Sintering of Two Drops of Model Fluids

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ABSTRACT: Sintering of various model fluids has been studied. 3 PDMS, 2 polybutenes and 4 Boger fluids were employed. The rheological properties of the 9 fluids have been studied. Measurements of the surface tension of these fluids have been done thanks to sessile drop method. The effects of viscosity, elasticity and surface tension have been explored on two substrates. Experimental data were compared to a physical model based on Maxwell constitutive equations. The viscosity is the main factor that acts against the sintering. We observed that the interfacial tension between the fluid and the substrate plays a non negligible role on the sintering kinetics.

Key words: sintering, model fluids, rheological properties, surface tension

1 INTRODUCTION

The coalescence is a phenomenon that occurs during a rotomolding cycle. The powder into the mold is heated and junctions between the powder particles are created. This has been studied by numerous authors. Frenkel first modeled the sintering for metals and ceramics [1]. Lontz extended this approach for polymers [2]. Pokluda *et al.* adopted Frenkel's approach but used the Upper Convected Maxwell Model (UCMM) and take into account the particle radii variation [3]. Bellehumeur *et al.* improved this model by introducing the viscoelastic behaviour of the polymers [4]:

$$8\left(\alpha\lambda K_1\theta'\right)^2+\left(2\alpha\lambda K_1+\frac{\eta_0 r_0}{\gamma}\frac{K_1^2}{K_2}\right)\theta'-1=0 \qquad (1)$$

x, r, t, γ, η_0 and λ are the neck radius, the particle radius, the time of sintering, the surface tension, the zero-shear viscosity and the relaxation time of the material. K_1 and K_2 are geometrical parameters. θ refers to the sintering angle as shown on Fig.1.

All these studies were performed by using various industrial polymers like PE, PVC, PC, copolymers [5]… Sintering achieved with such polymers present some technical difficulties: thermal degradation, experimental errors due to melt kinetics or particle shape… The idea is to use model polymers, liquid at room temperature, with a well-controlled rheological behaviour and surface tension.

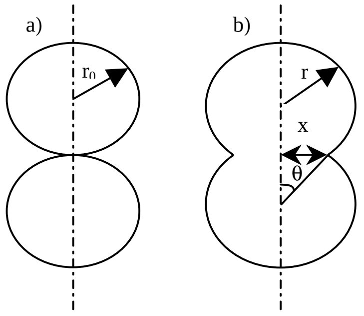

Fig. 1. Schematic geometry of two particles during sintering at a) t=0 s and b) t>0 s. r, x and θ represent the radius, the neck radius and the sintering angle respectively.

2 EXPERIMENTAL PROCEDURES

2.1 *Materials*

2 polybutènes PB and 3 poly(diméthylsiloxanes) PDMS were used in this study. Table1 presents the

nomenclature of the various samples with their zero-shear viscosities and relaxation times measured at 25°C. 4 Boger fluids BF have been formulated. Such fluids are a mix of a highly viscous polymer and a highly elastic one [6]. We used two PB's in order to examine the effect of the viscosity, and two amounts of poly(isobutylene) PIB for varying the elasticity. Table2 gives the composition of these fluids.

Table1. Rheological characteristics for PDMS and PB samples

Fluid	η_0 (Pa.s)	λ (s)
PDMS1	10,6	$1,5.10^{-4}$
PDMS2	28,9	$1,5.10^{-3}$
PDMS3	80,8	$3,1.10^{-3}$
PB1	23	10^{-5}
PB2	502	$2,6.10^{-3}$

Table2. Composition of the 4 Boger fluids

Fluid	% Kerozene	% PIB	% PB
BF1	6,98	0,22	92,8 (PB1)
BF2	6,2	0,8	93 (PB1)
BF3	6,98	0,22	92,8 (PB2)
BF4	6,2	0,8	93 (PB2)

2.2 *Rheological properties*

Small amplitude oscillatory shear tests were carried out on a stress-controlled rotational rheometer AR1000 from TA Instruments with a cone and plate geometry (diameter 60 mm, angle 2°). All rheological measurements were carried out in the linear viscoelastic regime as was verified by preliminary strain sweep tests.

