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Effect of preparation conditions on the thermal stability of an epoxy-functional inorganic–organic hybrid material system doped with Zr

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Abstract

An inorganic–organic hybrid material system consisting of (3-glycidyloxypropyl)trimethoxysilane, dimethyldimethoxysilane and zirconium(IV) *n*-propoxide was prepared by the sol–gel method. The influence of processing parameters including Zr content, UV irradiation and sol ageing on the thermal stability of the resultant thin films was characterised by thermogravimetry. It was demonstrated that the crosslinking of epoxy groups in the structure was the primary reason for variation in the thermal stability of the system. As Zr and/or UV irradiation may be employed to crosslink the epoxy groups in the structure, the thermal stability of the system can be tuned by the optimal combination of these two crosslinking methods.

Keywords: Sol–gel method; Organically modified silane; Crosslinking; Thermal stability

1. Introduction

Inorganic–organic hybrid sol–gel derived material systems play an important role in the development of optical waveguiding devices and are of considerable interest for possible photonic interconnect and sensor applications [1–7]. The sol–gel method has several advantages over conventional methods such as chemical vapour deposition or flame hydrolysis deposition to obtain such materials [8,9].

Inorganic–organic hybrid materials, which contain crosslinkable functional groups such as acrylate or methacrylate are most commonly used at present [10]. An advantage of epoxy-based systems is that, crosslinking of the epoxy functional groups can be achieved either by a suitable catalyst or by irradiation with UV or visible light in the presence of a suitable photo-initiator [11,12]. In addition to Si containing precursors, alkoxy compounds of transition metals such as Ti or Zr can also be involved in the sol–gel synthesis so that optical and physical properties can be tuned [10,11,13]. This is typically performed to optimise the refractive index of the cladding region in a planar waveguide device in order to minimise insertion losses. Currently Zr is the dopant of choice, as its reactivity can be more carefully controlled via complexation reactions, than that of Ti. Therefore, the compatibility of Zr dopant with epoxy-functionalised inorganic–organic hybrid material systems is of considerable interest.

In our previous study [14], a hybrid material system consisting of (3-glycidyloxypropyl)trimethoxysilane (GDPTMS), dimethyldimethoxysilane (DMDMOS) and zirconium(IV) *n*-propoxide ($Zr(OPr^n)_4$) was synthesised via the sol–gel route with different Zr compositions. The influence of Zr content, UV irradiation time, and sol ageing on the optical and physical properties of the system was evaluated. In this present article, the influence of the same parameters on the thermal stability of this material system is presented. The comparative crosslinking effects of Zr and UV irradiation on the thermal stability of the resultant films were detailed for the first time.

2. Experimental

The synthesis was described in detail previously [14], and is outlined in Scheme 1. The chemical structure of the precursors

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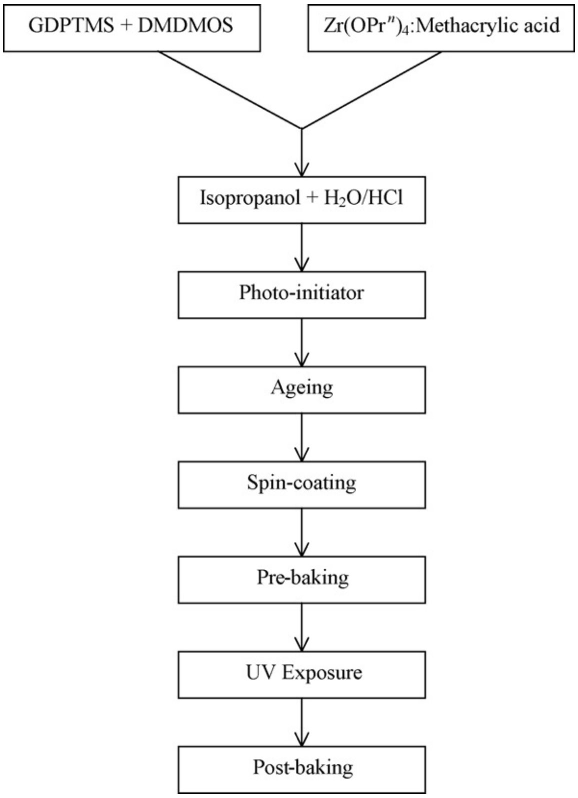

Scheme 1. Outline of the synthesis.

