Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Polymer 46 (2005) 4686–4694
polymer
www.elsevier.com/locate/polymer

Influence of the dispersion scale of reagents on the deformation of a reactive dispersed phase under shear flow

Y. Deyrail, A. Michel, P. Cassagnau*

Laboratoire des Matériaux Polymères et Biomatériaux, Université Claude Bernard Lyon 1, 15 Bvd. Latarjet, 69622 Villeurbanne, Cedex, France

Received 6 April 2004; received in revised form 13 January 2005; accepted 22 March 2005
Available online 19 April 2005

Abstract

Importance of the 'mixing scale' of reagents is shown through deformation experiments under shear flow on a reactive crosslinked dispersed phase. The EVA dispersed phase in a PDMS matrix can be crosslinked by ester–ester exchange reaction. Tetrapropoxyorthosilicate (TPOS) is used as the crosslinking agent and dibutyltin oxide (DBTO) is used as the precursor. Notion of 'droplet-reactors' is defined. Divergence of the reagents concentration in reactive EVA droplets from the bulk concentration is noticed. Diffusion of the liquid crosslinking agent (TPOS) from the reactive droplets into matrix is strongly inferred, as well as the heterogeneous dispersion of DBTO. First, influence of the mixing time on the dispersion of a powder catalyst (DBTO) in a highly viscous polymer is studied. Second, molecular mixing is experimented through distannoxanes formation when mixing DBTO and EVA. Microscale homogeneous reaction leads to an homogeneous deformation under shear flow of the crosslinked EVA droplets in PDMS matrix, meaning a homogeneous dispersion of the reagents in the EVA.

Keywords: Molecular mixing; Crosslinking; Droplets

1. Introduction

The reactive processing is now a widely used technique in industrial applications. For instance, in an immiscible polymer blends, crosslinking of one phase can enable the stabilization of the morphology. As regards TPV materials, they result from the phase inversion of the crosslinking phase during processing. The reactive phase becomes then the dispersed phase and crosslinking goes on in a multitude of reactive droplets, the size of which is microscopic. The final crosslinking extent of a droplet will therefore depend on the concentration of reagents in that droplet. Generally speaking, kinetics and final extents of crosslinking are discussed from a bulk point of view and not from a sample in dispersed conditions, essentially because of experimental facilities. Consequently, one can imagine that the concentration of reagents in the droplets may diverge from the concentration in the bulk: thus we define the concept of 'droplet reactor': each droplet is considered as a specific reactor. The reagents concentration in this reactor is 'supposed' equal to the concentration in the bulk. In this paper, it is proposed to show that the concentration of the reagents in the 'droplet reactor' diverges from the concentration in the bulk, depending on the mixing scale of those reagents.

In a previous work [1] on the same polymer system, it was showed that, under shear flow, no measurable deformation of a highly crosslinked dispersed phase was observed. However, it was also shown that for a crosslinking extent of the dispersed phase corresponding to an insoluble rate lower than 65%, its deformation was possible. In so far as this system is concerned, meaning reactive EVA, the crosslinking extent can be easily controlled through reagents concentration. Thus, let's consider a reagents concentration in the bulk so that the aimed crosslinking extent corresponds to a 85% insoluble rate. Assuming that the reagents concentrations in the bulk and in the droplets are the same, referring to our previous work [1], no measurable deformation under shear flow of those reactive droplets would be expected. On the other hand, if the

---

* Corresponding author. Fax: +33 4 78 89 25 83.
E-mail address: philippe.cassagnau@univ-lyon1.fr (P. Cassagnau).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.03.071

reagents concentration in the droplets diverges from that in bulk, the reactive droplets having a lower concentration of reagents would deform under shear flow. As a consequence, the evolution of the morphology of a reactive dispersed phase under shear flow can validate the existence of the 'macro-mixing' effect.

The purpose of this work is, basing on deformation experiments under shear flow, to show a mixing-scale effect in a particular immiscible polymer blend with a reactive dispersed phase. The main objective of this work will be to obtain a homogeneous reagents concentration in all 'droplet reactors' leading to stable crosslinked droplets under shear flow. For these reasons, mechanical and molecular-mixing will be experimented.

2. Experimental part

2.1. Materials

In this study, a high molecular weight polydimethylsiloxane (PDMS) was used as the matrix of the blend. Copolymer of ethylene–vinyl acetate (EVA; Evatane® 2840, 28% vinyl acetate, $M_w = 53.5$ kg/mol, $M_n = 19$ kg/mol, MFI 40), used as the dispersed phase, was supplied by Atofina in pellet form. The zero shear viscosities at 160 °C of EVA and PDMS are $\eta_0 = 570$ Pa s and $\eta_0 = 1650$ Pa s, respectively. The interfacial tension of the blend was measured using the drop retraction method described by Xing et al. [2]. More details on this method are given in a previous paper [3]. The interfacial tension of the pure EVA/PDMS blend is about 3.1 mN/m. Both crosslinking agents were commercial products. Dibutyltin oxide (DBTO) was obtained from Aldrich and tetrapropoxysilane (TPOS) was obtained from Roth Sochiel. The reactive EVA phase was then ground to powder ($\phi \approx 100$ µm) so that it could be dispersed in a PDMS sandwich for shear experiments.