2.3 *Surface tension measurements*

The surface tension of the fluids was measured at 25°C with sessile drop method. Preliminary measurements have shown that all fluids are non polar. This allows us to use only one substrate to deduce the surface tension of the materials. One drop of the fluid was deposited on a PTFE substrate, with a surface tension γ_S, and its profile was recorded thanks to a camera. The contact angle α was measured and the surface tension of the fluid γ_L was evaluated according to:

$$\gamma_L = \frac{4\gamma_S}{(1+\cos\alpha)^2} \qquad (1)$$

2.4 *Sintering experiments*

The sintering experiments were conducted on 2 different substrates: PTFE and a copper one. Two drops of the same fluid were deposited on the substrate and images of their coalescence were recorded at regular time. Images are then analysed and the sintering curves, *i.e.* x/r=f(t), are plotted. The accuracy of the experimental data is 4%. Data are compared with Bellehumeur's model (Eq.1).

3 RESULTS AND DISCUSSIONS

3.1 *Rheological behaviour*

Fig.2 reports the complex viscosity as a function of the frequency for the PDMS and PB's. All samples show a large Newtonian plateau, followed by a decrease of the viscosity for high frequency. This decrease is mainly observable for high molecular weight sample (PDMS3 and PB2). PB1 and PDMS1 are nearly Newtonian in the whole frequency domain. Table1 gives the rheological properties of these fluids.

Fig.3 shows the storage modulus and complex viscosity for BF2 and BF4. These two materials have the same concentration of PIB but are composed with PB1 and PB2. At low frequencies, both materials present a Newtonian plateau followed by a small decrease in viscosity to reach a second plateau for intermediary frequencies. Newtonian viscosities and relaxation times deduced from rheological curves are presented in Table3. At high frequencies, the BF's own the same behaviour that their constitutive PB's. As we can see in Table 3, λ_2 is similar to λ_{PB}. Rheological curves of BF1 and BF3 are similar to those of BF2 and BF4. We also observe that a small addition of PIB increases the viscosity and λ_1 especially.

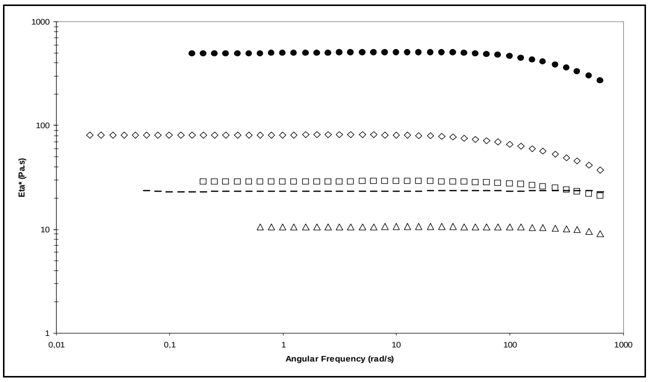

Fig. 2. Complex viscosity *vs.* angular frequency for PDMS1(Δ), PDMS2(☐) and PDMS3(◇), and for PB1(-) and PB2 (●).

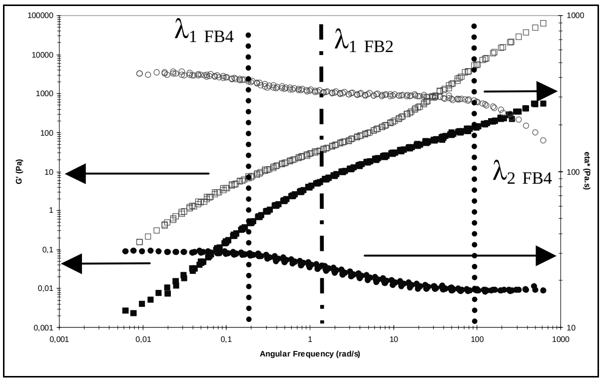

Fig. 3. Complex viscosity (●,○) and storage modulus (■,□) *vs.* angular frequency for BF2 (full symbols) and BF4 (open symbols).

Table3. Zero shear viscosity and relaxation times for Boger fluids. The relaxation time for PB's used in each Boger fluid are recalled in column 5.

