JOURNAL OF MATERIALS SCIENCE: MATERIALS IN MEDICINE **10** (1999) 91–98

Veneering composites – a thermoanalytical examination

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Differential thermal analysis and thermal gravimetric analysis were used to characterize veneering composites. Samples weighing 4–20 mg, made from the composite materials Visio-Gem (Espe, Germany), Sinfony (Espe, Germany), Artglass (Kulzer, Germany), Dentacolor (Kulzer, Germany) and Targis (Ivoclar, Liechtenstein), were examined. The samples were subjected to various thermal curing times of between 4 s and 25 min, using the relevant devices of the manufacturers. As a control group, samples of all materials were examined unreacted. In order to avoid post-curing during storage, all samples were subjected, immediately after manufacture, to the appropriate dynamic temperature programme of the thermoanalytical unit at a heating rate of 10 °C min^{-1}. The materials showed specific material characteristics which can, for instance, be used to analyse the curing behaviour of the materials. The position of the glass transition, polymerization and post-polymerization peaks at temperatures between 30 and 100 °C, as well as 150 and 300 °C, and the filler and matrix content, allow the classification of the veneering composites.

1. Introduction

Thermal analysis is a method of determining physical and chemical properties as functions of temperature (dynamic) or time (isotherm). The thermal analysis methods differential scanning calorimetry (DSC), thermogravimetry (TGA), differential thermal analysis (DTA), thermomechanical analysis (TMA), and thermodilatometry, have been described at length in a variety of publications, in general, for example, by Brazier [1], Baker and Lenkenby [2], Turi [3], Keattch and Dollimore [4], Mathot [5], and DIN 51005 [6], and with specific topics by, for example, Bischoff and Hennemann [7], Bourke *et al.* [8], Kaisersberger [9], and Fischer *et al.* [10]. The applications are directed principally at the synthetic and latex industries. DSC, DMA and TGA investigations of composites and light-curing composites, in particular, are described in dental literature by Taira *et al.* [11], Vaidyanathan *et al.* [12], Hosoya [13], Khan *et al.* [14], Clarke [15], Eliades *et al.* [16], Maffezolli *et al.* [17], McCabe and Wilson [18], Ruyter and Oysead [19], Watts *et al.* [20], and Ferracane and Greener [21]. The thermal analysis serves to determine the conversion processes (glass transition, curing behaviour, etc.), reaction heat and other thermal properties, as well as kinetic processes. Using these processes, the property changes (for instance, due to the effects of ageing, storage and processing) in various materials can be compared. Among other things, conclusions can be drawn from this material-specific evidence regarding mechanical or chemical behaviour (e.g. colour stability) [22]. Because of their complex structure of mono- and multifunctional monomers, inhibitors and photo-initiators, among other things, light-curing composite veneers are difficult to assess. The aim of this study was to carry out a thermoanalytical characterization of light/heat-curing dental composite veneers by the evaluation of the heat behaviour during the course of a dynamic investigation.

2. Materials and methods

Samples of the composite veneering materials Visio-Gem (Espe, Germany), Synfony (Espe, Germany), Artglass (Kulzer, Germany), Dentacolor (Kulzer, Germany), and Targis (Ivoclar, Liechtenstein), of weight from 4–20 mg, were produced. In the process due care was taken to restrict the thickness of the material on the sample to a maximum of 1 mm, because the thermal curing rate is partially dependent on the depth of light penetration [23]. The samples were subjected to various curing times lasting from 4 s to 25 min, using the appropriate manufacturers' appliances: Dentacolor XS (Kulzer), Targis Quick and Targis Power Oven (Ivoclar) and Alpha and Beta Ovens (Espe). In order to avoid post-curing, immediately after

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TABLE I Materials and methods. Overview of the study

