymères a attiré une attention considérable. Dans ce contexte, les procédés réactifs des polymères et plus spécifiquement la chimie des polymères à l’état fondu (tels que polymérisation en masse, modification de polymère, compatibilisation de mélange ...) se sont développés dans l’industrie et concurrencent les opérations en solvants du point de vue efficacité et économie. Toutefois, ces procédés réactifs restent difficiles à contrôler du fait du nombre de paramètres et de la multitude de phénomènes qui peuvent intervenir. Ils présentent aussi certaines limitations dues, d’une part, aux conditions opératoires dans les milieux visqueux qui sont souvent assez drastiques, et d’autre part, au manque de compréhension de ces phénomènes. Dans ce genre de réacteurs (à écoulement continu) les temps de séjour sont assez courts et puisque les écoulements sont laminaires, la modification de polymères exige, dans certains cas, l’introduction de petites molécules réactives ce qui induit une difficulté de mélange mécanique à l’échelle macroscopique (formation de striation, présence de zones hétérogènes ...), et une diffusion lente à l’échelle microscopique (miscibilité variable, gradient de viscosités, dissipation visqueuse, présence de réactions chimiques ...).

Si on s’intéresse à l’aspect fondamental de ces procédés, on constate que les phénomènes de mélange, diffusion et réaction sont reliés au sein d’un même processus. Ce processus est valable pour n’importe quelle chimie que ça soit dans le domaine des polymères ou celui du génie chimique. Dans le cas de ce dernier, l’étude du couplage de ces phénomènes a été largement abordée pour augmenter, d’une part, l’efficacité du mélange et pour, d’autre part, maîtriser l’aspect chimie des mélanges. Cette maîtrise du procédé est abordée dans le génie chimique en utilisant deux approches différentes. La première est purement empirique et se base sur les données expérimentales ; tandis que la deuxième (généralement la plus utilisée et...
la plus efficace) est basée sur la compréhension des phénomènes mis en jeu en couplant l’aspect expérimental et celui purement mathématique (modélisation et simulation). Entre ces deux extrêmités, il y a des approches intermédiaires qui sont plus ou moins expérimentales ou modèles.

Ce même raisonnement est utilisé dans le domaine des polymères. Par contre, ce dernier présente certaines spécificités qui le différencient du domaine du génie chimique du fait des viscosités élevées des milieux polymères comparés aux milieux solvants. En plus, ces milieux sont fortement réactifs et les profils de températures sont variables.

Ce travail est inspiré des démarches utilisées dans le génie chimique. Notre objectif est d’effectuer une démarche de compréhension pour identifier les relations existant entre mélange, diffusion et réaction sur des systèmes modèles dans des milieux visqueux fondus.

Une approche qui nous a paru intéressante, également inspirée du domaine du génie chimique, est basée sur l'utilisation des réactions modèles dans des milieux fondus et visqueux. L'idée est d’engager des réactions compétitives consécutives ou parallèles dans le polymère en présence d’un mélange mécanique et de mesurer l’indice de ségrégation.

Puisque le concept des réactions compétitives pour étudier le mélange a été développé pour le génie chimique, nous trouvons dans littérature que la plupart des systèmes de réactions compétitives consécutives ou parallèles étudiés sont effectuées en milieux homogènes de basse viscosité, aqueux ou organiques ([FOUR 96a]; [FOUR 96b]; [GUIC 00a]; [GUIC 00b]). Très peu d'auteurs appliquent cette approche micromélange dans des systèmes visqueux ([BOUR 95]; [BALD 98]; [GUIC 97]). Dans ces trois études la viscosité maximale atteinte (> 300 mPa.s) est plus faible que ce qu’on peut observer dans des milieux visqueux fondus. En outre, la plupart du temps le milieu polymère est constitué de polymère polaire, hydrophile ([BALD 98]; [GUIC 97]) dissout dans l'eau et mélangé à température ambiante. Les études sur les polymères apolaires à des températures élevées sont moins nombreuses [KOST 01] [FREY 88].
1. ETUDE PRELIMINAIRE

Puisque les études du micromélange sont appliquées avec succès pour caractériser le mélange dans le génie chimique mais rarement utilisées dans le cas des milieux fondu visqueux, nous avons essayé d'adapter ce concept en développant notre propre système modèle basé sur une imidisation d'un poly(styrène)-block-poly(ethene-co-1-butene)-block-poly(styrène) greffé anhydride maléique (SEBS-g-MAH) avec une diamine (MDEA). Un large excès d'une des diamines a été ajouté au polymère fondu variant de 0.1 à 0.9 en stoichiométrie. Le rapport stoichiométrique a été calculé selon l'équation 1 :

\[ r = \frac{n_{SEBS}}{n_{diamine}} \text{ en fonctions réactives} = \frac{m_{SEBS}}{m_{diamine}} \frac{M_{diamine}}{M_{SEBS}} \frac{10.2}{2} \]  

