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Acoustic emission analyses of the hygrothermal ageing of glass syntactic foams

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Abstract

In deepwater offshore production, thermal insulation of pipelines and risers is now commonly made with glass syntactic foams. These composite materials offer both good insulation properties and pressure resistance, and also provide buoyancy to the systems. But service conditions are increasingly severe, including pressure (up to 30 MPa at 3000 m water depth), water environment and temperature (up to 130°C in contact with the steel tube). These coupled loadings induce complex effects on the material and make the prediction of its long-term behaviour difficult. Over the past 10 years, many studies have been performed to better understand the behaviour of the glass syntactic foams used as thermal insulation of pipes for deepwater production. Ageing tests in hot water revealed some specific behaviour of these materials with coupled chemical and mechanical phenomena of degradation. The experimental techniques included gravimetry, mechanical and physicochemical characterisations, impedance spectroscopy, X-ray tomography. As the rupture of glass microballoons is relatively emissive, acoustic emission technique has also been used. The contribution of this latter technique to the understanding of the syntactic foam behaviour is presented in this paper. Some ageing tests in water at several temperatures and on several syntactic foams have been conducted. Mechanical characterisation has been performed using a confined compression set-up instrumented with an acoustic emission sensor to allow the monitoring of glass microballoons degradation vs. time and temperature of ageing. These results are analysed for syntactic foam materials having various compositions. The comparison to the information given by other techniques is also discussed.

Keywords: ageing; glass; insulation; syntactic foam.

1. Introduction

Increasing demand for oil and recent discoveries of huge reserves in deep water (Girasol and Dalia offshore Africa, Tupi and Carioca offshore Brazil) sustain the development of offshore deepwater fields. Over $80/barrel, all the kinds of oil can be economically produced, even the shale oil [1]. For these reasons, the ultra deep water (3000 m water depth) is becoming one of the next main issues.

The production of oil in ultra deep water faces lots of challenges. Among others is flow assurance which requires the use of thermally managed systems [2]. Due to multiphase flow in flowlines and risers, and consequently possible wax and hydrates formation, thermal insulation of subsea pipelines becomes increasingly important. This thermal insulation is used to maintain fluid temperature from subsea completion to floating platforms above a given temperature around 40°C to facilitate the flow.

Among the different thermal insulation systems, multilayer insulation systems are widely used. For shallow water, systems are made with raw materials (elastomer, polymer) or with polymeric foams. But increasing depths need improved systems which withstand higher hydrostatic pressure while keeping good thermal insulation properties.

Glass microballoons reinforced syntactic foams, initially used for buoyancy, are materials combining high pressure resistance and good thermal properties. For these reasons, they became widely used for thermal insulation of offshore oil pipes. These materials are nevertheless subjected to severe ageing conditions during service life: high pressure, contact with liquid water, thermal gradient between hot steel pipe surface (up to 130°C) and cold sea water (around 4°C).

Over the past 10 years, numerous studies were performed to better understand and discuss degradation mechanisms of syntactic foams due to combined effects of pressure, temperature gradient, and water ingress [3, 4]. Some of them revealed particular behaviours, for instance specific influence of the polymer nature, drastic evolution of properties during thermo-hydrolytic ageing tests, detrimental effect of combined solicitations including pressure, temperature and water [5].

Analyses of degradation phenomena has been performed using different techniques including weight gain during ageing [6], thermogravimetry, dielectrometry [7], X-ray tomography [8]. This last technique pointed out interesting features concerning the degradation of glass microballoons and the distribution of broken elements during loading. But this technique is very difficult to operate and analyzes only very small samples to get sufficient scan resolution.

As the break of glass microballoons releases elastic energy and then elastic waves, these events can be recorded by an acoustic emission analyser. This technique, classically used on composites reinforced by fibers, has been also used to study syntactic foam [9, 10] thanks to its ability to continuously monitor the mechanical degradation of the foams.

This paper presents new data obtained during ageing of different glass microballoons reinforced syntactic foams.

These materials have been aged in water at different temperature and their mechanical properties have been determined using a confined compression set-up. Acoustic emission has been recorded during these mechanical tests and evolution is related to hygrothermal degradation phenomena.

