Thermal stability of polymethacrylic based ELIUM® resin: Effect of comonomers, antioxidants and aluminum trihydrate filler

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ABSTRACT

This paper presents the study of the thermal degradation of methyl methacrylate resin based materials known as ELIUM® resin. Samples under investigation were made from MMA based resin (ELIUM® V1), ELIUM® V1 with a dimethacrylate comonomer (ELIUM® V2), and ELIUM® V2 with a stabilizer package (ELIUM® V3). They were used for trying to discuss the degradation mechanisms. Blocks differing by their thickness made from ELIUM® formulation filled with aluminum TriHydrate used as flame retardant were also investigated in order to better match some industrial materials. Degradation was observed to be mainly driven by unzipping, consistent with the methacrylic nature of ELIUM® resin. Occurrence of oxidation is also discussed depending on materials formulation and temperature. A blend of antioxidants was inefficient for limiting mass loss. At 200 °C, both ATH and ELIUM® degrade, which contributes to overall mass loss. At temperatures below 180 °C, ATH does not seem to induce new degradation mechanisms but would increase oxygen diffusivity. Finally, a first simple kinetic model is proposed to predict mass loss in thick composite blocks aged under air.

1. Introduction

Methacrylic resins based on methyl methacrylate (and in particular ELIUM® resins) are increasingly used as reactive matrices for manufacturing of composite materials with the process advantage of a low viscosity reactive mixture [1,2]. This latter can be polymerized at moderate temperature using an organic peroxide [3]. Their thermo-mechanical properties can be improved by introducing tetrafunctional acrylate comonomers allowing a certain crosslinking level [4].

It is known that methyl methacrylate-based polymers are thermally unstable. For example, it is well documented that Poly-MethylMethacrylate (PMMA) decomposes at temperatures as low as 200 °C [5,6] even under inert atmosphere due to an unzipping mechanism (cleavage of carbon-carbon bond leading to regeneration and release of MMA monomer). In presence of oxygen, an oxidative mechanism also occurs at the same time and accelerates the kinetics of isothermal ageing. It is known that unzipping may be limited using comonomers [7] and ageing under air can be slowed down by antioxidants [8,9]. There are however few reports addressing those topics in the case of ELIUM® resin to the best of our knowledge. The question of the stability under air of stabilized thick samples ELIUM® resin typically under 200 °C (where unzipping, oxidation, stabilization and oxygen diffusion are involved all together) remains thus fully open.

These resins may also suffer from the intrinsic low flame resistance, which is common to all polymers synthesized from methyl methacrylate [10]. Flame retardancy can be significantly improved by adding aluminum trihydrate (ATH). Its endothermic dehydration decreases the temperature in the burning polymer, which slows down its combustion, and releases water which dilutes toxic combustion gases in the external atmosphere. ATH can thus be used as flame retardant for ELIUM® [11]. It can however modify the long-term thermal stability: previous papers actually report increase of degradation temperature in the case PMMA/ATH [12] and thickening of oxidized layer in Vinyl Ester based composites [13]. In other words, there is no evidence if ATH positively or negatively influences ELIUM® stability, so that the effect of ATH on isothermal ageing of ELIUM® resin must be addressed.

Following our previous work on the thermal oxidation and unzipping of thin films of ELIUM® resin [14], the aim is here to understand the degradation of an ELIUM® based composite materials envisioned as a neutron polymeric shield used for packaging radioactive materials. For that purpose, materials with an increasing level of complexity will be investigated: base ELIUM® resin, ELIUM® with comonomers, ELIUM®

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with comonomers + antioxidants, ELIUM® with comonomers + antioxidants + ATH fillers… It is believed that this methodology will allow to separate the effect of "anaerobic" (unzipping) and aerobic (oxidation) in the overall degradation rate, together with a first screening of the effect of comonomers, antioxidants and fillers.

In terms of experimental methodology, bulky samples made from those 4 kinds of materials will be aged in order to:

- investigate mass and volume loss kinetics, in conjunction with elemental analysis focused to establish an ageing mechanism more clearly.
- observe the thickness of oxidized layer and discuss the effects of antioxidants and fillers on degradation profiles.

Those results will be helpful to address the thermal ageing (either under inert or oxidative atmosphere), which was less covered by literature than fatigue [15] or water ageing [16] for example. The study of materials made of "pure" ELIUM® resin will allow to have a better understanding of mechanisms meanwhile the study of compounds prepared with antioxidants and ATH fillers will allow to address the case of industrial materials.

2. Experimental

2.1. Materials

In the aim to understand factors improving the thermal stability, three kinds of unfilled acrylic resins were studied here as 4 mm thick plates samples:

- The resin ELIUM® V1 (also known as ELIUM 150 – see ref [2,17]) comprised a cast-grade monomer formula and a ketone peroxide thermal initiator. The ELIUM® V1 mixture contains MMA monomer with 20 to 30 wt.% acrylic copolymer chains, which serve as a thickening agent and an iron-based metallic salt, which acts as an accelerator. The redox system used allows the polymerization of the ELIUM® V1 at ambient temperature without the need of additional post-curing.
- ELIUM® V2 is synthesized from the reactive mixture used for ELIUM® V1 (MMA syrup) to which butanediol dimethacrylate (5% in weight) and methacrylic acid (5% in weight) were added. This comonomer induces crosslinking so that ELIUM® resin is no longer considered as thermoplastic.
- ELIUM® V3 is made from ELIUM® V2 reactive mixture with an antioxidant package (1500 ppm) which comprises a hindered amine light stabilizer (HALS) and a sulfur-containing, primary phenolic antioxidant as a heat stabilizer.

Those resins have similar densities: 1.185–1.19.

A composite (ELIUM® ATH) made of ELIUM® V3 resin containing both aluminum trihydrate and zinc borate as fillers (as described in Table 1) was also studied. Its composition is close to the one of composites used transport of storage casks [18,19] with an improved neutron shielding capability and fire resistance. The ageing of this latter was studied as 0.3, 0.5, 1, 2 and 4 mm thick samples. Some 10 and 20 mm thick samples were also aged for a more precise observation of the thickness of oxidized layer (TOL).

Table 1
Composition of ELIUM® ATH resin.

Component	Weight percentage (%)
ELIUM® v3	32
Aluminum trihydrate	62
Zinc Borate	6

2.2. Ageing conditions

Samples were aged in ventilated ovens at 160, 180 and 200 °C (AP60, System Climatic Service) under atmospheric air.

ATH and Zinc Borate powders were also aged in open vials at 160, 180, 200 and 250 °C.

2.3. Characterization

2.3.1. Gravimetric analysis

The residual mass of aged samples was measured after ageing using an AT261 DeltaRange balance (Mettler Toledo). Initial samples mass ranged from about 0.25 g (0.3 mm thick samples of ELIUM® ATH) to about 4 g (4 mm thick samples ELIUM®).

2.3.2. ThermoGravimetry analysis

TGA measurements were performed using a Q500 apparatus driven by QSeries Explorer (TA Instruments). Isothermal measurements were performed under 100% N_2 atmosphere supplied by a continuous 50 ml min^{-1} gas flow. Isothermal degradation was performed at a constant temperature (230 or 250 °C). Samples studied by TGA were 20 μm thin films microtomed in ELIUM® V1, V2 or V3.

2.3.3. Sample size

Size of samples was measured after ageing using a micrometre (OTMT).