(1)

où \( n_{SEBS} \) et \( n_{diamine} \) est le nombre de moles en fonctions réactives de SEBS et de diamine, \( m_{SEBS} \) et \( m_{diamine} \) les masses de SEBS et diamine et \( M_{SEBS} \) et \( M_{diamine} \) les masses molaires de SEBS et diamine. Avec ce processus, nous avons effectué beaucoup d'essais non décrits dans le manuscrit, qui ont enrichi et dirigé la suite de l'étude. L'amine a été ajoutée au SEBS-g-MAH fondu dans un mélangeur interne. Selon la concentration locale de la diamine dans le SEBS-g-MAH, la réaction de la diamine avec l’anhydride mène à une fonctionnalisation des chaînes de polymère (greffage) et à une réticulation d’une fraction du polymère. Différentes difficultés expérimentales sont apparues mais le problème principal est que la température matière mesurée différait fortement de la température consignée on raison de la dissipation visqueuse. De plus, dans les milieux polymères de hautes viscosités ce décalage de la température dépend fortement du cisaillement (et donc de la vitesse de rotation). C'est évidemment un problème majeur puisque le mécanisme de réaction peut être affecté par le changement de température ainsi que la viscosité du milieu. Le point critique ici est qu'objectivement nous ne pouvions pas attribuer le changement de la fraction insoluble à un changement du degré de ségrégation sans avoir vérifié que le mécanisme de réaction ne dépendait pas de la température. Ce problème existera toujours dans les milieux de hautes viscosités et nous croyons qu'il est réellement difficile (presque impossible) de définir un vrai système modèle de réactions compétitives adaptées aux polymères. Cette approche n’a pas eu de suite.
En second lieu, on a effectué l’analyse de la relation entre la diffusion et la réaction pour illustrer les difficultés rencontrées pour définir un système modèle ; également la complexité des interactions entre les phénomènes est soulignée.

2. REACTION ET DEVELOPPEMENT DE MORPHOLOGIE INFLUENCE PAR LA DIFFUSION DANS UN MELANGE THERMOPLASTIQUE / THERMODURCISSABLE

Dans de précédentes études [MEIN 04a], l’aspect mélange a été étudié en utilisant une méthode rhéologique par le biais d’un rhéomélangeur spécialement développé pour étudier l’effet du mélange dans un système thermodurcissable/thermoplastique. On a utilisé la rhéométrie dans une démarche complémentaire pour identifier le couplage diffusion/réaction dans ce mélange bien caractérisé pour lequel nous avions à disposition des données suffisantes (réactivité, miscibilité,…). De cet exemple particulier, on a voulu illustrer les difficultés liées à la définition d’un système modèle et la complexité des interactions entre les trois phénomènes cités plus haut.

2.1. Matériaux

Ce système est constitué de Diglycidyl éther du bisphenol A (DGEBA) et 4,4’-methylenebis [2,6-diethylaniline] (MDEA) dans du polystyrène (PS) comme polymère. Les deux liquides sont miscibles dans le polystyrène à la température consigne (177°C). Leur polymérisation conduit à la formation de sphères réticulées dispersées dans la matrice PS. Nous avons étudié comment leur diffusion dans une matrice fondu de polystyrène influence leur degré de polymérisation et la morphologie des particules thermodurcissables formées à la fin de la réaction.

L’influence de la diffusion des molécules réactives sur le développement de la morphologie et le comportement rhéologique du mélange dans le PS ainsi que le contrôle de la réaction par la diffusion a été démontré en comparant le temps de réaction dans un mélange initialement homogène à celui de différents échantillons en bicouche. Le principe de ces expériences est montré sur la figure 1.
2.2. Partie expérimentale et discussions

La réaction était contrôlée par la diffusion pour des couches relativement épaisses (0,3 mm). Cela a été identifié par des mesures en rhéologie de la viscosité complexe des bicouches où on a remarqué que moins les bicouche sont épaisse plus la viscosité augmente et tend à se rapprocher du système homogène (figure 2). Il faut noter que l’augmentation de la viscosité est due à la formation de nodules thermodurcissable dans le thermoplastique.
En raison des limitations diffusionnelles et du contrôle de la réaction par la diffusion, un gradient de morphologie a été observé dans les coupes des échantillons en bicouches (figure 3). L'asymétrie de ce gradient peut être due à trois facteurs différents :

- une vitesse de diffusion plus élevée de la MDEA dans la couche de PS/DGEBA comparée à la diffusion de la DGEBA dans la couche de PS/MDEA,
- une séparation de phase se produisant à des conversions faibles dans la couche PS/DGEBA. Cela est dû aux interactions moins favorables entre le PS et la DGEBA,
- La faible viscosité de la couche PS/DGEBA.

