J MATER SCI **41** (2006) 4047–4054

Hydrolytic ageing of syntactic foams for thermal insulation in deep water: degradation mechanisms and water uptake model

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This paper focuses on a novel syntactic foam formulation based on a model diepoxy-diamine matrix with a controlled architecture, discusses the factors governing the long-term performance of these materials and gives a predictive model to assist in the design of efficient and safe insulating systems.

Hygrothermal ageing in deionized water at 20°C, 60°C, 100°C and 120°C over 18 months (with no additional pressure) is followed by both gravimetric and impedance measurements. This original protocol provides the evolution with time of both mass gain and intrinsic material conductivity. Attention is paid to the degradation phenomenon observed after the matrix has reached saturation and the corresponding increase of both mass gain and conductivity. The latter suggests the occurrence of ionic extraction from the microsphere glass undergoing water leaching.

A model of mass gain is proposed to explain the gravimetric data and predict the long-term mass gain that governs the mechanical and thermal performances. The temperature dependence of fitting parameters follows an Arrhenius law and activation energies calculated support the scheme of glass corrosion by water during hygrothermal ageing, with respect to the literature. *© 2006 Springer Science + Business Media, Inc.*

1. Introduction

Syntactic foam materials based on hollow glass microspheres embedded in an organic matrix traditionally find application in marine environment for buoyancy. They are now being used for the thermal insulation of offshore pipelines and bundles which convey oil and gas resources [1–3]. As a matter of fact, syntactic foams can provide substantial heat loss resistance while withstanding external deep-water pressure (30 MPa at 3000 m deep) thanks to their closed-cell micro-structure.

The humid ageing of syntactic foams under hydrostatic pressure, up to 100 MPa, has been widely studied [4–7]. But the combination of high pressure/high temperature conditions (up to 30 MPa/130°C) is a recent concern: a pioneering research program including ageing in hot wet conditions has shown that traditional industrial syntactic foams were undergoing rapid and severe degradation in seawater at temperatures as low as 60°C [8]. There is experimental evidence that a key factor may be the chemical degradation of glass microspheres due to the "entrance"

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0022-2461 © *2006 Springer Science + Business Media, Inc.*
DOI: 10.1007/s10853-006-7618-0

of water [9]. In spite of this, there is only scarce literature focusing on the glass microsphere durability [3]. A new research program has started to study the thermal and mechanical properties of new industrial syntactic materials aged in a wide range of conditions including combined pressure and temperature [10]. However, a more fundamental approach is needed to understand how the hydrolytic ageing of glass microspheres may reduce the durability of syntactic foams used in hot wet conditions.

The syntactic foams are made with a model diepoxy-diamine matrix. The polymerisation kinetics are controlled thanks to the low reactivity of the diamine. Good dispersion of the microspheres is ensured by checking the viscosity when casting the foam. By formulating model syntactic foams with untreated glass microspheres, the influence of the glass hydrolytic ageing can be studied more clearly. This paper focuses on the effect of temperature on model syntactic foam ageing in deionized water, with respect to water sorption and electrical conductivity changes. The electrical conductivity calculated from impedance measured *ex-situ* at room temperature over several months of ageing is used in addition to gravimetry to investigate matrix plasticization and ageing mechanisms, in particular leaching of glass ions. Degradation mechanisms involved in syntactic foam during hot wet ageing are investigated and discussed, supported by experimental data available on pure aged glass microspheres. A simple model is proposed in order to determine the ageing kinetics and to predict the long-term mass gain that affects the mechanical and thermal performances. The ultimate objectives are (i) to improve syntactic foam formulations and design, and (ii) to provide kinetic data that would allow accurate model of thermo-mechanical properties under service conditions [11].

2. Experimental

2.1. Materials

The crosslinked matrix consisted of a mixture of a difunctional epoxy resin (Diglycidyl ether of bisphenol A, DGEBA) and a diamine hardener (4,4′-methylenebis(3-chloro-2,6-diethylaniline), MCDEA) at stoichiometric ratio (amine/epoxy = 1). It leads to a network with high glass transition temperature (Tg of 175°C) after full curing [7, 12, 13]. The filler material used was untreated sodium-borosilicate based glass microspheres of average diameter 34 μm and true density 0.35 $\text{g} \cdot \text{cm}^{-3}$.