2.3.4. Thickness of oxidized layer

Degraded layers were observed on 10 and 20 mm thick samples using a LEICA M80. Those later were previously cut and polished with 800 and 2400 granulometry disks. The oxidized layers were characterized from the brown layer. Those colour changes can be considered as an acceptable of oxidation and well correlated with other trackers (indentation modulus, or oxidized products for example) [20,21].

2.3.5. Elemental analysis

Carbon Hydrogen measurements were performed on a homemade Carbon / Hydrogen elemental micro-analyser (Institut des Sciences Analytiques, UMR5280 CNRS, Villeurbanne). About 1.5 mg of sample weighted in silver cups (3.2 × 6, Säntis Analytical AG, Teufen, Switzerland) dropped into a unit combustion in a flow of 50 ml/min of pure oxygen. The combustion system is equipped by two furnaces held at 1050 °c for the upper one and 850 °c for the lower and contain a vertical glass combustion tube, half filled with 11 cm of CuO oxidation catalyst (Copper oxide wire 0.7 mm, Säntis Analytical) and silver wool (Silberwolle Carl ROTH GmbH, Karlsruhe, Germany) used as halogens trap. Carbon and hydrogen have been respectively turned into carbon dioxide (CO_2) and water (H_2O). The measurements of both molecules have been done using a CO_2/H_2O non-dispersive infrared detector (Rosemount NGA 2000). A calibration has been daily established by measuring standards references (molecules pure at 99.9%). Then up to 8 samples were injected. To be sure of the lack of calibration-drift, 2 standards reference were introduced and measured as sample, every eight analyses. The uncertainty of measurements has been determined at +/−0.10 for H measurement and +/- 0.30 for carbon measurement. Reference standards used for calibration and stability controls are high purity compounds purchased from Sigma Aldrich corp. (Saint-Louis, Missouri, USA): Methionine (C: 40.25%, H: 7.43%), Glycine (C: 36.36%, H: 6.10%), Taurine (C: 19.20%, H: 5.20%), Cystine (C: 29.99%, H: 5.03%), Valine (C: 51.26, H: 9.46%), Tryptophan (C: 64.69%, H: 5.92%).

3. Results

3.1. Gravimetric analysis

Fig. 1 depicts the mass changes of acrylic resins ELIUM® V1, V2, V3 and the ELIUM® ATH composite in the case of 4 mm thick plates aged under air at 160, 180 et 200 °C. Results show that:

- ELIUM® V1 resin, which has neither comonomers nor antioxidants, is the less stable. Its strong mass loss is accompanied by strong geometrical changes due to its thermoplastic nature, presented later.
- There is a small difference for the thermal degradation of ELIUM® V2 and V3 resins. At 200 °C, the appearance of some cracks at long ageing time (150 days) is responsible for the re-start of mass loss.
- ELIUM® ATH composite is the more stable formulation. Since this latter contains ELIUM® resin and fillers, it means that fillers are more thermally stable and break down less easily than ELIUM ® resin. This will be confirmed in the following.

When comparing ELIUM® V1, V2 and V3, the difference of mass loss rate is very visible in the first stage (before 50 days at 200 °C, before 100 days at 180 and 160 °C) but at longer times (typically above 300 days at 180 °C and 200 at 160 °C) it seems to reach a comparable value for the 3 materials. For example, mass loss is about 5% for ELIUM® V1 after 2 days (2% for ELIUM® V2 and V3) and the mass loss rate tends towards 0.025%.day^{-1} after 100 days of ageing.

Data have been overlapped with a simple model for predicting mass loss from the unzipping rate presented later in the 'discussion' section. Differences with experimental results will be discussed later.

For better understanding the mechanisms responsible of mass loss, 20 µm thin films of ELIUM® V1, V2 and V3 were isothermally aged in TGA cell under inert atmosphere to investigate the kinetics of unzipping (« depolymerization ») [13]. Curves are given in Fig. 2 display two regimes. The first one corresponds to the mass loss of unreacted monomers and the second to the unzipping mechanism. Apart for the first stage, it indicates that ELIUM® V2 and V3 resins have very close unzipping rates (as suggested by the derivate of mass loss curves at long ageing times), consistently with the matter that antioxidants do not interfere with this degradation mechanism. A difference can however be observed at short exposure times when mass loss is due to evaporation of unpolymerized (volatile) groups suggesting that the presence of antioxidants might inhibit the polymerization and induce a greater quantity of unpolymerized monomers. As previously discussed [13], ELIUM® V2 is more stable than ELIUM® V1 due to the presence of dimethacrylate comonomer slowing down the unzipping, this latter being (as it will be seen in the following), the main source of mass loss. Another reason might be envisaged: ELIUM® V1 behaves as a real thermoplastic, and flows at high temperature, thus increasing the surface exposed to atmospheric air and further oxidation.

Kinetic curves of mass loss for ELIUM® ATH composites with different thicknesses are given in Fig. 3. Repeatability is illustrated in Supplementary Data. Three steps (separated by dashed lines in Fig. 3) are observed:

- a first step with a very fast mass loss at short ageing times.
- a deceleration of mass loss, this latter reaching a pseudo constant rate.
- an auto-acceleration of the degradation after this plateau. At 200 °C, the duration of the plateau is short and the auto-acceleration starts immediately after the first step. It is noteworthy that the auto-acceleration is less visible when samples thickness increases (apart at 200 °C where curves for 0.3 and 0.5 mm thick samples are very similar given the experimental incertitude). It suggests that this third stage could be due to oxidation. The differences between experimental results and the model describing the unzipping rate (see 'discussion') become more important in this last stage meaning here

