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THERMAL STABILITY OF ELIUM® RESIN AND ITS COMPOSITES

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Abstract: *This paper deals with the thermal ageing of ELIUM® based composites filled with mineral fillers (aluminium trihydrate in particular) and corresponding matrices. The ageing of thin films and thick blocks was investigated by gravimetry. The comparison of matrices with an incremental complexity highlighted the effect of comonomers and thermal stabilizers. In all cases, unzipping was shown to be the predominant source of mass loss but oxidation seems also to be involved in the case of ageing under air. The existence of this latter was confirmed by the existence of a brown surface layer. This oxidized layer was shown to be deeper for filled composites than unfilled matrices, suggesting that fillers favor the oxygen diffusion into the bulk.*

Keywords: Acrylic resin; Aluminium Trihydrate; Thermal oxidation; Kinetic modeling;

1. Introduction

ELIUM® resin is increasingly used as matrix for composites with the advantage of a low viscosity reactive mixture containing methyl methacrylate [1,2] which can be polymerized at moderate temperature using an organic peroxide [3]. It can thus be easily processed using the common tools used for thermoset matrix based composites (infusion, RTM…). Another of its great advantage is that the monomer can be recovered by the classical depolymerization method allowing to recover feedstock. Its use can for example be envisaged for manufacturing several parts needed for satisfying the societal need of low carbon energy: wind blades [4], or liquid hydrogen tanks [5].

ELIUM® resin suffers, however, from the well-known poor flame resistance common to all the members of the acrylic polymers family, such as PMMA for instance. This deficiency can be solved, for example, using flame retardants, among them aluminum trihydrate. Another issue is the relatively low feedback in terms of long term stability. In particular, the lifetime prediction makes necessary to determine the degradation rate, which can be achieved using a kinetic model based on the degradation mechanism.

Finally, the aim of this paper is to establish a first kinetic model for ELIUM® resin, and check its validity for Flame Retardant additivities resin. Since composites are usually thick parts, we will also address the so called diffusion limited oxidation effect. For that purpose, thin and thick samples of various kinds of ELIUM® resin (differing by the content of comonomers, stabilizers, and Flame retardant fillers) will be isothermally aged at several temperatures under several atmospheres (under nitrogen or in presence of oxygen) so as to derive a first kinetic model.

2. Materials and methods

Three kinds of unfilled acrylic resins were studied here as 4 mm thick plates samples:

- ELIUM® V1 is an acrylic resin synthesized from a MMA syrup.

- ELIUM® V2 is synthesized from the same reactive mixture than V1 (MMA syrup) to which butanediol dimethacrylate and methacrylic acid were added.

- ELIUM® V3 is made from ELIUM® V2 reactive mixture with an antioxidant package.

Composites (denoted by ELIUM® ATH) were made of ELIUM® V3 loaded with aluminium trihydrate (62% in weight) and Zinc borate (6% in weight). 4 mm thick plates were isothermally aged in ventilated ovens at 180°C.

50 µm thin films of ELIUM® V1 and V2 were obtained by micrototomy. They were in situ aged in TGA cell at temperatures ranging from 230 to 270°C either under pure nitrogen or pure oxygen flow.

4 mm thick ELIUM® V1, V2 V3 and ATH plates were isothermally aged in ventilated ovens at 180 under air. Their ageing was followed by gravimetry and microscopic observations. For ELIUM® ATH samples, 10 mm blocks were used for the microscopic observations.

To better understand the degradation of this composite, the stability of aluminium trihydrate and zinc borate was also investigated under air at those temperatures by gravimetry.

3. Results and discussion

3.1 Stability of thin films of pure ELIUM® resin under nitrogen

The stability of ELIUM® V1, V2 and V3 resin was first investigated by mass loss curves directly recorded in TGA cell. Examples are given in Figure 1 for ELIUM® V2 resin. It can be seen that samples display (i) a first very quick mass loss step expected to correspond to VOC loss in low content, (ii) an auto-decelerated mass loss step (Figure 1). Some T_g measurements were realized by DSC on ELIUM® V1 resin. It was verified that, even after significant level of mass loss (up to 40%). This mechanism was ascribed to an end chain unzipping mechanism [6].

