RHEOLOGY INNOVATION IN THE STUDY OF MIXING CONDITIONS OF POLYMER BLENDS DURING CHEMICAL REACTION

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ABSTRACT:
Polymer melts can be mixed with many monomers, plasticizers, antistatics or foaming additives. Properties of such mixtures can change during blending because of chemical reactions like polymerization or crosslinking. The process may be carried out either in stirred tanks, extruders or in motionless mixers. In this paper we focused on the mixing time and the diffusion time of reagent, plasticizer and polymer thanks to rheological tools, and on the way how rheological properties can be studied during chemical reaction in polymer blending. The concept of rheoreactor and Couette analogy were introduced since we have a reactor on our disposal that can mix solution and measure rheological properties without taking sample. This apparatus appears to be an appreciable tool in complement of internal mixers that are specific to polymer blending. For example, we show the importance of the competition between mixing time and reaction time for reactive systems.

ZUSAMMENFASSUNG:
Polymerschmelzen können mit vielen Monomeren, Weichmachern und antistatischen und schäumenden Additiven gemischt werden. Die Eigenschaften solcher Mischungen können sich während des Blendens aufgrund chemischer Reaktionen wie Polymerisation oder Vernetzung ändern. Die Verarbeitung kann entweder in Rührmischern, Extrudern oder statischen Mischern durchgeführt werden. Die Zielsetzung dieser Arbeit war die Untersuchung der Mischzeit und der Diffusionszeit des Reagens, des Weichmachers und des Polymers mittels rheologischer Methoden sowie die Möglichkeit, wie rheologische Eigenschaften während der chemischen Reaktion beim Blenden der Polymere untersucht werden können. Das Konzept des Rheoreaktors und der Couette-Analogie werden eingeführt, da uns ein Reaktor zur Verfügung steht, der Lösungen mischen kann und ohne Probenentnahme die rheologischen Eigenschaften messen kann. Dieses Messgerät scheint ein wertvolles Instrument zu sein in Ergänzung zu internen Mischern, die zum Blenden von Polymeren konstruiert worden sind. Beispielsweise zeigen wir die Bedeutung der Konkurrenz zwischen Misch- und Reaktionszeit für die reaktiven Systeme.

RÉSUMÉ:
French Abstract: Les polymères fondus peuvent être mélangés à différents monomères, plastifiants, aditifs antistatiques ou de moussage. Les propriétés de tels mélanges peuvent évoluer pendant l'opération de mélangeage si des réactions chimiques comme des polymérisations ou réticulations ont lieu. Ce procédé peut être mené dans des réacteurs agités, des extrudeuses ou des mélangeurs statiques. Dans cet article, nous avons étudié de près le temps de mélange, le temps de diffusion des réactifs, des plastifiants, des polymères grâce à des outils rhéologiques et la manière dont nous pouvions suivre les propriétés rhéologiques lors d'une réaction chimique dans un mélange polymère. Nous avonz alors introduit le concept de rhéoréacteur et d'analogie Couette. Il s'agit d'un réacteur sous forme de cuve agitée qui peut donc mélanger des solution et mesurer des propriétés rhéologiques en s'affranchissant du prélèvement d'échantillon. Cet appareil est un outil fort appréciable et permet un bon complément d'informations au mélangeur interne traditionnel qui est plus spécifique au mélange de polymères. Par exemple, nous montrons l'importance de la compétition entre le temps de mélange et le temps de réaction pour les systéms réactifs.

KEY WORDS: Polymer blend, rheoreactor, mixing conditions, crosslinking, diffusion

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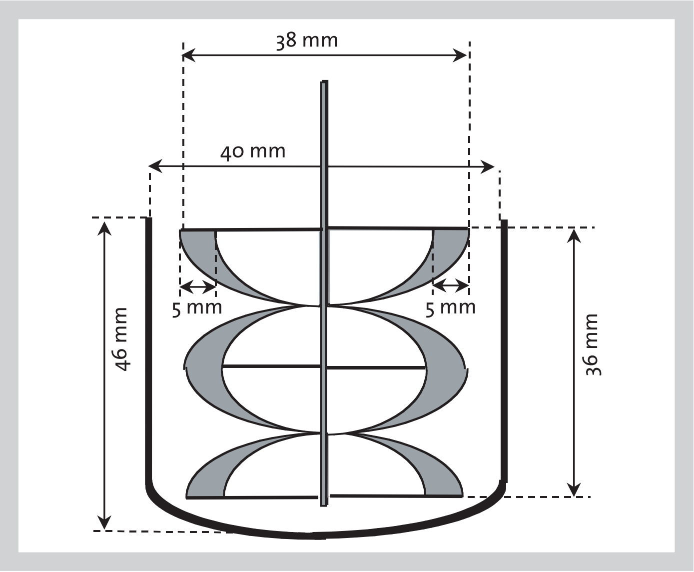
1 INTRODUCTION

Polymer processing usually takes place in internal batch mixer or in extruders. The mixing of additives into molten polymer matrices is of great interest, as a wide variety of commercial polymer materials are actually complex formulations [1]. From a processing point of view, these complex formulations involve the incorporation of low viscosity additives in a solid state, such as polymer themselves. The difficulties of mixing increases when low viscosity component is mixed with a polymer. The very low viscosity component tend to segregate to high shear rate area what delays mixing [2]. Furthermore, the different types of additives can be thermodynamically miscible or not with the molten polymer matrix. Consequently, the large mismatch between the different types of additives enhances the difficulties of tailoring the final polymer materials. Mc Kelvey [3] has studied the mixing of non-miscible Newtonian liquids by laminar flow in case of the viscosity of one of the components is very different of the other. He concluded that, when the viscosity of the minor component (the reagent) is much lower than the viscosity of the major component (the polymer), the shear rate in the minor component is determined by the rate gradient through the layer of reagent. This means that polymer, which is much more viscous, behaves like a rigid bound. Moreover, the products appearing in different industrial application fields are known to exhibit complex rheology. Reactive polymer processes, among other chemical modifications of polymers, polymer grafting, and reactive polymer blending, deal with highly viscous and rheologically complex media in geometrically complex reactors. In these reactors, laminar shear, elongational flow as well as distributive mixing occur simultaneously. Initial contacting is a very important problem and the reaction kinetics, together with transport phenomena and evolving rheological properties of the medium may be intricately influenced by the mixing conditions, affecting therefore the final product properties and quality. Thus, from formulation steps to final product, rheological behavior considerably vary from linear to viscous fluid (Newtonian) to linear elastic solid fluid (Hookean) including various non-linear and complex behaviors. Optimizing tailoring process and product quality requires at least the knowledge, or the control for the best, of the rheology of the product during each intermediate step. Rheology is one of the best tools used for the study of complex systems because, at macroscopic scale, it shows phenomena that appear at microscopic scale and particularly at the structural level. Until now rheology is mostly devoted to the study of dynamic systems at low strain and for linear viscoelastic response [4]. Mixing rheology have not been much studied. However, rheological characterization of complex fluids may, in certain circumstances, be a challenging task when conventional rheometers are used. Studies arecomplicated by several shortcomings such as the fact that media are not homogeneous, that they have non-negligible structural heterogeneity and that they are particularly sensitive to the thermomechanical history they had undergone. When adding, reagents, such as crosslinking reagent, the vulcanization of the polymer occurs while the measurement is in progress. Mixer-type geometry rotating in a fluid contained in a cylindrical tank, provides an alternative solution to such rheological characterization problems. We have developed new tools called “rheo-reactors” [5], which are mini-reactors installed on rheometers. In such device it is possible to reproduce aspects of processes and/or process conditions. That can be studied from both rheology and chemical engineering viewpoints. Mixing devices with large local spacing can indeed be used to handle fluids with relatively large heterogeneities while providing continuous mixing. Monitoring torque and rotational speed during the mixing process can provide a rheological signature of the material under evaluation, i.e. torque/speed curves that are similar in shape to those obtained with conventional geometries. However, a more detailed analysis is required to translate this information into a complete rheological characterization, i.e. viscosity/shear-rate curve as is the case when rheometers are used. Thus we suggest the following procedure to realize tailoring processes through rheological tools. This approach is based on the simulation of the whole or a part of the process in mini- or micro-reactor attached to advanced rheometers. This strategy comes under what we could called a systemic rheology (included knowledge and method of chemical engineering and of rheology). In this paper we deal with the concept of macromixing and not of micromixing. In order that a reaction goes off correctly and that the



