

Infiltration of Uncured Elastomers into Silica Agglomerates

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ABSTRACT: The degree of impregnation of an agglomerate by the suspending matrix is an important parameter because it influences the agglomerate cohesion and thus has a direct effect on dispersion mechanisms. Penetration kinetics reported in the literature were only measured in Newtonian or not very elastic matrices, although one of the main applications is the dispersion of porous filler in elastomers.

The aim of this article is to study the infiltration of porous silica agglomerates by uncured elastomers using optical microscopy. The application of the model of Bohin (infiltration of a Newtonian fluid into a porous sphere) is discussed. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3292–3300, 2004

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INTRODUCTION

The infiltration of a fluid into an agglomerate changes its cohesive strength.¹ This has a direct effect on its dispersion ability. Hydrodynamic stresses required to disperse impregnated agglomerates are larger than for dry agglomerates. The impregnation may also affect the type of dispersion mechanisms.^{2,3} For example, the erosion mechanism depends on the depth of impregnation of the agglomerate by the matrix.³ The rheological behavior of the penetrating matrix also has an effect on the cohesive force of the agglomerates, and consequently on the erosion mechanism. We recently showed that the more viscoelastic the matrix, the larger the stress required to erode agglomerates and the slower the erosion proceeds.⁴ This was observed in the case where the matrix infiltrated the agglomerate and the more difficult erosion was explained by an increase of the agglomerate cohesiveness due to the elastic character of the penetrated fluid. The knowledge of infiltration kinetics of a matrix inside the agglomerate is necessary to understand the dispersion of porous filler during mixing operations. One important field of application that involves dispersion concerns the incorporation of reinforcing filler such as silica or carbon black into elastomers. It is thus of prime importance to study the penetration of elastomers into agglomerates.

Bohin et al.² studied the kinetics of the penetration of a Newtonian silicon oil into silica agglomerates.

They proposed a model based on the capillary forces driving the penetration and viscous effects resisting it. The model predicts that the kinetics of the process can be described by the following equation:

$$F(X) = Kt \quad (1)$$

where

$$F(X) = -3X + 2X^{3/2} + 1 \quad (2)$$

with

$$X = \left(\frac{2R}{D_0}\right)^2 \quad (3)$$

and

$$K = \frac{36D_p \varepsilon^2 \gamma_{lv} \cos \theta}{150 \eta (D_0/2)^2 (1 - \varepsilon)} \quad (4)$$

where t is the impregnation time, R is the radius of the nonwetted core of the agglomerate, D_0 is the agglomerate diameter, D_p is the aggregate mean size, ε is the agglomerate porosity, γ_{lv} is the surface tension of the suspending fluid, θ is the contact angle between the fluid and the material forming the agglomerate, and η is the viscosity of the fluid.

This model assumes that the fluid is incompressible and Newtonian, and that the size of the polymer chains penetrating into the agglomerate are substantially less than the size of the pores through which the fluid flows.

If the infiltration kinetics can be followed, the model predicts that plotting $F(X)$ vs time should give a straight line which slope is equal to K [eq. (4)]. Know-

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TABLE I
Elastomer Characteristics

Elastomer name	BR neocis BR-40	IR Natsyn RNS7477	Oil extended SBR Buna VSL5025-1
M_w (kg · mol ⁻¹)	508	766	620
M_n (kg · mol ⁻¹)	132	205	260
γ_{lv} (mN/m)	32.5 ^a	35 ^a	30.6 ^b
Unperturbed radius of gyration (nm)	62 ^c	72 ^c	—
Reptation tube diameter (nm)	4.3 ^c	4.7 ^c	—

γ_{lv} is the surface energy of the elastomers, M_e is the mean molecular weight between two entanglements.

^a From ref. 8

^b Measurements performed on pure SBR.⁹

^c From ref. 10, data at 25°C.

ing D_{pr} , ϵ , and η , the term corresponding to the wetting property characterizing the filler-suspending fluid couple ($\gamma_{lv} \cos\theta$) can be determined. If in addition the surface energy of the fluid is known, the wetting angle, parameter that cannot be measured directly on this kind of substrates that are agglomerates, can be estimated.

A similar idea was used by Seyvet.⁵ But instead of determining the $\gamma_{lv} \cos\theta$ term from kinetics measurements, they used the fact that K can also be interpreted as the inverse of the total impregnation time. In this case, the wetting term can be determined from the proportionality between the total impregnation time and the square of the agglomerate diameter.

In any case, to follow the penetration kinetics, it is necessary to be able to visualize the impregnation. This is indeed possible for silica agglomerates. As soon as the matrix penetrates into the porous silica, the impregnated part becomes transparent, whereas the nonwetted part appears opaque because of the strong light scattering due to the air contained in the pores.

Penetration experiments were also reported on carbon black agglomerates. In this case due to the non-transparency of the agglomerates, the information on infiltration were obtained from sedimentation experiments.^{3,6}

The objectives of the present work are to investigate how the infiltration of a viscoelastic elastomer into agglomerates occurs and to measure impregnation kinetics. The aim is to determine the wetting angle between an elastomer and silica. Knowing this parameter should enable to estimate the adhesion energy between the two phases and thus the critical condition for the rupture at the filler–elastomer interface.