	Targis	Visio-Gem	Synfony	Artglas	Dentacolor
Colour code	Body	E55	DB1	DB1	HB10
Batch no.	825562	049F	TW0034966	021	23
Manufacturers	Ivoclar, Liechtenstein	Espe, Germany	Espe, Germany	Kulzer, Germany	Kulzer, Germany
Device for polymerization	Targis Quick, (Targis Power)	AlphaOven, (BetaOven)	AlphaOven, (BetaOven)	Dentacolor XS	Dentacolor XS
Treatment	None	None	None	None	None
	1 period	1 period	1 period		
	2 period	2 period	2 period	10 s	10 s
		3 period	3 period		
		5 period	5 period	90 s	90 s
	25 min, Targis Power	15 min, BetaOven	15 min, BetaOven	180 s	180 s

Measurement (open pan/5 ml min^{-1})	Temperature course (10 K min^{-1})
DTA 1 (air atmosphere)	25 °C/600 °C (heating)
DTA 2 (air atmosphere)	-100 °C/300 °C (heating)
DTA 3 (air atmosphere)	25 °C/300 °C/25 °C/300 °C (heating/cooling/heating)
DTA 4 (N_2 atmosphere)	25 °C/600 °C (heating/cooling)
TGA 1 (air atmosphere)	0 °C/600 °C (heating)
TGA 2 (air atmosphere)	0 °C/1000 °C (heating)

manufacture, all samples were subjected to the appropriate dynamic temperature programme of the thermoanalytical unit (Thermoscale TGA 1500, DSC Plus, Rheometric Scientific, GB) at a heating rate of 10 °C min^{-1}. As a control group, all materials were examined unreacted.

All experiments were carried out in open aluminium pans with a constant air flow of 5 ml min^{-1}. The temperature ranges, which were used in the experiments are listed in Table I. In order to eliminate the effects of oxidation, the uncured materials were additionally examined in a nitrogen atmosphere. For partial preparations, smaller temperature ranges were selected. So that the glass transition could be determined, DTA analysis was performed from -100 °C (cooling using liquid nitrogen) up to the beginning of the thermal decomposition reaction (300 °C). The thermal influence on the curing behaviour was examined by a dynamic heating/cooling/heating process at 25 °C/300 °C/25 °C/300 °C. The finally cured materials were subjected to DTA analysis after storage for 10 d under light exclusion. All analysis was carried out using an associated computer with the software Plus V 5.44 (Rheometric Scientific, GB). The initial, conversion and final temperatures were determined by means of the changes in weight, together with the percentage weight loss. The content of the filler results from the weight remaining after the last visible weight change at about 575 °C [24]. In order to analyse the DTA curves, the peak areas and positions in visible reactions were measured. Materials and processes are shown in Table I to give an overview.

3. Results

3.1. DTA

All the untreated materials show a glass transition, T_g, in the temperature range between -30 and -60 °C. In contrast to Artglas and Targis, this clear T_g stage disappears immediately after initial exposure for Synfony, Visio-Gem and Artglass. Due to exposure, in the temperature range from about 30–100 °C, a broad peak (magnitude 0.02 mcal) develops in all the materials, which is large and flatter in the case of the materials Targis and Dentacolor. In addition, Artglas shows, at around 50 °C in the uncured state, a level similar to glass transition. Following the longest exposure period, the broad peak between 30 and 100 °C is located at the highest temperatures.

All of the materials show a strong, variously distinguished peak (magnitude 0.5–8 mcal) between 150 and 300 °C in their uncured state. In the cases of Visio-Gem, Synfony, Artglas and Dentacolor, the peaks shift towards lower temperatures with increasing periods of exposure. In the case of Targis, such a peak occurs only in untreated material, although it is very slightly discernible. By comparison, Artglas shows a steep peak, Visio-Gem a markedly sharp peak and Synfony, subsequent to a distinct sharp swing, a flat, weaker one. With the increasing polymerization time of a material, the height of the peaks and the level of radiation heat transfer, decreases. This peak is no longer distinguishable after the initial exposure stage involving light curing in the case of Targis, but only following the concluding polymerization with heat treatment in the Beta Oven in the cases of Visio-Gem and Synfony. In the case of Synfony, both peaks are reduced to a substantially weaker peak following initial exposure. Artglas and Dentacolor continue to have peaks of about one-fifth of the peak area of unpolymerized material, even following the concluding polymerization (180 s) recommended by the manufacturer. Following further heating (25 °C/300 °C/25 °C/300 °C) up to the point below the beginning of the samples' decomposition as a typical indication of thermal curing, these peaks between 150 and 300 °C are likewise no longer discernible.