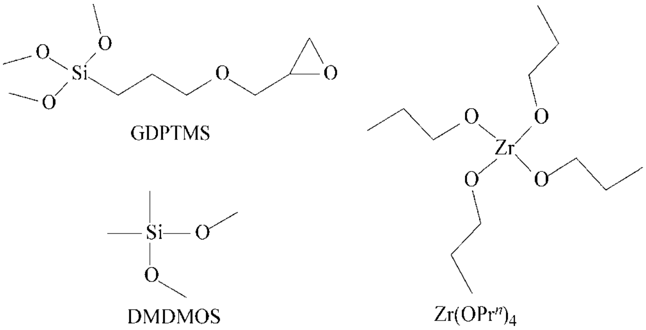

Fig. 1. Chemical structure of the precursors used.

used is given in Fig. 1. A Polymer Laboratories (Rheometric Scientific) TGA1000M model thermogravimetric analyser was employed to measure the thermal stability of the samples. The measurements were performed either in static air, in order to simulate the real conditions in which the materials would be used, or in nitrogen atmosphere. A heating rate of 10 °C/min was used in all analyses. The data reading from the TGA curves was done by taking the average of the numerical round-off limits; the plus–minus values in the tables correspond to these limits.

3. Results and discussion

3.1. Effect of Zr content and UV irradiation

The influence of Zr content on the thermal stability of both the unexposed and the UV-exposed (5 min) samples was investigated. Fig. 2(a) and (b) show the dynamic thermograms

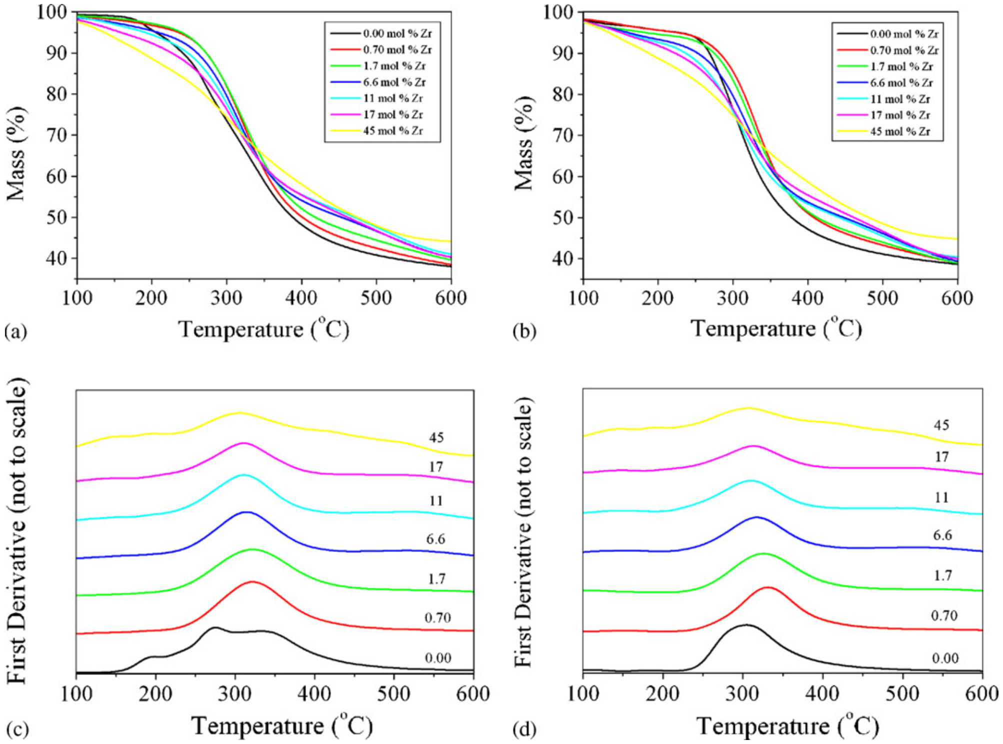

Fig. 2. Dynamic thermograms of the unexposed (a) and the UV-exposed (5 min) (b) materials in air. First derivative curves of the dynamic thermograms of the unexposed (c) and the UV-exposed (5 min) (d) materials in air. (Numbers on the curves correspond to Zr content (mol%).)