2. Experimental

2.1. Materials

All the tested materials have the same matrix consisting in a mixture of a difunctional epoxy resin (diglycidyl ether of bisphenol A – DGEBA, Hunstman Advanced Materials, Everberg, Belgium) and a diamine hardener (4,4′-methylenebis(3-chloro-2,5-diethylaninile – MCDEA, Lonza, Basel, Switzerland) at stochiometric ratio (amine/epoxyde=1).

This matrix chosen for its low water uptake (around 1.5 wt% at saturation) is filled with three different types of commercial sodium-borosilicate hollow glass microballoons (GM): one with particle density of 0.38 g/cm^3 (55% and 30% volume fractions), another with particle density of 0.60 g/cm^3 (55% volume fraction) and the last with also particle density of 0.60 g/cm^3 (55% volume fraction) but this microsphere batch underwent an additional sort to eliminate the biggest and the smallest balloons and get then a higher mechanical resistance (this batch was differentiated by the suffix HS for higher strength).

The monomers were mixed at 100°C before addition of microballoons. After degassing, the liquid mixture was cast in a mould and cured in oven at a maximum temperature of 200°C. Cure steps were progressive to prevent microballoons segregation from resin [11].

The true volume fraction of glass microballoons and homogeneity were controlled by thermogravimetry analyses (ramp at 10°C/min up to 650°C). The list of syntactic foam materials is given in Table 1.

2.2. Experiments

2.2.1. Compression test The compression solicitation has been applied using a confined compression set-up (Figure 1). The load was increased up to 25 MPa at a strain rate of 5.10^{-3} mm/min. The tests were performed at room temperature.

The samples were machined in cylindrical form with diameter of 10 mm and height of 10 mm (Figure 1).

2.2.2. Ageing Isothermal ageing in deionised water was performed over 3 months in closed and nitrogen inerted vessels at 60°C and 100°C. The mass gain was calculated from regular weight control on five samples normalised by the initial mass (ASTM D570) (each value is the mean of these five measurements).

Some samples were removed from vessels after 15 days, 1, 2 and 3 months for mechanical characterisation.

2.2.3. Acoustic emission A two-channel PCI-2 Aewin system from Euro Physical Acoustic (Sucy-en-Brie, France) was used. One resonant micro80 PAC sensor was fixed with elastic band onto the metallic chamber as on Figure 1. Silicon grease was used between the metallic surface and the sensor.

Table 1 Denomination and composition of materials under study.

Reference	Microballoons density (g/cm^3)	Volume fraction (%)
MS1	0.60	55.9±2.3
MS2	0.60 (HS)	55.7±1.9
MS3	0.38	55.4±0.2
MS4	0.38	30.2±0.4

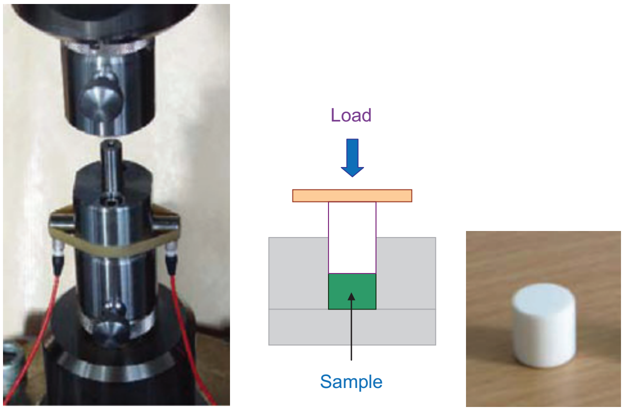

Figure 1 Confined compression set-up and sample.

3. Results and discussion

3.1. Influence of microballoon type

All the materials have been aged in deionised water over 3 months at 60°C and 100°C under 0.1 MPa. The gravimetry curves present the mass gain vs. the square root of time. In this representation, a Fickian behaviour which means a diffusion and absorption of water until a saturation level without any other side effect would give a linear increase of mass gain at short times and a plateau at long time.

The results obtained on the materials with 55% GM volume fraction at 60°C and 100°C are represented on Figure 2.

There is quite no difference between the three materials at 60°C. Water uptake remains below 5% in weight within experimental time but is not stabilised whereas water saturation of the resin is expected within only around 100 days at 60°C [12].