TABLE II DTA results; peak start, location and energy; glass transition (T_g) and decomposition starting temperature related to the treatment of the materials

Material	Treatment	Peak (A) (°C)	Energy ($\mathrm{mcal\,mg^{-1}}$)	T_g (°C)	Temperature (°C)		Energy [mcal/mg]	Decomposition start. temp. (°C)
					Start	Peak (B)		
Artglas	None	–	–	−39	190	200	−10.00	304
	10 s	49	−7.3	–	199	208	−3.66	299
	90 s	52	−9.4	–	174	193	−0.69	307
	180 s	88	−5.8	–	176	192	−2.23	304
Dentacolor	None	–	–	−48	160	175	−22.10	290
	10 s	–	–	−48 weak	156	178	−23.31	290
	90 s	–	–	–	160	170	−2.56	290
	180 s	–	–	–	159	171	−4.77	280
Synfony	None	–	–	−50	200	207	−28.76	322
	1 period	75	−13.4	–	188	195	−1.37	300
	2 periods	75	−13.4	–	176	187	−1.88	300
	3 periods	45	−13.2	–	178	188	−1.37	300
	5 periods	76	−13.4	–	176	187	−1.57	300
	15 min	88	−9.7	–	–	–		327
Visio-Gem	None	–	–	−57	180	188	−55.84	300
	1 period	84	−8.4	–	178	185	−6.54	300
	2 periods	84	−8.6	–	174	184	−2.36	280
	3 periods	73	−9.4	–	176	183	−2.84	274
	5 periods	78	−9.4	–	174	181	−2.07	285
	15 min	93	−6.0	–	–	–	–	344
Targis	None	–	–	−33	188	235	−5.04	308
	1 period	–	−19.6	−33 weak	–	–		309
	2 periods	–	−20.2	–	–	–		316
	25 min	–	−18.9	–	–	–		331

In all of the materials, an exothermic signal begins at a temperature of about 300 °C; this turns into a maximum of up to about 500 °C. The peaks in these areas of the graphs increase as the exposure period increases. In the materials Synfony, Visio-Gem and Targis, this peak is discernible at two stages; in the case of Dentacolor and Artglas a gradual increase in the path of the curve can be discerned. With Targis, following concluding polymerization, only one, albeit extremely marked, peak is discernible, whereas with Artglas, Synfony and Dentacolor, the starting point of this exothermic peak remains practically unchanged in comparison with untreated material and completely exhausted material. The initial temperature in the cases of Targis and Visiogem increases by about 30 °C. In comparison with the measurement under oxygen, under a nitrogen atmosphere, a softened peak for the reaction between 150 and 300 °C is shown for all materials. The line of the graph from 300–500 °C is less marked, because no oxidizing reactions have taken place.

The temperatures of the changes in the graph therefore correspond to the temperatures analogous to the measurements in the oxygen atmosphere. The temperatures and energies evaluated by means of the DTA curve are shown in Table II. As an example, the DTA curves of Targis and Visio-Gem are represented in Fig. 1.

3.2. TGA

The results of thermogravimetric analysis show a weight drop of up to a maximum of 50% between around 250 and 600 °C in all materials. The extent of the change in weight is not dependent on the length of exposure. The greatest differences in the TGA graphs are to be discerned between untreated material and material treated in the concluding phase. In the case of Synfony a difference is only distinguishable between untreated material and material following the shortest period of exposure: the further periods of exposure register no effect on the thermogram graphs. The established filler components vary depending on the material, from 50% in the case of Visio-Gem through 60% in Dentacolor, 51% in Synfony, 74% in Artglas, up to around 90% in Targis. In this connection all the materials demonstrate a further slight drop in weight even above 600 °C which was particularly marked in Targis and Dentacolor. The curves show two changes in weight each, in the cases of Targis and Synphony, where they are more strongly marked, and in the case of Artglas, where they are slighter, indicating different matrix components of the materials. We dispensed with a differentiation in the levels of weight changes because the graduation of the path of the curve was not sufficiently defined. In the case of Targis, a definite change in the path of the curve is shown following the final curing (Fig. 2).