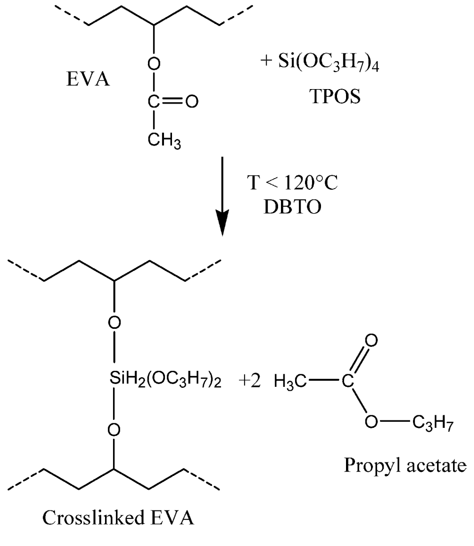

Fig. 1. Reactional scheme of the exchange reaction between ester group of EVA and alkoxide group from TPOS.

2.2. EVA crosslinking

The crosslinking system has been fully described in a previous paper [1]. Thus, EVA was crosslinked through ester–alkoxysilan interchange reaction described by Bounor-Legaré et al. [4]. They showed that a catalyst has to be used to start the crosslinking reaction for temperatures below 200 °C. The dibutyltin oxide (DBTO) enables crosslinking reaction starting from 120 °C. The reaction scheme is described in Fig. 1. Actually, the DBTO generates an organometallic bridge between the acetate groups through a metal–oxygen bond. In presence of alkoxy groups, this organometallic bridge is destroyed and crosslinking of the EVA occurs through formation of Si–O–C bonds. The reaction between DBTO and acetate groups of the EVA chains gives 1-alcoxy-3-acyloxytetrabutyldistannoxanes which are the true catalysts in the ester–ester interchange reaction (Fig. 2). The importance of distannoxanes was demonstrated by Bonetti et al. [5]. The formation of the distannoxanes results from a complex mechanism of 'licking' of the EVA melt with the solid particles of DBTO. There is no melting of the DBTO particles but a progressive consumption by the licking process. At temperatures below 140 °C, crosslinking kinetics are governed by the rate of distannoxanes formation. At higher temperatures, this reaction is fast and the crosslinking kinetics are then governed by the reaction between distannoxanes and alkoxy groups. The extent of crosslinking is controlled through the VA/OR ratio, which corresponds to the molar ratio of acetate groups (VA) of the EVA chains to alkoxy groups (OR) of the TPOS. Thus, the lower the VA/OR ratio is, the higher the extent of crosslinking is.

2.3. Preparation of the reactive dispersed phase

Reactive EVA was prepared using a Haake Plasticorder equiped with an internal mixer (Rheomix 600). The rotating speed and the resulting torque were recorded with blending time. In order to avoid the crosslinking of EVA during the blending process, the catalyst DBTO was first introduced and the crosslinking agent TPOS was added later, meaning in the last 3 min of mixing at 90 °C. So as to study the mixing-scale effects, various mixing times and temperatures of the DBTO with EVA melt were experimented. The so obtained reactive EVA was then mechanically ground into powder, the size of which was held between 50 and 300 µm with a mean diameter of about 100 µm. Incorporation of TPOS in PDMS matrix was carried out using a Scamia two roll-mills at 60 °C.

2.4. Viscoelastic studies

The crosslinking kinetic was studied at 160 °C through

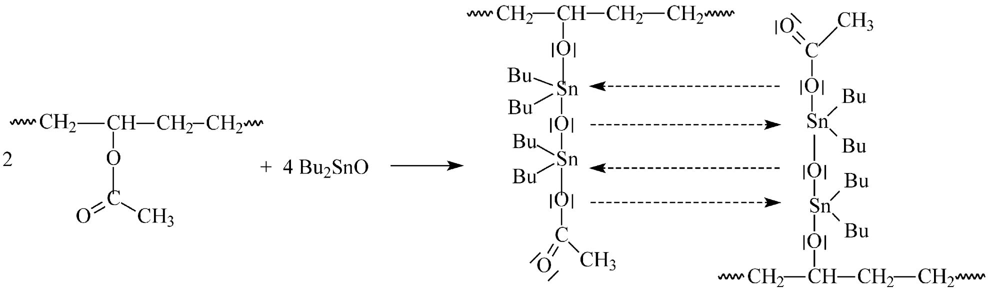

Fig. 2. Distanoxannes formation from reaction of DBTO (Bu_2SnO) with acetate groups of EVA.

evolution of the viscoelastic properties of EVA with time. Viscoelastic measurements were carried out with a Rheometrics strain controlled rheometer (RMS800) with parallel plate geometry (diameter: $\phi = 13$ mm). The thickness of the sample was about 1.5 mm. In all cases, the linearity of the sample response with respect to stress amplitude was verified and nitrogen gas was used to prevent thermal degradation. During crosslinking, the modulus varies about 4 decades so, in order to keep a good sensitivity on the evolution of the viscoelastic parameters, the applied strain has to be adjusted during the experiment.