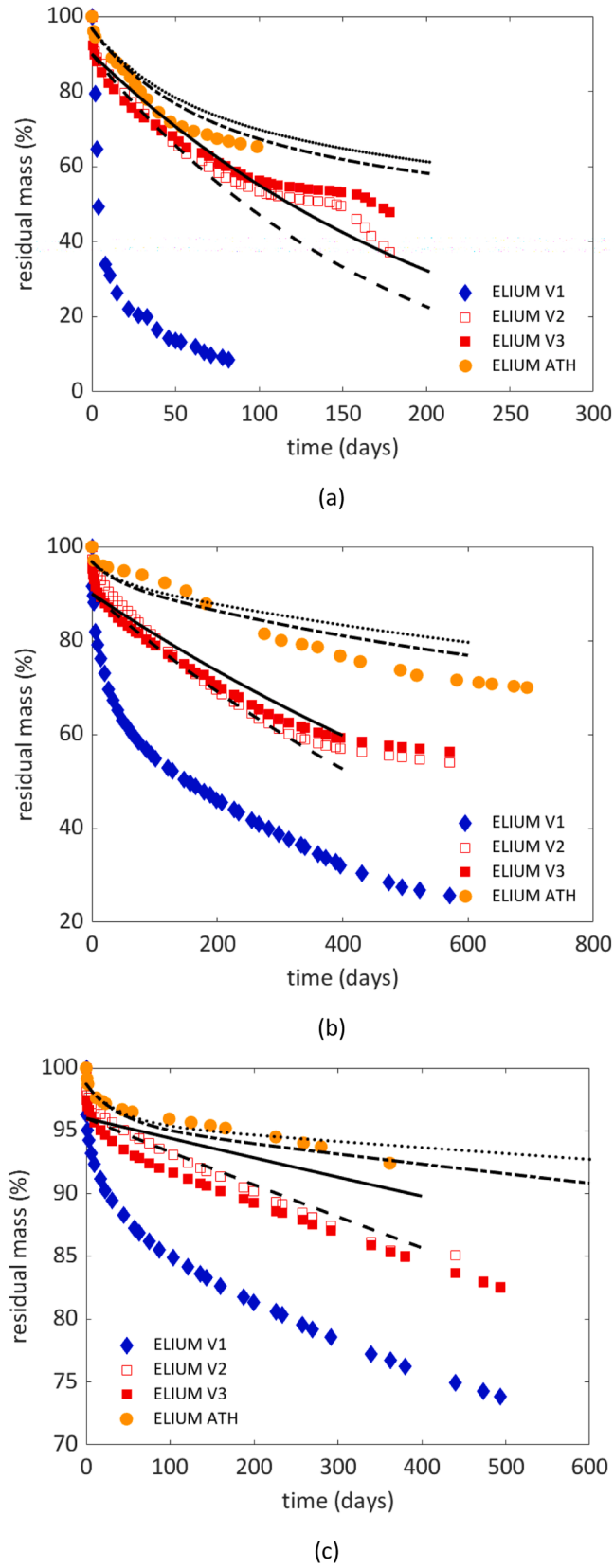


Fig. 1. Changes of residual mass of ELIUM® V1 (◆), V2 (■), V3 (×) and ELIUM® ATH (•) at 200 (a), 180 (b) and 160 °C (c). Lines correspond to modelling of mass loss either from extrapolation of high temperatures data for V2 and V3 (- -) (from ref [14]) and ELIUM® ATH (···), or best fitting for V2 and V3 (—) and ELIUM® ATH (·-) as developed in "Discussion".

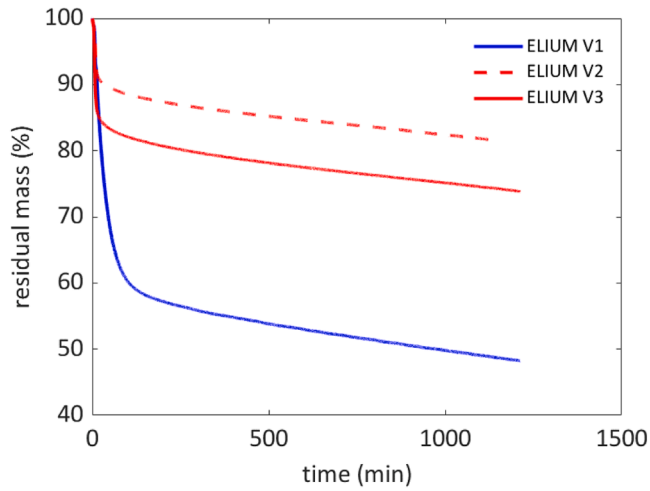


Fig. 2. TGA thermograms for ELIUM® V1, V2, V3 films aged at 250 °C under nitrogen.

also that they might come from an oxidative effect. Last, fillers seem to accelerate the degradation in this third stage.

For better understanding those results, degradation of fillers aged alone was studied separately (Fig. 4): ATH and Zinc Borate aged at 180 and 160 °C display a slight mass loss and a plateau with a final level very close to initial mass. It means that data in Figs. 3**b** and 3**c** are mainly explained by the degradation of the acrylic resin. Conversely at 200 °C, ATH degrades significantly which contributes to the strong mass loss of composite (Fig. 3**a**). It can be assumed that those results are intrinsic to the chemical nature of each kind of filler and can be generalized irrespectively of the manufacturer. To better comment those curves, let us recall that the degradation pattern of both fillers is:

- ATH degrades by dehydration: $2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$ corresponding to 34.6% mass loss.
- Zinc Borate degrades: $2ZnO,3BO_3,3H_2O \rightarrow 2ZnO,3BO_3 + 3H_2O$ corresponding to a 14.4% mass loss.

3.2. Elemental analysis

C/H analysis are used here to observe chemical changes in 0.3 mm thick ELIUM® V2, ELIUM® V3 and ELIUM® ATH before and after isothermal ageing, with significantly different mass loss level. In the case of oxidation, structural modifications are usually observed from FTIR, in particular in the carbonyl region. However, we believe that this approach is here of limited interest in methacrylic polymers where an intense carbonyl absorption is expected to hide modifications induced by oxidation. Reversely, chemical changes can be revealed by changes in elemental analysis as illustrated for example in [22,23].

Results are given in Fig. 5. 0.3 mm samples were chosen here because they can be considered as homogeneous in terms of oxidation profiles.

Hydrogen content loss increases linearly with mass loss. The factor is about 0.35 for ELIUM® V2 and V3 and 1.35 for ELIUM® ATH. At the same time, it was observed that C+H content keeps almost constant and close to 67% for ELIUM® V2 and V3 aged at 160 and 180 °C. In the case of unfilled ELIUM® resins, elemental composition is slightly modified.

Our interpretation is the following: in a homopolymer, if unzipping is the only degradation mechanism, the content in each element will remain unchanged. On the contrary, oxidation will induce more severe changes in elemental content. It is clear that at least H content will strongly decrease since C—H bonds will be oxidized in >C=O.

In the case of ELIUM® ATH, the elemental changes reflect both the degradation of ELIUM and its fillers. This will be discussed more in detail