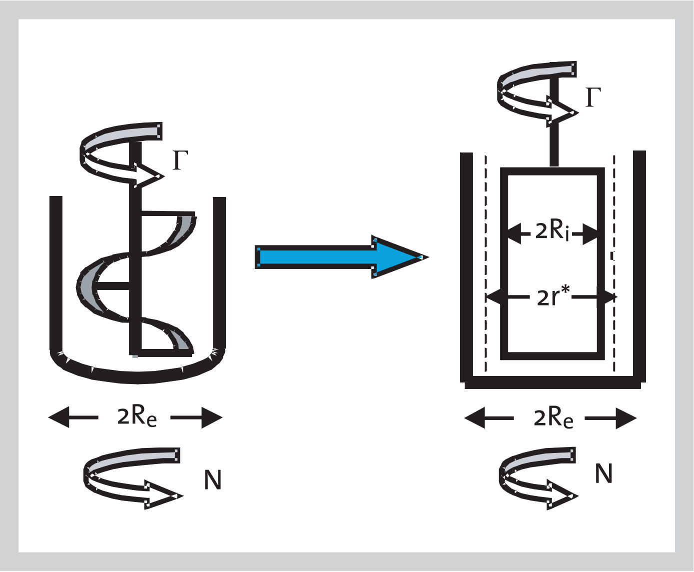


Figure 1 (left): Schematic of the rheo-reactor.

Figure 2: Couette analogy for a complex geometry.

expected quality of the product is respected, the concept of mixing or macromixing is not enough any more. We need to study more precisely what the vessel contains and to take into account the concept of micromixing. This is molecular state mixing. This concept, which represents the whole process at molecular scale, appeared in the fifties thanks to Danckerts [6], Zwietering [7] and Corrsin [8]. They showed that the knowledge of residence time distribution in a reactor is not enough by its own to predict the mixing state. The concept of micromixing and segregation have shown later that those two concepts have a decisive influence on the quality of the product, selectivity, the efficiency of polymer reactions, of crystallization or of organic synthesis. Aït-Kadi et al. [9] developed this new concept of mixing reactor: the rheoreactor. In order to illustrate this concept, this paper is devoted to study a polymer crosslinking reaction. The evolution of the rheological properties during the reaction will be followed-up. The influence of mixing and of the incorporation of reagents and plasticizer will be discussed. The performances and possibilities of the rheoreactor will also be compared with those of an internal mixer.

2 CONSIDERATION ON THE USED DEVICES

2.1 THE RHEOREACTOR

Consider a rheoreactor (Fig. 1) made of a cylindrical vessel and of a close-clearance impeller, such as a double helical ribbon for example (one of the most appropriate choice for highly viscous systems). An analytical method based on a Couette analogy allows to quantitatively analyze torque-rotational speed data in order to extract “absolute” viscosity-shear rate data in such a non-conventional geometry [9].

The Couette analogy consists first in determining a radius R_i of an equivalent Couette inner cylinder, having the same height L than the impeller, which gives, for the same rotational speed N, the same torque Γ, in a cylindrical vessel of radius R_e. This approach is illustrated in Fig. 2. Solving the equations of change in this virtual Couette geometry, assuming steady state, laminar regime and isothermal conditions for a power-law fluid (this last assumption is always valid for a limited shear rate range)

$$\eta = k\gamma^{n-1} \tag{1}$$

where k and n are the consistency and the flow index respectively, the following expression for R_i is obtained

$$R_i = \frac{R_e}{\left[1 + \frac{4\pi N}{n}\left(\frac{2\pi k L R_e^2}{\Gamma}\right)^{1/n}\right]^{n/2}} \tag{2}$$

For a given set of (N, Γ) values, R_i is a weak function of n, therefore the determination of R_i can be done in the particular case of n = 1, that is to say with a Newtonian fluid of known viscosity. Once R_i has been determined in such a virtual Couette geometry, we can calculate the shear stress and the shear rate profiles, from which it is easy to deduce the viscosity at a given position in the virtual gap. The shear stress is given by:

$$\tau = \frac{\Gamma}{2\pi L r^2} \tag{3}$$

and the shear rate, for a power-law fluid, by:

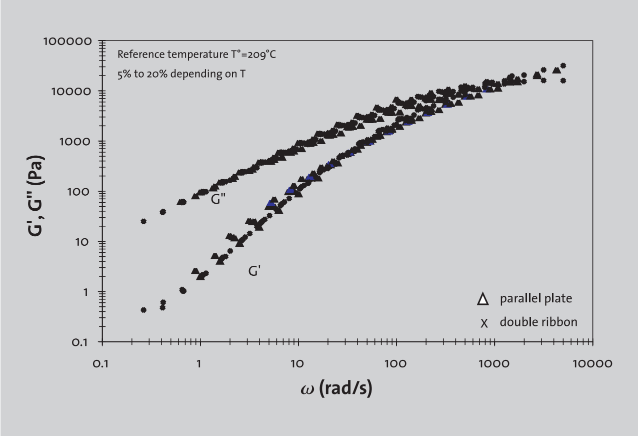


Figure 3 (left): Comparison of mechanical spectra of EVA 40-55 at a reference temperature of 209°C obtained with a parallel-plate geometry (triangle) and with the rheo-reactor