2.5. Optical shear device

Deformation experiments were carried out on a Linkam CSS 450 high temperature stage coupled with a Leitz Orthoplan optical transmission microscope with 20× lens. The sample consists of two disks of PDMS matrix between which ground reactive EVA powder was manually dispersed. The sample was held between two quartz windows and was sheared by rotating the bottom plate with a precision stepping motor, while the top plate remained fixed. To ensure a complete cohesion between the PDMS disks and as a consequence that reactive EVA droplets were totally imbedded, the gap between the windows was modified to a smaller value than the initial thickness of the PDMS films, using a stepping motor. In all of the experiments, the gap thickness varied between 1 and 2 mm. Deformation experiments were carried out at 160 °C at a shear rate varying from 0.1 to 0.3 s^{-1}.

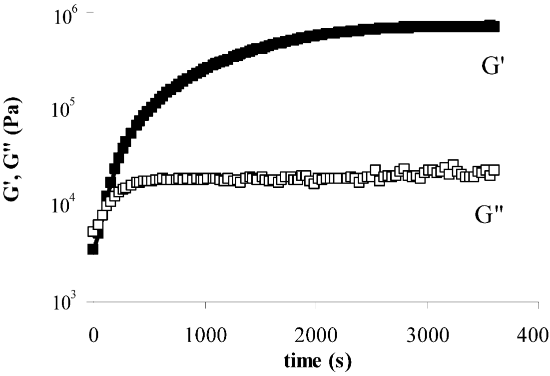

Fig. 3. Crosslinking kinetic. Dynamic time sweep tests on reactive EVA (VA/OR = 10, 1% DBTO. $T = 160$ °C).

3. Results and discussion

As described in the experimental part, the crosslinking kinetic of EVA and the crosslinking extent are obtained from rheogical analysis. In our previous work [1], it was shown that using different VA/OR ratio for the EVA reactive dispersed phase, the crosslinking kinetics were quite similar but the final rheological behaviors were completely different. Considering the aim of this work and the deformation results obtained previously [1], the following features were chosen for the reactive EVA: VA/OR = 10 and 1% DBTO (in weight). Therefore, regarding the crosslinking extent aimed, no measurable deformation of the EVA droplets under shear should be observed. At 160 °C, the crosslinking reaction is over after 1 h curing (Fig. 3). The final extent of crosslinking is characterized by a value of tan $\delta = 0.07$ at the equilibrium, corresponding to a high extent of crosslinking. Indeed, referring to Winter and Mours [6] and the work of Cassagnau [7] on the crosslinking of EVA, one might assume that the gel point is situated at tan $\delta = 1$. The relevance of the tan δ parameter with respect to the crosslinking level, was extensively discussed in our previous paper [1].

When the crosslinking of the dispersed phase is over and after applying the shear treatment (0.1 s^{-1} for 60 s), the morphology is set. For comparison purpose, the same deformation test was applied to each sample:

1. The sample PDMS/reactive EVA is cured at 160 °C, directly in the shear device, for 1 h.
2. A 0.1 s^{-1} shear flow is applied for 60 s at 160 °C.
3. The sample temperature was quickly decreased (30 °C/min) under 80 °C so as to prevent droplets from relaxing back to initial stage.
4. Pictures of the resulting morphology were taken randomly on the whole sample perimeter.

Regarding now the cooling rate in the step (3), it takes less than 3 min to freeze the morphology set during the shear treatment. In our previous work [1] about deformation of crosslinked EVA droplets in a PDMS matrix under shear flow, the relaxation times of the deformed droplets were studied. It was shown that, at 160 °C, the relaxation time of a neat EVA droplet, the diameter of which was close to the mean droplet diameter (100 μm), was about 1 min. When a similar droplet of reactive EVA was slightly crosslinked at 160 °C up to a extent of crosslinking corresponding to tan $\delta = 6.59$, the relaxation time after deformation at 160 °C was found to increase up to 39 min. Therefore, considering the crosslinking extent of the EVA droplets aimed in this study, the complete relaxation of the crosslinked droplets after deformation under shear flow is not to be expected. Moreover, it must be considered that the relaxation times previously mentioned were measured at 160 °C. In the present study, the relaxation times of the deformed crosslinked droplets will be much longer because of the fast cooling applied after shearing. As a consequence, the morphologies obtained after cooling can be compared to each other whatever the blending conditions were.

3.1. Macro-mixing

In order to demonstrate macro-mixing effect during blending of a reactive mixture, the following experiment has been carried out. First, the reactive EVA was prepared in the batch mixer in two steps:

1. $T = 110$ °C, $V = 50$ rpm: mixing of the EVA melt with the DBTO powder for 10 min.
2. $T = 110$ °C, $V = 50$ rpm: introduction of the liquid TPOS and additional mixing for 3 min.