In accordance with thermal activation, the mass gain at 100°C is higher than at 60°C. At 100°C, there is never stabilisation of the weight. This continuous increase of weight was explained [4, 11] by different phenomena occurring simultaneously: diffusion of water in the matrix (saturation expected within < 10 days) and at the interfaces, hydratation of glass, filling of voids created by microsphere breakage.

The material MS1 presents the higher mass gain at 100°C. This result is surprising because the microballoons are

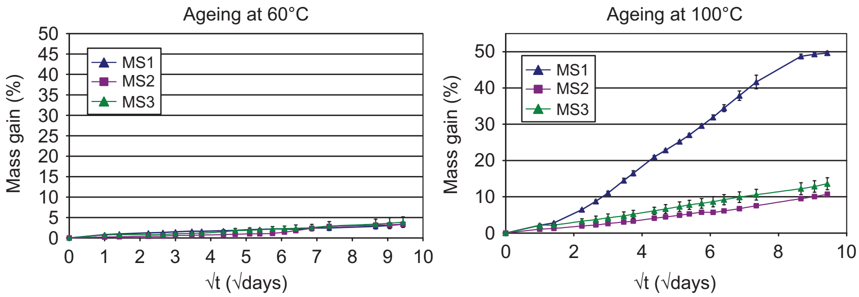

Figure 2 Gravimetry of syntactic foam with 55% volume fraction GM during ageing.

supposed to be the same than for MS2, except than the smallest and the biggest ones have been sorted for MS2. It might be a default in the batch of MS1 microballoons which induced a worse behaviour. The advantage was that this material was almost totally degraded (maximum mass gain obtained approaching theoretical saturated mass gain) during the duration of the study.

The confined compression curves of unaged materials are presented in Figure 3.

After a first increase of load, one can observe that there is more or less a plateau which corresponds to the rupture of the microballoons. When all the balloons are broken, there is compaction of the material and the load increases rapidly.

From this comparison, there is quite no difference between MS1 and MS2, the two foams with the high density GM. There is just a smaller deformation at 25kN for MS2, which can be related to the absence of the biggest GM in this material's batch.

The foam filled with 55% GM of density 0.38 g/cm^3 (MS3) presents a plateau at a lower load than MS1 and MS2. It is related to the mechanical resistance of the microsphere. The density is linked to the void volume inside the microballoons. It is worth noting that, as the outside diameters are almost the same (30 µm for GM of density 0.6 g/cm^3 and 40 µm for GM of density 0.38 g/cm^3 – manufacturer data), a smaller density means microballoons with bigger empty cavity, thinner glass thickness and then a smaller mechanical resistance controlled by the thickness diameter ratio. There is obviously a compromise between the mechanical resistance of the foam and the thermal insulation capacity, the strongest GM offering a poor insulation effect.

Ageing in hot water modified the mechanical resistance of foams. MS2 and MS3 show quite the same evolution (Figures 4 and 5). Ageing has induced more or less a decrease of the plateau and an increase of strain at 25 kN. The decrease of the plateau can be explained by the swelling of matrix induced by absorption of water. Indeed, GM acted as blockers which prevented the expansion of resin due to swelling. This caused a compressive load onto GM walls which was added to the mechanical compressive stress.

The stronger decrease of the plateau for MS3 after 3 months ageing at 100°C can be explained by the hydrolytic degradation of the glass walls. The GM of this foam have a lower density than MS2 ones, and then thinner microballoon walls. This hydrolytic degradation causes a decrease of the resistance of the microballoons [4] and then a decrease of the capability of the foam to resist to compressive load. As MS2 microballoons have thicker walls, the mechanical properties are less sensitive

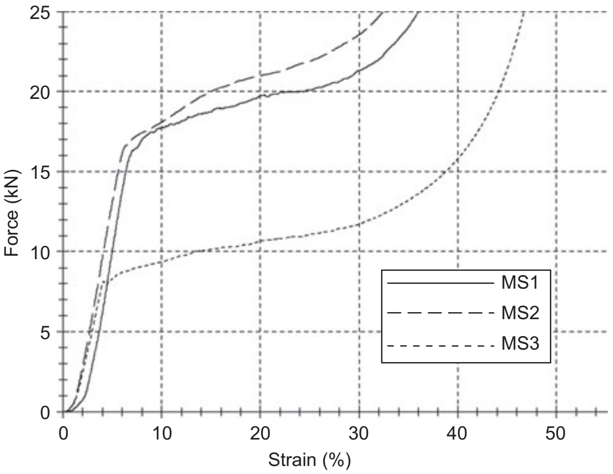

Figure 3 Compression curves of unaged syntactic foams with 55% volume fraction GM.