2.2. Processing

The monomers were heated to 90°C for 20 min and mixed in a reactor vessel while gently stirring before filler material was added at a volume fraction of 55% (classical filler amount in the application). A mixing time of 20 min in vacuum resulted in a homogeneous mixture, free of bubbles. The liquid mixture was then cast in large moulds ($160 * 100\ \text{mm}^2$) of 2 mm thickness at 150°C for 8 h and post-cured at 200°C for 4 h, followed by a quick cooling to room temperature. For comparison purposes, a pure diepoxy-diamine network was prepared following the same protocol. The density of the pure polymeric material measured by helium pycnometry was 1.20 $\text{g} \cdot \text{cm}^{-3}$. The pycnometric density of syntactic foam materials was very close to the value calculated from a simple mixture law, namely 0.72 $\text{g} \cdot \text{cm}^{-3}$, suggesting there was no significant porosity in the samples. All syntactic foams manufactured were also systematically characterized by thermogravimetric analysis to check the microsphere content and parallelepiped samples of $50 * 50 * 2\ \text{mm}^3$ were cut for both gravimetric and impedance measurements from the core of the plate produced. Extensive morphological control of these laboratory cast glass/epoxy syntactic foams, including 3D X-ray microtomography control, is reported elsewhere [14].

3. Measurements

3.1. Differential scanning calorimetry

A differential scanning calorimeter (DSC Q100 from Waters) was used with hermetic cells (up to 3 MPa) to determine the dry and wet glass transition temperatures (Tg) of the materials (taken at the onset during ramp of $10^\circ\text{C} \cdot \text{min}^{-1}$). Non-hermetic cells allow having a constant pressure where melting and vaporisation temperatures are well-known. They were used in order to evaluate the amount of water inside the samples.

3.2. Gravimetry

Isothermal ageing experiments in deionized water (ionic conductivity $10^{-6}\ \text{ohm}^{-1} \cdot \text{cm}^{-1}$) were carried out over 18 months at temperatures ranging between 20°C and 120°C in hermetic vessels. The water uptake in percentage (%mass gain) was calculated from regular mass gain determined by blotted dry samples with consistent procedure and normalised by the initial mass. With this calculation, the following hypothesis is used: there is no concomitant mass loss from the aged sample.

3.3. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed (with a TG 209 device from Netzsch) on the materials. The experimental conditions for the heating ramp for these measurements were: $10\ \text{K} \cdot \text{min}^{-1}$ from 30°C to 200°C and a plateau of 4 h at 200°C under nitrogen, followed by a ramp at $10\ \text{K} \cdot \text{min}^{-1}$ from 200°C to 700°C under air.

3.4. Impedance spectroscopy

It has long been known that electrical impedance measurements can successfully monitor water diffusion into polymeric membranes or coatings. High frequency capacity curves versus time can reveal the quantitative water uptake thanks to Brasher and Kingsbury's law [15], provided the experimental temperature differs sufficiently from the polymer's glass transition temperature [16]. Indeed, an increase of the polymer's permittivity of several orders of magnitude, associated with the cooperative backbone mobility, is typically related to glass transition. This capacity change overwhelms the signal's increase associated to water uptake, if phenomena occur in the same temperature range.

In addition, the electrical resistance of polymeric membranes or coatings is known to decrease with the introduction of water. Indeed, ionic impurities appear in the polymer during the synthesis of the prepolymers [17] and their mobility is related to the polymer's chain mobility. In the glassy state in particular, there is only local mobility within diepoxy-diamine networks; therefore ion transfer through polymeric coatings and membranes is limited. But matrix plasticization due to water uptake favours chain mobility and induces a lowering of the glass transition temperature. Thus, some enhanced mobility related to water diffusion is expected for internal ionic species as well. Changing the water activity is necessary to determine whether the resistance measured reflects the bulk polymer's internal resistance or directly follows the solution resistance due to some porosity effect [18]. Indeed, when the polymer resistance decreases with diffusing water, irrespective of solution activity, conduction must involve internal ionic species.

Impedance measurements were performed at 0.1 V between 10^5 Hz and 0.1 Hz using a Solartron 1260 FRA device equipped with a Solartron 1296 impedance interface. *Ex-situ* impedance measurements at 20°C were systematically conducted on the same specimens as those used in gravimetry measurements using a parallel-plate set-up with 2 electrodes (3 measures for each control). Ionic conductivity was calculated from impedance data and sample geometry. Attention was paid to apply a low potential value thus avoiding any disturbance that could provoke interfacial polarisation or surface conduction effect [19]. Moreover, water desorption during impedance measurement (20 min in a sandwich device) was checked and found to be negligible.

4. Results and discussion

4.1. Humid ageing for a pure diepoxy-diamine network

Firstly, dry Tg of the polymer was ~170°C suggesting that the network had reached maximum cure extent [12–13]. The wet Tg value for the polymer dropped to almost 135°C when aged at 100°C in deionized water (1.8% mass gain) which corresponds with a drop of Tg of 20°C for each 1% mass gain [20].