Following this, the reactive EVA was ground into powder and dispersed manually on a PDMS disk, the diameter of which was about 25 mm. A second disk of PDMS is laid on the first one in order to imbed the EVA particles. Then, a curing at 200 °C for 30 min was achieved directly in the hot shear stage to complete the crosslinking reaction. During the first minutes of curing at 200 °C, polymorphous droplets issued from the mechanical grinding were allowed to relax into spherical droplets due to interfacial forces. Theoretically, at the end of curing and according to the crosslinking extent aimed, the spherical nodular morphology generated should be undeformable under shear flow. Experimentally, the resulting morphology is presented in Fig. 4(a). It can be seen that some 'reactors' have reached a high level of crosslinking (no deformation of the droplet under shear flow) whereas some reactors were only slightly crosslinked (high deformation of the droplets, even leading sometimes to filaments). In Fig. 4(b), an additional shear treatment was applied with respect to the Fig. 4(a). It can be seen that if the shear rate is increased from 0.1 to 0.3 s^{-1}, the droplets-reactors with a low crosslinking level can still deform. On the other hand, the highly crosslinked reactors keep their spherical shape whatever the shear rate is. Basing on these observations, it can be assumed that dispersion of the reagents in the EVA, obtained in the batch mixer, is very heterogeneous from a microscopical point of view. The droplet-reactors are not identical and the reagents concentration in the droplets substantially diverges from the concentration in the bulk: therefore 'macroscale-mixing' is demonstrated. Actually, such effect can be explained first, by a heterogeneous dispersion of the DBTO powder in the EVA melt in the internal mixer and second, by the diffusion of liquid TPOS from the droplet-reactors into the PDMS matrix. In the droplet reactors, a lack of TPOS or DBTO automatically leads to an extent of crosslinking lower than the one aimed (tan $\delta = 0.07$). Therefore, in order to obtain a homogeneous extent of crosslinking for all the droplet-reactors, new mixing conditions must be experimented.

3.2. Diffusion of TPOS

Previous studies conducted in the laboratory (Bounor-Legaré et al. [4]) tend to show that the mixing of EVA melt and liquid TPOS is homogeneous from the molecular scale point of view. In so far as the PDMS/EVA blends are concerned, the reactive EVA phase consists of microscopic droplets diluted in the PDMS matrix. As the TPOS is a liquid, a diffusion process was expected from the more concentrated environment (EVA droplets) to the lower concentrated one (PDMS matrix). Actually, the diffusion process is pretty fast at high temperatures. Obviously, this phenomenon leads to a lower concentration of TPOS in the droplet-reactors than initially aimed. Basically, an easy way

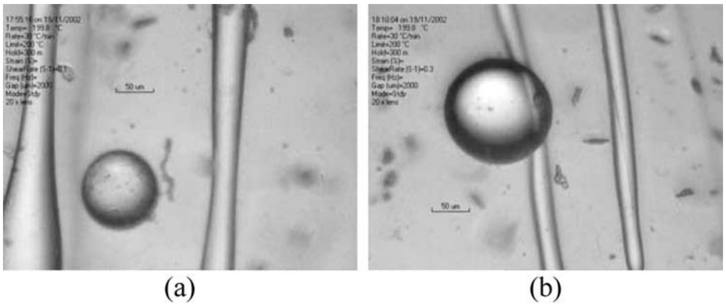

Fig. 4. Macro-mixing effect. Curing at 200 °C for 30 min. (a) shear flow at 0.1 s^{-1} for 60 s, (b) shear flow at 0.3 s^{-1} for 60 s. The black scale line on the pictures is equal to 50 μm.

of getting rid off this diffusion process is to incorporate some TPOS in the PDMS matrix. Although the quantity added is small, its inertia with respect to the rheological behavior of the matrix was checked and confirmed. Of course, the amount of TPOS added to the matrix was calculated so as to have the same concentration of TPOS in the matrix and in the droplets. In order to verify the validity of this technique, the reactive EVA blends have been prepared in the following way:

1. DBTO was mechanically mixed with EVA melt at 110 °C for 10 min ($V=50$ rpm).
2. TPOS was introduced at 90 °C and blended for three additional minutes.

The so obtained reactive blend was then ground into powder in order to be dispersed manually between two disks of matrix. For the deformation experiments, two different matrix were used:

1. neat PDMS matrix (B1).
2. PDMS + TPOS, called PDMS' in the following (B2).

The deformation experiments were carried out after a curing at 160 °C for 1 h directly in the hot shear stage. As can be seen in Fig. 5, there is a great difference in homogeneity of the morphologies obtained from the pure PDMS matrix (Fig. 5(a) and (b)) and from the PDMS–TPOS matrix (Fig. 5(c)). A statistical study of the deformed and non-deformed droplets has been performed after the shearing process. The morphology after cooling is analyzed basing on two different states of deformation of the droplets:

1. The droplet has kept its initial shape after shearing/cooling: it means that its crosslinking level his equal or higher (called aimed) than the aimed one.
2. The droplet has an ellipsoidal shape after shearing/cooling: it means that its crosslinking level is lower (called lower) than the aimed one.