Fluid	η_0 (Pa.s)	λ_1 (s)	λ_2 (s)	λ_{PB} (s)
BF1	17	0,6	$3,6.10^{-5}$	$1,5.10^{-5}$
BF2	30,8	0,9	10^{-4}	
BF3	275	3,6	4.10^{-3}	$2,6.10^{-3}$
BF4	420	5,3	10^{-2}	

3.2 Surface tension measurements

The surface tension of the 9 fluids was evaluated. The sessile drop method has the advantage of being simple, but its main disadvantage is its poor accuracy. The average error is about ±0,2 mN/m.

Table4 gives the surface tension measured. The surface tension for the 3 PDMS are quite similar, whereas the 2 PB's have different surface tension. This variation can be explained by their difference on molecular weight. The surface tension of BF's has a value equal to that of their respective matrixes. BF1 and BF2 have the same surface tension than PB1, and BF3 and BF4 have the same than PB2. The addition of PIB doesn't modify significantly the surface tension.

Table3. Surface tension for all samples.

Fluid	γ_L (mN/m)
PDMS1	23,3
PDMS2	23,8
PDMS3	23,6
PB1	26,3
PB2	27,4
BF1	26,5
BF2	26,3
BF3	27,2
BF4	27,3

3.3 Sintering kinetics

3.3.a Effect of the viscosity

The effect of the viscosity on the sintering rates is shown on Fig.4 for the 3 PDMS on a PTFE substrate. Similar curves are obtained on the copper substrate. PDMS1 coalesces faster than PDMS2 and PDMS3 as indicated by t_{99} on Table4. If we use a reduce time t_r which takes into account the viscosity, surface tension and initial radii of drops, it appears that they are quite similar. We can conclude that only the viscosity and surface tension play a role on the sintering of the PDMS. Bellehumeur's model agrees with the experimental data.

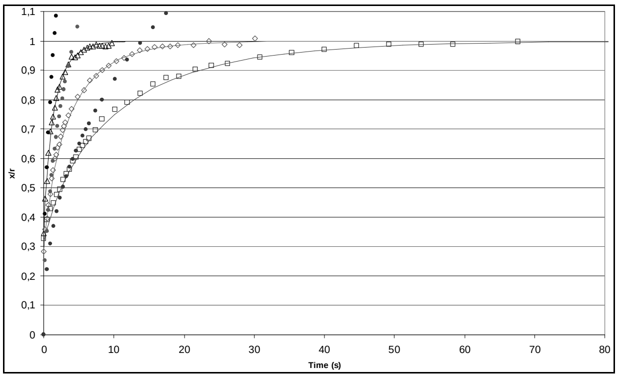

Fig.4. Coalescence curves for: PDMS1 (Δ),PDMS2 (◇) and PDMS3 (□) on a PTFE substrate. The solid lines represent the Bellehumeur et al. model for each PDMS material and the full circles are the Frenkel's model.

3.3.b Effect of the viscosity and interfacial tension

As shown on Fig.5 and Fig.6, PB's samples display sintering kinetics similar to that of PDMS, and depend also on viscosity. We observe a deviation of the model for PB2. We attribute that to the interfacial tension between the fluid and the substrate. On a non wetting substrate (PTFE), sintering kinetics of PB2 is slow down and Bellehumeur's model over predict sintering rates. On a wetting one (copper), the sintering seems to be accelerated and the model underestimates the sintering kinetics. The comparison of t_{99} and t_r for PB2 on the 2 substrates confirms that fact. This effect does not appear for PB1, as for the 3 PDMS, since their viscosities are too low.