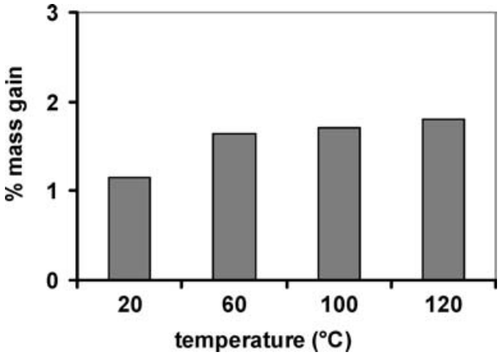

Figure 1 Mass gain at 20°C of pure DGEBA-MCDEA network after 150 days ageing in deionized water at 20°C, 60°C, 100°C and 120°C.

Secondly, the short-term behaviour in water of the pure diepoxy-diamine network under consideration as revealed by gravimetric experiments was not the main issue of this paper. Previous experiments [20] showed that water diffusion follows the Fick's law independent of temperature, as expected for the diepoxy-diamine network [21]. The long-term mass gain values for a pure diepoxy-diamine network after 150 days of immersion in deionized water at 20°C, 60°C, 100°C and 120°C are presented in Fig. 1.

The reversibility of mass gain was checked by drying the samples until mass reached an equilibrium. Thus, it can be said that the pure diepoxy-diamine network under consideration admitted a low water content at equilibrium in the saturated state (<2 wt.%) and exhibited long-term stability.

Fig. 2 illustrates the ionic conductivity at 20°C calculated from *ex-situ* impedance measurements for a pure diepoxy-diamine network before and after 150 days of immersion in deionized water at 20°C, 60°C, 100°C and 120°C.

A weak conductivity increase (around 2 decades) was observed at all temperatures tested. This effect could not be related to the ingress of external ionic species since ageing experiments were conducted in deionized water. Thus, it revealed the increase of the internal ionic mobility

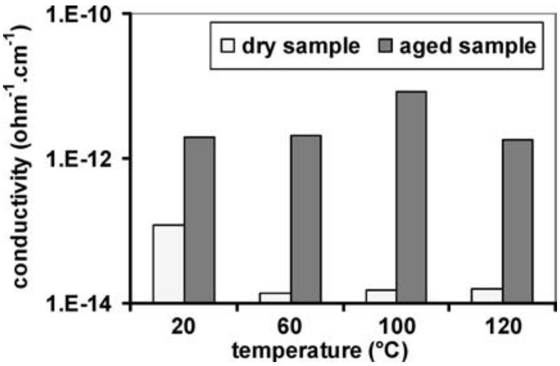

Figure 2 Conductivity at 20°C of pure DGEBA-MCDEA network before and after 150 days ageing in deionized water at 20°C, 60°C, 100°C and 120°C.

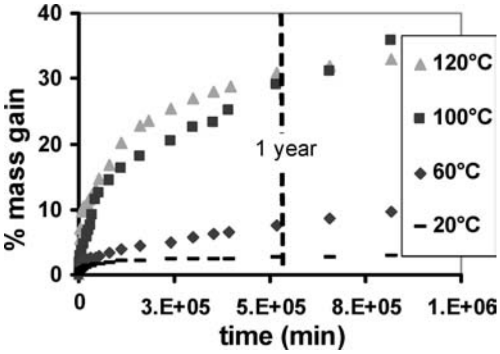

Figure 3 Mass gain at 20°C versus time for 55 vol.%. syntactic foams aged in deionized water at 20°C, 60°C, 100°C and 120°C.

in the diepoxy-diamine network as a consequence of the polymer's plasticization (enhancement of chain mobility) due to water absorption. The ionic mobility of the polymer stems from the ionic impurities appearing during the synthesis of the prepolymers [17].

4.2. Humid ageing for syntactic foams

The dry Tg of syntactic foams reaches the same value as the polymer (fully cured network).

Values of wet Tg of syntactic foams are not available because water inside the microspheres causes a wide endothermic transition coming from the vaporization of this "not linked" water. This peak hides the glass transition of the matrix.

Fig. 3 represents the mass gain for a 55 vol.% filled syntactic foam as a function of immersion time in deionized water at 20°C, 60°C, 100°C and 120°C over 18 months.