Table 1
Statistical study of the droplet deformation after shearing

Level of crosslinking mixing method	Lower (%)	Aimed (%)
B1	62	38
B2	33	67
B3	75	25
B4	48	52
B5	10	90
B6	30	70
B7	18	82

B1, without optimisation; B2, addition of TPOS in the matrix; B3, mixing time of 5 min; B4, mixing time of 10 min; B5, molecular mixing + PDMS'; B6, optimisation for tan $\delta=6.59$, B7, optimisation for tan $\delta=0.57$.

The results are presented in Table 1. Considering the sample B1 and B2, the strong influence of the diffusion of TPOS from the droplets into the matrix is clearly demonstrated. Indeed, regarding the sample with neat PDMS matrix (B1), the diffusion of the TPOS leads to low levels of crosslinking of most of the EVA droplets (62%), resulting in a substantial deformation under shear flow. Considering now the PDMS–TPOS matrix (B2), the resulting morphology after shearing is significantly more homogeneous. Most of the crosslinked droplet-reactors (67%) do not deform under shear flow (Fig. 5(c)). It means that the crosslinking extent aimed has been reached for most of the droplet-reactors. As a consequence, the addition of TPOS in the PDMS matrix drastically limits the diffusion of TPOS from the droplet-reactors into matrix. In the following discussion, the PDMS matrix containing TPOS will be called PDMS'. An interesting point that deserves to be discussed is the droplet size dependence of this diffusion process. Indeed, a faster diffusion of the TPOS is expected in the smaller droplets. However, due to experimental constraints, such study was not conducted. Indeed, if the diffusion process is really faster in the smaller droplets, the crosslinking extent obtained after curing is very small and the droplet then turns into a filament during shearing. Most probably, this filament breaks up during shearing or at least before the end of the cooling step. The critical point is that the break-up process of the fiber seems to be somewhat perturbed by the crosslinking of EVA (Fig. 5(b)), leading to droplets of various size after break up (Fig. 5(a)). Thus, from the final morphology, it is very difficult to know about the size of the initial droplet. The second point that harms the study of size dependence of the diffusion process is that it also depends on the concentration of DBTO in the droplets. So, if the concentration of DBTO is equal or higher than 1 wt%, the crosslinking reaction will occur before diffusion of the TPOS into the matrix. Moreover, the increase in viscosity resulting from the running crosslinking reaction in the droplet prevents further diffusion of the TPOS. So as a conclusion, if the importance of stopping the

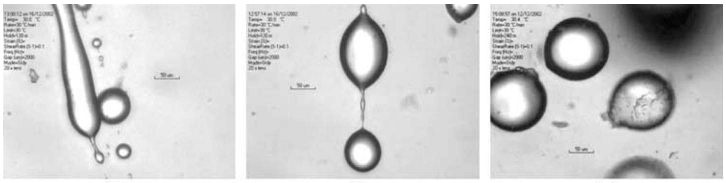
(a) (b) (c)

Fig. 5. Diffusion of TPOS into matrix. Curing at 160 °C for 1 h. Shear flow at 0.1 s^{-1} for 60 s. VA/OR = 5 (tan $\delta=0.05$). (a) pure PDMS, (b) PDMS + TPOS. The black scale line on the pictures is equal to 50 μm.

diffusion of TPOS so as to get identical droplet-reactors is clearly shown, the influence of the droplet size could not be demonstrated.

3.3. Dispersion of DBTO

Knowing that the catalyst DBTO is in powder form and that the melt viscosity of EVA is rather high, a homogeneous dispersion of the DBTO in the EVA melt is most probably not achieved through a simple mechanical mixing. Moreover, the difference in droplets size of DBTO and that of EVA dispersed in the PDMS matrix is only of about one order of magnitude. So, knowing the particles size of DBTO and EVA, the number of DBTO particles incorporated in one reactive EVA droplet can be calculated. Obviously it is assumed that both EVA and DBTO droplets are spherical. Considering that V_{DBTO} represents the volume of DBTO introduced in the internal mixer then V_{DBTO} contains N_{DBTO} particles so that:

$$N_{\mathrm{DBTO}} = \frac{V_{\mathrm{DBTO}}}{\frac{4}{3}\pi D_{\mathrm{DBTO}}^3} \tag{1}$$

These N_{DBTO} particles were then dispersed in V_{EVA}; V_{EVA} representing the volume of EVA introduced in the internal mixer. Thus, N_{p} which is the number of particles of DBTO contained in one EVA droplet, the diameter of which is D_{EVA}, can be calculated by the following expression:

$$N_{\mathrm{p}} = \frac{N_{\mathrm{DBTO}}}{V_{\mathrm{EVA}}}\frac{4}{3}\pi D_{\mathrm{EVA}}^3 \tag{2}$$