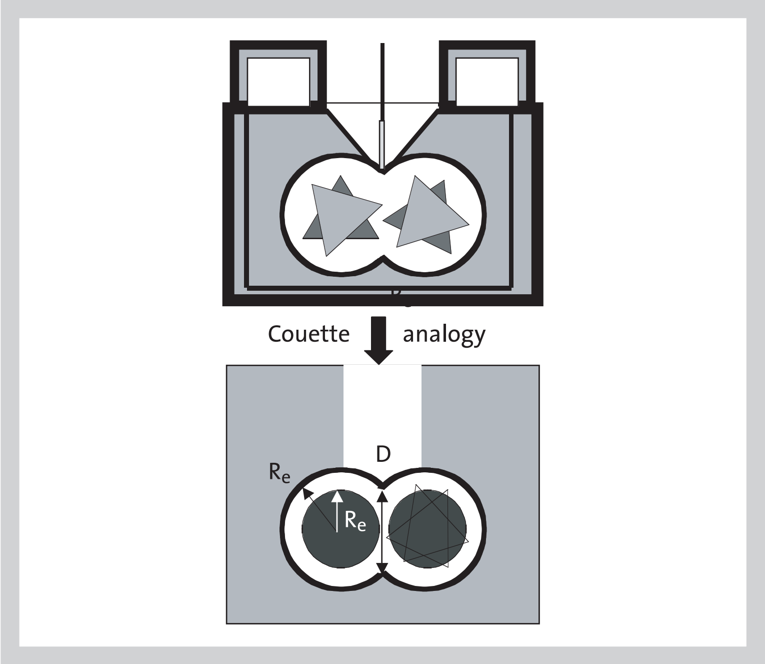


Figure 4 : Couette analogy for internal mixer.

$$\gamma = \left[\frac{\frac{4\pi}{n}\left(\frac{R_i}{r}\right)^{2/n}}{1-\left(\frac{R_i}{R_e}\right)^{2/n}} \right] N = K_r N \tag{4}$$

Even for a large virtual gap, it has been found [9] that a specific position $r = r^*$ exists in the gap at which the term in brackets K_r in this last equation is independent on the power-law index n, in other words on the rheology of the fluid. This r^* value can be graphically or analytically determined. Equation 4 shows that in general case, K_r depends on n and r for a given Couette cell, i.e. $K(r, n)$. The independence of K_r on n can be written as $K(r, n_1) = K(r, n_2)$ with $n_1 \neq n_2$. Then we can calculate r^* by:

$$r^* = \left(\frac{n_1}{n_2} \frac{\left(R_e/R_i\right)^{2/n_1} - 1}{\left(R_e/R_i\right)^{2/n_2} - 1} R_e^{\left(\frac{2}{n_2}-\frac{2}{n_1}\right)} \right)^{1/\left(\frac{2}{n_2}-\frac{2}{n_1}\right)} \tag{5}$$

and then both shear stress and shear rate are evaluated at this specific r^* value:

$$\tau_{r^*} = \frac{\Gamma}{2\pi L (r^*)^2} \tag{6}$$

$$\gamma_{r^*} = \frac{4\pi N \left(\frac{R_i}{r^*}\right)^2}{1-\left(\frac{R_i}{R_e}\right)^2} \tag{7}$$

The viscosity is then obtained by the ratio between τ_{r^*} and $\dot{\gamma}_{r^*}$. This analytical method has also been transposed to small amplitude oscillatory strain tests. In this case, the complex modulus is expressed as follows:

$$G^* = G' + iG'' = \frac{\tau}{\gamma_o} e^{i\delta} \tag{8}$$

Storage modulus, G', and loss modulus, G'', can be calculated knowing the expressions of stress τ and strain γ_O, in our virtual Couette geometry, for $r = r^*$ and $n = 1$. Stress is obtained directly and strain is given by the following expression

$$\gamma_o = \frac{2\theta}{1-\left(R_i/R_e\right)^2} \left(\frac{R_i}{r^*}\right)^2 \tag{9}$$

where θ is the angle of deformation angle. In the linear viscoelasticity area, the mechanical spectra obtained with a standard geometry and with a rheoreactor configuration compare fairly well [9]. This Couette analogy was successfully verified in the case of an ethylene vinyl-acetate copolymer melt (EVA) as shown in Fig. 3.

Using the values of the dimensions of the specific rheoreactor we used, which is a curved bottom vessel 46 mm height and 40 mm diameter (R_e = 20 mm) equipped with a double helicoïdal ribbon of 38 mm diameter and of L = 36 mm height (see in Fig. 2). The calculated parameters for the Couette analogy are r^* = 18.32 mm and R_i = 17.24 mm. Those parameters have been found from calibrations with silicon oil (which is a Newtonian fluid) by measuring the torque versus the deformation angle. The apparent shear rate and viscosity are given by $\dot{\gamma}_p = 43.3N$ and $\eta_p = 304\Gamma/N$ where N is the number of revolutions per minute (rpm) of the rotor and Γ is the torque (Nm).

2.2 HAAKE INTERNAL MIXER

Considering an internal mixer, Bousmina et al. [10] succeeded in creating a model corresponding to a Couette analogy. Figure 4 illustrates the geometry of the virtual Couette equivalent to the internal mixer. Thanks to this analogy, one can

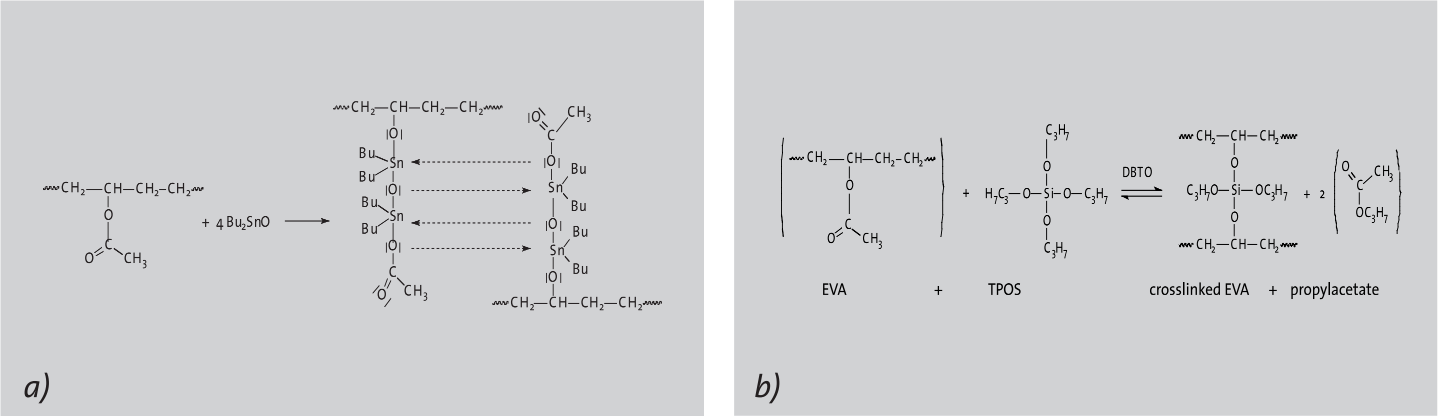


Figure 5:
Crosslinking reaction of EVA:
a) Formation of the real catalyst between EVA and DBTO,
b) Crosslinking of EVA by exchange reaction with TPOS.