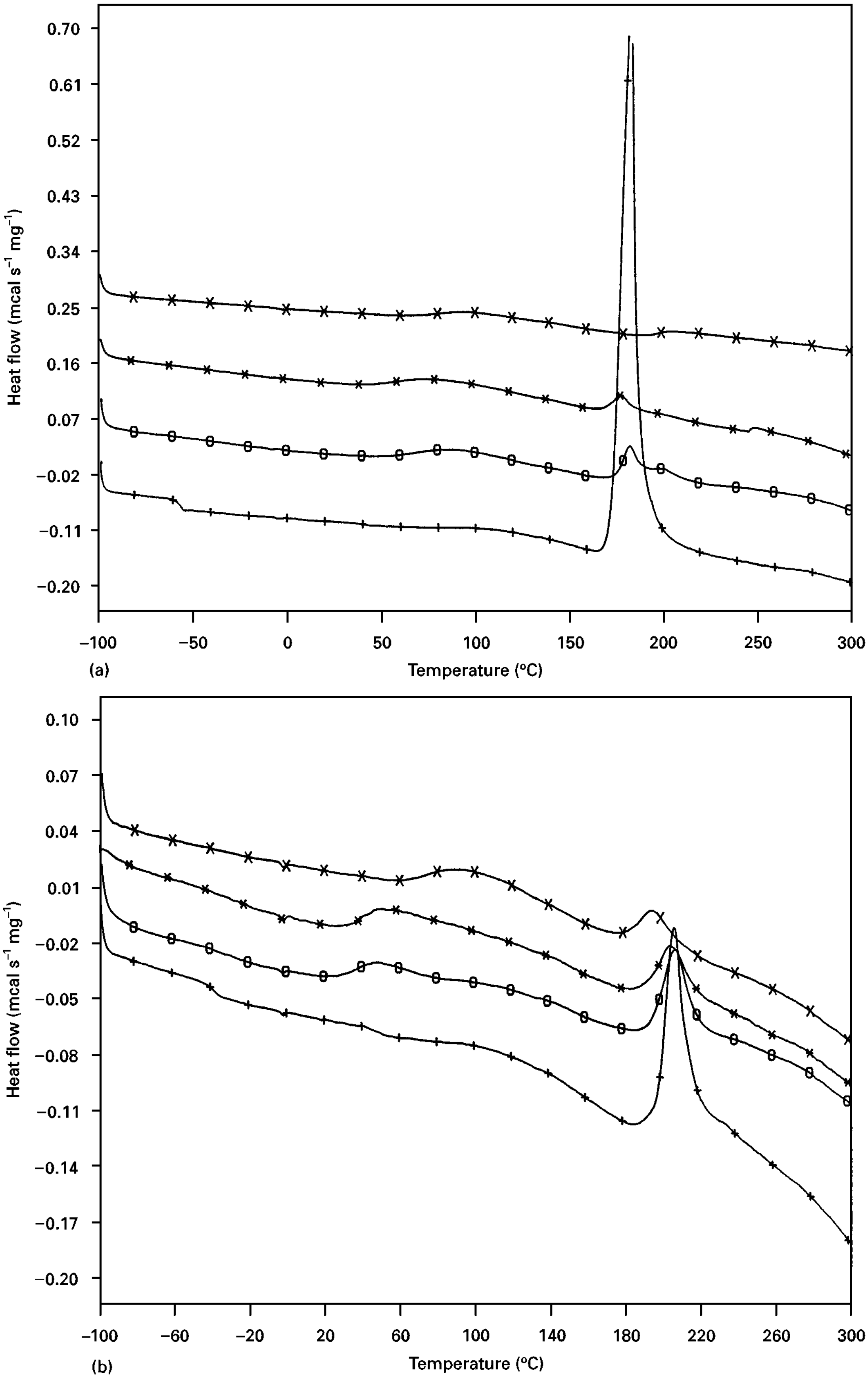

Figure 1 DTA graphs between −100 and 300 °C of the veneering composites (a) Visio-Gem and (b) Artglass. (a) (+) No treatment, (×) 15 min, (○) 1 phase, (∗) 4 phases. (b) (+) No treatment, (×) 180 s, (○) 10, (∗) 90 s.