Knowing N_{DBTO} from Eq. (1):

$$N_{\mathrm{p}} = \frac{V_{\mathrm{DBTO}}}{V_{\mathrm{EVA}}}\frac{D_{\mathrm{EVA}}^3}{D_{\mathrm{DBTO}}^3} \tag{3}$$

In our blending conditions, $V_{\mathrm{EVA}} = 50\ \mathrm{cm}^3$, $V_{\mathrm{DBTO}} = 0.5\ \mathrm{cm}^3$ (meaning 1% in volume assuming that the densities are equal to 1). It is assumed that the average diameter of EVA droplets is of about 100 μm and that of DBTO particles is approximately 3 μm (given by the supplier). It is found that one EVA droplet contains $N_{\mathrm{p}} = 370$ particles of DBTO. Thus, all droplet-reactors should contain some catalyst and consequently should be able to crosslink. Nevertheless, it can be seen from Eq. (3) that N_{p} varies with the cube of the ratio of the particles average diameters. From the granulometry (Fig. 6) of the DBTO powder determined by scanning electron microscopy (SEM), the average droplets size is found to be approximately 13 μm. The value of N_{p} then fall to 4.5: considering the very broad size distribution of the DBTO particles, some particles having a diameter of 50 μm, some reactive EVA droplets may not contain any DBTO and consequently cannot crosslink at 160 °C. Therefore, a good dispersion of DBTO powder in the EVA melt must be achieved in order to obtain a homogeneous crosslinking of all the droplet-reactors dispersed in the PDMS matrix. Considering this, two different methods have been experimented: first, fitting the mixing time of DBTO and EVA melt and second, dispersion of DBTO through molecular-mixing with EVA melt.

3.3.1. Influence of mixing time

Blending of DBTO and EVA melt was performed at 90 °C in the internal mixer with a rotating speed of 50 rpm. The TPOS was introduced in the mixing chamber for the last 3 min of blending in order to limit the crosslinking of EVA. During the first minutes of blending, the complete melting of the EVA can be attributed to the stabilization of the mixing torque. Following this, the DBTO powder is incorporated. In order to demonstrate the influence of mixing time on the dispersion of DBTO particles, the mixing was proceeded for 5 or 10 min. Then, the reactive blends were ground into powder and manually dispersed between two PDMS' disks (containing TPOS) in order to

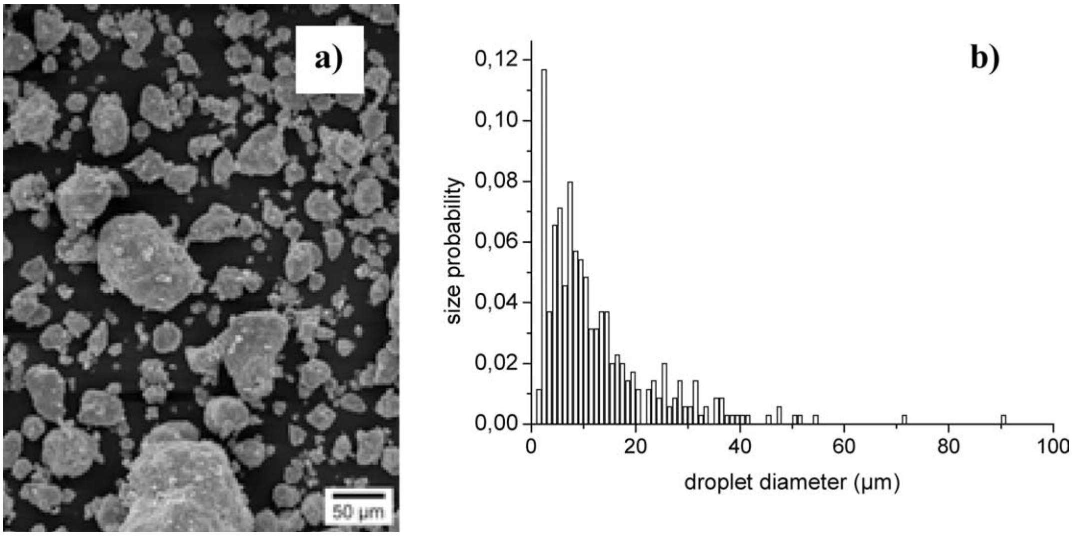

Fig. 6. Granulometry of DBTO powder: (a) SEM picture. (b) Size distribution.

carry out the deformation experiments. The resulting morphologies are shown in Fig. 7. For each morphology, three characteristic pictures have been chosen. It can be seen from the irregular shape of the EVA particles that they were not able to relax into well-defined spherical droplets during the 1-h curing at 160 °C. It can be attributed to a partial crosslinking of EVA due to the self-heating phenomena during mixing with TPOS. However, despite of these experimental difficulties, the differences between the two mixing time remains quite clear (Table 1 and Fig. 7). A short mixing time (5 min) leads to a very heterogeneous morphology. Indeed, only 25% EVA droplets were highly crosslinked and did not deform under shear flow (Fig. 7(a)). On the other side, 75% of the EVA droplets were slightly crosslinked and could even turn into fibers under shear flow (Fig. 7(c)). As one can see in Fig. 7(b), the crosslinking development seems to be heterogeneous in the droplet itself since under shear flow only a part of the droplet was deformed.