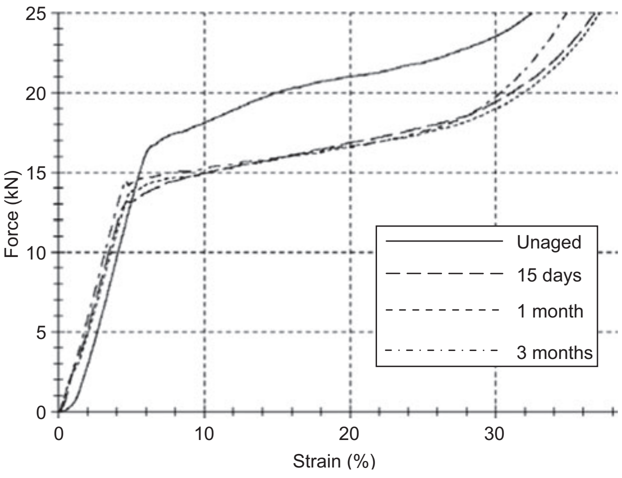

Figure 4 Compression curves of MS2 aged at 100°C.

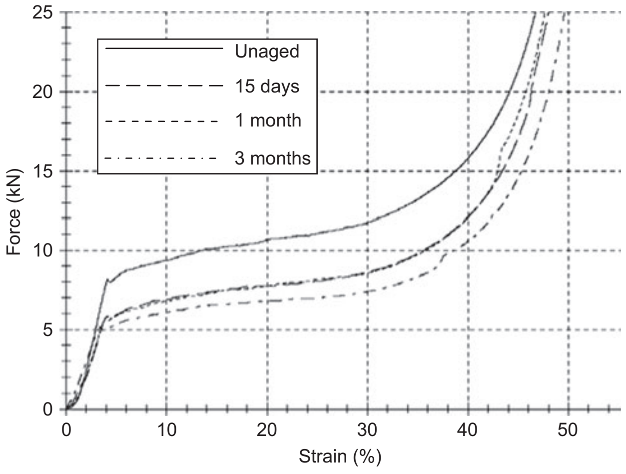

Figure 5 Compression curves of MS3 aged at 100°C.

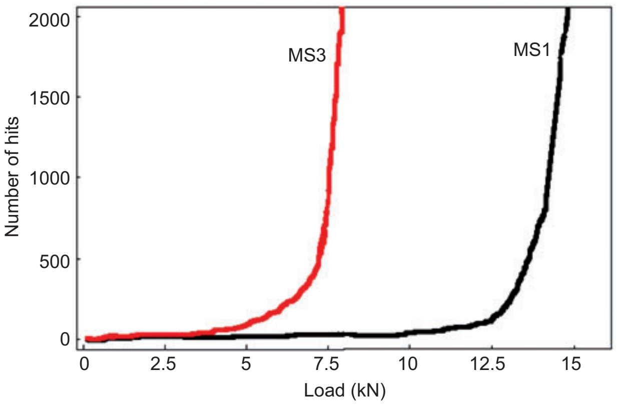

Figure 7 Acoustic emission activity of MS1 and MS3 [number of hits vs. load (kN/10)].

to glass hydrolysis within the experiment duration but a longer ageing time would probably have the same effect.

The compression curves obtained after ageing of MS1 foam give another indication of the hygrothermal degradation of syntactic foam materials (Figure 6). After 15 days, one can observe the plateau decrease related to the swelling of the matrix and also to ongoing hydrolytic ageing of GM. One month ageing has caused a further decrease of the plateau which can be explained by more hydrolysis of glass walls. In addition, there is a decrease of the slope in the first part of the curve which can be related to the hydrated glass exhibiting degraded mechanical properties. Considering the strain at 25 kN load, a substantial decrease appears after 3 months ageing. By this time, the compression curve has become almost linear and more representative of the behaviour of a massive material. This reveals that the syntactic foam MS3 contains damaged microballoons filled with water in complete agreement with gravimetry date discussed previously.