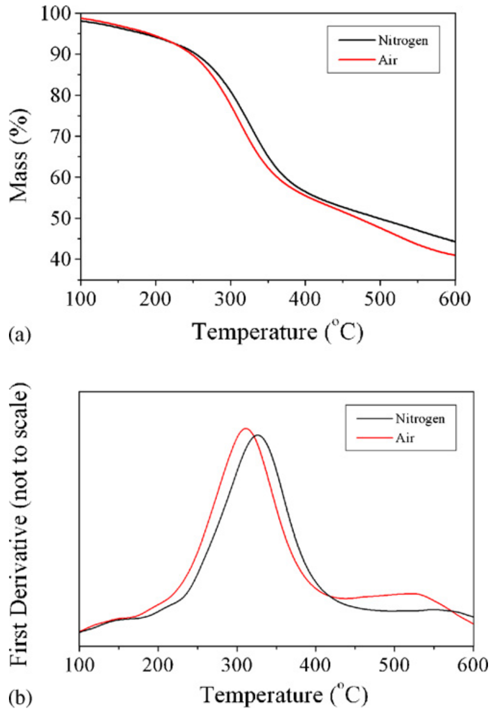

Fig. 3. Dynamic thermograms of the sample containing 11 mol% Zr, in air and in nitrogen (a). First derivative curves of the dynamic thermograms of the sample containing 11 mol% Zr, in air and in nitrogen (b).

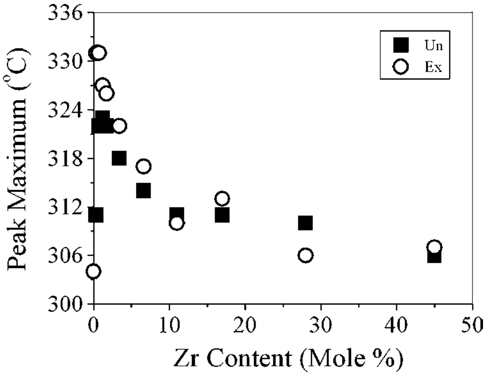

Fig. 4. Variation of temperature, at which the decomposition rate is maximum, with Zr content (Un: unexposed; Ex: UV-exposed (5 min)).

of the samples in air. The unexposed sample, which contained no Zr, exhibited multi-step mass loss upon heating. This was also evident from the first derivative curve in Fig. 2 (c). The peak around 200 °C most likely corresponds to the thermal decomposition of the species related to the epoxy rings in the structure [15]. The other peaks correspond to the thermal decomposition of the remaining organic structure. The UV-exposed sample, which contained no Zr, exhibited a one-step mass loss that corresponds to the thermal decomposition of the main organic structure. This can also be seen from its first derivative curve in Fig. 2(d). This difference between the unexposed and the UV-exposed samples indicates that the crosslinking occurred via epoxy ring opening upon irradiation with UV light. When Zr was involved in the structure, the thermal decomposition profile became two-step for both the unexposed and the UV-exposed samples. The formation of a second step around 520 °C showed that the decomposition profile changed upon addition of Zr. This can be explained as the thermooxidative decomposition of the residual, which forms in the first decomposition stage [16,17]. Increasing the amount of Zr increased the amount of the residual. The comparison of the thermograms and their first derivative curves of the unexposed sample, containing 11 mol% Zr, obtained in air and nitrogen atmospheres, respectively, further supported this idea (Fig. 3(a) and (b)). It was observed that the decomposition at around 520 °C did not occur in the sample, which was run under nitrogen atmosphere.

The determination of the temperatures, at which 10 and 50% mass losses occurred, was also investigated to further assess the thermal stability of the materials. Table 1 shows the variation of the temperature, at which 10% mass losses occurred, with Zr content. (This table includes some additional data, since not all the thermograms and their first derivative curves are presented in Fig. 2(a)–(d), for the sake of clarity.) An increase, up to around 1 mol% Zr, and then a gradual decrease was observed. This increase can be ascribed to the crosslinking of epoxy groups in the structure. It is known that Zr has a catalytic effect on epoxy crosslinking [11,14]. The disappearance of the first peak, upon addition of Zr, in the first derivative curve of the unexposed sample was also evidence for that effect. With Zr contents lower than approximately 2 mol%, this effect increased the thermal stability of the materials in terms of the temperature, at which 10% mass loss occurred, whereas further addition of Zr decreased it. One factor for this decrease is the relative dilution of epoxy crosslinks in the structure with increasing Zr content. Another probable factor is that transition metals can promote the thermooxidative decomposition of organic polymers [18]. This latter effect could also have resulted in the increase in the amount of the residual, which decomposed at higher temperatures. This,