calculate the effective shear rate $\dot{\gamma}_p$ and viscosity η_p,knowing the torque and the rotational speed N of the blade:

$$\gamma_p = 16\pi \; N \frac{\beta^2}{(1+\beta)^2(\beta^2-1)} \tag{10}$$

with $\beta = R_e / R_i$ where R_e is the external radius of the chamber of the internal mixer (m) and R_e is the internal radius of the Couette geometry (m)

$$\mathrm{R}_i = \frac{\mathrm{R}_e}{\left(1+\frac{4\pi N}{n}\left(2\pi k L \mathrm{R}_e{}^2 \frac{1+r_N{}^{n+1}}{\Gamma}\right)^{1/n}\right)^{n/2}} \tag{11}$$

with n as power-law index (taken equal to 1 for the polymer used here), n as consistency index (Pas^n), Γ as torque (Nm), L as blade length (m), and r_N as the two blades rotational speed ratio (< 1). The effective viscosity is calculate as follows

$$\eta_p = \frac{\Gamma}{N} \frac{(\beta^2-1)}{8\pi^2 L R_e^2 (1+r_N)} \tag{12}$$

The Haake Plasticorder (of our laboratory) is fitted out with a “Rheomix 600” internal mixer with two rotors running in a contra-rotating way. This instrumental apparatus allows to follow-up the change of the viscosity of a molten blend through the measurement of the torque. The mixing chamber can be regulated in temperature and the rotor speed can be well controlled. The thermocouple located in the mixing chamber allows to determine the temperature of the molten blend (melt temperature). Consequently, we can follow-up in real time the changes of the torque and of the melt temperature during the mixing of the studied formulation. The parameters for our system are L = 47.6 mm, r_N = 2/3, and R_e = 20 mm.

Bousmina et al. [10] did the analogy using different polymers in their batch mixer, which is exactly the same than ours. The data obtained with PS, LDPE, and PPhv under different processing conditions gave a mean value of R_1 = 17.6 mm, which is very close to the value of 17.3 mm found by Goodrich and Porter [11] using Newtonian fluid for calibration. So we took for our model R_i = 17.6 mm and β = 1.136 while the apparent shear rate inside the chamber can be calculated as $\dot{\gamma}$ = 0.82N. Bousmina’s model [10] allows us to know an effective shear rate and the corresponding viscosity in an internal mixer, however it is not possible to obtain the complex moduli of our material in-situ. In this paper, the studies of polymer blending undergoing chemical reaction in both rheoreactor and internal mixer will be compared.

3 EXPERIMENTAL SECTION

3.1 MATERIALS AND REAGENTS

The polymers were commercial products and were used as delivered. An ethylene vinyl acetate copolymer (EVA) was used as the rubber phase. Evatane 40-55 (Mw = 32000 g/mol) and Evatane 33-400 were supplied by Ato-Fina. EVA copolymers were crosslinked by an exchange reaction between silane groups of tetrapropoxyorthosilicate (TPOS) and vinyl acetate functions of EVA [12]. This reaction is catalysed by dibutyl-tin-oxide (DBTO). TPOS was supplied by Sigma-Aldrich (purity of 98%). DBTO was supplied by Sigma-Aldrich (purity of 98%) or by Goldschmidt under the trademark Tegokat® 248 (purity of 98%). Both of them were used without any further purification. The concentration of TPOS was given by the AV/OR ratio equal to 10 (AV/OR is the ratio between the mole number of ester groups of EVA and the mole number of alcoxy groups of TPOS) and the concentration of DBTO was 0.5 phr (gram per hundred grams of rubber). Experimentally, the sample was immerged in toluene (a good solvent at room temperature for the EVA 33-400) at 40°C until the complete extraction of free EVA chains (48 hours). Then, the gel fraction of EVA phase, which is a quantitative measurement of the cross-linking reaction of the elastomer phase, was calculated. On the other hand, we used the diethyl 2hexyl phtalate (DOP) as a plasticizer oil of the EVA 40-55.

3.2 EVA CROSSLINKING

The cross-linking reaction of EVA copolymers was carried out through an interchange reaction between the ester groups of EVA and the alkoxy groups of TPOS, as described in Fig. 5. This exchange reaction is catalyzed by DBTO as precursor of alcoxy-acyloxydistannoxane (Fig. 5a), the true catalyst of the reaction for temperatures above 100°C. Consequently, the rate of the transesterification reaction, i.e. the crosslinking reaction, is governed by the kinetics of distannoxanne formation. Furthermore, the kinetics of this type of reaction can be made suitable for a discontinuous process (for example, in an internal mixer where the reaction times can last until thirty minutes and so we can realize a sampling experiment to well control the extent of the reaction) or for a continuous process (for example, in an extruder where the reaction times are only about a few minutes).

3.3 MIXING TIME MEASUREMENT

The determination of macromixing time of the plasticizer or liquid reagent has been made in the rheoreactor. A simple method of conductimetry has been established by using a differential probe plunged in the vessel. The model viscous fluid, used here at room temperature, was the glucose. The mixing of plasticizer or reagent in EVA is here simulated by an injection of 1 ml of saturated salt water solution (viscosity of 1.2 mPas) in the vessel full of a more or less concentrated glucose solution. We measure a conductivity signal during the incorporation of the salt solution (Fig. 6). When a stable signal is obtained, the corresponding time (estimated by computing calculations over the whole signal curve in Fortran language in order to cast off background noise) is called the macromixing time t_m.

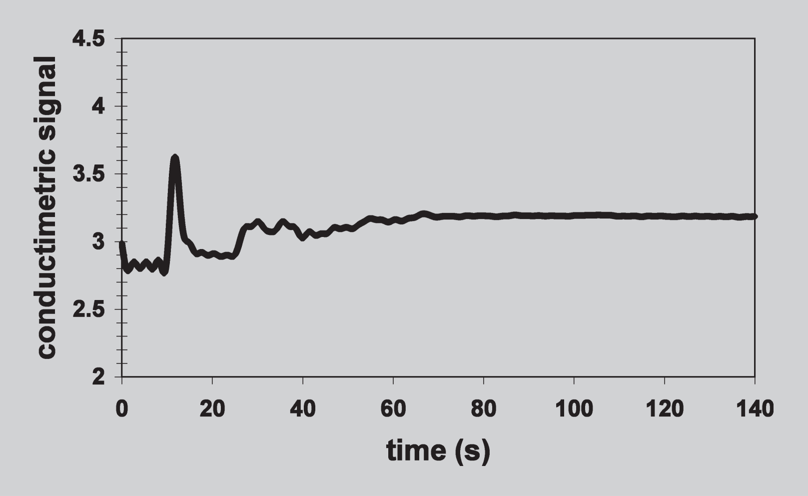


Figure 6: Conductivity signal curve during the mixing of 1 ml saturated salt solution (1.2 mPas) injected in 60 ml of glucose solution (here 1.6 Pas).