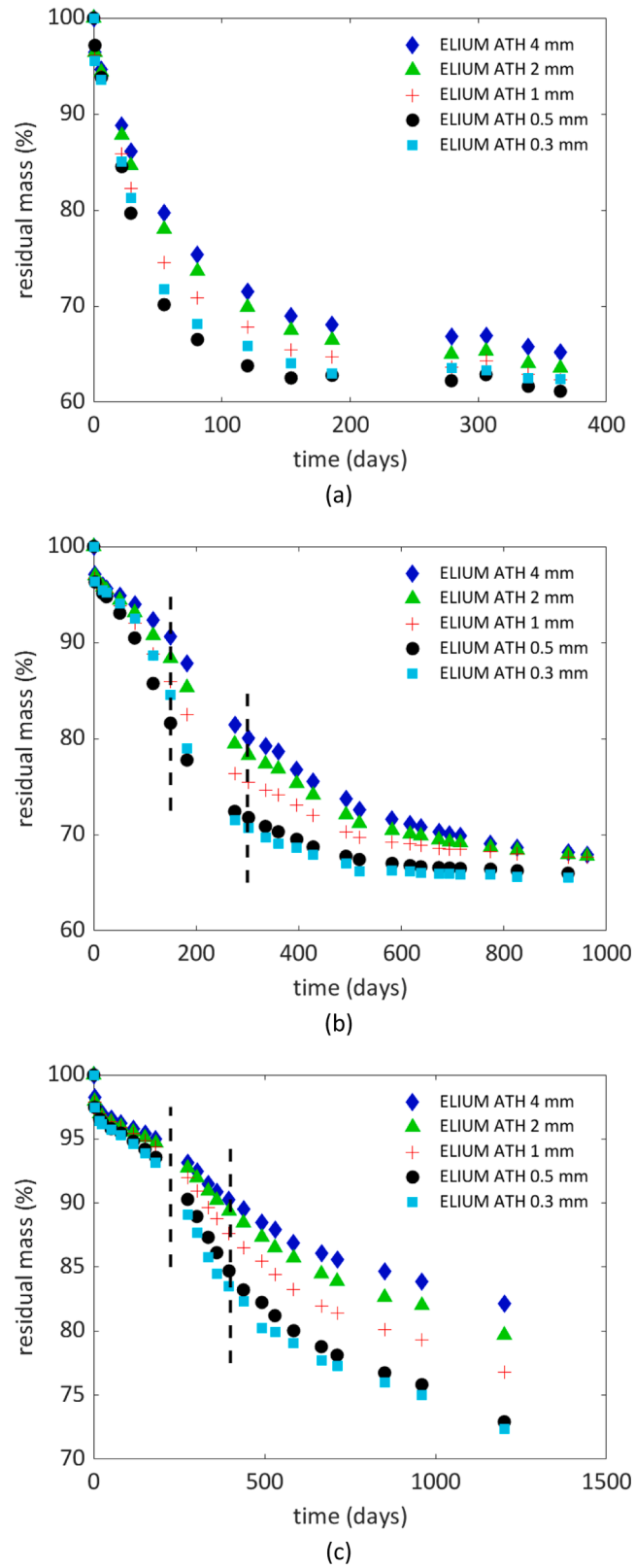


Fig. 3. Changes of residual mass for ELIUM® ATH composites aged under air at 200 (a), 180 (b) and 160 °C (c). Dashed lines indicate three distinct regimes of mass loss (see text).

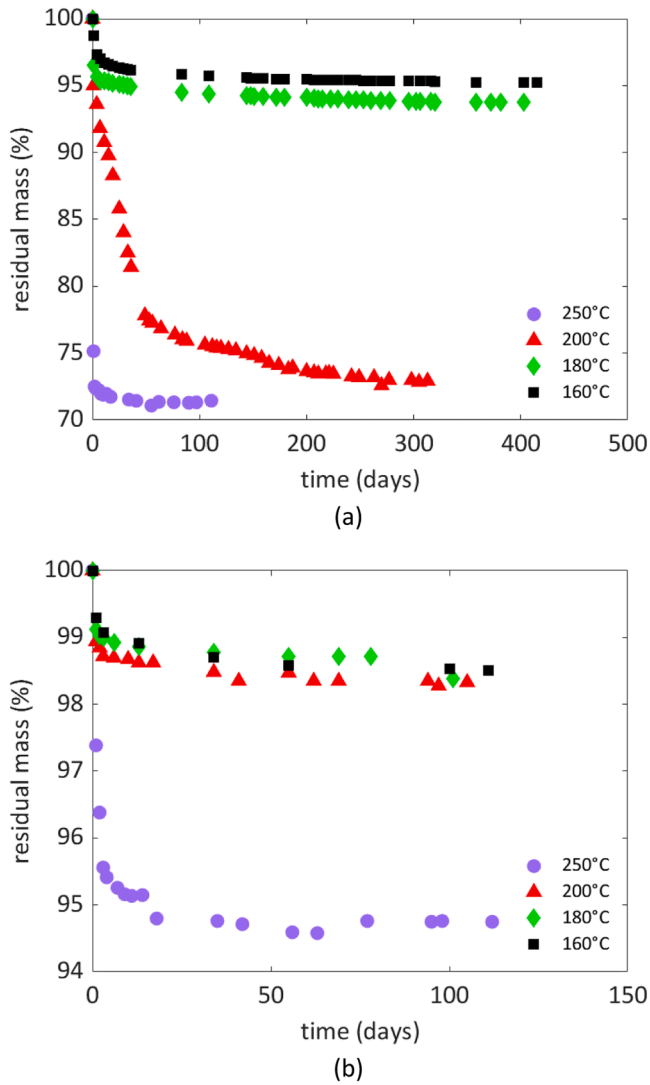


Fig. 4. Changes of residual mass of ATH (a) and Zinc Borate (b) at 250 (•), 200 (◆), 180 (■) and 160 °C (▲).

later regarding the mass loss of ELIUM® resin and its fillers (Figs. 1 and 2) and its impact on hydrogen content.

3.3. Observation of oxidation profiles

Thicknesses of Oxidized Layers (TOL) were measured at 160, 180 and 200 °C (Figs. 6 and 7). Let us precise that even if TOL were mainly observed on 4 mm thick parts, some complementary measurements were performed on thicker samples of ELIUM® ATH (10 mm) in order to (to) better characterize TOL value. It must also be stressed that such optical measurements constitute a very rough estimation of degradation depth. Example of observations at 160 °C are given in Fig. 6 and all available data are given in Table 2. It can be observed:

- A brown layer, characteristic of the oxidation of thermosets [24].
- A « white » surface layer, the thickness of which remains constant and almost independent of temperature (270–300 μm). It could be formed of neat ATH, since this latter seems stable below 180 °C (Fig. 4).
- In any case, it can be observed that in terms of thickness of oxidized layer: ELIUM® ATH > ELIUM® V2 > ELIUM® V3 (even without considering the thickness of this "white" surface layer). It means that the oxidation effects are more significant for filled ELIUM® resins than unfilled ones (in line with the suspected effect of oxygen (the deviation compared to prediction of unzipping rate) in ELIUM® ATH observed in Fig. 3.
- At relatively high conversion degrees, cracks seem to favour a supplementary access to oxygen, allowing a stronger penetration of the oxidized layer to deeper layers (Fig. 7). It means that samples can initially be subjected to the Diffusion Limited Oxidation effect but can become homogeneously oxidized. At this stage, measuring the TOL for such samples becomes for us questionable, which is the reason why values are not given for ELIUM® ATH aged 8 months or more.

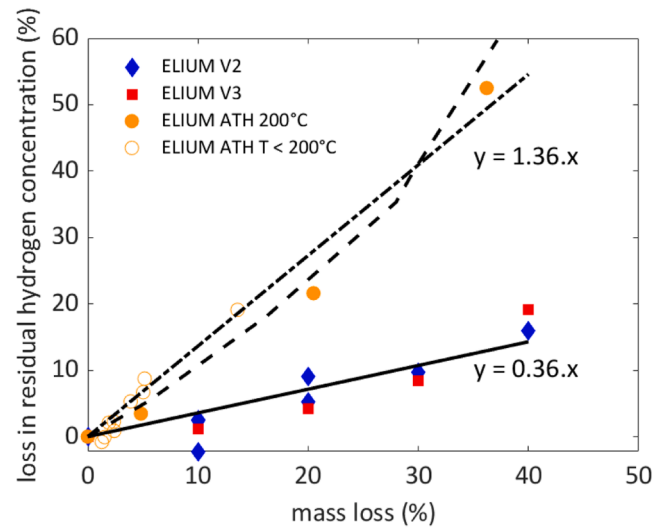


Fig. 5. Loss of elemental concentration in hydrogen in residual polymer vs mass loss for ELIUM® ATH aged below 180 °C, ELIUM® ATH aged at 200 °C, ELIUM® V2, ELIUM® V3. Dashed line corresponds to the prediction using Eqs. (5) and (7).