The mass gain curves related to hot wet ageing conditions increased steadily with time and did not present a plateau as expected through the classical Fick's law. Only the 20°C curve presented a Fickian behaviour over the ageing time similar to a pure diepoxy-diamine network. The water content at the plateau (∼2 wt.%) remained close to the saturated polymer water content (1.3 wt.% corrected by the real amount of matrix), suggesting that long-term aged syntactic foams at 20°C mainly exhibited a saturated matrix. Besides, it is well known that water diffusion in the matrix is thermally activated, which could account for the different initial slopes that can be observed with increasing temperature when mass gain remains below 2–3 wt.%. But other mechanisms must be identified to explain the steady mass gain occurring in hot wet ageing conditions. Since the volume expansion of one year aged syntactic samples was quite similar at any ageing temperature and remained below 5%, it seemed obvious that water did not only hydrate the polymeric matrix but possibly hydrated the interfaces, the glass material and filled in microsphere interiors as well [9].

The ionic conductivity at 20°C calculated from *ex-situ* impedance measurements during immersion in deionized water at 20°C, 60°C, 100°C and 120°C is represented as a function of time in Fig. 4.

The syntactic material aged at 20°C exhibited a weak increase in conductivity (one decade) during the initial water diffusion, then remained almost constant over the ageing time corresponding to the Fickian plateau. Therefore, the matrix saturation was shown to be the predominant governing factor of water diffusion into syntactic foams aged in deionized water at low temperature, in agreement with gravimetric results. The consideration of hot wet ageing curves, namely 100°C and 120°C, highlighted markedly different behaviour, with a significant increase in conductivity of almost 7 decades over the ageing time. The conductivity measured during ageing at intermediate temperature (60°C) also tended to substantially increase but after a longer time. Since there is no ionic ingress from external deionized water, the internal conductivity increase was attributed to the extraction of alcalinous species from the glass used for the microspheres [22–25].

The representation of the conductivity as a function of the mass gain, as illustrated in Fig. 5, is shown for a better understanding of possible water uptake mechanisms.

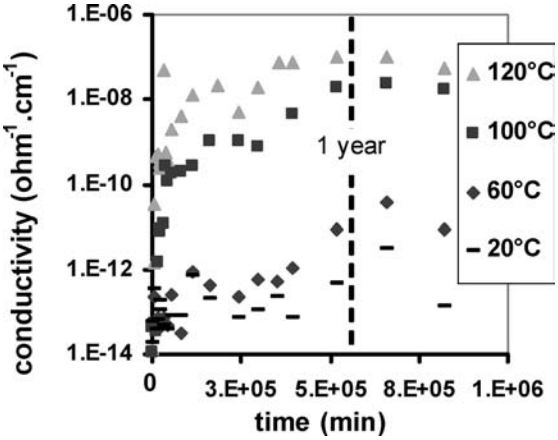

Figure 4 Conductivity at 20°C versus time for 55 vol.% syntactic foams aged in deionized water at 20°C, 60°C, 100°C and 120°C.

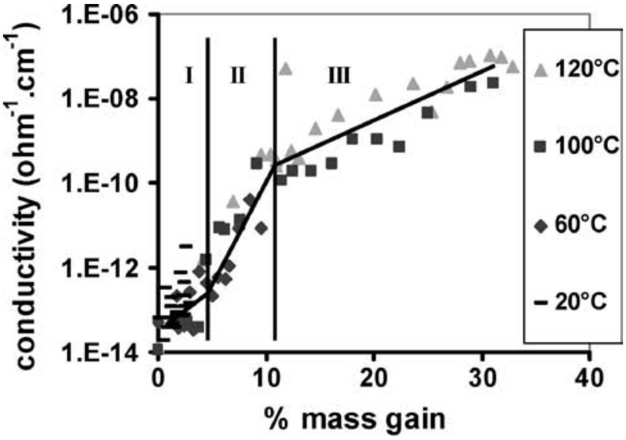

Figure 5 Conductivity at 20°C versus mass gain at 20°C for 55 vol.% syntactic foams aged in deionized water at 20°C, 60°C, 100°C and 120°C.

A remarkable feature was that all curves tended to follow a unique master curve, independent of the ageing temperature, suggesting that mechanisms governing the mass gain of syntactic foams during ageing in deionized water are under kinetic control. This means that such degradation phenomena could occur in immersed syntactic foams at any ageing temperature, but their effective occurrence is a matter of time. Three regions could be distinguished from the master curve drawn with the experimental data in Fig. 5, suggesting predominant mechanisms governing the water uptake of syntactic materials:

(I) polymeric matrix plasticization, as the initial stage,
(II) interface and glass hydration (hydrogen bonding to silanol and to ionic species, extraction of alcalinous ions, hydration of extracted ions . . .) as the intermediate stage,
(III) filling of hollow microspheres (failure of glass shell or permeation) with stabilisation of the conductivity because ions are no longer extracted, as the final stage.