3.4 DIFFUSION TIME MEASUREMENT

The question of molecular diffusion as a mechanism of mixing miscible plasticizers into polymers has been raised by several authors [13, 14, 15] But they generally concluded that diffusion into polymers is too slow or acts on too short distances to be considered as a mechanism of effective transport. It is clear that the incorporation of plasticizer into polymer matrix is not a simple mixing with laminar flow. Therefore, it is essential to know those mechanisms of molecular diffusion. The most known theory of transport is the one of Ventras and Duda [16, 17]. This model precisely describes the diffusion assuming that the free volume of a system is available. This hypothesis was first introduced in 1959 by Cohen and Turnbull [18]. Though this model was initially built in case of liquids characterized by a set of hard spheres, the biggest development of their theory was in the description of mass transfer in case of solutions of long chain polymers mixed with little molecules of solvent. The molecules of hard spheres, which constitutes an ideal liquid, exist in holes made by their closest neighbors. The self-diffusion coefficient is an exponential function of the ratio of the diffusing molecule size and the free volume per molecules. In previous works [4], we developed a technique for determining the self-diffusion coefficient of DOP plasticizer. A free volume approach of the diffusion of organic molecules in polymers above their glass transition temperature, T_g, was addressed. We consider that the diffusion of small molecules, like plasticizers, in a polymer, here the copolymer of ethylene and vinyl acetate (EVA), above T_g, can be described by Fick's classical law. The experiments were carried out on a parallel plate rheometer. We studied the diffusion of the diethyl 2hexyl phtalate (DOP) into the melted EVA at four different temperatures. Using Fick's law, the concentration of the plasticizer was established at any point of the thickness of the swelling elastomer at any time. Using a one dimensional grid to solve continuous equations that describe the different rheological contributions of each abscissa, we determined the linear viscoelastic response of the whole sample. Comparing the experimental loss modulus to the values calculated from the rheological model, we found the values of the three parameters of the free volume expression of the diffusion coefficient

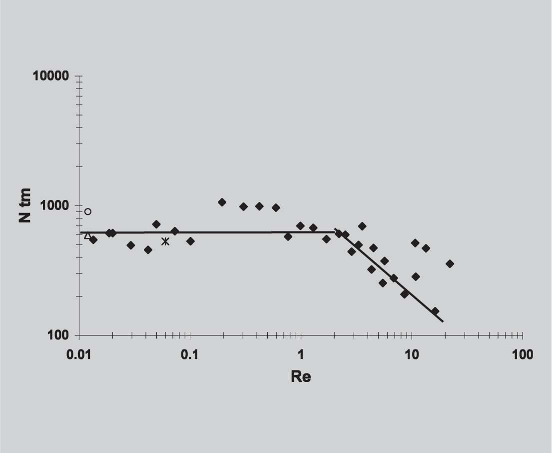


Figure 7 (left): Nt_m versus Re (Full symbols: mixing of 1 ml of saturated salt solution (1.2 mPas) injected in glucose solutions of different viscosities in the rheo-reactor (double helicoïdal ribbon agitator; Clear triangle: mixing of 7.5 ml of DOP injected in EVA 40-55 melt (135 Pa.s at 200°C) in the internal mixer at 50 rpm; Clear circle: mixing of 12.5 ml of DOP injected in EVA 40-55 melt (135 Pa.s at 200°C) in the internal mixer at 50 rpm; Star: mixing of 7.5 ml of DOP injected in EVA 40-55 melt (135 Pa.s at 200°C) in the internal mixer at 250 rpm).

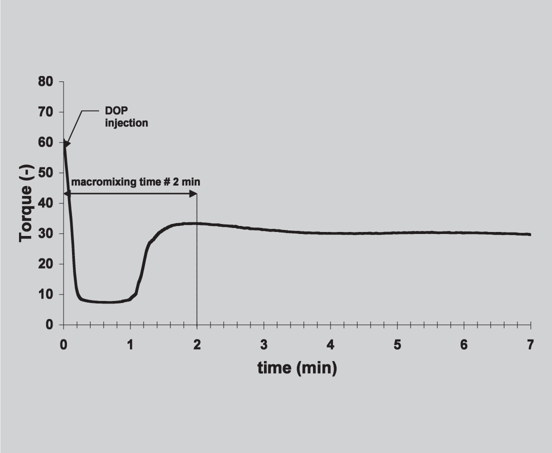


Figure 8: Macromixing curve for the incorporation of 7.5 ml of DOP injected in 50 ml of EVA 40-55 melt at 160°C and 50 rpm.

$$D_1 = D_0\, \mathrm{e}^{(-E/RT)}\, \mathrm{e}^{\left(-\frac{\omega_1\left(1-\gamma\left(RT/E_1^f\right)\right)V_1^t+\xi\omega_2\left(1-\gamma\left(RT/E_2^f\right)\right)V_2^t}{\omega_1\left(RT/E_1^f\right)V_1^t+\omega_2\left(RT/E_2^f\right)V_2^t}\right)} \tag{13}$$

with ω_1 and ω_2 being the weight fractions of plasticizer and polymer, E_1 and E_2 the activation energies of plasticizer and polymer, $V^t{}_1$ and $V^t{}_2$ the densities of plasticizer and polymere, R the gas constant, E the critical energy which a molecule must possess to overcome attractive forces. The values of the three parameters in Eq. 17 are $\gamma = 1$, $\xi = 1.76$, and $D_0 = 2.5\ 10^{-2}$ m²/s. A simple relation, which describes the mutual diffusion coefficient of DOP into melt EVA and depends exponentially on 1/T and on the weight fraction of solvent, ω_1, was established as

$$D = 0.157\,\mathrm{e}^{\left(-90.3\mathrm{i}10^3/RT\right)}\, e^{\left(15.8\omega_1\right)} \tag{14}$$

Finally, at 180°C and in infinite dilution conditions, $D = 10^{-8}$ m²/s .