Cependant, il est difficile d'attribuer cette asymmetricité du gradient avec certitude à l'un des trois paramètres précédemment cités.
2.3. Conclusion

La présente partie du travail illustre très bien les complications que nous pouvons rencontrer dans de tels systèmes complexes. La définition d'un système réactif plus simple (sans...
séparation de phase) et également le découplage des processus de diffusion et de réaction de n'importe quel autre phénomène semblent être une nécessité. Ceci sera discuté en détail dans la prochaine partie.

3. DIFFUSION DE LIQUIDES DANS DES POLYMÈRES FONDUS : DEPENDANCE DU COEFFICIENT MUTUEL DE DIFFUSION AVEC LA MISCIBILITÉ ET LA MASSE MOLAIRES DU POLYMÈRE

La suite de l'étude a été menée sur un système modèle dans lequel nous avons pris soin de vérifier les miscibilités de petites molécules monofonctionnelles dans un thermoplastique à différents grades pour une réaction simple. Le but ultime de ce système modèle est de découpler la diffusion et la réaction pour pouvoir définir indépendamment les paramètres qui peuvent régir la diffusion et la réaction. En fait, on a besoin de ces paramètres pour pouvoir modéliser et simuler l’interaction entre ces différents paramètres dans un système simplifié comparé à ce qui se produit dans une extrudeuse.

Sachant que les coefficients de diffusion sont difficilement mesurables et calculables, une partie spécifique de l’étude est dédiée à déterminer les coefficients de diffusion de nos réactifs. Théoriquement, la diffusion est décrite par la théorie des volumes libres [VREN 77a].

3.1. La Diffusion

La diffusion d’un liquide dans un polymère fondu peut être mise en évidence à partir du schéma expérimental suivant (Figure 4). L’échantillon sollicité en mode dynamique dans le domaine linéaire de la viscoélasticité est un bicouche formée d’une couche de polymère et d’une couche de liquide dont on veut étudier la diffusion. Avant le début du processus de diffusion, la viscosité initiale mesurée reflète la viscosité du liquide. Durant le processus de diffusion, le gradient de concentration qui est établi dans tout l’échantillon induit une augmentation de la viscosité apparente. Lorsque la concentration devient homogène dans tout l’échantillon, la viscosité tend alors vers une valeur constante. En conséquence, la variation de la viscosité en fonction du temps traduit la diffusion du liquide dans le polymère fondu (figure 4).
3.2. Les matériaux

Des poly(éthylène-co-vinyle acétate) (EVA) de masses molaires différentes ont été utilisés dans cette étude. Le composé monoamine est la (N-éthylaniline) (NEA) et le composé monoépoxyde est le 2,3-époxypropyl-phenylether (PGE). Les caractéristiques de ces produits sont regroupées dans le tableau 1.

<table>
<thead>
<tr>
<th>Matériaux</th>
<th>Abbreviation</th>
<th>η₀ à 110°C (Pa.s)</th>
<th>Mᵥ (g.moF⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(Ethylene-co-vinyle acétate)</td>
<td>EVA2803</td>
<td>5.1·10⁷</td>
<td>53500</td>
</tr>
<tr>
<td>(avec 28% d’acétate)</td>
<td>EVA2840</td>
<td>5.3·10³</td>
<td>27500</td>
</tr>
<tr>
<td></td>
<td>EVA28800</td>
<td>7.4·10³</td>
<td>7900</td>
</tr>
<tr>
<td>N-éthylaniline</td>
<td>NEA</td>
<td>7·10⁻⁴</td>
<td>121</td>
</tr>
<tr>
<td>2,3-époxypropyl-phenylether</td>
<td>PGE</td>
<td>1.5·10⁻³</td>
<td>150</td>
</tr>
</tbody>
</table>
3.3. Procédure expérimentale

Les expériences ont été conduites sur un rhéomètre RMS800 utilisant une géométrie plan-plan de 50 mm chauffée par convection sous un flux d'azote. La couche d'EVA est mise en contact avec le plateau inférieur. Une fois que l'échantillon d'EVA a atteint la température expérimentale, le liquide (amine ou époxy) est transféré entre l'échantillon d'EVA et le plateau supérieur. La variation de la viscosité complexe est alors suivie pendant la diffusion du liquide dans l'EVA à la fréquence de $\omega=10$ rad/s.