Table 1
Variation of temperatures at 10 and 50% mass loss with Zr content

	Zr content (mol%)										
	0.00	0.35	0.70	1.2	1.7	3.4	6.6	11	17	28	45
10%											
Un	241 ± 3	266 ± 2	273 ± 2	274 ± 2	272 ± 2	268 ± 2	261 ± 3	248 ± 4	226 ± 5	205 ± 5	187 ± 5
Ex	269 ± 1	285 ± 2	282 ± 3	272 ± 3	275 ± 3	270 ± 3	253 ± 4	241 ± 4	223 ± 5	206 ± 6	188 ± 5
50%											
Un	388 ± 3	397 ± 4	401 ± 4	406 ± 4	418 ± 5	422 ± 6	453 ± 7	471 ± 6	461 ± 6	463 ± 5	475 ± 6
Ex	378 ± 3	399 ± 4	408 ± 4	396 ± 4	412 ± 5	430 ± 6	448 ± 7	448 ± 7	461 ± 6	470 ± 6	482 ± 6

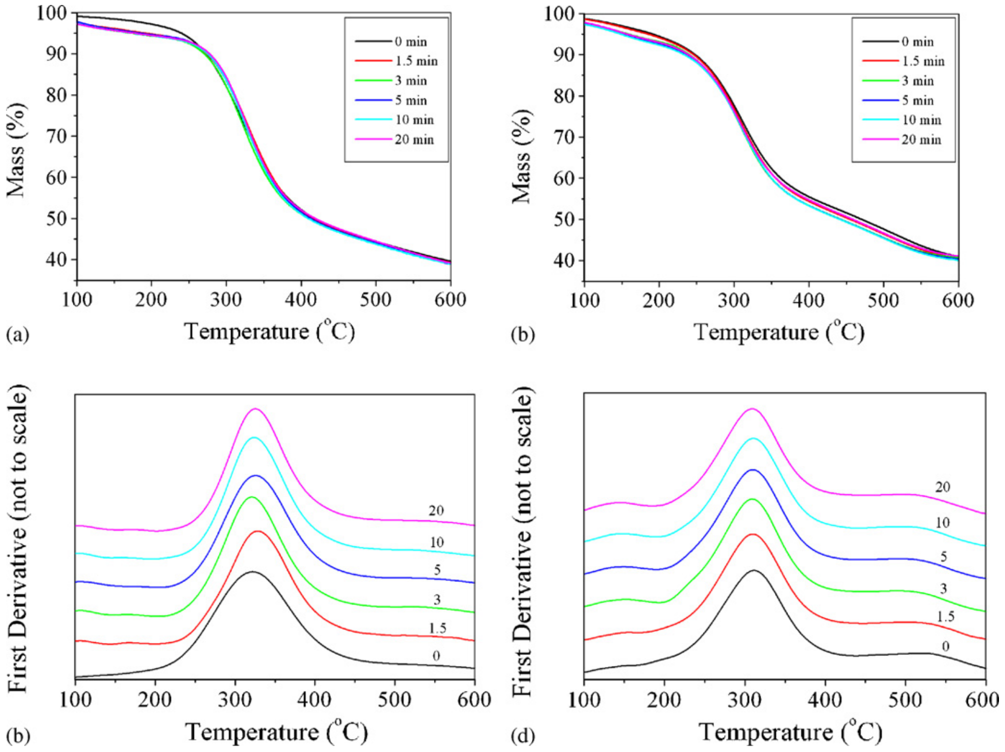

Fig. 5. Dynamic thermograms of the materials containing 1.7 and 11 mol% Zr (a) and (b), respectively, in air. First derivative curves of the dynamic thermograms of the materials containing 1.7 and 11 mol% Zr (c) and (d), respectively, in air. (Numbers on the curves correspond to the UV exposure time in minutes.)

therefore, increased the temperature, at which 50% mass loss occurred (Table 1). The results were more or less the same for both the unexposed and the UV-exposed samples except those, which did not contain Zr. In this case, UV irradiation was dominant in the crosslinking of the epoxy groups.