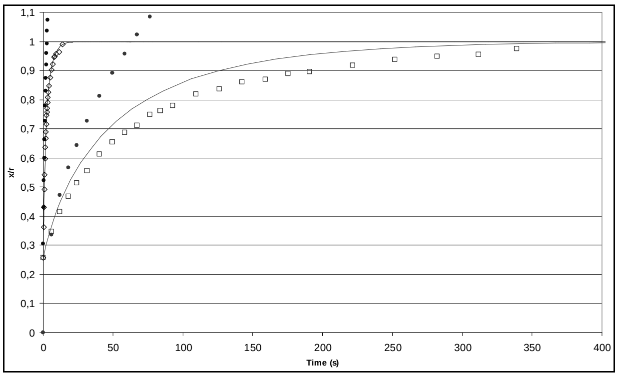

Fig.5. Coalescence curves for: PB1 (◇) and PB2 (□) on a PTFE substrate. The solid lines represent the Bellehumeur et al. model for each PB material and the full circles are the Frenkel’s model.

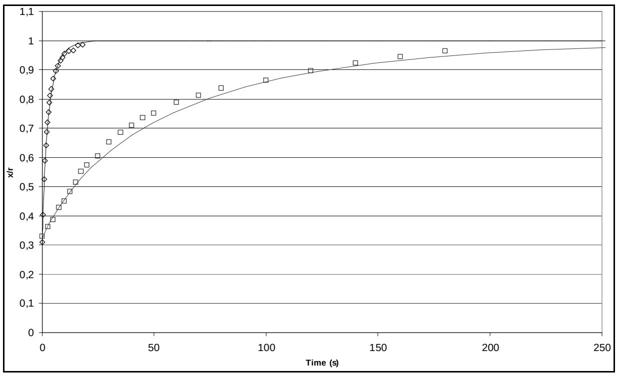

Fig.6. Coalescence curves for: PB1 (◇) and PB2 (□) on a copper substrate. The solid lines represent the Bellehumeur model for each PB material.

3.3.c Effect of the elasticity

Fig.7 illustrates the sintering of BF’s on a PTFE substrate. Similar curves are obtained on a copper one. BF1 and BF2 coalesce faster than BF3 and BF4. This can be explained by their large difference in viscosity. In order to examine the effect of the elasticity, it is necessary to compare fluids that have similar viscosities and surface tension. As we can observe in Table4, reduced sintering times are different for BF1 and BF2. The main difference between these fluids is their relaxation time. They can also be compared with PB1. We observe the same trend for BF3 and BF4. An increase of the relaxation time leads to a slowest sintering process.

4 CONCLUSIONS

The study of the sintering process of 9 well characterized model fluids has pointed out the influence of the viscosity, relaxation time and interfacial tension. The limits of Bellehumeur’s model were tested. Further studies with industrial polymers are in progress.

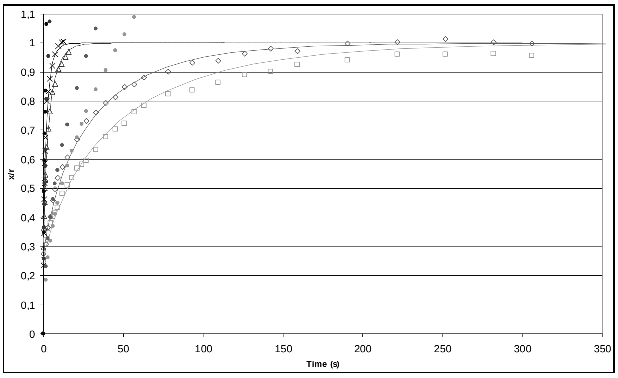

Fig.7. Coalescence curves for: BF1 (**x**), BF2 (*Δ*), BF3 (▱) and BF4 (□) on a PTFE substrate. The solid lines represent the Bellehumeur et al. model for each PB material and the full circles are the Frenkel’s model.

Table4. Sintering times and reduced times for all fluids on PTFE and copper substrate.

Fluid	$t_{99\ (s)}$ (PTFE)	t_r (PTFE)	t_{99} (s) (copper)	t_r (copper)
PDMS1	6,2	3,15	7,3	3,25
PDMS2	14,7	3,03	17,3	3,17
PDMS3	42,3	3,09	50,0	3,25
PB1	9,5	2,58	11,4	2,90
PB2	322,5	4,19	217,5	2,83
BF1	7,3	2,76	8,2	3,04
BF2	14,9	3,04	16,0	3,18
BF3	130,5	3,15	145,0	3,26
BF4	225,0	3,48	192,5	2,91

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