3.4. Modèle de diffusion

Le processus de diffusion d'une petite molécule dans un polymère fondu est généralement de type Fickien. En conséquence, la deuxième loi de Fick peut être utilisée pour décrire les variations de la concentration avec le temps:

$$\frac{\partial C}{\partial t} = \frac{\partial C}{\partial x} \left( D_{12} \langle C \rangle \frac{\partial C}{\partial x} \right)$$

Où $D_{12}$ est le coefficient mutuel de diffusion. $D_{12}$ est directement relié au coefficient de diffusion $D_1$ :

$$D_{12} = D_1 \phi^2 \left( 1 - 2 \chi (1 - \phi) \right)$$

où $\chi$ est le paramètre d’interaction de Flory-Huggins et $\phi$ la concentration du polymère.

Le coefficient $D_1$ s’exprime à partir de la théorie du volume libre selon l’équation suivante :

$$D_1 - D_0 \exp \left( -\frac{E}{RT} \right) \exp \left( -\frac{\alpha V_m^* + \beta V_m^*}{V_m^*} \right)$$
où $D_0$ est une constante, $E$ est l’énergie critique qu’une molécule doit avoir pour surmonter les forces d’attractions (en général : $E=0$), $R$ est la constante des gaz parfaits, $T$ est la température absolue, $V_1^*$ et $V_2^*$ sont les volumes spécifiques de l’espèce diffusante et du polymère respectivement à $T = 0K$, $\omega_{1,2}$ sont les fractions massiques de l’espèce diffusante et du polymère et finalement $\xi$ est le rapport des volumes molaires des unités sautantes du solvant et du polymère.

Cette équation nécessite de connaître les fractions de volume libre et donc la loi de Williams-Landel-Ferry (WLF) de chaque espèce. Plus simplement, cette expression peut être décrite [JOUB 02] en terme d’énergie d’activation dans un domaine de température bien précis.

\[
D_1 = D_0 \cdot \exp\left(-\frac{E_i}{RT}\right) \cdot \exp\left(\frac{a_1}{1 + \frac{T}{E_1}} \cdot V_1^* + \xi \cdot \frac{a_2}{1 + \frac{T}{E_2}} \cdot V_2^*\right)
\]

où $E_i$ et $V_i^*$ sont respectivement l’énergie d’activation à l’écoulement et le volume spécifique (à la température $T$) de l’espèce $i$. Les détails concernant cette expression sont décrits dans la référence [PONS 05].

Pour prédire le coefficient de diffusion $D_1$ il est donc nécessaire de déterminer les coefficients $D_0$ et $\xi$. Le coefficient $D_{12}$ nécessite de déterminer en plus le paramètre d’interaction de Flory-Huggins $\chi$. Ces paramètres sont alors déterminés par une méthode de rhéologie inverse consistant à ajuster $D_0$ et $\xi$ (voir $\chi$) afin que le modèle rhéologique décrive au mieux la variation du module complexe de la viscosité en fonction du temps de diffusion.

3.5. Résultats et discussion

Durant la diffusion, le module de la viscosité complexe change de manière significative allant de la viscosité du liquide (amine ou époxy) au début de l’expérience, à celle du mélange homogène EVA/liquide à la fin du processus de diffusion (figure 4). Cette courbe rhéologique traduit le phénomène de diffusion du liquide dans le polymère.
Par exemple, l'influence de la température sur la diffusion de l'amine et l'époxy dans l'EVA est montrée sur les figures 5 et 6. Comme attendu, la diffusion est activée par une augmentation de la température. Toutefois, les courbes de diffusion de l'époxy dans l'EVA sont sensiblement différentes. En effet elles présentent des allures très différentes et montrent apparemment deux régimes de diffusion.

D'autre part, la figure 7 montre que le processus de diffusion de l'amine ne dépend pas de la masse molaire des échantillons d'EVA, du moins dans la gamme des masses molaires étudiées ici (voir le tableau 1). En effet, les courbes rhéologiques de diffusion se superposent parfaitement en début d'expérience. Au contraire, le processus de diffusion de l’époxy est dépendant de la masse molaire de l’échantillon d’EVA comme le montre clairement la figure 8. D’autre part, on peut préciser qualitativement que le processus de diffusion de l'époxy est plus lent que celui de l'amine.
La théorie du volume libre prédit que le coefficient de diffusion $D_1$ ne dépend pas a priori de la masse molaire du polymère. Cela est uniquement vrai si la $T_g$ du polymère ne dépend pas de sa masse molaire. Nous avons effectivement mesuré que la $T_g$ de nos EVA était sensiblement constante ($T_g \approx -25^\circ C$). D’autre part, leur énergie d’activation à l’écoulement aux environ de 110°C est également très proche. Le coefficient $D_1$ est alors indépendant de la masse molaire. Toutefois, rappelons que les courbes rhéologiques de diffusion traduisent les variations du coefficient mutuel de diffusion $D_{12}$. Nos résultats montrent alors que le paramètre d’interaction de Flory-Huggins ne dépend pas de la masse molaire de l’EVA dans le cas de l’amine. Pour ce système là, $\chi$ a été calculé à partir de la théorie des groupes de Van Krevelen : $\chi_{EVA/amine}=0,40$. Le calcul par rhéologie inverse (figure 7) donne pour l’ensemble des expériences à différentes températures de diffusion de l’amine dans l’EVA : $D_1=0,8 ~m^2/s$ et $\xi=2,5$.