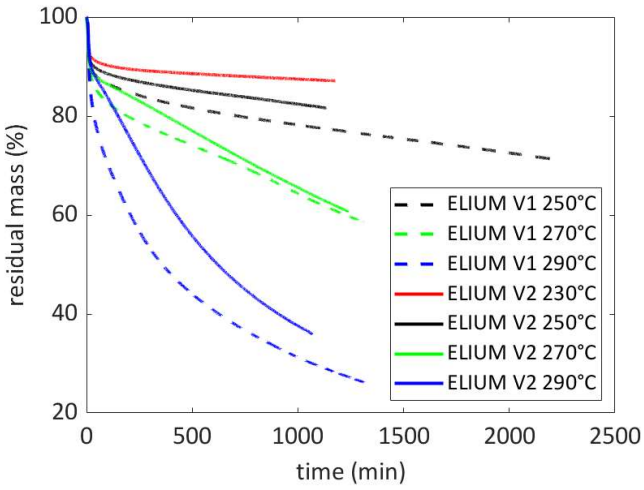


Figure 1. Mass loss curves of thin ELIUM® samples recorded by TGA under inert atmosphere.

In a first approach, its kinetics was depicted by the following equation:

$$\frac{m}{m_0} = \frac{m_{v_0}.\exp(-k_v.t)+m_{p_0}.\exp(-k_{unzipping}.t)}{m_{v_0}+m_{p_0}} \quad (1)$$

m_{v0} and m_{p0} corresponding respectively to the initial mass of residual VOC's and of polymer, k_v being the rate constant for the volatilization of VOC's and $k_{unzipping}$ corresponding to the apparent rate constant for the overall unzipping process.

This latter was estimated for both ELIUM® V1 and V2 and found higher for ELIUM® V1, in good agreement with the well-known role of acrylic comonomers for slowing down the unzipping rate as illustrated for example in PMMA [7].

3.2 Stability of thin films of pure ELIUM® resin under oxygen

In presence of oxygen, the mass loss curves display the same shape at early stage, but a strong auto-acceleration of mass loss is observed (Figure 2). The depletion of T_g was here clearly higher under air than under inert atmosphere indicating that a random chain scission occurs

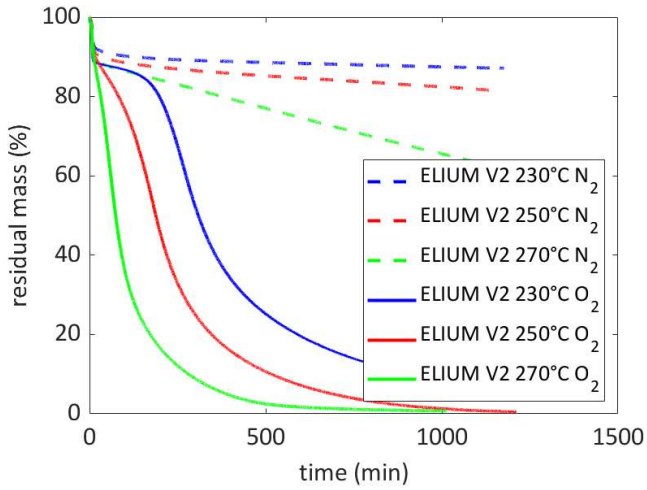


Figure 2. Mass loss curves of thin ELIUM® V2 samples recorded by TGA under N_2 or O_2 atmosphere.

3.3 Stability of thick blocks of ELIUM® resin and its composites under air

Those investigations were used to understand the ageing behavior of thick blocks of ELIUM® and its composites at high temperatures under air, i.e. in conditions closer to the service condition of organic composites. Figure 3 depicts the mass loss of 4 mm blocks.

ELIUM® V1 resin, which has neither comonomers nor antioxidants, is the less stable meanwhile there is a weak difference between ELIUM® V2 and V3 resins. The difference in terms of mass loss between ELIUM® V1, V2 and V3 is very visible on the first stage (before 100 days). After this duration, the apparent mass loss rate seems to reach a value which is almost constant for the 3 systems under investigation at longer times.

There is no evidence of the very strong auto-acceleration associated to oxidation suggesting that the oxidation plays only a negligible role on mass loss.