An important point concerns the beginning of the degradation of the microballoons. The observations made by X-ray tomography [8] showed that the large diameter microballoons (which are of primary interest for buoyancy and insulation) break first. Acoustic emission is expected to be a powerful technique to check this early degradation, not detectable by global mechanical characterisation.

Acoustic emission activity for MS1 and MS3 foams is represented in Figure 7. The mechanical degradation starts around 4200 N for MS3 and over 11,000 N for MS1 whereas the plateau observed on compression curves for these materials appears, respectively around 8000 N and 16,000 N. Therefore, acoustic emission allows one to detect more precisely the beginning of GM degradation.

As mentioned above, MS3 foam degradation starts around 4200 N (55 MPa). This value is substantially higher than the hydrostatic pressure at 3000 m water depth (30 MPa), which is the expected depth for production of oil but one must pay attention to the evolution occurring with ageing.

Figure 8 presents the early acoustic activity of MS3 foams at different ageing durations at 100°C. As soon as the first sampling (after 15 days ageing), the degradation starts at very lower load (approx. 1000 N–15 MPa). This level seems to be the same during all the ageing duration. At 60°C (Figure

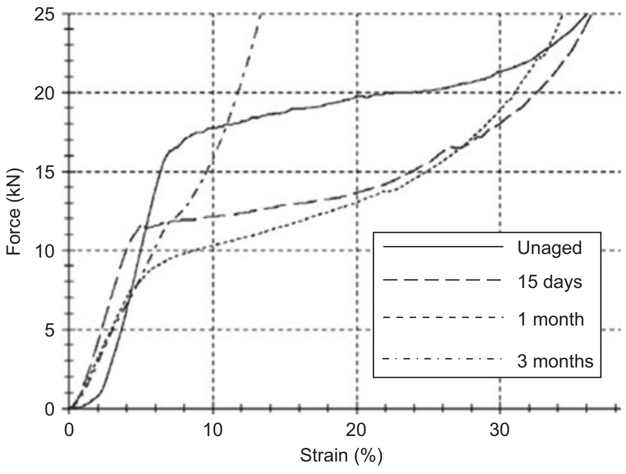

Figure 6 Compression curves of MS1 aged at 100°C.

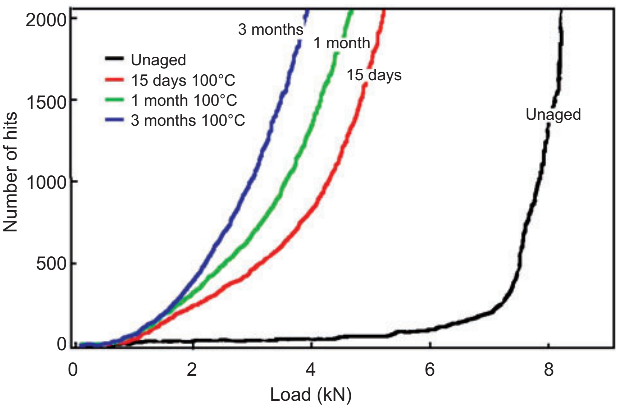

Figure 8 Acoustic emission activity of MS3 aged at 100°C [number of hits vs. load (kN/10)].

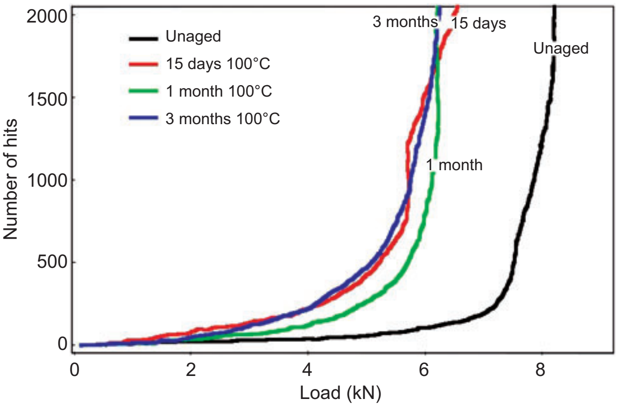

Figure 9 Acoustic emission activity of MS3 aged at 60°C [number of hits vs. load (kN/10)].