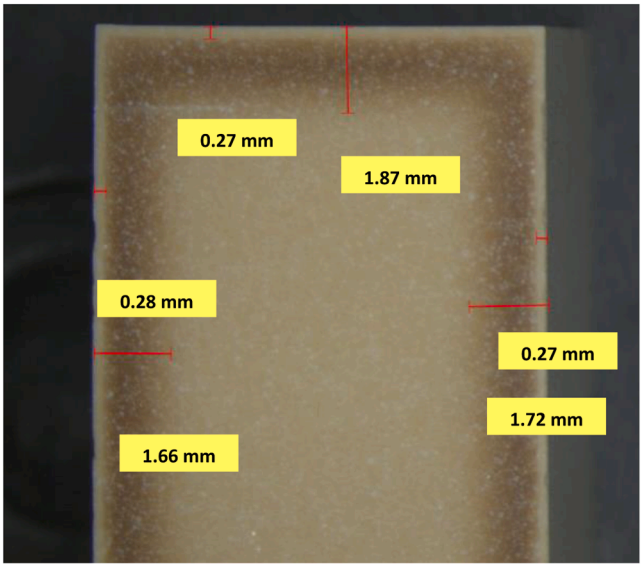
3.4. Volume changes

Fig. 8 depicts changes in relative thickness (e/e_0) and volume changes vs mass loss. Let us recall that ELIUM® V1 was not studied here because of its thermoplastic behaviour inducing dramatic shape changes at the exposure temperatures. Thickness changes (Fig. 8a, c and e) are consistent with mass loss results, i.e. ELIUM® V2 is less stable than V3 resin, in line with stabilizer effects. Fig. 8b, d, and f show some noticeable results:

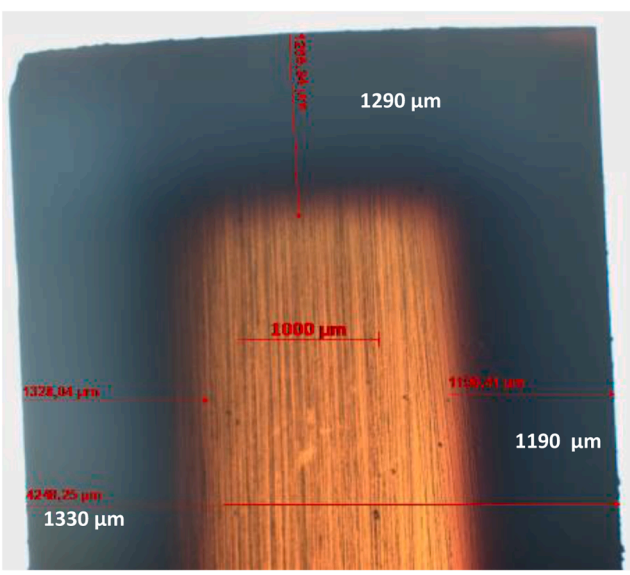
- Volume loss changes linearly with mass loss regardless of ageing temperature. Proportionality ratio is close to 1 for ELIUM® V2 resin. This ratio is not changed by antioxidants.
- Despite a significant shrinkage, no crack is detected. It seems in link to the presence of sub-glassy relaxation [25] and the possible fact that groups responsible for this sub-glassy motion are not destroyed by ageing.
- The presence of ATH decreases the shrinkage as shown on the comparison of ELIUM® ATH and ELIUM® V3. In particular, for a given mass loss level, the volume loss is lower in particular at high temperatures.

4. Discussion

The main aims of this section are to explain the observed differences between ELIUM® V1, V2, V3 and filled with ATH in terms of mass and volume loss, basing on the changes in carbon and hydrogen content linked to the mechanism of degradation.



(a)



(b)

Fig. 6. Microscopic observations of ELIUM® resins aged at 160 °C: ELIUM® ATH 2 months (a) ELIUM® V2 4 months (b) (NB: values of TOL were rounded given the uncertainty of the microscopic measurements).

4.1. Degradation of ELIUM® V1 and V2

Let us start by commenting the mass loss curves regarding our previous work on ELIUM® resin (without mineral filler) [13] according to which:

① first step corresponds to the loss of (unpolymerized) volatiles,

② second step corresponds to unzipping (depolymerization), which can be modelled by a first order equation:

$$\frac{dm}{dt} = -k_{unzipping}.m \tag{1}$$

$k_{unzipping}$ is here an apparent constant for the depolymerization rate. Using data acquired by TGA measurements for ELIUM® V2 aged under nitrogen at 230–290 °C (see Fig. 2), its value was extrapolated from as illustrated in Fig. 9. The extrapolated values (given by the circles in Fig. 9) were incorporated in a global mass loss equation for ELIUM® V2 and V3.

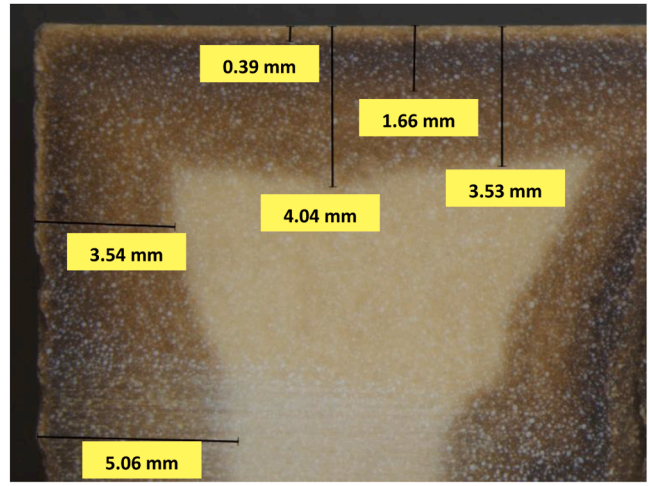


Fig. 7. Microscopic observations of ELIUM® ATH aged 8 months at 180 °C. (NB: values of TOL were rounded given the uncertainty of the microscopic measurements).

$$\frac{m}{m_0} = \frac{m_{v_0}.\exp(-k_v.t) + m_{p_0}.\exp(-k_{unzipping}.t)}{m_{v_0} + m_{p_0}} \tag{2}$$

Where m_{v0} (accounting for initially present volatiles) was estimated from the early-stage mass loss. Eq. (2) allowed fair simulations as it can be seen in Fig. 1. NB: k_v was shown here to play a negligible role as long as $k_v >> k_{unzipping}$.

They are three options for improving the simulations:

- Increasing the value of $k_{unzipping}$: this option was tried with values in the margin of error of the extrapolation and experiments (as it can be seen in Supplementary Information file). Resulting extrapolations are given by the squares in Fig. 9, corresponding simulations are given as "best fit" in Fig. 1 and Table 3).
- Using the non-empirical model for unzipping (see Supplementary information files). Very good fits were obtained but it remains to validate them in particular by adjusting the set of rate constants for all simulations of available results [14] so as to have excellent Arrhenius behaviour for all rate constants.
- Considering a mechanistic reason in agreement with the presence of an oxidized layer. The possible degradation mechanisms can be discussed basing on their consistency with elemental analysis results.

In the virgin polymer, molar mass of a monomer (MMA) is 100 g.mol^{-1} with 8 H. It means that the hydrogen content (number of monomer per mass unit) is 0.08 hydrogen/(g.mol^{-1}).

For unfilled resins, if unzipping (Scheme 1) is the only mechanism, both the hydrogen and carbon content will keep unchanged meanwhile mass will decrease. This trend is inconsistent with Fig. 5.

Let us now discuss on the possible effects of "pure" oxidation. A qualitative reasoning can be done for a structural unit close represented in Scheme 2. If oxidation occurs on a methyl group: the new hydrogen content is close to 0.075, meaning that the loss in hydrogen content is almost 6% whereas mass increases which is also inconsistent with experimental results.