The peak maxima, which correspond to the maximum decomposition rate, of the first derivative curves of the thermograms were also used to follow the effect of Zr content on the thermal stability of the materials and are given in Fig. 4. (This figure includes some additional data for the same reason as for Table 1.) A sudden increase and then a gradual decrease in the peak maximum temperature resulted from the same factors as for that at 10% mass loss. This effect could be followed only after the incorporation of the Zr into the structure for the unexposed samples, since the epoxy crosslinking was carried out only by the catalytic effect of Zr.

3.2. *Effect of UV exposure time*

The influence of UV exposure time was investigated for two representative sample sets, containing 1.7 and 11 mol% Zr. Fig. 5(a) and (b) show the dynamic thermograms of the samples, in air. The thermograms of the materials with 11 mol% Zr showed two-step decomposition profiles consistent with the previous results. UV irradiation was only effective at lower Zr concentrations (in this case 1.7 mol%). UV irradiation for 1.5 min was adequate to achieve the maximum epoxy crosslinking. After that irradiation time, there was no change in the materials in terms of thermal stability. This can also be seen from the first derivative curves of the corresponding thermograms in Fig. 5(c) and (d). The temperatures, at which 10 and 50% mass losses occurred, did not change significantly with increasing UV exposure time for both sets (Table 2). In addition, the peak maximum of the first derivative curves of the thermograms remained almost constant with UV irradiation time for both sets (Fig. 6). It can be said that, in general, UV exposure time has little or no effect on the thermal stability of the materials, which contain Zr. However, it has an appreciable effect on the thermal stability of the materials with no Zr, as, in this case, the epoxy crosslinking is carried out only by UV light.

3.3. *Effect of sol ageing*

The influence of sol ageing on the thermal stability of the material system, with 11 mol% Zr, for both the unexposed and

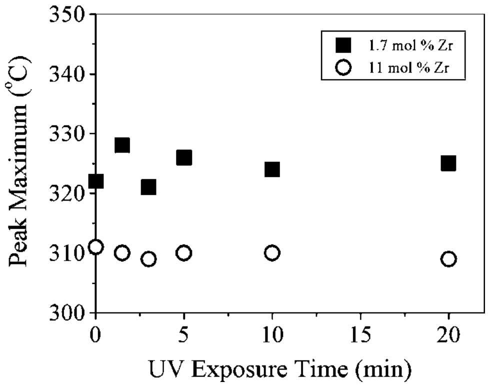

Fig. 6. Variation of temperature, at which the decomposition rate is maximum, with UV exposure time.

Table 2
Variation of temperatures at 10 and 50% mass loss with UV exposure time

	UV exposure time (min)					
	0	1.5	3	5	10	20
10%						
1.7 mol% Zr	272 ± 2	274 ± 3	271 ± 3	275 ± 3	275 ± 3	277 ± 3
11 mol% Zr	248 ± 4	242 ± 4	240 ± 4	241 ± 4	238 ± 5	239 ± 5
50%						
1.7 mol% Zr	418 ± 5	416 ± 5	410 ± 5	412 ± 5	409 ± 5	418 ± 5
11 mol% Zr	471 ± 6	455 ± 6	449 ± 7	448 ± 7	448 ± 7	453 ± 6