EXPERIMENTAL

Materials

Silica agglomerates, Z1165MP produced by Rhodia, were used in this study. This silica is characterized by a surface area of 148 m²/g (measured by BET), a mean

aggregate size of 48 nm (centrifuge sedimentometry) and a porosity of 66% (mercury porosimetry). Silica particles were not submitted to any particular thermal treatment before their use.

Three commercial elastomers representing the main families of elastomers used in the formulation of tyres were chosen: a butadiene rubber (BR) produced by EniChem, an isoprene rubber (IR) produced by Good-year, and a vinyl–styrene–butadiene rubber prepared in solution (SBR) produced by Bayer. SBR contains 25% of styrene and is extended with 37.5 p.h.r. of aromatic oil. Some characteristics of these elastomers are presented in Table I. All experiments were conducted on uncured elastomers.

The rheological behavior of the three elastomers was characterized by oscillatory experiments using a RMS800 Rheometrics rheometer (25 mm in diameter) at a constant temperature of 140°C. Measurements were performed at a strain of 1% (linear viscoelastic regime) and for a frequency range of 0.1–100 rad/s. The complex viscosity (η^*) and the modulus ratio (G'/G'') are plotted vs frequency on Figure 1 for the three elastomers.

The oil extended SBR has the lowest apparent viscosity for the frequency range investigated. BR has probably the lowest zero shear viscosity. Below 20 rad/s, IR is the most viscous elastomer. For larger frequencies, BR becomes the most viscous.

A lower viscosity matrix was also used for sake of comparison with the elastomers: polydimethylsiloxane (PDMS) Rhodorsil 47V200000 from Rhodia, characterized by a 200 Pa.s viscosity. The behavior of this PDMS at low shear rates is Newtonian.

Experimental setup and procedures

Samples consisted of a sandwich of two thin films of elastomer with a few agglomerates (less than 0.1 p.h.r.) randomly placed in between. The sample is set between two glass plates and its thickness is controlled. Observations were recorded via a CCD camera and a video recorder. Because elastomers are very

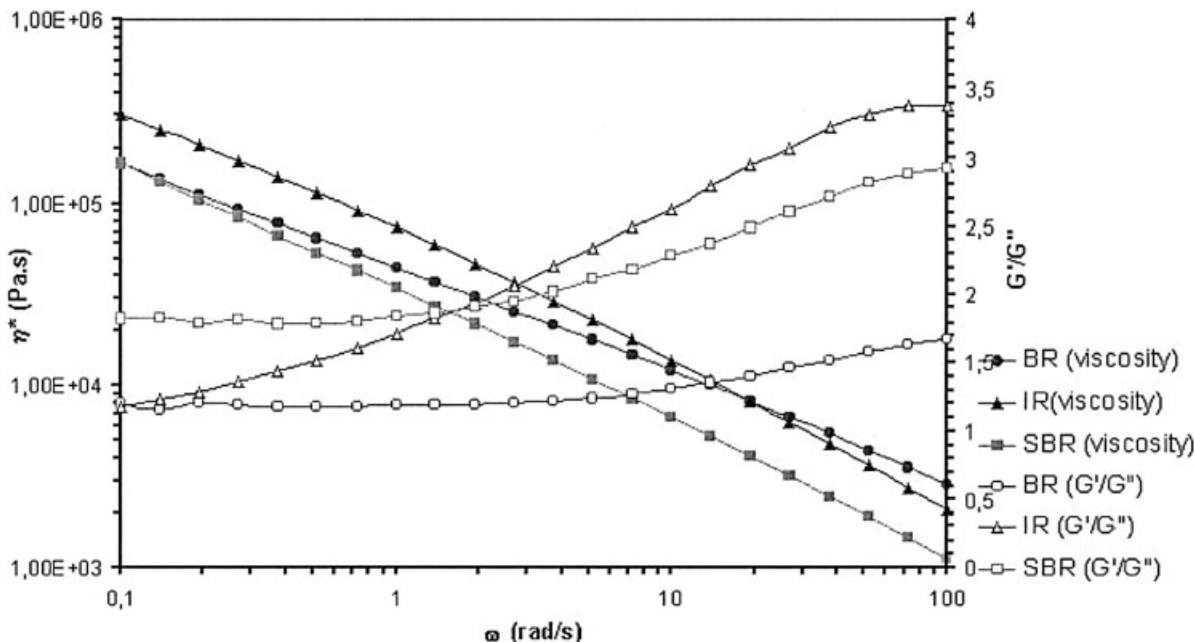


Figure 1 Complex viscosity (η^*) and ratio of storage over loss moduli (G'/G'') vs frequency (ω) at 140°C for BR, IR, and oil extended SBR.

viscoelastic, very large sample thicknesses (more than half a millimetre) were used to minimize the time necessary for the system to relax when the sandwich is set between the two glass plates. During the sample setup, the contact between the two films and between the elastomer and the silica particle is checked by optical microscopy. But once the contact was ensured, the sample was not squeezed further in order not to apply any external pressure on the sample (outside the pressure linked to the long relaxation time of the elastomers). Kinetics could start to be recorded 10 min after the contact between the agglomerates and the matrix. This time also took into account the time necessary to reach the equilibrium temperature.