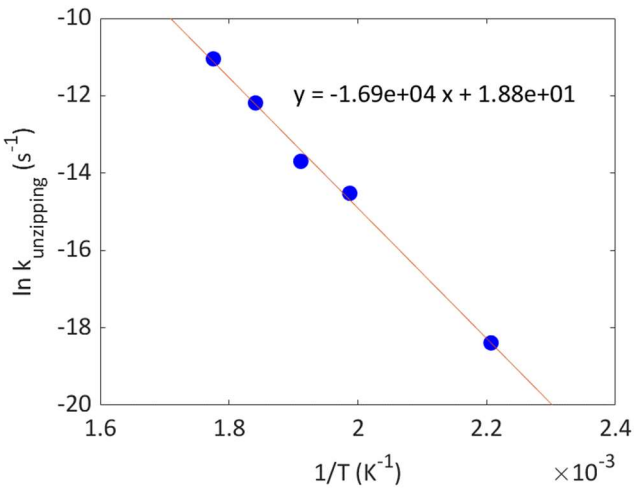


Figure 3. Arrhenius diagram of unzipping rate constant estimated for ELIUM® V2 samples from TGA under N_2 (from Figure 1).

For example, the extrapolation of $k_{unzipping}$ from estimated from Figure 1 allows a very reasonable fitting of ELIUM® V2 and V3 (Figure 4). The slight difference between experimental curves and simulation could be testimony of the existence of a minor oxidation process with a negligible effect on mass loss. Interestingly, the fact that antioxidants present in ELIUM® V3 do not modify the mass loss rate compared to ELIUM® V2 also confirms this hypothesis.

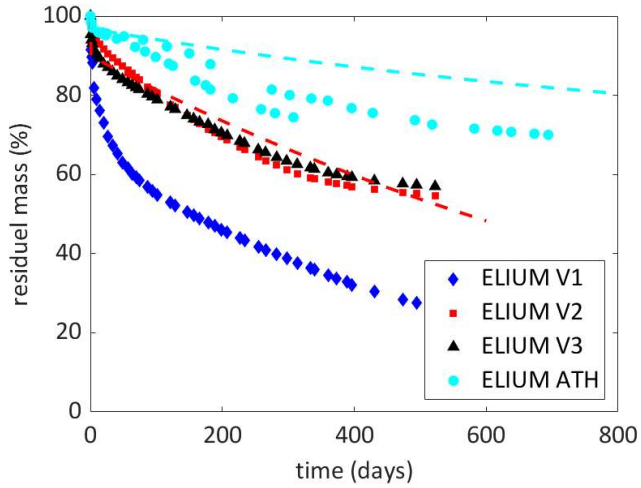


Figure 4. Mass loss curves of 4 mm thick ELIUM® V1, V2, V3 and ELIUM ATH samples at 180°C under air. Dashed lines correspond to simulated mass loss using Eqs. 1 and 2.

ELIUM® ATH composite is the more stable formulation, which can be discussed in the following, having in mind that ELIUM® resin on one side, and fillers on the others, can degrade. To better understand the behavior of this composite, fillers were aged alone (Figure 5). They can be

observed to be almost stable at the temperature under investigation, keeping in mind that, for example, aluminium trihydrate degraded by dehydration:

$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$ so that the total process induces a mass loss equal to 35%.

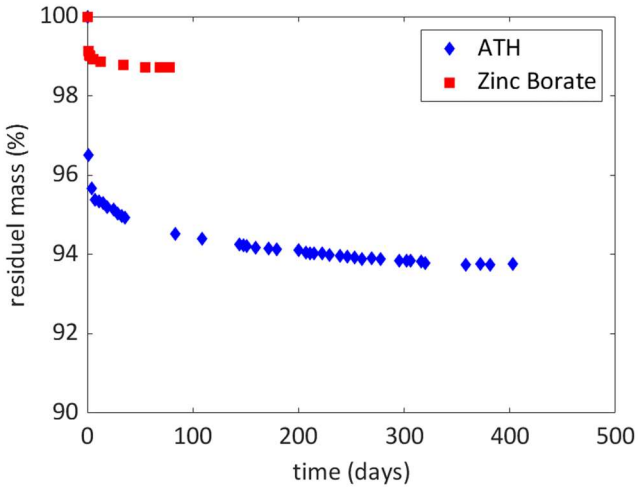


Figure 5. Mass loss curves of zinc borate and aluminium trihydrate at 180°C under air.