4 RESULTS AND DISCUSSIONS

4.1 MACROMIXING AND DIFFUSION TIME ON NON-REACTIVE SYSTEMS

Scott and Young [19] have studied the mechanism of blends of low viscosity polyethylene into more viscous polystyrene in an internal mixer. Besides usual pick of polyethylene melting and of inter-diffusion of polystyrene pellets, the authors underlined another pick which is associated with a phase inversion : the incorporation of the low viscosity polymer into the matrix. In the same way, Couvreur [20] has studied the incorporation of glutarate α,ω diol polypropylene in polypropylene. The more low viscous product they put, the later the phase inversion appears. Above a certain concentration, a lubrification of the surface of the vessel and of the blades is observed. That phenomenon leads to a nearly zero torque The viscosity of the glucose solution is evaluated before each injection of salt solution so as to calculate the dimensionless Reynolds number:

$$Re = \frac{\rho N D^2}{\eta} \tag{15}$$

with ρ as the glucose solution density (kg/m³), N as the rotational speed of the vessel (rad/s), D as the agitator diameter (m), and η as the viscosity of the glucose solution (Pas). By bringing together all the mixing time data versus *Re*, we obtain a dimensionless representation of the macromixing time as shown in Fig. 7. In laminar conditions (for *Re* approximately smaller than 1 to 10), it is well known that $Nt_m = constant$ [21]. In our case, we obtain $Nt_m \cong 700$. In order to justify the use of rheoreactor instead of an internal mixer to understand the rheological properties of polymer material which evolves with time during a chemical reaction, we added three experimental points corresponding to the mixing of DOP injected in the EVA 40-55 melt (135 Pas at 200°C) in the internal mixer at 50 rpm and 250 rpm at 160°C. An example of a curve of mixing in internal mixer is given in Figure 8. The fact that these points fit pretty well with those obtained from measurements made in the rheoreactor leads us to conclude that, in this range of rotational speed and viscosity, the rheoreactor and the internal mixer behave in a similar way for the incorporation of small quantities of low viscosity substances in an higher viscosity mixture. Using the obtained value of Nt_m the macromixing time of small quantities of DOP into melt EVA is equal to 135 s at 50 rpm. In the other hand, we can estimate physically a macromixing time due to diffusion only. Considering a static layer of a polymer with a 2L-thickness surrounded by an infinite quantity of plasticizer whose self-diffusion coefficient is *D*, Ficks law predicts the time at which the gradient of concentration in the polymer would be less than 1% as [1, 22]

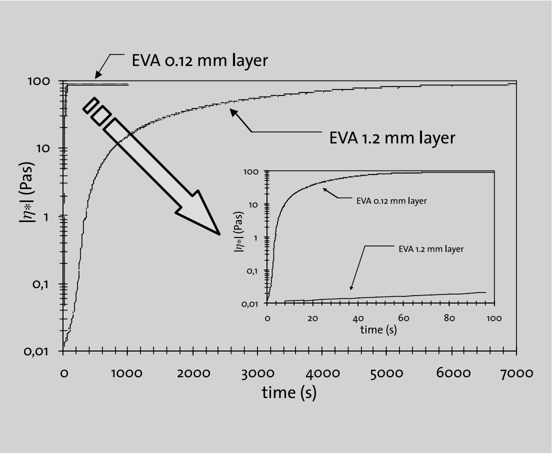


Figure 9 (left): Diffusion times for different thickness of the initial EVA layer (from simulation).

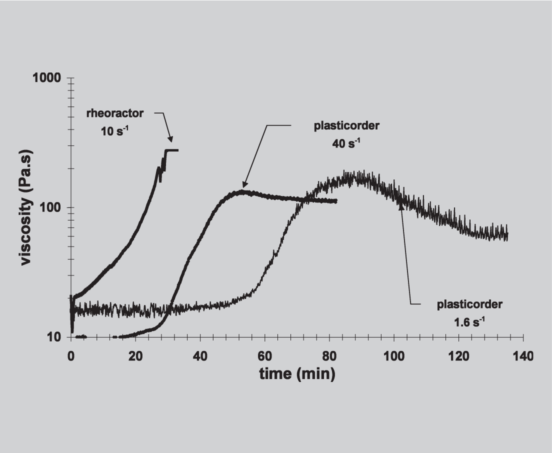


Figure 10: Comparison between kinetics of EVA crosslinking in the rheo-reactor and in the plasticorder (EVA 33 400, AV/OR = 10, DBTO = 0.5 phr, T = 180°C).

$$t_{macromixing} \approx t_D = \frac{2L^2}{D} \tag{16}$$

In previous works [4], where DOP was not in infinite quantity but where DOP constituted a layer over the EVA's one, the diffusion time was consequently two times bigger. Indeed, DOP can get into EVA film just from one side so it would take two times more to reach an equilibrium state

$$t_D = \frac{4L^2}{D} \tag{17}$$

Nevertheless, our experimental data fitted much better with the following relation as illustrated in Fig. 9

$$t_D = \frac{16L^2}{D} \tag{18}$$

Previous simulations (at 180°C, where the proportion between EVA/DOP was 60/40 and $D = 2.74 \cdot 10^{-9}$ m²/s [4]) give for two different thickness of EVA the following values: $t_{D\,1.2\,mm} = 7500$ s and $t_{D\,0.12\,mm} = 70$ s. We do have a ratio of 100 between these two values that agree with the L^2-law in Eq. 18. Thus the diffusion time decreases rapidly when the polymer thickness decreases. Mixing, which consists in diminishing the polymer thickness under shear rate, will lead to a significantly shorter macromixing time. Under shear, the thickness of layers decreases with time as follows [1]

$$L = \frac{2L_o}{t\gamma} \tag{19}$$

with L_O as the initial thickness of the polymer (m), $\dot{\gamma}$ as the shear rate (1/s), and t as the mixing time (s). By rearranging Eqs. 18 and 19, we obtain the expression of the macromixing time under shear:

$$t'_D = \sqrt[3]{\frac{64L_o^{\,2}}{D\gamma^2}} \tag{20}$$

Considering that EVA layers have a thickness of approximately of 1.5 mm in an internal mixer, the macromixing time of 7.5 ml of DOP into 50 ml of melt EVA will be close to 150 s at 50 rpm and 160°C ($D = 3.25 \cdot 10^{-14}$ m²/s [4]) using Eq. 20. One can observe that this macromixing time is of the same order of magnitude than the one found in Fig. 8.

In short, the rheoreactor allowed us to estimate a macromixing time law and the experimental points obtained in an internal mixer agree with this law. The study of plasticizer diffusion in parallel plate geometry with classical rheometer allowed the determination of its self-diffusion coefficient and the establishment of a law that estimates a macromixing time under shear rate that can be compared with the one found in the rheoreactor.

4.2 REACTIVE SYSTEM: CROSSLINKING EVA

On the one hand, in an internal mixer such as a Haake plasticorder, it is quite difficult to understand what is happening at the beginning of the crosslinking reaction because the torque sensors cannot detect too small variations and it is also difficult to distinguish whether the increase of crosslinking kinetics with increasing shear rate is a consequence of viscous dissipation or of mechanical energy. On the other hand, the knowledge of rheological properties of EVA during its crosslinking would be of great help to understand its mechanism and, in later works, how inversion phase takes place when an EVA/thermoplastic vulcanizate (TPV) is tailored.