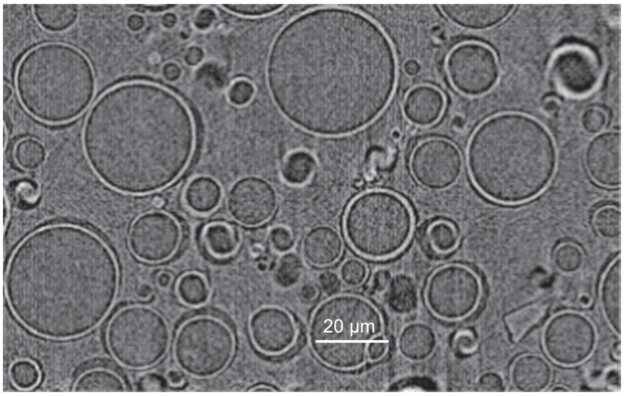

Figure 11 Decohesion at interface after 7 days ageing in deionised water at 100°C -300 bar. Observation by X-ray microtomography at ESRF (Grenoble, France) on ID19 beamline [13].

9), even if the massive increase of acoustic activity occurred at higher load (around 6000 N), the degradation recorded by acoustic emission started also at lower load. The same trend is observed for MS1 foam after ageing (Figure 10) where acoustic activity begins at a lower load, around 2500 N – 30 MPa.

This early detection cannot be attributed to the degradation of glass wall because it is not related either to the ageing temperature, or to ageing time or to the type of fillers. Observations made by X-ray tomography on aged samples have shown that the first phenomenon is decohesion of the interfaces between matrix and glass spheres (Figure 11). As the microballoons volume fraction is high for these materials, the sphere can be often in contact, as revealed by analysis of the three-dimensional granulometry of the thickness of the matrix from X-ray tomography scans [14]. On unaged materials, the compressive load is transferred from sphere to sphere through the matrix. When the interface has been degraded by water, this load transfer would occur at the contact points, inducing high stress concentration which would break the microballoons from early loading.

3.2. Influence of macroballoon volume fraction

The effect of glass microballoon volume fraction on the mass gain during ageing at 100°C is presented on Figure 12. For both foams, there is no stabilisation of the weight and the mass gain for MS3 is higher than for MS4. When the volume fraction is higher, there is obviously more interfaces and potentially more broken microballoons.

If MS4 mass gain is normalised to the same GM volume fraction than MS3 one, there is only superposition of the curves at the beginning of the ageing (Figure 13). This first stage corresponds to the Fickian absorption of water by the epoxy resin. The later divergence of the two curves means that other phenomena have occurred, not related only to the volume fraction of GM. At this stage, it is without doubt the hydration of interface and glass surface, phenomena which are proportional to the surface of the microspheres.

The beginning of the degradation recorded by acoustic emission on unaged materials is also sensible to the GM volume fraction (Figure 14). MS3's activity begins around 4200 N (55 MPa) whereas MS4's activity appears only at 6500 N (80 MPa). Even without ageing, a smaller GM volume fraction leads to a better resistance of the foam, due to less contact between GM in MS4.

The protective effect of the matrix located between microballoons is also visible on aged results of MS4 samples

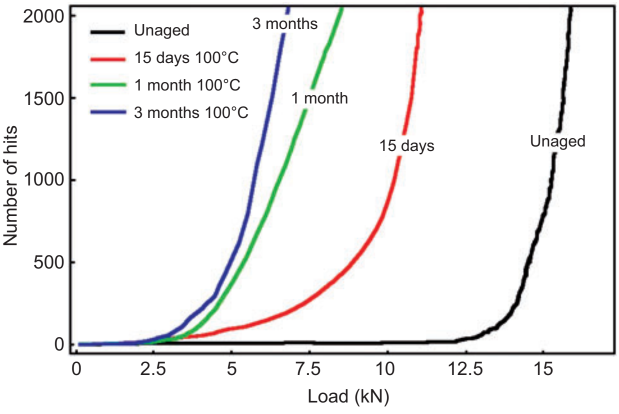

Figure 10 Acoustic emission activity of MS1 aged at 100°C [number of hits vs. load (kN/10)].