The kinetics of impregnation was followed by optical microscopy by measuring the size reduction of the dry part of the silica agglomerates vs time. Nonembedded parts of the agglomerates appear black (due to the large difference of refractive index between air and silica), whereas, once penetrated by the matrix, imbedded parts are transparent (small difference of refractive indices between silica and the fluid).

Image analysis procedure

The determination of nonwetted area (dark parts of the agglomerates, see Fig. 2) for a given image was performed using an image analysis system (Visilog 5.3 software) for a given threshold value. But as it can be seen from Figure 2, the determination of the radius of the nonpenetrated part is not obvious. Two difficulties had to be solved.

First, after some impregnation time, there were a lot of remaining nonwetted areas in the middle of the infiltrated part. To take these areas into account for the calculation of the dry volume, the image analysis software measured the total 2D dark area. From this surface, the radius of an equivalent full sphere was calculated. By doing this, we artificially gathered all remaining nonwetted spots in the centre of the agglomerate.

Second, the nonwetted areas did not change abruptly from black to transparent, the effect of the threshold value on the impregnation kinetics was thus investigated. An example of analysis of a set of kinetic data is shown in Figure 3. Kinetics measurements are represented according to the model proposed by Bohin et al. [see eqs. (1) to (3)].

However, the start of penetration, and more particularly, the slope of the central part of the curve, are not very sensitive to the threshold value. Because these are the two important parameters, we consider that the image analysis operational parameters do not influence the obtained results.

RESULTS

Elastomers can infiltrate into a porous filler, although they have a very large viscosity, as seen in Figure 2.

Impregnation seems to happen in a different way in elastomers in comparison with Newtonian matrices. In low viscosity and elasticity fluids, the matrix penetration is a gradual and homogeneous process^{2,5} (infiltrated depth at the agglomerate periphery in-

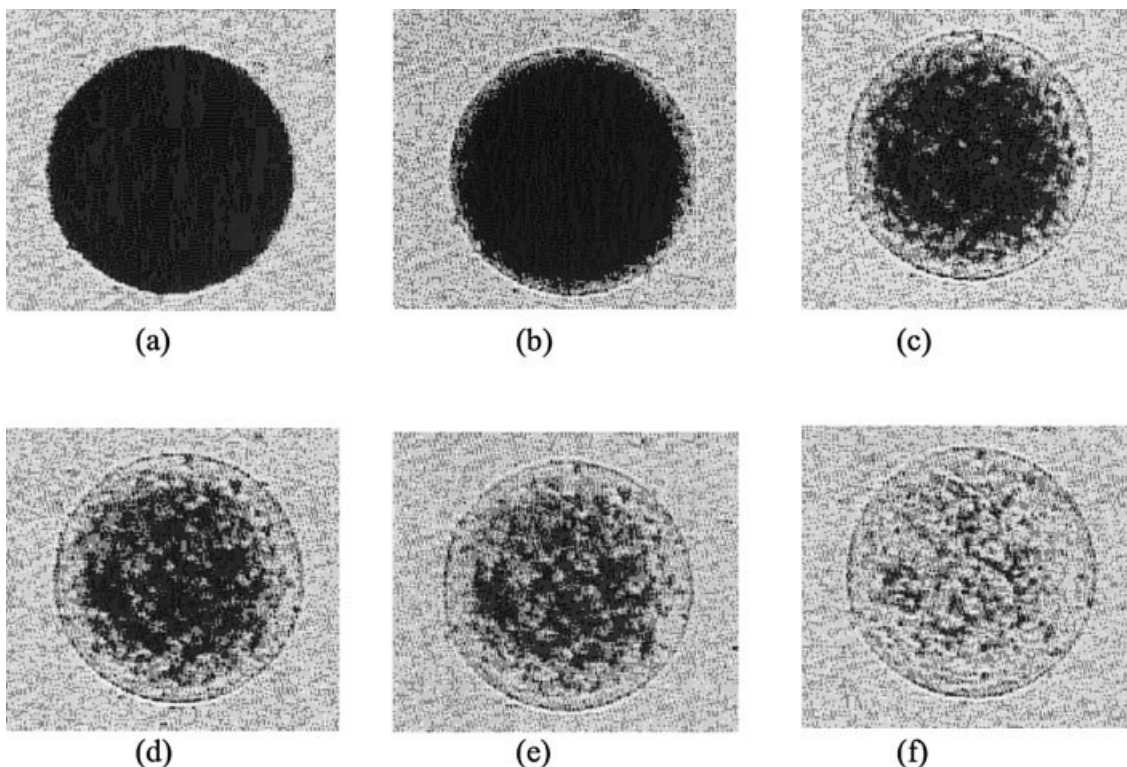


Figure 2 Infiltration of BR into a silica particle ($D_0 = 153 \mu\text{m}$) at different times, (a = 15 min), (b = 165 min), (c = 250 min); (d = 295 min); (e = 320 min); (f = 540 min).