These possible mechanisms can overlap and are proposed to explain why such a great amount of water is driven into immersed syntactic foams (for instance, 30 wt.% after one year at 100°C, see Fig. 3). For example, if glass has previously undergone mechanical damage, due to hydrostatic pressure, the filling of microsphere may superpose with other water uptake factors. Moreover, the way water molecules enter the microspheres remains unclear (failure of glass shell, permeation, etc.). Under service conditions, microsphere breakage could occur due to overloaded hydrostatic pressure, or possible stress concentration phenomena related to local heterogeneity. Differential swelling between matrix and fillers when water diffuses and temperature increases may also induce stress concentration on glass microspheres. Last but not least, the osmotic pressure (Π) in the interfaces between matrix and microspheres is expected during glass leaching, according to Equation 1 [26]:

$$\Pi = \frac{RT}{V_m} \ln \frac{a}{a_i} \tag{1}$$

where V_m is the molar volume of water, a_i is the water activity at the interface and a is the water activity of the external solution. Some authors [27] pointed out that increase of the water activity a causes an increase in the osmotic pressure and therefore an increase in the interfacial gap, which leads to an increase in the reservoir for more incoming water. An additional effect should be taken into account: when glass leaching occurs, the activity of the interfacial water steadily decreases. This induces an increase of osmotic pressure which can quite rapidly reach the maximum pressure resistance of microspheres. Note that glass hydrolytic ageing could be a direct factor for microsphere breakage due to the mechanical weakening of the glass shell, but also an indirect factor as a promoter for increasing osmotic pressure in the matrix-microsphere interfaces.

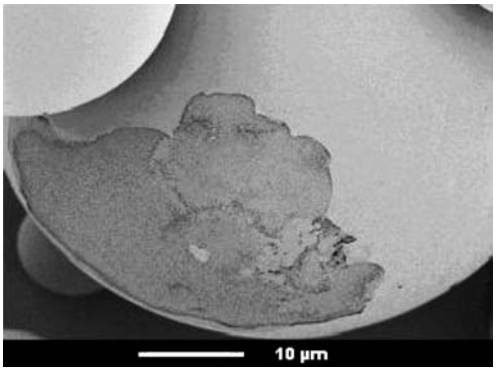

Figure 6 Scanning electron microscopy (SEM) of a microsphere aged in deionized water at 120°C over two months (after 2 h superficial drying at 60°C) with apparent local degradation of the glass surface.

4.3. Humid ageing for microspheres

To assess previous interpretations, additional ageing experiments were conducted on microspheres immersed for 2 months in deionized water at 120°C. Aged microspheres were superficially dried for two hours at 60°C prior to characterisation by thermogravimetric analysis and differential scanning calorimetry in order to be properly handled and weighed.

The TGA curve revealed that aged microspheres could lose up to 60 wt.% on the initial heating ramp. This value was probably underestimated because of the superficial drying previously performed at 60°C. However, this experiment confirmed the particularly high sensitivity of microsphere glass to water, supporting the mechanism of glass hydration as a major driving factor for water entrance into syntactic foams.

Scanning electron microscopy (SEM) was also used to complete the analysis of glass microspheres after hot wet ageing (and superficial drying). As shown in Fig. 6, part of the microspheres exhibited apparent local degradation features on the glass surface, that are likely to be the signature of glass degradation initiated by leaching.

In addition, DSC was performed on aged microspheres including a cooling step down to −80°C prior to heating up to 550°C (Fig. 7), in non-hermetic pans.

This scan revealed two exothermal peaks at 0°C and −40°C attributed to water crystallisation (the latter being shifted toward negative temperatures due to capillary effect in the smallest glass spheres [28]), one endothermal peak at 0°C related to the melting of ice, and two endothermic peaks with a maximum around 100°C and 270°C related to water vaporisation. As observed previously in the literature [29], the peak at 100°C corresponds

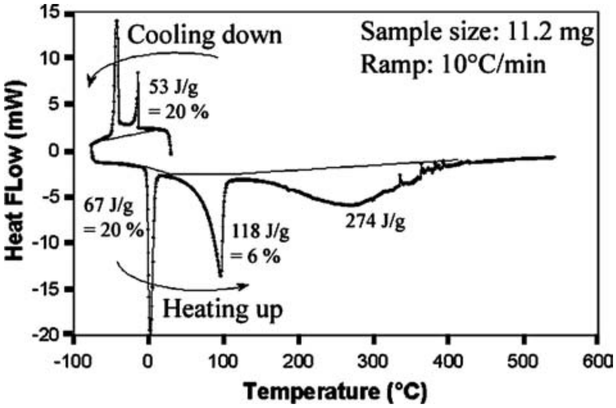

Figure 7 Differential scanning calorimetry (DSC) scan of microspheres aged in deionized water at 120°C over two months (after 2 h superficial drying at 60°C).