La diffusion du composé époxy s’avère beaucoup plus délicate à étudier compte tenu du fait que le composé époxy est partiellement miscible dans l’EVA. La diffusion du liquide n’est plus alors gouvernée par le gradient de concentration et les interactions polymère/liquide mais également par la thermodynamique de la séparation de phase.

Pour donner une explication, la géométrie expérimentale peut être assimilée à deux couches macroscopiques où une diffusion Fickienne classique se produit, séparées par une interface mince où le profil de concentration est très étroit. Notez également que quand une des espèces diffuse plus rapidement que l’autre, ou si la concentration globale des espèces est différente de la composition critique, l’interface se décale vers le côté du composant qui a la diffusion la plus rapide ou vers le composant minoritaire (figure 9). Pour récapituler, pour notre système, l’immiscibilité partielle de l’EPPE dans l’EVA influence profondément le profil de la concentration produit. Nous ne pouvons plus considérer une variation continue de la concentration.
Figure 9. Description schématique des profils de concentration du système partiellement miscible. L’axe $z$ est perpendiculaire au bicouche. L’état initial se compose d’une couche supérieure liquide pure séparée de la couche pure de polymère par une interface étroite ($t=0, w\approx 0$). Pour des temps longs ($t \to \infty$) le profil de concentration à l’équilibre est établi avec une couche riche en liquide concentration $C_{2eq}$ et une couche riche en polymère de concentration $C_{1eq}$. L’épaisseur de l’interface, $w$, a augmenté ($w > 0$). Les profils de non-équilibre sont représentés à deux étapes intermédiaires (courbes discontinues). Puisque le liquide diffuse beaucoup plus rapidement que les chaînes de polymère, le gradient de concentration dans le polymère est établi plus rapidement que dans la couche liquide.


Le calcul par rhéologie inverse montre bien que $D_1$ ne dépend pas de la masse molaire comme attendu ($D_0=0,1m^2/s$, $\xi=2$). En revanche, le paramètre d’interaction de Flory-Huggins $\chi_{EVA/époxy}$ dépend de la masse molaire (tableau 2), ce qui explique la dépendance du coefficient mutuel de diffusion $D_{12}$ en fonction de la masse molaire.

Tableau 2. Variation du coefficient d’interaction $\chi_{EVA/époxy}$ de Flory-Huggins avec la masse molaire à 110°C.

<table>
<thead>
<tr>
<th>EVA</th>
<th>$M_w$ (g/mol)</th>
<th>$\chi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2803</td>
<td>53500</td>
<td>0,58</td>
</tr>
<tr>
<td>2840</td>
<td>27500</td>
<td>0,55</td>
</tr>
<tr>
<td>28800</td>
<td>7900</td>
<td>0,34</td>
</tr>
</tbody>
</table>
3.6. Conclusion

La compréhension des mécanismes diffusionnels est très importante pour identifier leurs effets sur la réaction dans les milieux réactifs de haute viscosité notamment en extrusion réactive. Dans cette optique, il est indispensable d'identifier les paramètres gouvernant les mécanismes réactionnels se manifestant dans les procédés réactifs (continus ou discontinus).

Dans cette partie, nous avons fait l'étude rhéologique de la diffusion de réactifs de type amine et époxyde dans des EVA de masses molaires différentes. Le coefficient mutuel de diffusion $D_{12}$ a été calculé par une méthode de rhéologie inverse. Comme prédit par la théorie de volume libre, $D_{12}$ dépend fortement de la concentration des deux monomères dans le milieu polymère et pour une même concentration le monomère amine diffuse plus vite que le monomère époxyde. D’autre part, nous avons montré que le coefficient de diffusion $D_{12}$ de l’amine ne dépend pas de la masse molaire (viscosité) de l’EVA contrairement à celui de l’époxyde. Cela est tout simplement dû au fait que le paramètre d’interaction de Flory-Huggins dépend de la masse molaire pour le système époxyde/EVA.

Nous avons déterminé les paramètres clefs de la diffusion de liquides monomères dans un milieu fondu de haute viscosité. Nous allons donc utiliser ces données fondamentales pour étudier le couplage diffusion/réaction de tels monomères dans des milieux de viscosité différente.