creases gradually). This is true even if Seyvet observed that the penetration occurred with Jerks (depending on the silica origin) except if a certain hydrostatic pressure was applied to the sample.⁵ In the case of elastomers (Fig. 2), the infiltration does not happen in a homogeneous manner. Some spots corresponding to a deeper infiltration of the matrix into the porous filler can be observed. This leads to the presence of transparent areas (i.e., impregnated) in the middle of the dry core. Vice versa, nonwetted spots can also be

observed in the infiltrated areas. Some of these non-wetted spots are still present at the end of the infiltration process. The apparent difference of behavior between low viscosity and elastomeric matrices will be discussed in the following.

Observations during infiltration also show that the fluid penetration does not start immediately after the macroscopic contact between the silica and the matrix (contact followed by optical microscopy). There is a certain time before the infiltration really takes place.

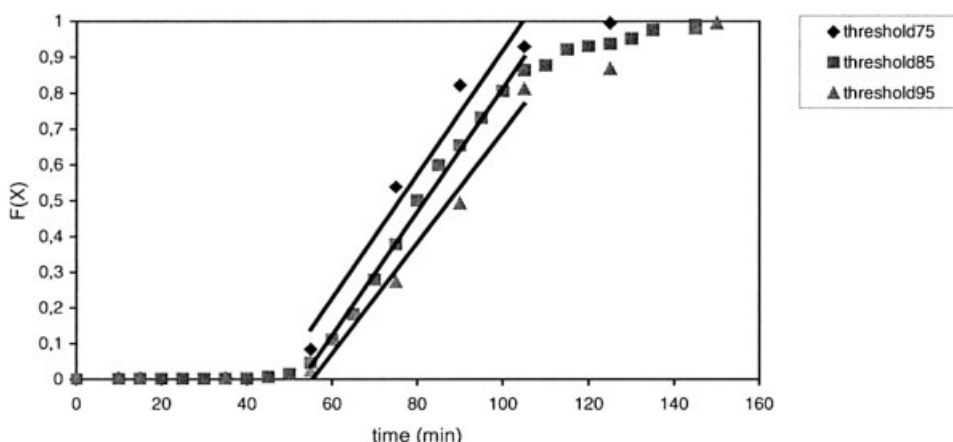


Figure 3 Effect of different threshold values on the slope of the curve $F(X)$ vs time (experiment on a silica particle with $D_0 = 83 \mu\text{m}$ in BR).

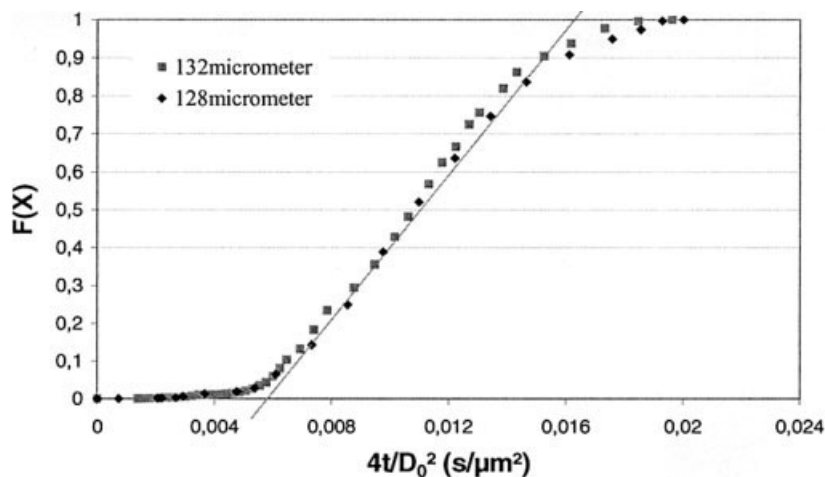


Figure 4 Infiltration of polydimethylsiloxane into two silica particles. Kinetics data plotted according to eqs. (1) to (3).

This is very clear in elastomeric matrices where latent times as long as several hours for the SBR matrix can be observed. This is better seen for a low viscosity fluid by looking at the $F(X)$ vs time representation of the infiltration process [no infiltration corresponds to $F(X) = 0$] (see Fig. 4). This latent period was not previously reported for low viscosity fluids, but it does exist.

Kinetics of impregnation of the three elastomers into silica agglomerates are very different. Figure 5 shows a comparison of the infiltration stages for the three matrices.