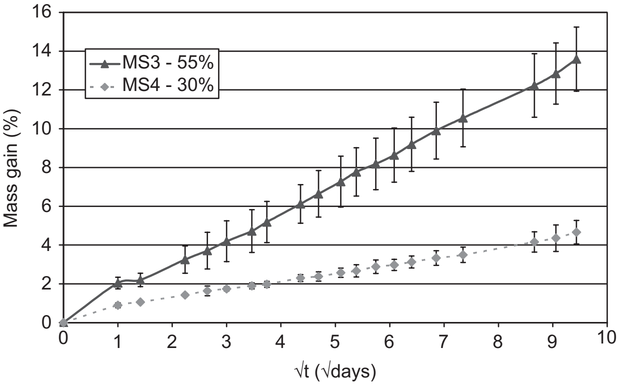

Figure 12 Gravimetry of syntactic foams (30% and 55% GM volume fractions) during ageing at 100°C.

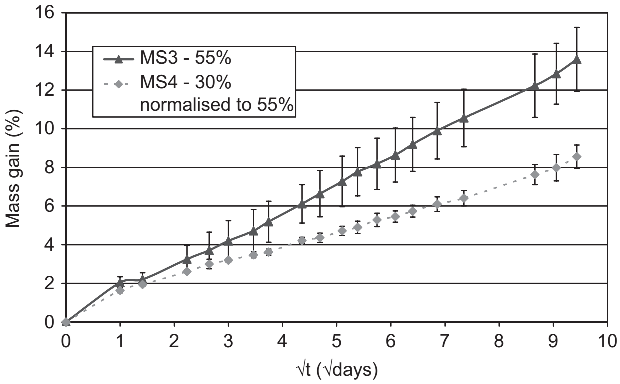

Figure 13 Gravimetry of MS3 and MS4 normalised to the same volume fraction (55%) during ageing at 100°C.

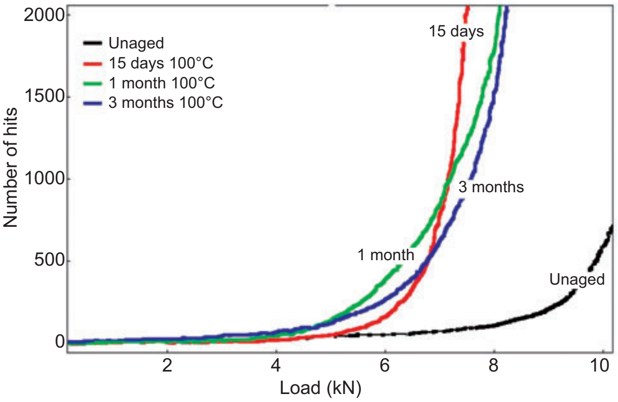

Figure 15 Acoustic emission activity of MS4 during ageing [number of hits vs. load (kN/10)].

(Figure 15). One should bear in mind that the beginning of the acoustic emission for aged MS3 samples appeared around 1000 N from the first sampling (Figure 8). For MS4, the load for which the acoustic activity appears is dependent on the ageing time. It appears around 5000 N after 15 days ageing, 3500 N after 1 month and 2000 N after 3 months ageing. This progressive decrease reveals that the effect of water absorption is not the same than for MS3. As there was more matrix between microballoons and then less contact between them, decohesion of the interfaces had less influence on the stress concentration.

The mechanical behaviour of MS4 (Figure 16) is also different than MS3's one (Figure 5). First of all, looking at unaged materials, the plateau of the compression curve is at higher load for MS4, illustrating the protective role of the matrix. This plateau is also shorter than for MS3, because the number of GM to break is smaller and then the compaction step is reached earlier. Looking at aged MS4 materials, a point to be highlighted is the decrease of strain at 25 kN, previously observed on MS1 (Figure 6) and related to the filling of microballoons by water. This behaviour, not detectable by the others measurements, could be explained by higher compressive load induced on GM by the swelling of matrix in larger volume fraction [14] which then could break the spheres.