In fact, the co-existence of mass loss and decrease in hydrogen content means that both unzipping (mass loss) and oxidation (hydrogen loss) are involved as depicted in Scheme 3. Despite quite speculative, this scheme depicts the situation where one monomer is released and one radical is oxidized (for 4 monomers). The corresponding mass loss would be 32.2%. Hydrogen content would decrease from 8 to 7% (−13%). Finally, the ratio of hydrogen loss to mass loss would be about 0.35, in line with Fig. 5. It suggests that oxidation rate and unzipping

Table 2
Average values of Thickness of Oxidized Layers from Fig. 6. NB: For ELIUM® ATH, TOL is obtained by subtracting the thickness of white zone to the value of total degraded zone.

			1 w	2 w	4 w	2 m	4 m	8 m	11 m	16 m
200 °C	**ELIUM® ATH**	brown		1300	1100					
		white								
	V3		600	700	800		600			
	V2		700	700	900					
180 °C	**ELIUM® ATH**	brown		1500	1500	1200	1600			
		white		300	300	400	300			
	V3					1000	1300		1200	
	V2				900	1100	1100		1000	
160 °C	**ELIUM® ATH**	brown				1400	1500	1500		
		white				300	300	300		
	V3				1100	1400			1500	1500
	V2				1400		1300	1500	1400	1400

rate would be on the same magnitude order in the temperature range under investigation.

Oxidation seems to moderate compared to unzipping in the temperature range under investigation. When lowering the temperature, it seems however clear that oxidation will become more and more predominant, keeping in mind that activation energy for unzipping reaction is about 100 kJ.mol^{-1} vs 70 kJ.mol^{-1} for the propagation reaction of oxidation process [14].

Finally, it seems interesting to comment here the stability of ELIUM® resin: The mass loss of a Vinyl Ester (4 mm thick, after 1000 h of ageing at 160 °C under air is about 2%, i.e. significantly lower than for ELIUM® blocks (5%). This can be explained by two reasons: oxidized layers are deeper for ELIUM® thick blocks (more than 1 mm) than for vinyl ester (less than 500 μm) and vinyl ester resin seems more stable in those conditions since they cannot undergo unzipping contrarily to methacrylic resins, as discussed in the last paragraphs.

4.2. Degradation of ELIUM V3: Effect of antioxidants

According to Fig. 2, antioxidants favour the presence of volatile "unpolymerized" compounds meanwhile they do not change unzipping rate. According to the comparison of shrinkage for ELIUM® V2 and V3 (Fig. 8), it seems that the volume loss is higher for ELIUM® V3 than V2 (at a given mass loss). A possible explanation is that antioxidants modify the polymerization route and generate more "defects" (oligomers, dangling chains) more likely to induce volatiles.

The first result is in line with the inhibiting role of phenol groups on polymerization. It might be surprising to consider that phenols inhibit the polymerization but would not unzipping mechanisms meanwhile both mechanisms involve the same kind of radicals. A simple explanation can be proposed by comparing the rate of unzipping reaction and the rate of the reaction during which phenols give a hydrogen to an alkyl radical.

$$k_{DP}[P^{\bullet}] >> k_{abst}[P^{\bullet}][AH] \tag{3}$$

Here, the weight fraction in stabilizers is typically on the order of 0.1% so that *[AH]* is clearly lower than 0.01 mol.l^{-1}, and k_{DP} is around 500 s^{-1} at 250 °C. It means phenols could block unzipping if k_{abst} > 50,000 lmol^{-1}.s^{-1} which is clearly unreasonable for an abstraction reaction [26]. Some simulations were performed in Supplementary Information file. They show that if antioxidants would be efficient, they would induce an "induction period'' and a higher residual mass, which is contrary to the experimental results.

Under air, antioxidants hardly induce a decrease the rate of mass loss, in line with the fact that mass loss mainly comes from unzipping. They however slightly increase the thickness of degraded layer. This is not surprising since the Thickness of Oxidized Layer (*TOL*) is often approximated by:

$$TOL^2 = D_{O2}.[O_2]/r_{OX} \tag{4}$$

Where D_{O2} is the oxygen diffusivity, $[O_2]$ the concentration in surface and r_{OX} the oxidation rate in surface. Here, it seems that *TOL* is hardly increased for ELIUM® V3 compared to ELIUM® V2. A possible explanation would be that $(D_{O2})_{ELIUM\ V2} \sim (D_{O2})_{ELIUM\ V3}$ and $(r_{OX})_{ELIUM®\ V3} < (r_{OX})_{ELIUM®\ V2}$. This difference in oxidation rate is expected since ELIUM® V3 contains antioxidants.

4.3. Degradation of ELIUM® ATH

The aim of this section is to comment on the effect of ATH on the degradation of ELIUM® resin. Let us start by discussing the mechanisms responsible for mass loss in ATH filled composites. Three mechanisms can be proposed:

- Dehydration of filler.
- Thermolysis of matrix (for instance by unzipping).
- Thermal oxidation of matrix.

To understand the oxidation effects, mass loss can be plotted vs reciprocal thickness (Fig. 10) for the domain where thickness plays the most important effect (in other words where oxidation might the more visible).

Let us recall that if thermal processes (unzipping) are negligible compared to oxidation, the plot of mass loss rate vs reciprocal thickness would display a "plateau" at low thicknesses and a linear increase at high thicknesses with mass loss rate tending towards 0 for very high thicknesses. Interestingly, we observe here that:

- The ratio between the rates corresponding to fully oxygenated sample (0.3 mm thick) and 4 mm thick sample i.e. 13 times thicker) is almost 2 which is considerably lower than epoxies for example [27].
- The limit when reciprocal thickness tends towards 0 (k_0) is very close to the extrapolated value from Fig. 9 (see Table 4). For the samples of high thickness, the comparison of k_0 and "true" mass loss rate proves the coexistence of unzipping compared to oxidation, oxidation being lower than unzipping but not negligible.

The ageing rate was thus discussed from data given in Figs. 1 and 4 using:

$$\frac{\Delta m}{m_0} = w_A.\left(\frac{\Delta m}{m_0}\right)_A + w_{ATH}.\left(\frac{\Delta m}{m_0}\right)_{ATH} + w_B.\left(\frac{\Delta m}{m_0}\right)_B \tag{5}$$

where A, ATH and B correspond to acrylic resin, aluminum trihydrate, and zinc borate respectively, w_i are the relative fraction in weight of each component and ($\Delta m/m_0$) their relative mass loss (estimated from Fig. 4).