After 26 min of contact between the elastomers and the silica agglomerates, an impregnated depth of about 10 microns is already observed in BR [Fig. 5(a)], whereas in IR [Fig. 5(c)] and in oil-extended SBR [Fig. 5(e)] no impregnation can be observed by optical microscopy. After a longer immersion time (145 min), a 83- μm agglomerate is almost completely penetrated by the BR matrix [Fig. 5(b)]. For the same time of immersion, only a thin layer is infiltrated by IR [Fig. 5(d)] or by oil-extended SBR [Fig. 5(f)]. Kinetics of impregnation into silica is thus the fastest in BR and the slowest in oil-extended SBR. This is also quantitatively confirmed by plotting kinetics data according to Bohin's model (see Fig. 6). To compare the kinetics measured for different agglomerate diameters, the function $F(X)$ [see eqs. (1) to (3)] is plotted vs time divided by the agglomerate diameter squared.

Three infiltration regimes can be thus distinguished in the infiltration process: (1) a first regime where there is no impregnation, referred as the latent time; (2) a second regime where the infiltration occurs, which plotted according to the infiltration model gives straight lines; (3) a third regime corresponding to the slowing down of the process.

The three infiltration steps are discussed separately in the following.

DISCUSSION

Latent period

The existence of a certain delay time before the infiltration of the matrix into the agglomerate starts was

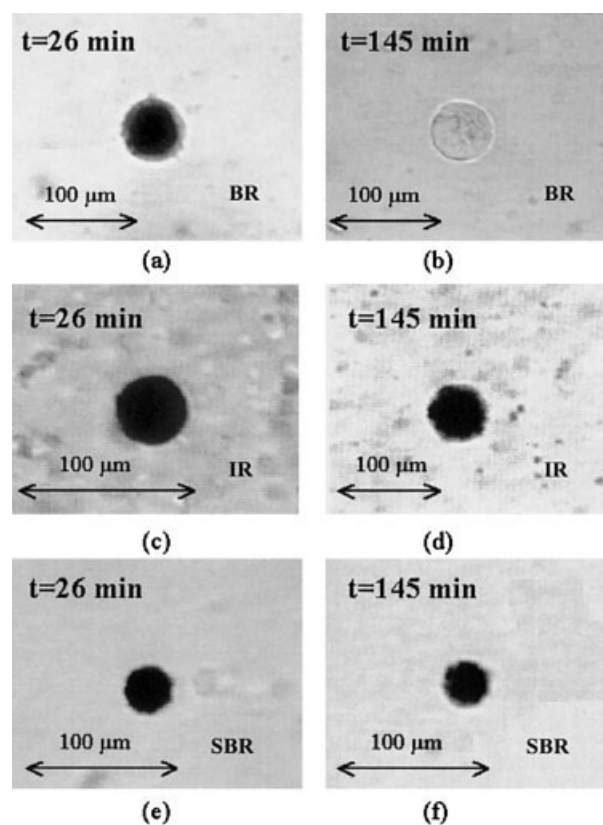


Figure 5 Comparison of the levels of impregnation of silica agglomerates in the three elastomers at two different immersion times (after 26 and 145 min). (a) and (b) correspond to observations performed in BR, (c) and (d) in IR, (e) and (f) in oil extended SBR.

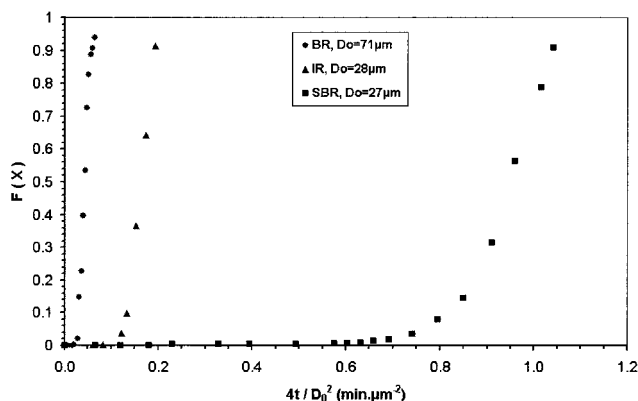


Figure 6 Kinetics of impregnation of silica agglomerates embedded in elastomers at 140°C. $F(X)$ vs $4t/D_0^2$ in BR ($D_0 = 71 \mu\text{m}$), in IR ($D_0 = 28 \mu\text{m}$) and in oil extended SBR ($D_0 = 27 \mu\text{m}$).

not previously reported.^{2,5} To check if the delay time was not due to an experimental artefact, two measurements were performed at room temperature with the PDMS matrix. Impregnation kinetics with this fluid are reported in Figure 4. Even if this delay period is much shorter than for the elastomeric matrices, this time with no infiltration is also observed for this low viscosity fluid. This latent time was also observed for other low viscosity fluids (polyisobutylenes).

The presence of this latent time for the PDMS shows that the latent time is not an artefact due to the heating and homogenization of the temperature in the sample because these experiments were performed at room temperature. In addition, if this time was linked to the heating and temperature homogenization, similar latent times should be found for the three elastomers, which is not the case.