4. CARACTERISATION ET MODELISATION DE LA DIFFUSION ET DE LA REACTION DE REACTIFS A FAIBLE POIDS MOLECULAIRE DANS UN POLYMERE FONDU

Dans cette partie, nous avions considéré la réaction de deux réactifs de faible masse moléculaire initialement séparées et miscible ainsi que leurs produit de réaction dans un milieu fondu de viscosité élevée. Nous voulons aussi modéliser la compétition diffusion/réaction et comparer les prévisions de ce modèle aux données expérimentales collectées sur ce système réactif modèle soigneusement choisi.
4.1. Modèle

La réaction de ces deux réactifs est du deuxième ordre et suit deux mécanismes parallèles : un mécanisme non catalytique et un mécanisme auto catalysé par les groupes OH formés après l’ouverture des cycles oxirane des époxydes.

\[ r_A = \frac{dC_A}{dt} = \left( k + k' (C_{OH} - C_A) \right) C_A^2 \]  \hspace{1cm} (6)

D’un point de vue de la modélisation de la compétition réaction diffusion, nous avons maintenant toutes les données expérimentales, à savoir les coefficients de diffusion mutuels des deux espèces réactives et la cinétique chimique en milieu homogène, afin de simuler la cinétique de réaction d’un système bicouche a priori non homogène. Cette modélisation consiste à résoudre le système d’équations différentielles suivant :

\[ \frac{\partial C_j}{\partial t} = D_{12} \frac{\partial^2 C_j}{\partial x^2} + r_j \]  \hspace{1cm} (7)

\( r_j(x,t) \) est la vitesse de production (ou consommation) des entités \( j \) (\( j = A, B, C \)). \( D_{12} \) est le coefficient mutuel de diffusion. Toutefois, pour simplifier la résolution de ces équations on admettra que le coefficient de diffusion mutuel des deux espèces est constant pendant le processus de diffusion/réaction et ne dépend que de la concentration initiale en réactifs. En effet on admet que la réaction époxyde amine conduit à la formation d’un composé de réaction dans le milieu qui a priori ne va pas changer la \( T_g \) du milieu réactif, et donc le coefficient d’autodiffusion ni les interactions polymère réactifs, c’est à dire le coefficient de diffusion mutuel. Dans la partie précédente, nous avons étudié la diffusion du N-éthylaniline (NEA) et du 2,3-epoxypropyl-phenylether (EPPE) dans des EVAs de différents poids moléculaires [BELL 06]. Ici, basé sur la même équation modèle nous avons calculé \( D_{12} \) dans l’EVA à \( T = 150^\circ C \). \( D_{12} \) a été trouvé égal à \( 1.8 \times 10^{-11} \), \( 1.2 \times 10^{-10} \), et \( 1.25 \times 10^{-11} \) m².s⁻¹ respectivement pour les trois entités, EPPE, DPA et produit.
4.2. Expérimental

4.2.1. Matériaux

Le polymère utilisé est le poly (ethylene-co-vinyl acetate) avec 28wt % d'acétate de vinyle et un d'indice de fluidité de 800 g/10min (190°C-2,16 kg). Les deux réactifs employés sont le 2,3-epoxypropyl-phenylether (EPPE) et la dipentylamine (DPA).

4.2.2. La réaction époxyde/amine

L’étude cinétique a été suivie par DSC (PYRIS Diamond) à différentes températures sur le système époxyde amine liquide en concentration stœchiométrique et à 150°C en présence de milieux viscosant.

Les géométries utilisées dépendent de la répartition initiale des réactifs. L’étude cinétique a été faite sur un mélange liquide (en masse) des réactifs pour identifier les cinétiques intrinsèques des réactifs purs, un système homogène avec des réactifs uniformément dissous dans EVA de sorte que la reaction se produise dans un milieu visqueux homogène et un système où les réactifs étaient séparés dans des couches adjacentes de polymère fondu (échantillons en bicouche), de sorte que les réactifs diffusent dans la couche voisine pour réagir. En outre, l'utilisation de bicouches vise à approcher une vision mélange laminaire d'une manière simplifiée (figure 10).

![Diagram](image.png)

Figure 10. Le système réactif de bicouche

A partir des courbes expérimentales, différents paramètres expérimentaux ont été identifié (Figure 11) dont l’enthalpie de réaction (\(\Delta H_\infty=400\ \text{J.g}^{-1}\)), et les constantes cinétiques k et k’ respectivement des parties non catalytique et auto catalytique. Cette cinétique en masse est comparée sur la figure 11 à la cinétique en milieu fondu EVA de ce même système réactif. Cette figure montre que la réaction est accélérée en milieu polymère fondu car on remarque que lors de la dilution de ces réactifs dans un solvant (dodécane) à même concentration que...
dans le polymère, on retombe sur les prévisions du modèle pour le système pur avec effet de dilution. En effet la modélisation établie sur la base de l’équation 6 prédit une cinétique plus lente en prenant en compte la concentration des réactifs dans le milieu fondu supposé homogène. L’origine de cette catalyse peut être de plusieurs natures (stabilisants, fonctions esters). Pour modéliser ce comportement, nous avons ajusté l’équation 6 en milieu polymère fondu en re-calculant la constante k’. Le tableau 3 regroupe les constantes calculées pour les deux systèmes et la figure 11 montre cette modélisation cinétique. Un bon accord est observé mais cette partie de l’étude montre toute la difficulté d’étudier une cinétique en milieu polymère dont les polymères sont d’origine commerciale et donc formulés. D’ailleurs ce dernier point mériterait d’être plus souvent pris en compte et intégré dans les études sur les procédés réactifs.