If the mixing time is now increased up to 10 min, the resulting morphology is nicely more homogeneous. Even if only 52% of the EVA droplets are not deformed after shearing (Fig. 7(e)), those that are deformed exhibit approximately the same deformation (Fig. 7(d) and (f)). After shearing, less than 2% of EVA fibers are observed. This means that all the droplet-reactors have crosslinked with a sufficient extent of crosslinking, which means that they all contained some DBTO. As with less than 1 wt% of DBTO the crosslinking reaction of EVA is not completed after the 1 h curing at 160 °C, these droplet-reactors remain deformable under shear. On the contrary, the droplet-reactors containing at least 1% of DBTO are undeformable. Thus, the better dispersion of the DBTO powder is achieved with a mechanical mixing of 10 min. However, it must be pointed out that, as most of the EVA droplets were still deformable after curing, another route to obtain a homogeneous morphology has to be considered: molecular-mixing of DBTO and EVA.

3.3.2. Molecular-mixing

In the experimental part, more precisely about the crosslinking chemistry of EVA, the importance of the formation of distannoxanes was pointed out. They are the true catalyst of the crosslinking reaction and no crosslinking can take place at 160 °C without their beforehand formation. It could be expected that the formation of such molecule (Fig. 2) during the first step of mixing with EVA should improve the dispersion of the catalyst in the EVA melt: in the following, this process is called 'molecular-mixing'. As explained in Section 2.2 of Section 2, the formation of the distannoxanes results from a 'licking process' of the solid DBTO by the EVA melt. This reaction starts at 140 °C and lasts for few minutes. Thus, to prepare reactive EVA blends through 'molecular-mixing', a mechanical mixing of the DBTO powder with EVA melt was performed at 140 °C and carried on for 10 min at least. This way, the catalyst of the crosslinking reaction is homogeneously incorporated in the EVA phase. Actually a mechanical mixing is coupled to a molecular-scale mixing: this blending process could be also called 'micro-mixing'.

After this blending step, the temperature of the mixing chamber is decreased to 90 °C so as to incorporate the TPOS. The time needed to cool down the blend to 90 °C is rather long since the rise in the blend's viscosity generates a strong self-heating phenomenon. To enable a faster cooling, the rotating speed of screws was decreased to 30 rpm. Then, as described for previous blends, the so-obtained reactive EVA blend was ground into powder and dispersed manually between two PDMS' disks in the hot shear stage. After the curing for 1 h at 160 °C and the shearing treatment, the morphology presented in Fig. 8 is generated. The efficiency of the micro-mixing process is clearly demonstrated since 90% of undeformed EVA droplets (Table 1) could be seen after the shearing/cooling steps. It means than only 10% of the droplet-reactors contained a lower reagents concentration than the bulk aimed one. It can also be observed that the reactive droplets issued from mechanical grinding are unable to relax into a spherical shape during the curing at

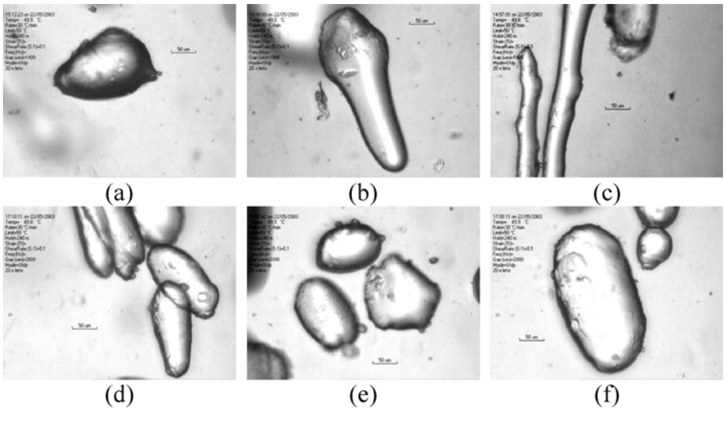

Fig. 7. Influence of mixing time, tan $\delta = 0.07$, shear at $0.1\ \mathrm{s}^{-1}$ for 60 s. (a)–(c) $t = 5$ min, (d)–(f) $t = 10$ min. The black scale line on the pictures is equal to 50 μm.

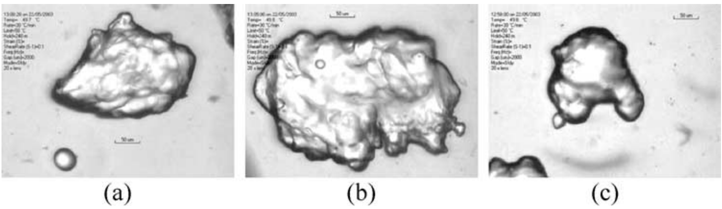
(a) (b) (c)

Fig. 8. Micro-mixing, tan $\delta = 0.07$, shear at 0.1 s^{-1} for 60 s. The black scale line on the pictures is equal to 50 μm.