The latent time seems to depend on the viscosity of the fluid (very short latent time for PDMS and very long for elastomers), but must depend on other parameters. To better understand the origin of this time where no infiltration takes place, an extended study of this phenomenon (varying the fluid viscosity, the temperature, the pellet size) is presently carried out.

Impregnation stage

The penetration of elastomers does not seem to happen homogeneously as for low viscosity fluids. It seems to proceed through preferential pathways. This nonhomogeneous penetration of the chains can be explained by the relative dimensions of the polymer chains towards the pore size. Two different situations can be at the origin of a nonhomogeneous infiltration:

1. the existence of larger pores in the agglomerates, which would be the location of preferred pathways for the matrix infiltration, as suggested by

Yamada et al.⁶ These large pores should first be infiltrated because of their lower resistance to penetration. As soon as larger pores are penetrated, infiltration should continue through smaller pores.

2. the difference in the polymer chain dimensions between PDMS and the elastomers relatively to the pore size distribution can also explain this fact. For the same size distribution of pores, low molar mass chains should penetrate "everywhere," whereas larger chains should only penetrate through large pores.

Impregnation kinetics

First, it is interesting to note that although the infiltration process looks nonhomogeneous in elastomeric matrices, kinetics data plotted according to the model of Bohin do give straight lines. This is obtained even if the nonwetted parts in an agglomerate at a given moment are summed to calculate the radius of an equivalent sphere.

Analysis of the data according to Bohin's model

Because plotting $F(X)$ versus time results in a straight line, as soon as the impregnation really starts, we tried to use Bohin's model to interpret the infiltration kinetics and from the slope of the curve, knowing the viscosity, to estimate the wetting term.

For the PDMS matrix, a wetting term around 17 mN/m is obtained from the linear part of the $F(X)$ vs time curve. The surface tension of a PDMS being around 21 mN/m,⁷ a wetting angle of PDMS on silica around 30° is found.

Elastomers being non-Newtonian, we estimated the shear rate submitted to the elastomer during infiltration to determine the viscosity during the process. This was done by considering a Poiseuille flow in a tube representing the pore (mean hydraulic pore radius taken as

$$R_h = \frac{\varepsilon D_p}{6(1 - \varepsilon)}, \quad (5)$$

with D_p the aggregate mean size and ε the porosity) and a power law to estimate the rheological behavior of the elastomers. Table II summarizes the results obtained from the infiltration kinetics plotted according to Bohin's model. The indicated results are averaged values taking into account all measurements performed for a given elastomer. An example of a complete set of kinetics (measurements performed on eight silica pellets) is given in Figure 7 for the BR matrix.

TABLE II
Averaged Parameters of Kinetics of Impregnation and Wetting Terms ($\gamma_{lv}\cos\theta$)
Calculated with the Estimated Viscosity (η)

Elastomer D_0 range (μm)	BR 65–153	IR 28–60	Oil extended SBR 27–30
Latent period ($\text{min} \cdot \mu\text{m}^{-2}$)	0.025 ± 0.005	0.115 ± 0.025	0.61 ± 0.05
K ($\mu\text{m}^2 \cdot \text{min}^{-1}$)	59 ± 44	18 ± 5.4	4.4 ± 0.3
$\gamma_{lv}\cos\theta/\eta$ ($\text{m} \cdot \text{s}^{-1}$)	$(6.6 \pm 4.9) \cdot 10^{-5}$	$(2.0 \pm 0.6) \cdot 10^{-5}$	$(4.9 \pm 0.3) \cdot 10^{-6}$
η ($\text{Pa} \cdot \text{s}$)	$4 \cdot 10^4$	$4.2 \cdot 10^4$	$5.3 \cdot 10^4$
$\gamma_{lv}\cos\theta$ ($\text{N} \cdot \text{m}^{-1}$)	2.6	0.84	0.26

D_0 is the agglomerate diameter, and K is the slope of the $F(X)$ vs time curve, γ_{lv} is the surface energy of the elastomer, θ is the contact angle and η is the viscosity of the elastomer.

This table shows that the wetting term is larger in BR than in IR and in oil-extended SBR. However, if we use the respective surface tension of BR and IR (taken from the literature and given in Table II), we find cosine values much larger than 1, which is impossible.

Critical analysis of the infiltration model relative to our experiments

These impossible cosine values lead us to question the validity of the assumptions on which the infiltration model is based and of values of some parameters characterizing the system. Different assumptions of the model can be examined: (a) a Newtonian fluid, (b) a homogeneous porosity, (c) a constant flow rate during the process, (d) a continuum mechanical description of the flow.

The non-Newtonian character of the elastomer is disregarded as being at the origin of the failure of the interpretation. The integration of a power law expression for the viscosity variation in the infiltration model or considering a viscoelastic fluid should lead to larger frictional pressures in a porous medium and, conse-

quently, to worse estimated values for the wetting term.

The method used to determine the agglomerate porosity (mercury porosimetry) must overestimate the porosity available to the elastomer. Variations of the porosity or of the mean aggregate size (parameters that fix the hydraulic diameter of the pores) were also considered, but the resulting variations on the wetting term are not sufficient to explain the model failure. The homogeneity of the porosity can be questioned.