A shift in weight change to a later starting point and a reduction to one weight level is discernible. The values for the weight changes and the temperatures at the beginning, turning point and end, are depicted in Table III.

When the temperature ranges of the DTA measurements were compared with the TGA measurements, weight changes together with exothermal reactions were established from the beginning of the exothermal curing reactions between 150 and 300 °C up to the

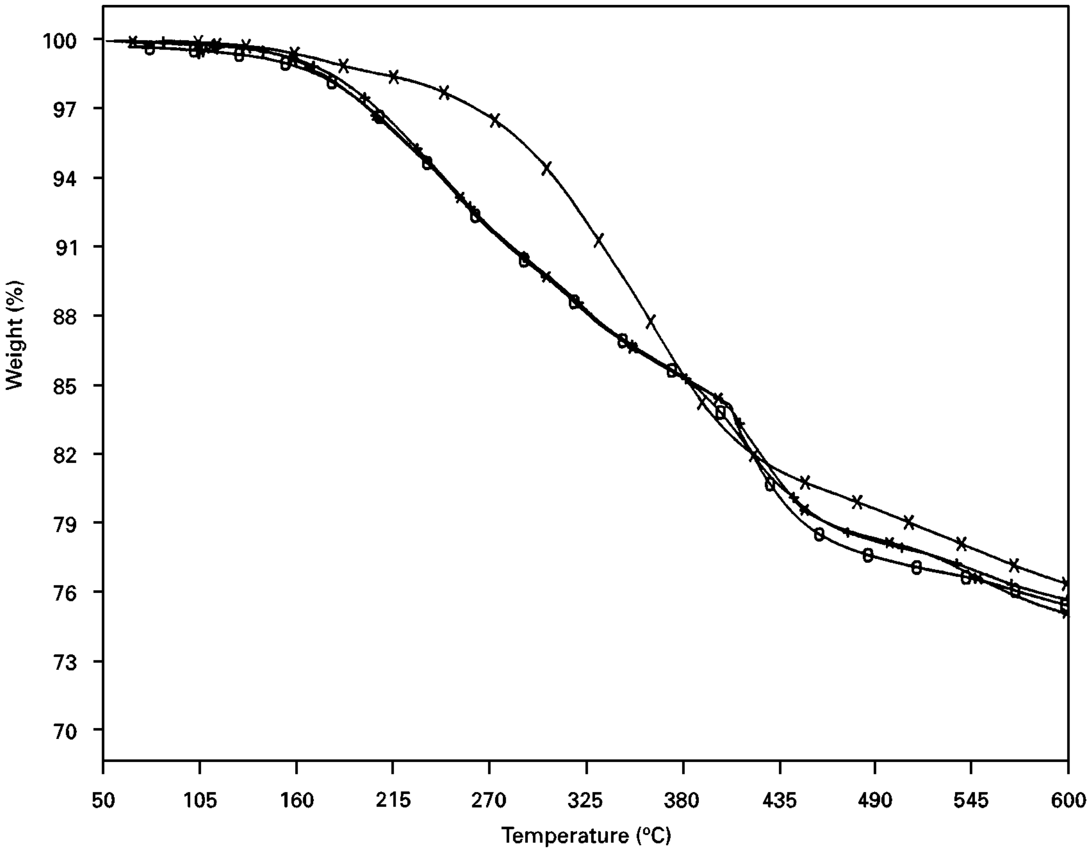

Figure 2 TGA graph of the veneering composite Targis between 50 and 600 °C. (+) 1 phase, (×) 25 min, (○) 2 phases, (∗) no treatment.