The mass loss of A-ATH was thus simulated using:

$$\frac{\Delta m}{m_0} = w_A.\left(\frac{\Delta m}{m_0}\right)_A + w_{ATH}.\left(\frac{\Delta m}{m_0}\right)_{ATH} + w_B.\left(\frac{\Delta m}{m_0}\right)_B \quad (2)$$

where A, ATH and B respectively correspond to ELIUM® resin, aluminium trihydrate, and zinc borate, and w_i are the relative fraction in weight of each component and $(\Delta m/m_0)$ their relative mass loss. The mass loss of ELIUM® composite was thus predicted using Eq 1 for the mass loss of ELIUM part, $k_{unzipping}$ extracted from Figure 3 (as a direct extrapolation of values derived from TGA measurements under inert atmosphere at 230-290°C), $(\Delta m/m_0)_{ATH}$ and $(\Delta m/m_0)_B$ from Figure 4.

The discrepancy between experimental results and this very simple simulation can be interpreted by two ways:

- either the extrapolated $k_{unzipping}$ value is not reliable.

- or there is a “synergy” between degradation of ELIUM® resin and degradation of fillers. One could imagine, for example, that ATH favors the degradation of acrylic group, or that degradation products of ELIUM polymer degrade the ATH filler.

- either oxidation has a more pronounced effect in A-ATH blocks than in ELIUM® samples of comparable thickness, which can be discussed in terms of thickness of degraded layers

This last hypothesis was discussed from the thickness of oxidized layers observed by optical microscopy (Figure 6). The following observations were made:

- for ELIUM® V2 and ELIUM® V3, the overall thickness decreases in line with unzipping and oxidation induced mass loss.

- the existence of dark edges is characteristic of the oxidation of surface layers, meanwhile the progressive browning observed in the “core” region of the thick blocks is testimony of the existence of chemical modifications in zones where no oxidation occurs.

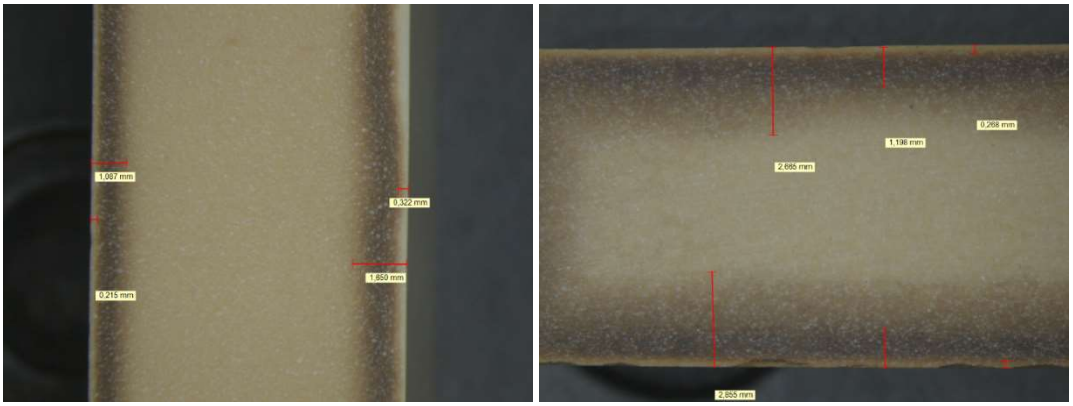
- the thickness of degraded layer is slightly higher for ELIUM® V3 than for ELIUM® V2. Keeping in mind that the thickness of oxidized layer (TOL) can be approximated from:

$TOL^2 = Pe_{O2}/r_{OX}$, Pe_{O2} being the oxygen permeability and r_{OX} the rate of oxygen consumption in surface, results given in Figure 6 may come from the fact that either stabilizers inhibit the polymerization and induce a lower “crosslinking density in ELIUM® resin, and thus a high value for oxygen permeability or (ii) stabilizer decrease the oxidation rate in surface.