Before undertaking any further experiments, we compared the crosslinking kinetics of EVA which took place in a Haake plasticorder and in the rheoreactor. In Fig. 10, we can see that kinetics slopes are the same in the two cases. However, there is no latent period in the rheoreactor exper-

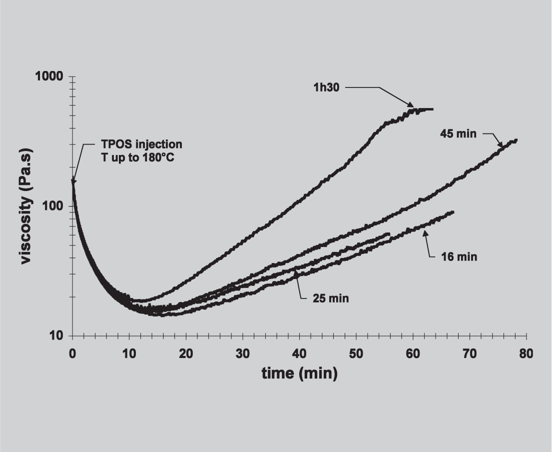


Figure 11 (left above): Influence of premixing time of DBTO (0.5 phr) in EVA 33 400 melt (100°C, 20 s^{-1}) on EVA crosslinking (TPOS AV/OR = 10, 180°C, 5.8 s^{-1}) in the rheo-reactor.

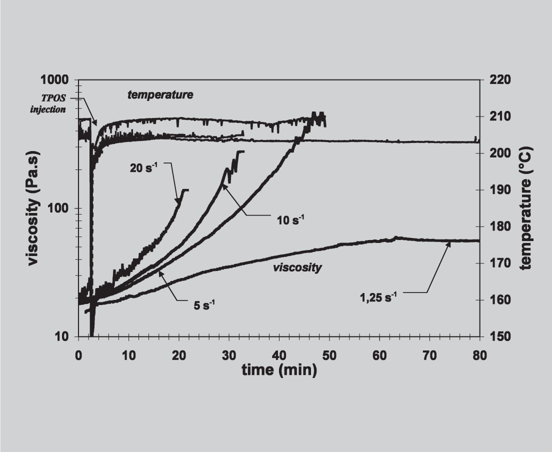


Figure 12 (right above): Influence of shear rate after TPOS injection in EVA 33 400 melt/DBTO (TPOS: AV/OR = 10; DBTO: 0.5 phr, T = 200°C).

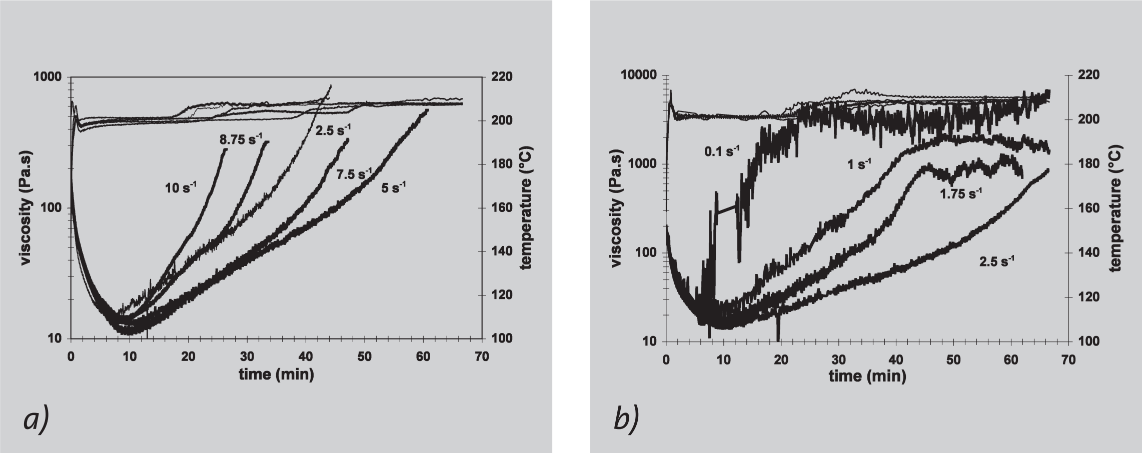


Figure 13 (below): Influence of shear rate in the rheo-reactor during the crosslinking of EVA 33 400 at 200°C after premixing of reagents (TPOS: AV/OR = 10 and DBTO: 0.5 phr) at 100°C and 20 s^{-1} for 15 min:
a) Shear rate varying from 2.5 to 10 s^{-1} and
b) Shear rate varying from 0.1 to 2.5 s^{-1}.

iments, the viscosity increases as soon as TPOS is injected. In each case, TPOS was injected in an EVA melt. It is true that the rheoreactor is more sensitive to a little variation in viscosity, but this could not explain this difference completely. We will see further that the quality of the reagent mixing has an impact on the kinetics.

As it was mentioned previously in this paper, the catalyst DBTO is not the true catalyst, but it is used to build the real catalyst of the crosslinking by generating a complex with EVA (with its acetate functions) at temperatures higher than 140°C [23]. Though this catalyst would become miscible in the matrix, one can ask for its concentration homogeneity in the media. This is particularly true that the dispersion of a powder is difficult in a viscoelastic media of high viscosity. Thus, we studied in the rheoreactor the influence of a premixing time of DBTO with EVA at low temperature (100°C). In these conditions, we do not see any viscosity change in the DBTO/EVA blend. After different given times, TPOS was injected and temperature was brought up to 180°C so as crosslinking can start (Fig. 11). The kinetics of crosslinking depends remarkably on the DBTO dispersion in the EVA matrix. This experiment yielded to the fact that catalyst acts at molecular scale and a simple macromixing is not enough to crosslink EVA in the best conditions provided the dispersion of the DBTO powder is extremely difficult because EVA is quite viscous. Considerations at a micromixing scale are needed.

In other respects, in a plasticorder, studying the influence of shear rate on crosslinking kinetics is hard to exploit. Indeed, from 20 to 225 s^{-1}, temperature gradient between the two extremes can grow up to 40°C. So, it is difficult to say whether the kinetics acceleration is due to the shear rate or to viscous dissipation. However, lower shear rates can be used in the rheoreactor compared to the plasticorder, since the rheoreactor has a highest sensitivity to the variation of the rheology at the earlier stage of the crosslinking reaction. Figure 12 shows the influence of shear rate on the crosslinking kinetics. One can verify that temperature effects are not concerned by those experiments. Shear rate has consequently a real impact on the kinetics. It could be attributed to a better dispersion of the crosslinking reagent. From $Nt_m \cong 700$, we know that mixing TPOS with EVA for 15 min at 10 s^{-1} is sufficient to have a good macromixing. Thus, in order to rid of dispersion aspect on kinetics, a premixing of TPOS at low temperature (100°C) in EVA/DBTO blend was made before looking at the influence of shear rate at 180°C (Fig. 13). Note that two cases depending on the shear rate rangecan be considered . For shear rates larger than 2.5 s^{-1} (Fig. 13a) the crosslinking kinetics increases with shear rate, whereas for smaller shear rates

(Fig. 13b) the contrary is observed. To explain this phenomenon we have assumed that, at very low shear rate, reagent and EVA are in contact during a long time. Consequently, the crosslinking appears to be faster in those area. At higher shear rate, the meeting frequency of the reactive zone increases and the kinetics can grow up. Unfortunately, the rheoreactor cannot afford very high shear rates because its torque sensor is quite rapidly saturated.