TABLE III TGA results; starting, turning point and end temperature, filler content and weight loss between 0 and 300 °C related to material and treatment

Material	Treatment	Temperature (°C)			(%) Filler	Weight loss (%) (0–300 °C)
		Start	Turning point	End		
Artglass	None	360	394	428	74	2
	10 s	343	401	461	74	–
	90 s	364	399	433	73	–
	180 s	334	400	467	74	2
Dentacolor	None	257	312	367	60	12
	10 s	272	324	374	61	–
	90 s	273	324	373	61	–
	180 s	274	328	377	60	7
Synfony	None	301	414	444	49	2
	1 period	300	420	446	51	–
	2 periods	300	417	449	51	–
	3 periods	300	417	445	52	–
	5 periods	300	416	445	50	–
	15 min	300	416	441	50	2
Visio-Gem	None	396	418	440	51	<2
	1 period	401	422	442	51	–
	2 periods	401	423	445	49	–
	3 periods	398	420	442	49	–
	5 periods	404	425	446	50	–
	15 min	400	421	442	51	<2
Targis	None	214	268	327		8
		434	456	472	75	–
	1 period	229	283	344		–
		428	455	481	78	–
	2 periods	227	291	342		–
		441	463	484	79	–
	25 min	305	336	368		4
		425	449	472	79	

point of the beginning of the declining reaction of each material. These changes in weight are around 2% of the total weight in the cases of Artglas, Synfony and Visio-Gem in both cured and uncured states, while in the case of Dentacolor, taking into account the shifts in temperature, a weight loss of 12% takes place in the uncured material and of around 7% in the cured material. Targis behaves in a similar fashion, with an 8% change in weight prior to curing and a change of around 4% following it.

4. Discussion

Shifts in glass transition [23, 25, 26] and the peaks produced dependent on the polymerization temperature in the range 40–100 °C (A), characterize various curings and post curings of synthetic materials. That the area and height of the exothermal peaks between 150 and 300 °C (B) are reduced with increasing periods of exposure, has likewise been indicated in curing reactions previously described by Vaidyanathan and Vaidyanathan [27] and Mallon *et al.* [28].

The different glass transitions and the consistency of the material Targis, Artglas and Dentacolor (highly viscous) and Visio-Gem and Synfony (of a low viscosity) allow conclusions to be drawn regarding a variable level of pre-curing or differing monomer contents in the state the materials are in when delivered. According to Antonucci and Tooth [29] the levels of the exothermal peaks between 150 and 300 °C (B) can be judged and calculated as a measurement for the conversion rate of the polymer. A steep peak, as in the case of Artglas and Visio-Gem, tends to indicate a strong reaction, whereas a gentler, broader peak as in the case of Dentacolor, or even more markedly in the case of Targis, tends to indicate a weak reaction [30]. The different activating energies can be traced back to varying initiator or inhibitor components or to the varying translucencies of the materials [11, 31, 32]. The shift in the peaks to lower temperatures with increasing periods of exposure indicates that with increasing lengths of exposure a greater amount of radicals are formed. These radicals can cause an earlier start of the thermal curing reaction due to thermal activation or greater mobility of the molecules due to thermal influx [28].

A comparison of the materials indicates, in the case of Targis, a relatively flat but broad exothermic peak between 150 and 300 °C. This weak reaction of the partially thermal curing material Targis (90% filler) can be traced to a high filler or a corresponding low monomer component, as established by Ban *et al.* [30] and Vaidyanathan *et al.* [12] for thermal curing polymers. That this peak already disappears after initial light curing when compared with the other materials can perhaps be explained by different high components of champherchinon. This photoreagent has a slight potential for heat curing in which reagents or monomers can already vaporize through heat. Ban *et al.* [30] assume in this context that the exothermic reaction is not dependent on the conversion of champherchinon but of the monomer itself.

This particular characteristic of Targis compared to the other composite materials makes it perhaps suitable for special use not only as a veneering composite for metals but also for fibreglass-reinforced composite materials (Vectris, Ivoclar, Liechtenstein).

As has already been shown by Mallon *et al.* [28], the path of the curve of the curing reaction after longer radiation periods becomes flatter, the curing energy decreases and the mobility of the radicals is, in the process, greatly reduced. Owing to the longer radiation period, the rate of conversion of the curing reaction increases.