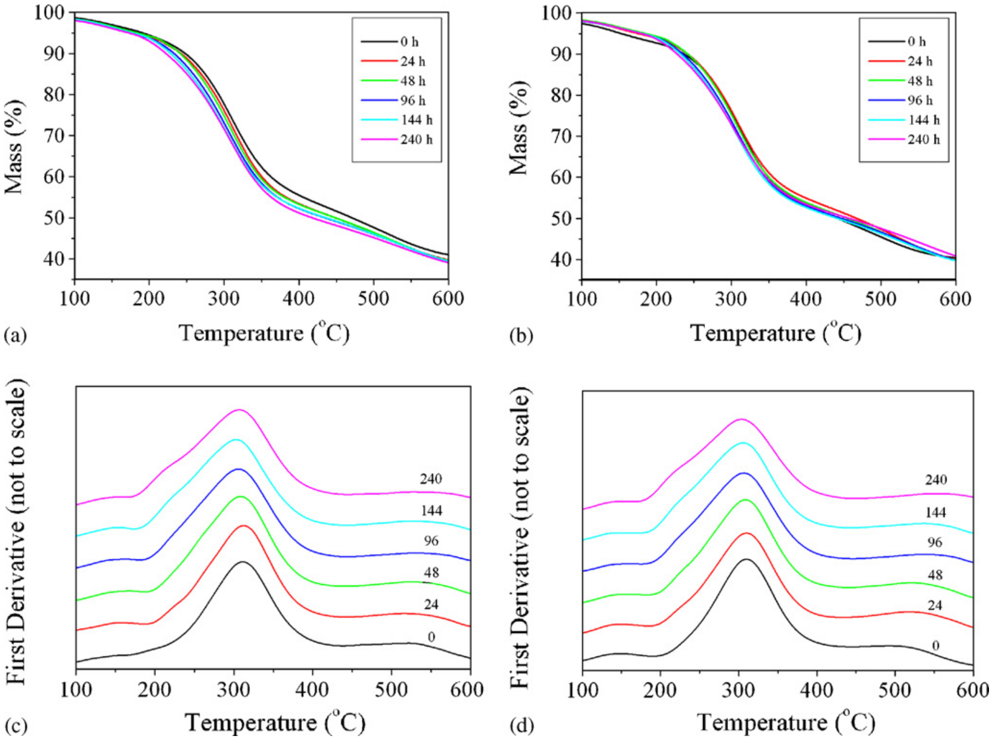

Fig. 7. Dynamic thermograms of the unexposed (a) and the UV-exposed (5 min) (b) materials in air. First derivative curves of the dynamic thermograms of the unexposed (c) and the UV-exposed (5 min) (d) materials in air. (Numbers on the curves correspond to the sol ageing in hours.)

the UV-exposed (5 min) samples, was also investigated. Fig. 7(a) and (b) show the dynamic thermograms of the samples, in air. The thermograms showed a two-step decomposition profile. The reason is as explained previously. The derivative curves of the corresponding thermograms are given in Fig. 7(c) and (d). It can be seen from Table 3 that the temperatures, at which both 10 and 50% mass losses occurred, tend to decrease with increasing sol ageing time. Increasing sol ageing time increased the relative number of –OH groups in the structure [14], which could have led to lower thermal stability. This could also result in the peak maximum of the first derivative curves of the thermograms shifting to lower temperatures (Fig. 8).

Table 3
Variation of temperatures at 10 and 50% mass loss with sol ageing

	Sol ageing (h)					
	0	24	48	96	144	240
10%						
Un	248 ± 4	242 ± 3	241 ± 3	233 ± 3	229 ± 3	222 ± 3
Ex	241 ± 4	242 ± 3	242 ± 3	235 ± 3	232 ± 3	228 ± 3
50%						
Un	471 ± 6	448 ± 8	448 ± 8	434 ± 8	436 ± 8	418 ± 8
Ex	448 ± 7	461 ± 7	455 ± 7	447 ± 8	441 ± 8	448 ± 9

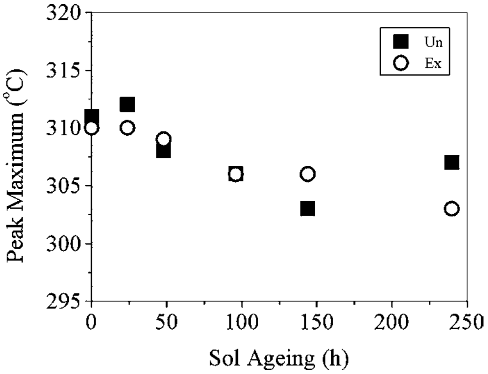

Fig. 8. Variation of temperature, at which the decomposition rate is maximum, with sol ageing (Un: unexposed; Ex: UV-exposed (5 min)).

4. Conclusions

An inorganic–organic hybrid material system with epoxy functional groups was prepared by the sol–gel method. The thermal stability of the system was characterised as a function of process variables including Zr content, UV irradiation, and sol ageing. It was shown that Zr, besides its role as a network former and a catalyst for epoxy crosslinking, can also promote the thermooxidative decomposition of the organic segments of the structure. UV irradiation time had little or no effect on the thermal stability of the materials, which contained Zr. However, it had an appreciable effect on the thermal stability of the materials with no Zr, as, in this case, the epoxy crosslinking was carried out only by UV light. Even though the sol ageing process did not change the decomposition profile of the materials, since the amount of –OH groups in the structure increased, the thermal stability of the materials decreased to some extent with increasing sol ageing time.

As both Zr and UV irradiation may be employed to crosslink the epoxy groups in the structure, the thermal stability of the system can therefore be tuned, to some extent, by adjusting the combination of these two crosslinking methods.

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