to water superficially sorbed on the glass surface and easily desorbed, referred to as "free water", while the one at 270°C is related to water linked to glass by hydrogen bonding on silanol or cation hydration, referred to as "linked water". The amounts of water undergoing crystallisation, melting and vaporisation (at 100°C) were calculated from the experimental enthalpic values (integration under peaks) and the enthalpy values for pure water reported in the literature. Note that these three peaks are a sign of "free water". The water content calculated from both crystallisation and melting peaks reached 20 wt.% of the aged microspheres under consideration while the amount of water undergoing vaporisation at 100°C was only 6 wt.%. One possible explanation is that most of the "free water" was accumulated in the interior of aged microspheres where it froze and melted but it did not diffuse rapidly enough through the glass nor vaporise within the cavity upon heating. Moreover the vaporisation peak of "linked" water at 270°C could also partly result from the late diffusion of water trapped in microspheres or from its vaporisation once the internal pressure inside the spheres became high enough to break the glass shell. As a conclusion, the existence of different kinds of water linkage with glass material has been clearly demonstrated during microsphere ageing, including tight linkage (chemisorption) that may modify the mechanical resistance of glass spheres towards pressure. Further work is in progress in order to better understand this behaviour in comparison with aged foams.

4.4. Model of the anomalous behavior of syntactic foam water uptake

The model of water uptake in syntactic foams is a key issue since the entrance of water directly affects their thermal and mechanical properties, reducing their performances as thermal insulating material in deep water. In this work, the objective was to propose and validate a simple model of water uptake versus time focused on the hydrolytic degradation of syntactic foams, beyond Fickian diffusion already widely studied [9, 30]. Therefore, the water content related to the matrix was considered constant throughout the ageing experiment and equal to matrix saturation, explaining the initial water content in the model (1.3 wt.% for a 55 vol.% syntactic foam).

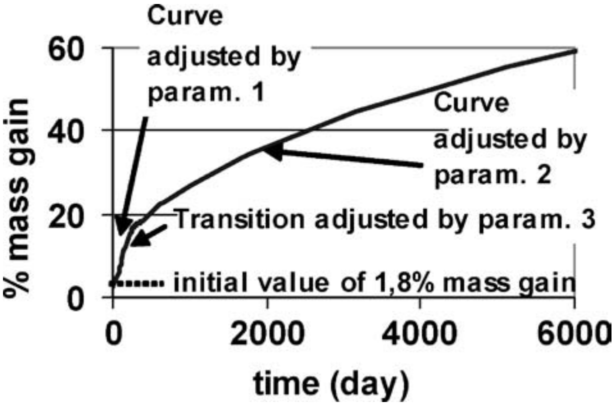

Figure 8 Typical curve shape of the mass gain versus time obtained from IFP model for syntactic foams.

4.4.1. Basis of the model

The model, called IFP model after Institut Français du Pétrole in the following paragraphs, is based on analytic calculations taking into account the granulometry of the microspheres, the glass thickness, as well as the volume fraction of spheres. Water diffusion in the glass and water filling of the internal cavities in the microspheres are clearly separated in the IFP model which may be an approximation of what happens in reality.

Three adjustable parameters were integrated into the model in order to obtain a fit-for-purpose curve (Fig. 8) and to reflect the mechanisms discussed previously:

- "parameter 1" fits the first part of the mass gain, related to the hydration of microspheres' glass,
- "parameter 2" fits the second part of the mass gain, related to the internal sphere filling issued from water permeating through the glass of the microspheres,
- "parameter 3" adjusts the water content in the glass at the transition between both water uptake regimes given above. It reflects the hydrophilic nature of the glass before water enters the internal cavities of the microspheres and it is linked to the type of microspheres used, whatever their volume fraction is.

4.4.2. Validity of the model

Validation of the model was performed by using syntactic foams with volume fractions of 30% and 45% in comparison to 55% (Fig. 9).

The IFP model fits all experimental curves obtained at the temperature of 100°C in deionized water with the same values for the 3 parameters.

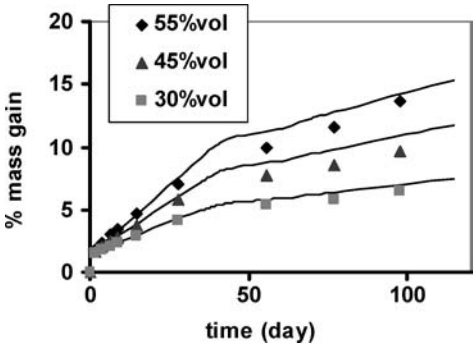

Figure 9 Comparison of IFP model (black line) and experimental data for model syntactic foams containing 30 vol.%, 45 vol.% and 55 vol.% of microspheres, aged in deionized water at 100°C.