160 °C. Indeed, as the distannoxanes are the catalyst of the ester–alkoxysilane exchange reaction, a partial crosslinking of EVA occurred during blending with TPOS at 90 °C. However, as no deformation of the crosslinked particles could be achieved, even at high shear rates, it means that the micro-mixing process leads to homogeneous highly crosslinked EVA droplets. Actually, this also means that a homogeneous dispersion of the DBTO in the EVA melt was achieved.

3.3.3. Generation of a homogeneous dispersion of reagents in reactive EVA droplets

Basing on the conclusions discussed above, the blending conditions necessary to achieve a homogeneous dispersion of the reagents in the reactive dispersed phase are the following ones:

1. First EVA is introduced in the mixing chamber at 140 °C. The rotating speed of screws is fixed at 50 rpm. Self-heating makes the temperature increase above 140 °C.
2. When resulting torque is constant, the DBTO powder is introduced. Mixing is carried on for 10 min at least. Formation of distannoxanes takes place.
3. The temperature of the blend is then decreased to 90 °C in order to incorporate the TPOS. The rotating speed of screws is decreased to 30 rpm so as to limit the self-heating.
4. At 90 °C, TPOS is added in the mixing chamber and proceeds for three additional minutes.
5. TPOS was introduced into the PDMS matrix using a two roll-mill at 60 °C. The TPOS concentration in PDMS' is the same than in the corresponding reactive EVA.

Using these mixing conditions, deformation of a reactive EVA dispersed phase with a higher value of tan δ leads to a nicely homogeneous morphology of slightly deformed droplets as can be seen in Fig. 9. However, due to the very small quantity of TPOS added to the reactive blend, less identical droplet-reactors are obtained: 82% for tan $\delta = 0.57$ and 70% for tan $\delta = 6.59$. In both cases, less than 10% of droplets having a low extent of crosslinking were found, which is still a very good result.

4. Conclusion

This work aimed at obtaining a homogeneous dispersion of crosslinking reagents in highly viscous droplets dispersed in another viscous phase. The reactive phase is first prepared by mixing in an internal mixer and then ground into powder so as to be dispersed in the other polymer phase. The quality of the dispersion of the reagents in the droplets was qualified through deformation experiments under shear flow after the crosslinking step. Thus, the mixing conditions of a liquid crosslinking agent (TPOS) with a powder catalyst (DBTO) in EVA melt was studied. Notion of 'droplet-reactor' was defined. Each droplet of reactive EVA can be considered as a 'reactor'. A substantial divergence of reagents concentration in 'droplet-reactors' compared to reagents concentration in the bulk has been showed. Diffusion of the TPOS from reactive droplets into PDMS matrix was demonstrated. Addition of TPOS into PDMS prevents reactive droplets from diffusion of TPOS. Influence of the mixing time on the dispersion of DBTO was experimented. It has been showed that a mechanical mixing for 10 min is necessary to get a rather good dispersion of the DBTO in the EVA melt. Finally micro-mixing was experimented. Mixing of DBTO and EVA at 140 °C leads to the formation of distannoxanes and leads to a molecular dispersion of the catalyst into the EVA melt. In this fashion, homogeneous morphologies of

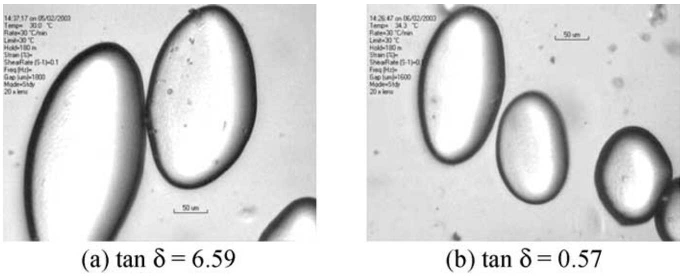
(a) tan δ = 6.59 (b) tan δ = 0.57

Fig. 9. Homogeneous morphology of crosslinked EVA droplets deformed under shear flow (0.1 s^{-1}). (a) tan $\delta = 6.59$, (b) tan $\delta = 0.57$. The black scale line on the pictures is equal to 50 μm.

underformable crosslinked droplets were achieved, meaning a homogeneous dispersion of the reagents in the EVA droplets.

References

[1] Deyrail Y, Cassagnau P. J Rheol 2004;48:505–24.

[2] Xing P, Bousmina M, Rodrigue D. Macromolecules 2000;33:8020–34.

[3] Deyrail Y, Fulchiron R, Cassagnau P. Polymer 2002;43:3311–21.

[4] Bounor-Legaré V, Ferreira I, Verbois A, Cassagnau P, Michel A. Polymer 2002;43:6085–92.

[5] Bonetti J, Gondard C, Petiaud R, Llauro MF, Michel A. J Organomet Chem 1994;481:7–17.

[6] Winter HH, Mours M. Adv Polym Sci 1997;134:165–234.

[7] Cassagnau P. Handbook of advanced material testing 1995.