The evolution of the volumetric flow rate of fluid through the porous medium can be calculated from the advancement of the wet-dry interface (see Fig. 8). It shows that, once the penetration has started, the flow rate first increases, reaches a maximum, and then decreases. The variation of the volumetric flow rate for the PDMS matrix should be similar to that shown for BR in Figure 8, because kinetics follow the same tendencies. The fact that physical values are obtained in the case of PDMS tends to show that the constant flow rate assumption, although crude can, however, be used.

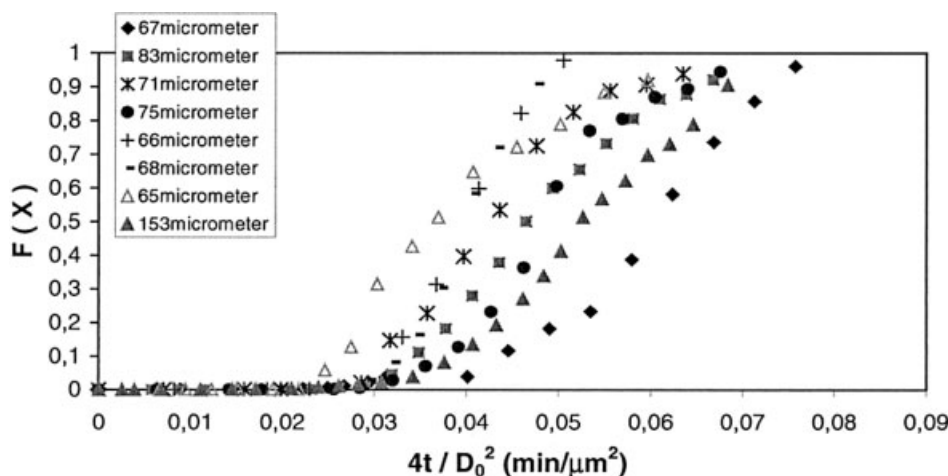


Figure 7 Infiltration of BR into eight silica particles, data plotted according to the model of Bohin [see eqs. (1) to (3)].

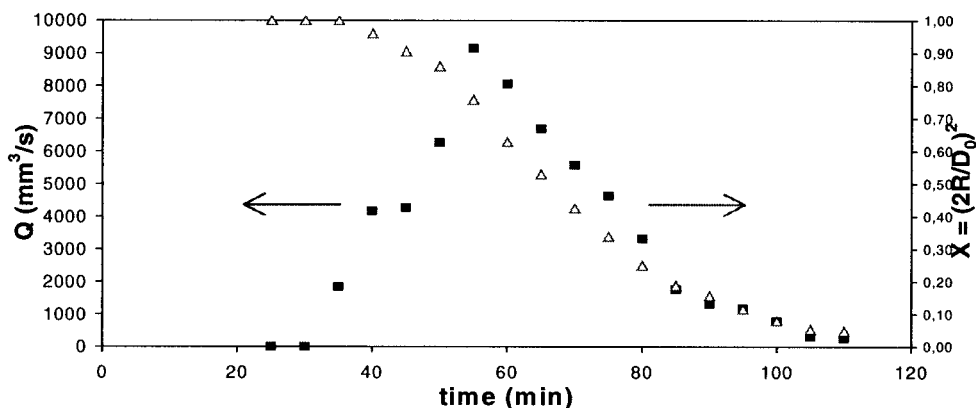


Figure 8 Variation of the flow rate versus time during the impregnation process (squares). Data corresponding to the infiltration of BR into a silica 83- μm large particle. The evolution of the X parameter (triangles) is reported for sake of understanding the variation of the flow rate as the impregnation proceeds.

A last classical implicit hypothesis is that a continuum description of the fluid should be valid. This means, for example, that the size of the molecules penetrating into the agglomerate should be substantially less than the size of the pores through which the fluid flows. But the comparison of the mean hydraulic pore radius ($R_h = 15.5$ nm) with the characteristic dimensions of the polymer chains (see Table I) shows that the size of the polymer chains penetrating into the agglomerates are not substantially less than the size of the pores. The unperturbed radius of gyration are larger than the average pore diameter. Also, considering the size of the tube of reptation, the hydraulic radius is only less than four times larger than this characteristic size. The model considers that the force resisting the impregnation process is the viscosity. However, the relative dimensions of the polymer chain towards the pore size shows that a viscosity measured in the bulk is not characteristic of what happens inside the agglomerate. Two facts can be at the origin of this discrepancy:

1. the behavior of the polymer chains in a flow with a gap size comparable with the chain characteristic dimension cannot represent the bulk viscosity measured by classical rheometry. It would be very tempting to think that a rheological measurement carried out at a nanoscale would solve this problem. However, the common idea is that the viscosity in a nanoscale gap is larger than the bulk viscosity, and this would lead according to the impregnation model to an even larger wetting term. Outside this point, such measurements are performed by imposing an external force. In our case, the fluid velocity is driven by the capillary force, and one should not forget that chains may adsorb on the walls of the pores. Due to the narrow geometry relative to the chain size, the question is to know which characteristic dimen-

sion of the chain should be considered to correctly represent the force resisting the impregnation.