4.4.3. Temperature dependence

The fitting of the experimental gravimetric data available for different temperatures (discussed previously) was done as a function of the ageing time and results are presented in Fig. 10.

Note that parameter 3 had a constant value independent of temperature, as expected, because the microspheres used are similar. The comparison between experimental data and model showed very good agreement at 20°C, 60°C and 100°C during the entire ageing period. However, divergences were observed after 200 days ageing at 120°C. Thermogravimetric analysis were performed on the sample aged at 120°C for 460 and 560 days and revealed a mass gain of 30 wt.% and 40 wt.%, respectively, with a substantial general mass loss recalculated from the glass fraction of the samples. The corresponding true mass gain was, 40 wt.% and 49 wt.%, respectively, underlining that the long-term mass gain given by gravimetry was underestimated at 120°C due to significant mass loss upon ageing. In addition, the model proposed could fit experimental data very well on the basis of the true mass gain values at 120°C given by TGA (Fig. 10). Therefore, the IFP model is expected to show good predictive agreement.

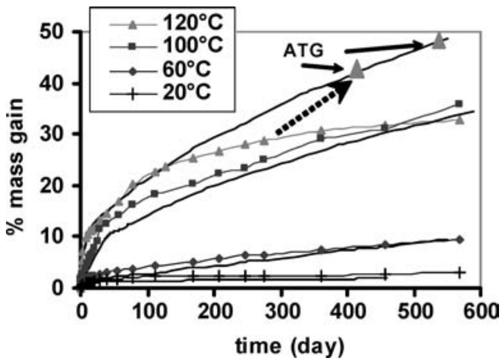

Figure 10 Comparison of IFP model (black line) and experimental data for 55 vol.% syntactic foams aged in deionized water at 20°C, 60°C, 100°C and 120°C.

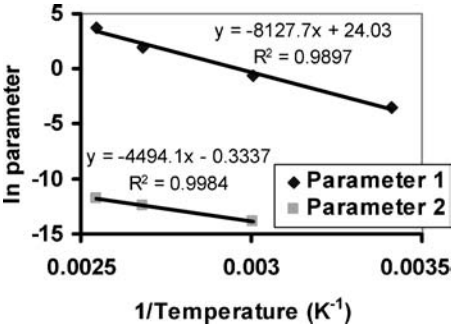

Figure 11 Temperature dependence of the adjustable parameters "parameter 1" and "parameter 2" of the IFP model obtained for syntactic foams aged in deionized water at 20°C, 60°C, 100°C and 120°C.

The temperature dependence of the model parameters referred to as "parameter 1" and "parameter 2" was studied. Both were expected to follow a classical Arrhenius law since they are related to diffusional mechanisms. The representation of their logarithms as a function of reciprocal temperature (1/Temperature), given in Fig. 11, confirmed this point.

Note that parameter 2 could not be evaluated at 20°C because the sample had not yet reached the filling of hollow spheres. The activation energies related to both diffusional regimes were calculated from the slopes. The value of 68 $\mathrm{kJ \cdot mol^{-1}}$ related to the glass hydration stage was close to values reported in the literature for hydrolytic ageing of glass, around 75 $\mathrm{kJ \cdot mol^{-1}}$ [24–25]. This again supports the proposed mechanisms, where the glass hydration is a governing factor for the syntactic foam water uptake. An activation energy of 37 $\mathrm{kJ \cdot mol^{-1}}$ was calculated for the water uptake related to sphere filling. This latter value is almost comparable to the activation energy of water diffusion inside the diepoxy-diamine matrix, approximately 40 $\mathrm{kJ \cdot mol^{-1}}$ [21], suggesting that the filling stage could be limited by the water diffusion through the matrix. Additional work is in progress to gain a better understanding of this point.

5. Conclusions

The diepoxy-diamine formulation used as matrix presents a low water content in hot wet ageing conditions. Its controlled architecture and well-known curing kinetics are helpful to formulated a model of epoxy/glass syntactic foams for studying purposes.

Impedance spectroscopy using a two electrode set-up is an innovative technique for studying hydrolytic ageing of epoxy/glass syntactic foam. Evidence of glass leaching was found using *ex-situ* measurements at room temperature on aged samples. The conductivity increase presented an interesting dependence on mass gain, building a master curve involving three main regions. Possible mechanisms accounting for the water uptake of syntactic foams during hydrolytic ageing were identified and discussed, and supported by experimental data obtained by ageing of glass microspheres.

Water uptake was modelled upon previous assumptions and exhibited good agreement with gravimetric experimental data. The model was validated by comparison of experiments with different volume fractions of microspheres. Good predictive agreement was obtained. Further work is in progress to take into account the diffusion inside the matrix as well as the effect of pressure on the mass gain of syntactic foams.