**Table 3.** k et k’ calculées pour EPPE-DPA pur et pour 20 wt% de EPPE-DPA dissous dans l’EVA (T=150°C).

<table>
<thead>
<tr>
<th>Système réactif</th>
<th>k (L.mol(^{-1}).s(^{-1}))</th>
<th>k’ (L^2.mol(^{-2}).s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPPE/DPA et dodecane/EPPE-DPA 80/20</td>
<td>5.55 x 10^-4</td>
<td>6.43 x 10^-4</td>
</tr>
<tr>
<td>EVA/EPPE-DPA 80/20</td>
<td>5.55 x 10^-4</td>
<td>6.57 x 10^-3</td>
</tr>
</tbody>
</table>

**Figure 11.** taux d’avancement de la réaction (mesuré et calculé) à T=150°C

(□) EPPE-DPA pur, (○)EVA/EPPE-DPA 80/20 homogène, (☆)dodécane/EPPE-DPA 80/20

Homogène

La conversion de la réaction époxyde amine en fonction du temps est présenté sur la figure 12 et les résultats des simulations sont montrés sur la figure 13.

**Figure 12.** avancement de la réaction en fonction du temps à T=150°C. (□) EPPE-DPA pur, (⊙) EVA/EPPE-DPA homogène 80/20, (●) système en Bicouche de 0.5/0.5 mm avec 20 wt% de EPPE et DPA, (△) système en Bicouche de 0.5/0.5 mm avec 10 wt% de EPPE et DPA, (●) système en Bicouche de 1/1 mm avec 20 wt% de EPPE et DPA.

**Figure 13.** Comparaison entre l’avancement expérimental et calculé de la réaction en fonction du temps. Les courbes pleines représentent la modélisation de la réaction. (□) EVA/EPPE-DPA homogène 80/20 (△) système de bicouche de 1/1 mm avec 20 wt% de EPPE et DPA.

Le processus de diffusion/réaction a été modélisé et l'avancement calculé de la réaction a été comparé aux données expérimentales. La vitesse apparente de la réaction s'est avérée fortement dépendante de la valeur du coefficient de diffusion.

Notez finalement que le modèle n'intègre pas le transfert de matière par mélange convectif mais il est possible d'évaluer si la diffusion limite toujours la réaction lorsqu'un mélange laminaire convectif est appliqué au système (mélange dans une extrudeuse bi-vis par exemple). Le temps de diffusion, \( t_D \), et l'évolution de l'épaisseur de striation, \( e(t) \), dans un écoulement laminaire et le temps nécessaire pour l'homogénéisation, \( t_M \), peuvent être estimés et calculés à partir des expressions suivantes (figure 14):

\[
\begin{align*}
\dot{e}(t) &= \frac{2 \cdot \varepsilon^2(t)}{D_{12}} \quad e(t) = \frac{2 \cdot \varepsilon_0}{t \cdot \gamma}, \\
\gamma &= \sqrt{\frac{8 \cdot \varepsilon_0^2}{D_{12} \cdot \varepsilon^2}} \quad t_D = \frac{e(t)}{\dot{e}(t)} \\
\end{align*}
\]

**Figure 14.** Représentation simplifiée du mélange laminaire avec la diminution de l'épaisseur de striation en cisaillement simple.

Nous considérons deux couches de polymère fondu avec une dimension caractéristique initiale de 1 mm (épaisseur) contenant respectivement 20 wt% d'époxyde et 20 wt% d'amine.
Ces couches fondues sont mélangées dans une extrudeuse. En considérant les coefficients de diffusion respectifs des réactifs à cette concentration et avec un taux de cisaillement de 10 s\(^{-1}\), on trouve que l'état homogène est atteint en 13 à 25 secondes ce qui est très court comparé au temps caractéristique de réaction. En appliquant un cisaillement de 100 s\(^{-1}\) (ce qui est généralement le cas dans une extrudeuse), on arrive à des temps d'homogénéisation de 3 à 5 secondes.