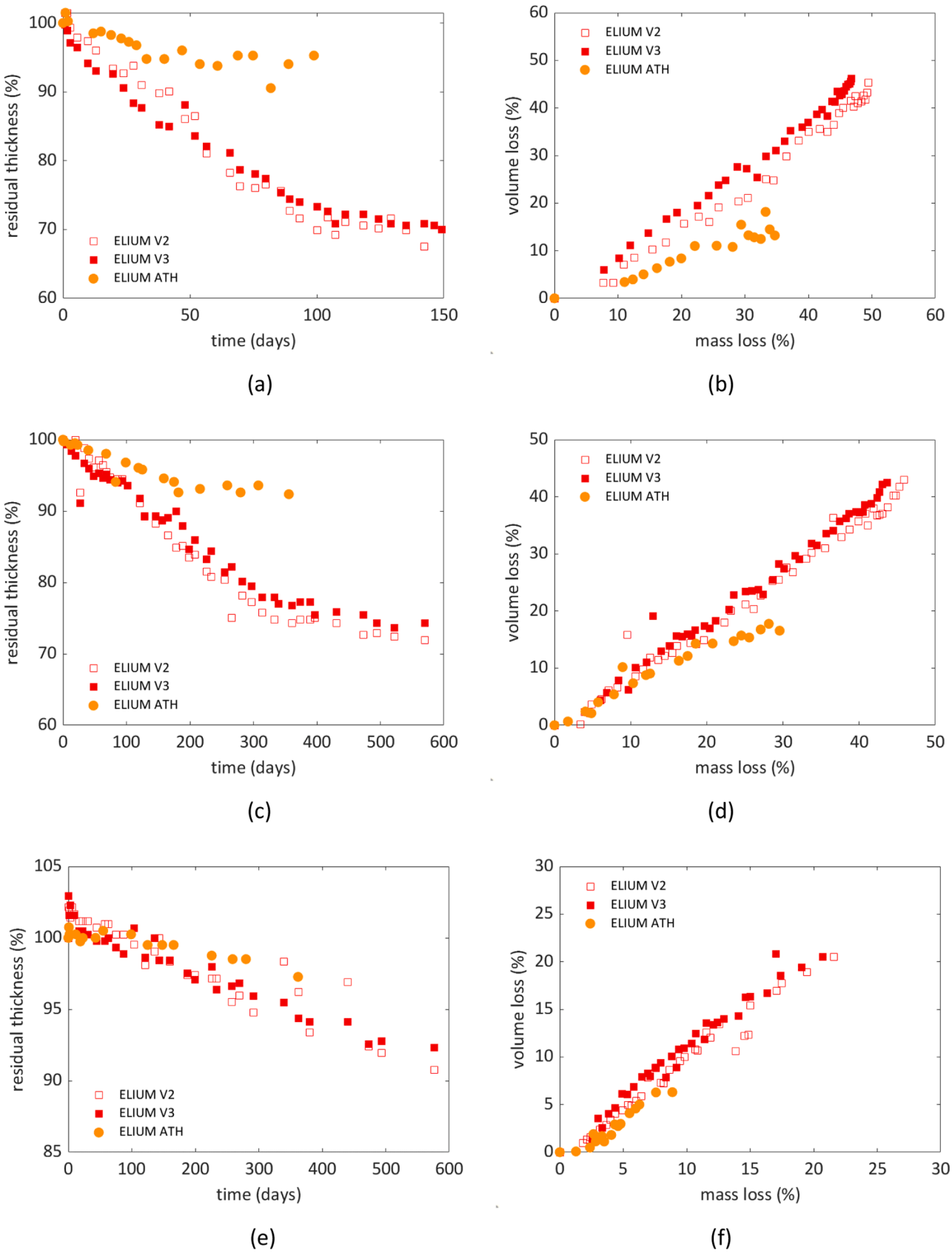


Fig. 8. Residual thickness changes versus exposure time (a, c, e) and volume changes vs mass changes (b, d, f) at 200 °C (a, b), 180 (c, d) and 160 °C (e, f) for ELIUM® V2, ELIUM® V3 and ELIUM® ATH composite.

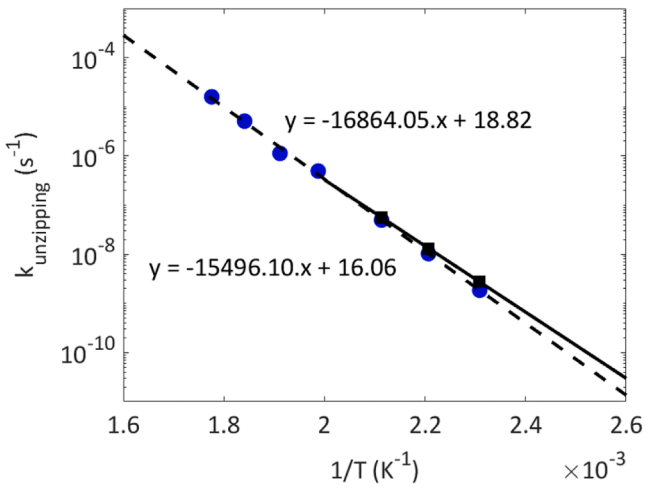


Fig. 9. Arrhenius diagram of the apparent rate constant for unzipping measured by TGA under nitrogen (•: data at 230–290 °C [13]) and from gravimetric curves fitting (■: 160–200 °C - Fig. 3) for ELIUM® V2.

Table 3
Code for simulations in Fig. 1.

Simulation	Direct extrapolation of Fig. 9 data	Best fit	Direct extrapolation of Fig. 9 data + Eq. (4)	Best fit for ELIUM® V3 + Eq. (4)
Resin	ELIUM® V2 and V3	ELIUM® V2 and V3	ELIUM® ATH	ELIUM® ATH
Graphical code	–	- -	•••	• -

It is noteworthy that extrapolations using Eqs. (1) and (4) (i.e. in the case of pure unzipping process) underestimate the mass loss, even if at low degradation levels (steps 1 and 2), there is a certain agreement between experimental data and those coming from the theoretical value of unzipping rate. The discrepancy between model and experimental data is more important for ELIUM® ATH than for ELIUM® V3 in particular at high conversion degrees. This can be explained from the fact that oxidized layers are deeper for ELIUM® ATH composites than for ELIUM® V3 (which is unfilled). The oxidized layers can be predicted from Eq. (4). This suggests that the difference of TOL between ELIUM® V3 and ELIUM® ATH is due to a higher oxygen diffusivity in the composite than in the pure matrix. Since oxygen diffusion becomes significant for ELIUM® ATH samples, Eqs. (1) and (2) were considered as oversimplified and no simulations are given (for example in Fig. 3).

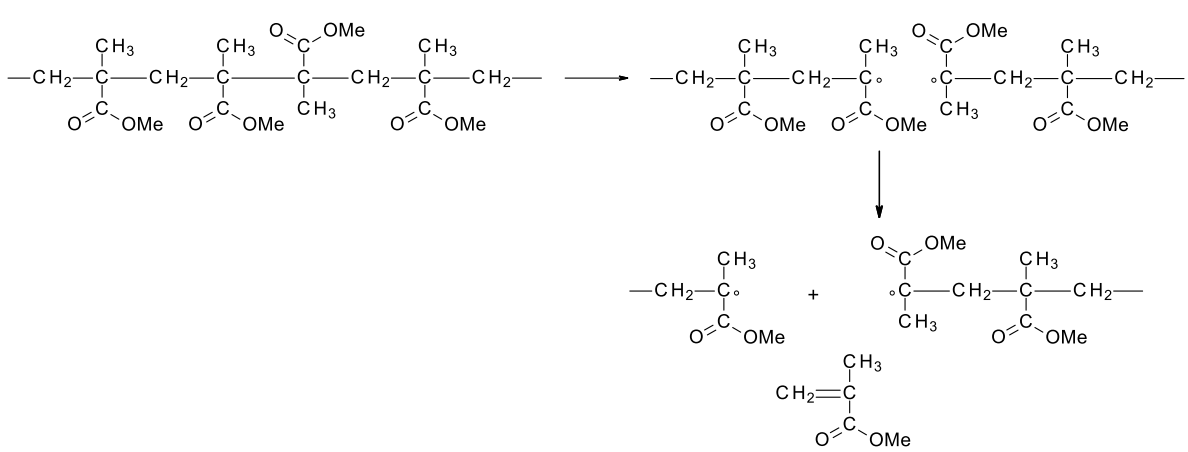
Let us now turn to the prediction of hydrogen content, which an important requirement for example for neutronic shields used in the transports of radioactive wastes [18]. For ELIUM® ATH, hydrogen content is about 5%. This value is in good agreement with the estimate made for each single component (Table 5) using Eq. (7):

$$\%H = \Sigma w_i.H_i \tag{7}$$

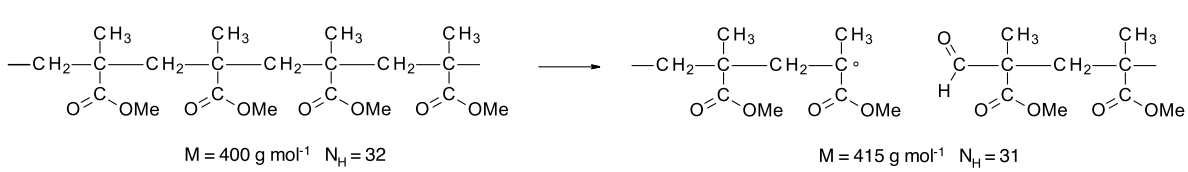
w_i being the mass ratio of each component and H_i the hydrogen content.