The conversion of the light- and heat-curing materials Targis, Synfony and Visio-Gem appears to be concluded after 15 and 25 min polymerization, whereas the conversion of the materials Artglas and Dentacolor from this point of view is not completely finished even after 180 s light curing. A further conversion following concluding light-curing can be expected; whether the reaction continues up to a maximum conversion point when used *in vivo* ought to be investigated in long-storage experiments, for example. After a storage of 10 d in darkness we found no further conversion for the materials Artglas and Dentacolor. Owing to the obstruction of reactive groups in the exhausted network formation, the conversion rate aimed at can, however, never reach the level which can be expected with an immediate final reaction and perhaps thermal influx [26, 32, 33]. Moore [34] showed that, in general, polymers achieve higher conversion rates due to greater heat movement or easier sterical mobility. This also explains why higher conversion rates and with them improved properties of the materials are often achieved by the subsequent thermal treatment [30, 35–40]. The incompleted curing, however, leaves a high proportion of unreacted double bonds and monomers [23, 41], which can, in turn, lead to discoloration and oxidative decomposition *in vivo* [29, 42]. DTA investigation of damaged or discoloured materials can, therefore, contribute to explaining the causes of damage and failure in *in vivo* situations. It should be noted, however, that the influence of oxygen on small samples might be so great that a partial inhibition of the sample surface could have a negative effect on the conversion rate [33, 42, 43]. If the experiment is carried out in a nitrogen atmosphere, i.e. under oxygen exclusion, the exothermic reactions observed between 150 and 300 °C are less pronounced.

An examination of the DTA graphs of materials treated with only marginally different short exposure times (e.g. 4 and 8 s) is only possible to a limited extent. Because the polymerization reactions can take place quickly and immediately following initiation, the transfer of the samples from the light oven to the DTA system can have an influence on the conversion rate, particularly with shorter exposure times. Thus, equipment in which light curing can be carried out directly can have great advantages even in dynamic measurements [44–47].

The exothermic reactions of the DTA measurements over 300 °C show the beginning of the declining and decomposition reactions of the materials [14].

TABLE IV DTA measurement; summary of the observed reactions

	Temperature range (°C)			
	-100–0	30–100 °C	150–300 °C	$\geqslant 30$ °C
Peak		(A)	(B)	(C)
Peak magnitude (mcal mg^{-1})	0.01–0.1	0.02	0.5–8	> 5
Peak stands for;	glass transition	polymerziation	polymerziation	decomposition
Peak behaviour;	disappears or shifts towards higher values	peak generates with increasing conversion rate	peak reduces because of higher conversion	peak area according to conversion rate
Indicating;	transition soft/solid	curing temperature	curing conversion	temperature standing

The width and height of the curves increase with the higher conversion rate, i.e. stronger curing. The multiple graduations of this peak have an extremely complex nature and are perhaps an indication of the different polymer components of the individual materials. The TGA results supplement this, giving good testimony in support of ISO 4049 regarding the filler and matrix components of the material, as well as the characterization of the materials in terms of the initial temperature of the decomposition [27]. It has been shown that the weight curve following the decomposition results in a blur and a further lingering drop in the weight level, perhaps because of the bonding of filler over silan to the matrix.

In the comparison of the temperature levels in DTA and TGA measurements, it is shown that curing reactions described accompany a very slight change in weight. This can, however, also point to monomers breaking free, or slightly volatile auxiliary materials in curing reaction, as they already take place from about 150 °C. Clinical effects can be expected in the long term, at best due to the diffusion of these auxiliary substances, for example. Investigations of light curing taking place directly in the thermoscales might provide further explanations.

Combinations of DTA and TGA measurements allow final judgements of veneering composites not only with exact classification and characteristics, but also with statements concerning the conversion rate of the reactions. The position of the glass transitions, peaks resulting from curing between 30 and 100 °C, peaks dispersing due to curing between 150 and 300 °C and the filler and matrix component, enable a classification of the composites (Table IV). In this way comparative judgements of veneering composites can be made not only for the purpose of academic studies, but for quality control measure, and in order to estimate, for example, the biological incompatibility of a material.

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Received 26 August
and accepted 25 September 1997