Acknowledgements

The authors would like to thank the Institut Français du Pétrole and the Association Nationale de la Recherche Technique for financial support. The contributions of S. Schweitzer and J. Grenier are gratefully acknowledged.

References

1. J. F. FRANKLIN and A. WRIGHT, in Proceedings of the 13th International Conference on Pipeline Protection, edited by BHR Group Limited, (Edinburgh, UK, September 1999).
2. L. WATKINS and E. HERSHEY, *World Pipelines* **4** (2004) 49.
3. B. VAN BELLE, in "Offshore Technology Conference", Houston, Texas (USA) May 2002.
4. A. AVENA, Ph.D. Thesis, Ecole Nationale Supérieure des Mines de Paris, 1987.
5. G. FONBLANC, Ph.D. Thesis, Université Bordeaux I, 1986.
6. L. WATKINS, in 7th International Conference on Offshore Mechanics and Arctic Engineering, Houston, Texas (USA) 1988.
7. T. FINE, H. SAUTEREAU and V. SAUVANT-MOYNOT, *J. Mat. Sci.* **38** (2003) 2709.
8. D. CHOQUEUSE, A.CHOMARD and C. BUCHERIE, in Offshore Technology Conference, Houston, Texas (USA) May 2002.
9. V. A. KOCHETKOV and R. D. MAKSIMOV, *Mechanics* **32** (1996) 61.
10. D. CHOQUEUSE, A. CHOMARD and P. CHAUCHOT, in *Offshore Technology Conference*, Houston, Texas (USA) May 2004.
11. A. BRINI, F. PRADEL, A. BENHAMIDA and H. DUMONTET, in ICCM-14, (San Diego, California (USA), July 2003).
12. A. BONNET, J. P. PASCAULT, H. SAUTEREAU, M. TAHA and Y. CAMBERLIN, *Macromolecules* **32** (1999) 8517.
13. E. GIRARD-REYDET, C. C. RICCARDI, H. SAUTEREAU and J. P. PASCAULT, *Macromolecules* **28** (1995) 7599.
14. E. MAIRE, N. GIMENEZ, V. SAUVANT-MOYNOT and H. SAUTEREAU, "Phil. Trans. of the Royal Society of London" (London, UK, November 2004), published under doi 10.1098/rsa.2005.1691.
15. D. M. BRASHER and A. H. KINGSBURY, *J. Appl. Chem.* **4** (1954) 62.
16. S. DUVAL, M. KEDDAM, F. ROPITAL, V. SAUVANT and H. TAKENOUTI, in Eurocorr 2001 (Riva Del Garda, Italy, October 2001).
17. B. ELLIS, in "Chemistry and Technology of Epoxy Resins" (Chapman & Hall, 1993).
18. S. DUVAL, M. KEDDAM, F. ROPITAL, V. SAUVANT-MOYNOT and H. TAKENOUTI, in Eurocorr 2003 (Budapest, Hungary, October 2003).
19. H. OCHS, J. VOGELSANG and G. MEYER, *Progr. Org. Coat.* **46** (2003) 182.
20. V. SAUVANT-MOYNOT, S. SCHWEITZER, J. GRENIER and S. DUVAL, in Eurocorr 2004 (Nice, France, September 2004).
21. J. P. PASCAULT, H. SAUTEREAU, J. VERDU and R. J. J. WILLIAMS, in "Thermosetting Polymers" (Marcel Dekker Inc., New York, 2002).
22. R. J. CHARLES, *J. Appl. Phys.* **29** (1958) 1549.
23. A. PAUL, in "Chemistry of Glasses" (Chapman & Hall, 1990), p. 179.
24. B. C. BUNKER, *J. Non-Cryst. Solids* **179** (1994) 300.
25. G. I. COOPER and G. A. COX, *Applied Geochemistry* **11** (1996) 511.
26. K. KAMIDE, in "Thermodynamics of Polymer Solutions—Phase Equilibria and Critical Phenomena" (Elsevier, Amstedam, 1990), p. 651.
27. A. LEKATOU, S. E. FAIDI, D. GHIDAOUI, S. B. LYON and R. C. NEWMAN, *Composites* **28A** (1997) 223.
28. K. SAKAI, *J. Membrane Sci.* **96** (1994) 91.
29. R. BATTISTELLA, *Ph.D. Thesis, Ecole de Mulhouse* (1971).
30. D. LUO, J. FRANKLIN and A. WRIGHT, in "Proceedings of the 14th International Conference on Pipeline Protection, edited by BHR Group Limited", (Edinburgh, UK, October 2001).