In the case where the only possible degradation occurring in the ELIUM® ATH composite would be the dehydration of ATH, the relative mass loss would become equal to 21%. ATH ratio becomes 0 meanwhile Al_2O_3 ratio increases up to 51.6%. Hydrogen content drops from 5.05% to 2.75% (−45%) meaning that $(\%H - \%H_0)/\%H_0 \sim 2.\Delta m/m_0$ which is clearly higher than in Fig. 5, because the decrease in H content also originate from the degradation of ELIUM® resin.

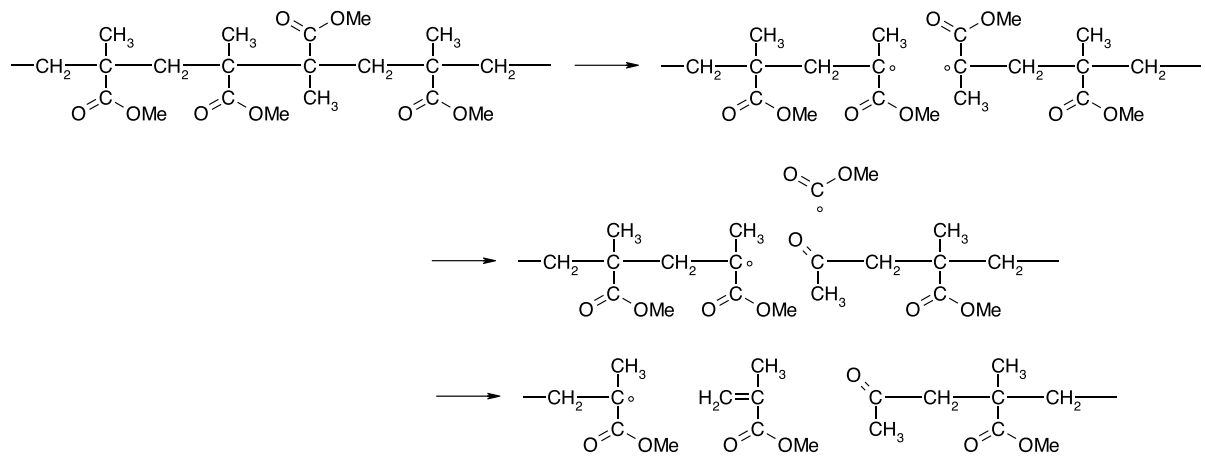
Let us consider at the same time the degradation of ELIUM® V3 resin, ATH and Zinc Borate. By selecting data in Figs. 1 and 5 for some well-chosen degradation times, the mass loss for each component, the mass loss in the composite (Eq. (5)), and the residual hydrogen content (Eq. (7)) were estimated. The resulting hydrogen content (for a given mass moss) is represented by dashed line in Fig. 5 and simulates particularly well the small positive concavity experimentally observed. The capability of those simple equations to predict this specific trend from the degradation of each simple component suggests that ATH, Zinc Borate and ELIUM® resin degrade separately without any interaction with the other components. Even if it remains to be studied more carefully, this preliminary result suggests that a simple model allowing to predict the degradation rate of each component can be later used to predict the residual hydrogen content.



Scheme 1. Unzipping mechanism.



Scheme 2. Depicted degradation of ELIUM® resin by oxidation.



Scheme 3. Depicted degradation of ELIUM® resin by oxidation + unzipping.

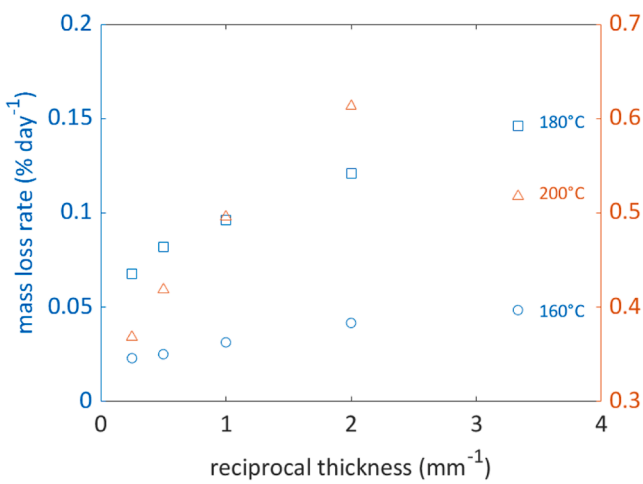


Fig. 10. Mass loss vs reciprocal thickness for ELIUM® ATH blocks aged at 160, 180 (left axis) and 200 °C (right axis).

Table 4
Comparison of apparent unzipping rate constant (%.day^{-1}) and mass loss rate for infinite thickness sample (from intersect value at origin in Fig. 10).

T (°C)	k_{obs} (%.day^{-1})	k_0 (%.day^{-1})
200 °C	0.43	~ 0.3
180 °C	0.089	~ 0.05
160 °C	0.016	~ 0.02

Table 5
Estimate of hydrogen content in ELIUM® ATH. w_i is the weight fraction,%H the hydrogen content of each component and%$H \times w_i$ the resulting hydrogen content in the composite.

	ELIUM®	ATH	Zinc Borate	ELIUM® ATH
w_i	0.32	0.62	0.06	
%H	8	3.85	1.6	
%$H \times w_i$	2.56	2.38	0.096	5.04

5. Conclusions

This paper describes the thermal degradation of ELIUM® resin and its composites loaded with mineral filler. Using an incremental approach, it was observed that this polymer is more stable when co-monomers are added, provided those latter slow down the possible thermally induced unzipping. On the contrary, thermal stabilizer do not significantly slow down the degradation kinetics, which has been explained from the fact that thermal unzipping predominates over oxidation effect. In the case of particle filled composites, the oxidation seems to be more important, in relation with the possible increase of oxygen diffusivity due to the presence of fillers (this effect might be more or less visible depending on fillers granulometry). Basing on a previous work, a set of equations was then used for the first time for describing mass loss in ELIUM® resin and its composites.

CRediT authorship contribution statement

Mohamed Souheib Chebil: Formal analysis, Investigation, Data curation. **Pierre Gerard:** Resources, Writing – review & editing. **Hervé Issard:** Conceptualization, Methodology, Supervision. **Emmanuel Richaud:** Formal analysis, Investigation, Conceptualization, Methodology, Validation, Visualization, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.polymdegradstab.2023.110367.

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