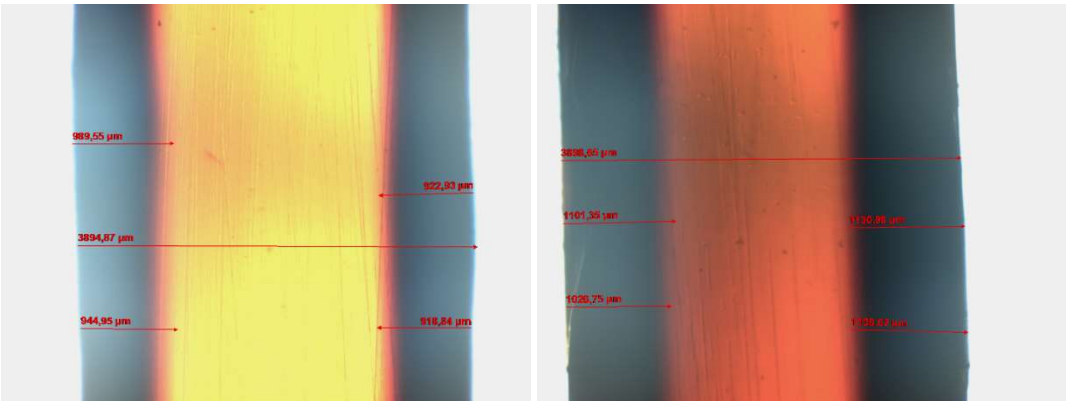
In the case of ELIUM® ATH, a white surface layer is observed. This layer could be constituted of ATH, this latter being almost stable at 180°C (Figure 4) or Al_2O_3. The degraded layer is slightly more degraded (1.5 – 2 mm) than for unfilled resins (about 1-1.2 mm). Since ELIUM® ATH is made from ELIUM® V3, the only possible explanation is that the presence of filler favors the diffusion of oxygen from edge to the bulk.

4. Conclusions

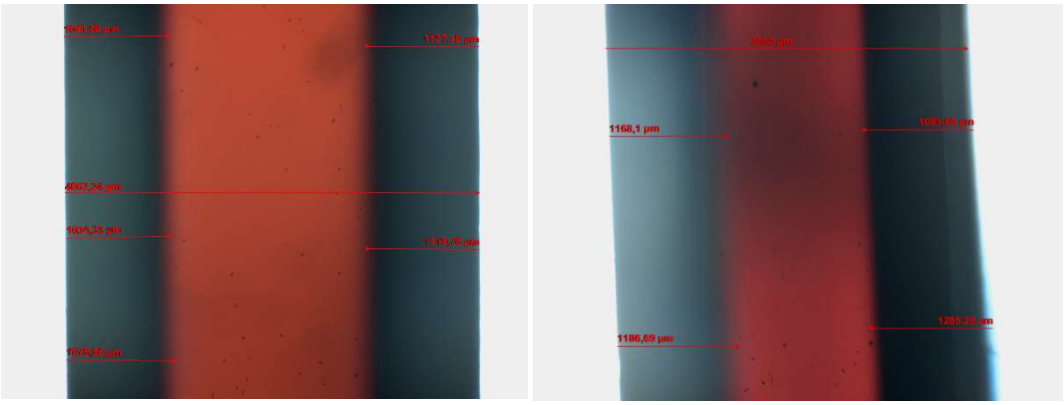
This paper describes the thermal ageing of ELIUM® and its composites. By using an incremental approach, it was observed that this polymer is more stable when comonomers are added, provided those latter slow down the possible thermally induced unzipping. On the contrary, thermal stabilizer hardly slow down the degradation kinetics, which was explained from the fact that thermal unzipping predominates over oxidation effect. In the case of particle filled composites, the oxidation seems increases, in link the possible increase of oxygen diffusivity due to fillers presence.



(a) (b)



(c) (d)



(e) (f)

Figure 7. Microscopic observations of ELIUM® ATH aged 1 month (a) and 4 months (b), ELIUM® V2 aged 1 month (c) and 3 months (d), ELIUM® V3 aged 1 month (e) and 11 months (f) at 180°C under air (thickness of samples is close to 4 mm for ELIUM® V2 and ELIUM® V3 and 10 mm for ELIUM® ATH).

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