5. Conclusion

Il est vrai que le choix d'un système modèle reste compliqué en raison des différents paramètres qui doivent être pris en considération (miscibilité, absence de réactions secondaire, absence de dégradation…); mais on est parvenu à identifier quelques interactions entre diffusion et réaction. Nous avons remarqué que la réaction est contrôlée par la diffusion et que cela dépendait de l'épaisseur des couches et que pour cette raison la conversion dans les bicouches était plus lente par rapport à un système homogène. L'aspect mélange laminaire était pris en considération par une géométrie multicouche simplifiée utilisée pour calculer le temps et l'épaisseur de couches à partir desquels un bicouche peut être assimilé à un système homogène. Cependant, la réaction utilisée est trop lente pour la caractérisation du mélange dans de tels mélangeurs en considérant que la viscosité du polymère utilisé (EVA 28800) est basse ce qui implique des coefficients de diffusion élevés des espèces réactives (EPPE et DPA). Pour une meilleure caractérisation du mélange, il serait intéressant d'augmenter la viscosité du milieu en utilisant des EVA de masses molaires plus élevées (EVA 2840 ou EVA 2803) pour ralentir la diffusion de l’EPPE. L'utilisation d'espèces de hautes réactivité est également une solution à condition que nous puissions encore mesurer facilement la conversion en fonction du temps.
CONCLUSION ET PERSPECTIVE

Ce travail avait pour but d’ouvrir un chemin pour la compréhension des phénomènes de mélange/diffusion/réaction en développant de nouveaux outils (rhéologie) et des systèmes modèles expérimentaux pour comprendre le couplage de la diffusion et de la réaction en utilisant une géométrie simple pour prendre en considération l’écoulement laminaire.

En s’inspirant du génie chimique, on voulait caractériser le mélange en utilisant des réaction compétitives et consécutives de petites molécules dans un milieu visqueux. Cette tentative avait échouée en raison des complications (problèmes de caractérisation et d’auto échauffement) et des limitations (doute sur les mécanismes réactionnels) qui étaient survenues. En fait, ces limitations peuvent être rencontrées dans n’importe quel système en extrusion réactive.

Fort de ces constatations, nous nous sommes intéressés à illustrer les difficultés liées à la définition d’un système modèle et la complexité des interactions entre les trois phénomènes cités plus haut. Un système thermorçissable / thermoplastique a été étudié. La comparaison entre un système homogène et des système en bicouches montre que du point de vu réaction ou morphologie la diffusion a une large influence. Cela a été attribué à trois phénomènes différents : la différence de vitesse de diffusion des réactifs, la séparation de phase qui est initié dans des milieux de faibles interactions et la viscosité du milieu.

Après cette partie, la définition d’un système plus simple et le découplage des phénomènes de diffusion et réaction s’imposaient.

Nous avons montré qu’une expérience de rhéologie pouvait être utilisée pour quantifier la diffusion d’un liquide dans un polymère fondu. De plus, une méthode inverse de calcul basée sur la théorie des volumes libres nous a permis de calculer des coefficients mutuels de diffusion $D_{12}$. Ce coefficient de diffusion ne dépend pas de la masse molaire du polymère pour un système parfaitement miscible (EVA/amine). En revanche pour un système partiellement miscible (EVA/époxy), $D_{12}$ dépend de la masse molaire à travers la variation du paramètre d’interaction de Flory-Huggins.
Après avoir rassemblé les différents coefficients de diffusion, l’étape suivant était le couplage de la diffusion et de la réaction tout en en utilisant une géométrie multicouche pour prendre en considération le mélange. Un modèle mathématique pour la diffusion d’espèces réactives dans un polymère a été développé.

Il a été possible d’identifier la forte influence de l’épaisseur des bicouches et de la concentration initiale des réactifs sur l’avancement de la réaction considérant qu’un système polymère est en régime laminaire lorsque le mélange est pris en considération. Dans ce cas-ci, il était possible de répondre si le système était contrôlé par la réaction ou la diffusion. Pour finir, nous pouvions prévoir l'épaisseur à partir de laquelle le système en bicouche est assimilé à un système homogène et le temps nécessaires pour être homogène dans des conditions dynamiques.

Avec ces résultats, la porte reste toujours ouverte à plusieurs perspectives :

- Il sera intéressant d'étudier l'influence du polymère sur la réaction des petits réactifs (présence de liaisons hydrogène, interaction polymère réactif) ;
- Présenter un modèle plus global prenant en considération l'aspect convectif dans les mélangeurs ;
- Utiliser les nouveaux outils pour étudier en ligne dans une extrudeuse l'interdépendance mélange, diffusion et réaction (ultrasons, NIR, RAMAN, mapping...)

Ce domaine de recherche reste à ses débuts et les combinaisons des produits sont innombrables en extrusion réactive. Nous espérons que ce travail ouvrira de nouvelles perspectives à d'autres chercheurs pour multiplier les pas vers la compréhension des systèmes réactifs visqueux.
REFERENCES
REFERENCES


REFERENCES


REFERENCES