3.3. Tentative of interpretation of AE signals

Previous paragraphs have presented different mechanisms of degradation of syntactic foams during hydrothermal ageing. Indeed several phenomena occurred during ageing and obviously during mechanical testing.

Acoustic emission technique is commonly used to detect and discriminate different phenomena vs. the type of events recorded [15–18]. The clustering of acoustic signals is performed by unsupervised or supervised methods and help to classify the data in regards to the expected physical mechanisms. The correlation to establish between cluster and these physical mechanisms is often the more difficult step. The main studies which led to the identification of different signals include mechanical characterisation in tension [18–20]. Other kinds of solicitations led to more difficulties [21].

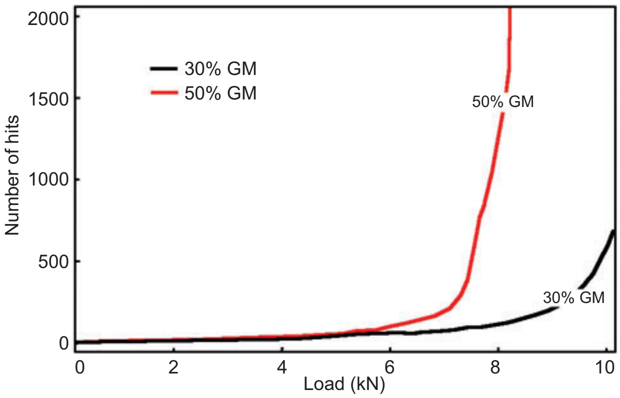

Figure 14 Acoustic emission activity of MS3 and MS4 [number of hits vs. load (kN/10)].

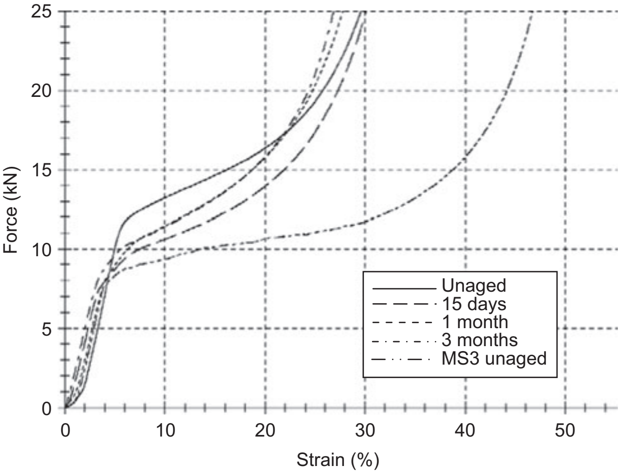

Figure 16 Compression curves of MS4 aged at 100°C.

In this study, attempts were made to apply the k-means method to AE data with the hope, first to define some class of signals, second to look at evolution of these classes in function of ageing time.

Unfortunately, the acoustic data obtained during the compression tests on foams were not clusterable. And there was almost no evolution of the signals maps during ageing, even for MS1 foam for which there has been the more degradation.

4. Conclusion

An experimental investigation was carried out to characterise the ageing behaviour of syntactic foams made of epoxy resin reinforced by hollow glass microballoons. Materials with different microballoon density and volume fraction were tested. Characterisation was carried out by gravimetry and confined compression test instrumented with acoustic emission. Comparisons of compressive behaviour during ageing with unaged results and based on previously published data, have shown the possibility to attribute the modification of the curves to the different degradation mechanisms. The decrease of the plateau is related to additional compressive load borne by glass microballoons, induced by swelling of the matrix due to absorption of water. Further decrease can be explained by hydrolytic ageing of glass reducing the glass microballoons mechanical resistance. The decrease of overall strain is related to the filling of broken microballoons by water. Acoustic emission activity allowed the detection of early degradation during the mechanical test. It was shown that a high volume fraction of microballoons led to stress concentration between spheres which is particularly detrimental to wet aged samples. For these samples, first microballoons were broken under small loadings, far lower than 30 MPa which is the hydrostatic pressure in service. Acoustic emission has also shown that a lower volume fraction of microballoons prevents this early degradation by stress concentration, however, thermal properties would be diminished. It was nevertheless not possible to identify different classes of acoustic signals related to the different degradation mechanisms.

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