The rheoreactor is then very useful to follow-up rheological changes with the reaction time while blending. In addition, mechanical spectra can be obtained in the rheoreactor at different mixing times. The measured mechanical spectra at any mixing time are shown in Fig. 14. This is undoubtedly a huge advantage as compared to the possibilities of an internal mixer for which a sampling procedure has to be undertaken, followed by different processing steps in order to produce a disk with which measurements of the complex moduli can be obtained in conventional rheometers. At the gel point, according to Winter et al. [24], the storage and loss moduli have the same power-law frequency dependence $G'(\omega) \propto G''(\omega) \propto \omega^n$ where n is the relaxation exponent. Note that a complete review of the rheology near the liquid-solid transition was published by Winter et al. [25]. Figure 14b shows the variation of dynamic moduli and loss tangent distribution at different extents of the reaction. Limitations of the experiments at low frequencies comes from the long experimental times, during which the extent of crosslinking may change so much that the entire experiment becomes no more relevant. We did the experiment from 100 to 0.25 rad/s (or to 0.1 rad/s if we were far from the gel point). Thus each experiment lasts 3 to 5 minutes. These dynamic mechanical data allow us to accurately determine the n exponent at the gel point

$$\tan\delta = \frac{G"}{G'} = \tan\left(\frac{n\pi}{2}\right) \qquad (21)$$

since G' and G'' depend on pulsation in the same way ($G'(\omega) \propto G''(\omega) \propto \omega^n$). From Fig. 14b the variation of $\tan\delta$ versus time can be calculated at different frequencies and Fig. 14c shows that the gel point occurs at $\tan\delta = 2.5$ when all curves intersect. Then we find $n = 0.75$. This value is close to

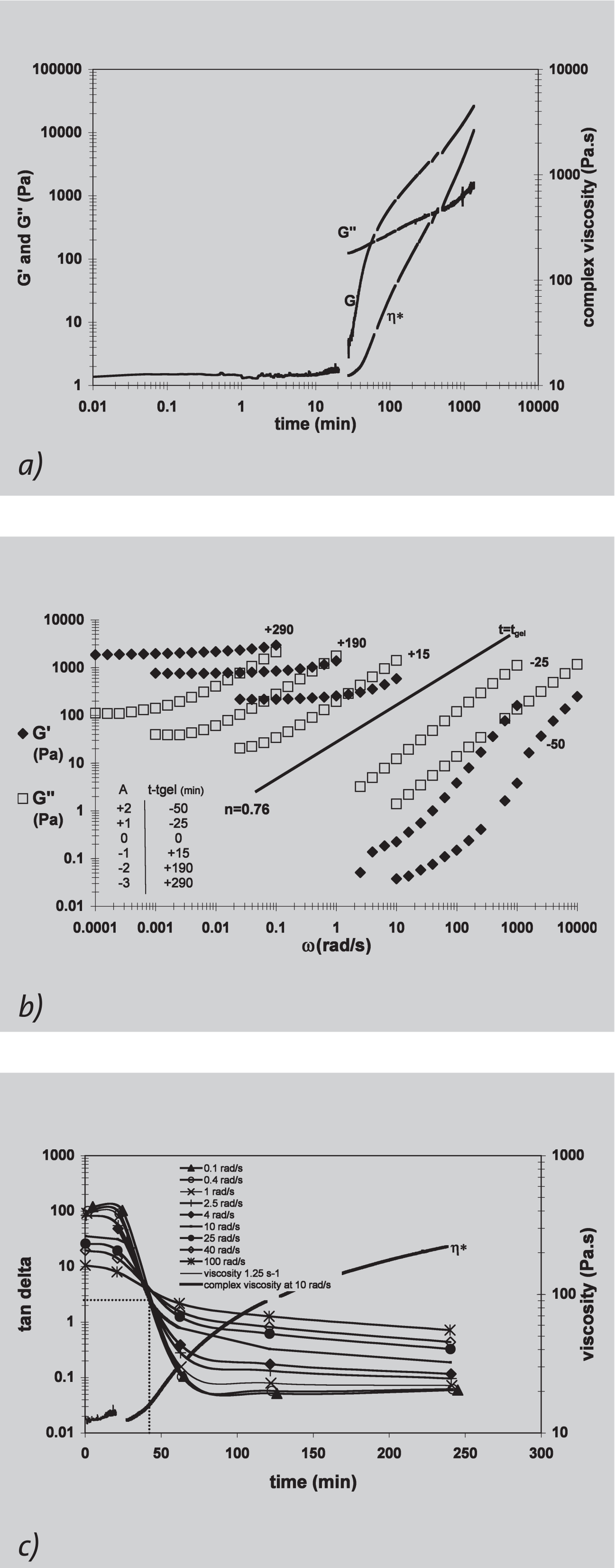


Figure 14:
Evolution of rheological properties during the crosslinking of EVA 33 400 (TPOS: AV/OR = 10, DBTO: 0.5 phr, T = 200°C, 10 rad/s) after dispersion of reagents at 1.25 s^{-1} for 18 min:
a) Evolution of rheological properties at 10 rad.s-1 during crosslinking time,
b) Complex moduli variation versus pulsation at 180°C. In order to better read the data, a shift A has been applied on pulsation, and
c) Gel point determination (crossing of tan d versus time for different pulsations.

that of literature data for networks based on low molecular weight precursor ($n \approx 0.7 - 0.8$ [25]), whereas EVA33-400 can be assimilated to an intermediate molecular weight precursor ($n \approx 0.4 - 0.7$). In a previous work [26] we have reported a value of $n = 0.5$ for a high molecular weight precursor.

5 CONCLUSION

On the one hand, a comparison between rheological data from classical parallel plate geometry and those from a rheoreactor permitted to justify the use of the rheoreactor with melt polymer. On the other hand, the complementary uses of a rheoreactor, a classical rheometer and an internal mixer allowed to establish a mixing law for the incorporation of small quantities of low viscous liquid into highly viscous polymer melt. The more in-depth study of diffusion in polymer helped us to understand the relationships between macromixing and diffusion and the effect of the striation thickness on the diffusion rate.

Besides these results, the rheoreactor allowed us to point out mixing phenomena and reagent dispersion during a polymer crosslinking. Without considering viscous dissipation, the kinetics of EVA crosslinking is all the more fast that shear rate is high when crosslinking reagent are not premixed. Moreover, when the reagents are premixed at low temperature in order to melt EVA, we should distinguish two cases depending on the shear rate range. At very low shear rates, EVA crosslinks faster when shear rate decreases, and a more usual tendency is observed for higher shear rates, that is to say the kinetics increases with shear rate. This was possibly due to a competition between frequency meeting and contact time between active functions. In addition, this phenomenon shows the importance of the competition between mixing time and reaction time. Finally, a very interesting advantage of the rheoreactor concerns the measurement of the viscoelastic properties of a material during mixing. For example, the gel point can be accurately determined in situ.

On the other hand, we have focused in this paper on the diffusion and mixing time in an EVA matrix. Indeed, as the material experiences a shear rate action during mixing, a relation between mixing time and diffusion time was established.

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