2. The relative dimensions of the pores towards the polymer chain dimensions, and more particularly the distribution in chain length, question whether all macromolecules can penetrate inside the pores. If there is a selection of molecular weight, the bulk viscosity cannot be again the right parameter.

Comparison between the three elastomers

Although quantitative information on the wetting term characterizing the matrix/agglomerate couple cannot be obtained, infiltration kinetics give access to qualitative information. The comparison of the infiltration kinetics for the three elastomers (Fig. 6) shows that the latent period is the shortest in BR and the longest in oil-extended SBR and the slope of the $F(X)$ vs time curves is the largest in BR and the lowest in oil-extended SBR. The impregnation of silica by the BR matrix is thus the fastest and the longest by the oil-extended SBR matrix. This order gives an idea of the wetting property of the matrix towards the silica substrate and of the affinity between the two constituents.

It is interesting to note that even if the SBR matrix is oil extended, the low molar mass oil does not penetrate at first into the agglomerates. Otherwise, the infiltration of the matrix would be more rapid and homogeneous. It is clear that it is not the case.

Final degree of filling

Yamada et al.⁶ suggested a description for the evolution of the air trapped in the agglomerate as impregnation proceeds. First, the air contained in the large pores should easily find its way either being evacuated from the agglomerate through similar large pores

or through smaller pores or being diffused through the matrix. However, as smaller pores get infiltrated, and some of them corresponding to close pores, the air entrapped should be compressed until an equilibrium pressure should be found. Once this pressure has been reached, the infiltration of the matrix should stop. From this description, it is expected that the final state of impregnation should correspond to a less than complete saturation of the pores by the fluid. The authors reported that this degree of filling should depend on the viscosity of the fluid, the affinity of the fluid with the porous medium, and the volume of voids between the aggregates. For low viscosity fluids having a good affinity towards the filler, a degree of saturation close to 100% is expected. Outside the affinity between silica and an elastomer, it is clear that the degree of saturation in elastomeric matrices should be far less than 100%. This corresponds to our observations. However, the exact degree of filling cannot be estimated from our experiments at the scale accessible by optical microscopy.

CONCLUSION

This work shows that elastomers do infiltrate into agglomerates despite their very high viscosity. This result is important because the cohesion of a porous filler is changed by the presence of interstitial fluid and the depth of infiltration determines dispersion mechanisms of the agglomerate.

The infiltration process looks different in elastomeric matrices (not homogeneous penetration of the fluid into the agglomerate), despite the physics behind this process is the same (infiltration driven by capillary forces and resistance linked to the matrix "viscosity"). The apparent difference in behavior between elastomers and low viscosity fluids can be explained by the relative dimensions of the polymer chains towards the pore size.

There exists a latent period before impregnation really takes place. This time is observed for low viscosity and elastomer matrices. This latent period was not previously reported in literature for low viscosity fluids.

Once the infiltration process has started, kinetics data plotted according to the model of Bohin (proposed for Newtonian fluids) give straight lines, as predicted by the model. This is also found for elastomeric matrices, although the process does not happen homogeneously.

From the curve slopes, the ratio $(\gamma_{1v} \cos \theta / \eta)$ can be calculated giving access on the principle to the wetting angle. In the case of elastomeric matrices, cosine values much larger than 1 were found. The use of this model for elastomeric matrices and the assumptions related to the model were discussed. Our opinion is

that, although simple, the model is valid to describe the infiltration process at a macroscopic scale. Infiltration is driven by the capillary force and the viscosity is resisting this process. However, we can question if the bulk viscosity (determined by classical rheometry) is the right parameter to characterize the resisting force in the case of chains infiltrating a nanoscale gap where the driving force is the capillary force. The fact that not all chains may penetrate inside the pore also questions the use of the bulk viscosity. To access the wetting angle, a way to measure the proper viscosity should be found. Vice versa, if the wetting angle is known, infiltration kinetics may give a way to measure the rheological behavior of fluids in complex nanoscale geometries.

It should be noted that even if the experiments do not presently enable us to determine wetting angles, large differences in the impregnation process are found between the three elastomers. Assuming that the viscosity term is not too different, this also gives an indication of the wetting property of the matrix towards the filler and thus its affinity.

A practical question to be addressed is to know whether infiltration can happen during the filler dispersion in an internal mixer because very long total infiltration times are found in elastomers. The effect of additional external parameters, as the presence of pressure or flow, should be considered. Seyvet⁵ showed that pressure accelerates the infiltration kinetics, whereas shear has no effect in the case of Newtonian matrices. It will be interesting to know the effect of these parameters not only on infiltration kinetics but also on the latent period, and also in the case of elastomeric matrices. This will be considered in a forthcoming work.

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