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Characterization of a nanoparticle-filled resin for application in scan-LED-technology

Eva Kolb · Claudia Kummerlöwe · Martin Klare

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Abstract Scan-LED-technology is a new rapid prototyping technique with increasing applications in the production of custom-made medical products. The present work is dealing with the examination of a silica/urethandimethacrylate (UDMA) nanocomposite for application in scan-LED-technology. The use of specific LED in a photo-DSC unit enables the simulation of crucial parameters of nanoparticle-filled resins for their application in scan-LED-technology. The conversion of double bonds during the curing reaction and the rate of conversion were studied as a function of radiation intensity, silica nanoparticle content, and silanization of the nanoparticles with 3-methacryloyloxypropyl-trimethoxysilane (MPTMS). The conversion of double bonds is increasing with increasing radiation intensity. The increasing conversion of the nanoparticle-filled resins is discussed as a combined effect of increasing nanoparticle content, alternated initiator/double bond ratio and increasing radiation intensity. A significant dependence of the reaction rate on nanoparticle content could not be found. Only for the unfilled resin, the rate was increasing at higher radiation intensities. The influence of residual solvent on conversion and rate of reaction was also analyzed. TGA measurements combined with FTIR were used to study the silanization of the nanoparticles. The silane layer thickness on the surface of the silica nanoparticles was determined.

E. Kolb · C. Kummerlöwe (✉)
Faculty of Engineering and Computer Science, University of Applied Sciences Osnabrück, 49076 Osnabrück, Germany
e-mail: c.kummerloewe@hs-osnabrueck.de

M. Klare
Dreve Dentamid GmbH, 59423 Unna, Germany

1 Introduction

The rapid progress in the development of imaging techniques, which leads to an enhanced availability of three dimensional data sets, is one of the key factors for the fast development of digital medical technology. In combination with powerful CAD systems the generative fabrication techniques, often termed as rapid prototyping, will gain influence on various medical applications [1, 2]. Currently the field of applications of these technologies is limited on the one hand side by the materials available and on the other hand side by process related drawbacks which are assigned to the chosen generative fabrication technology. For example, particle-filled materials cannot be used in three dimensional printing whereas they can be applied for stereolithographic or image projection systems. The new scan-LED-technology presents a hybrid of the above mentioned systems and offers possible future solutions in order to enhance the spectra of medical applications of generative fabrication. The principle of scan-LED-technology is depicted in Fig. 1. It consists of a vat (Fig. 1c) with a light curing material, a coating system (Fig. 1b) similar to the well known stereolithographic systems and a projection system (Fig. 1a). The projection head is moving in *x*, *y* direction over the vat comparable to a three dimensional printing device. The scan head contains a combination of a high power UV-light emitting diode (UV-LED) with a wavelength of 365 nm (NCSU033A, Nichia Corp.), a direct light projection device (DLP©, Texas Instruments), and an optical system. In this new system, images of 29.16 mm edge length and a pixel size of 27 μm are projected onto the liquid surface and induce the photopolymerization.

In order to optimize the process, it is important to understand the correlations between the composition of the resin, its curing reaction and the processing parameters.

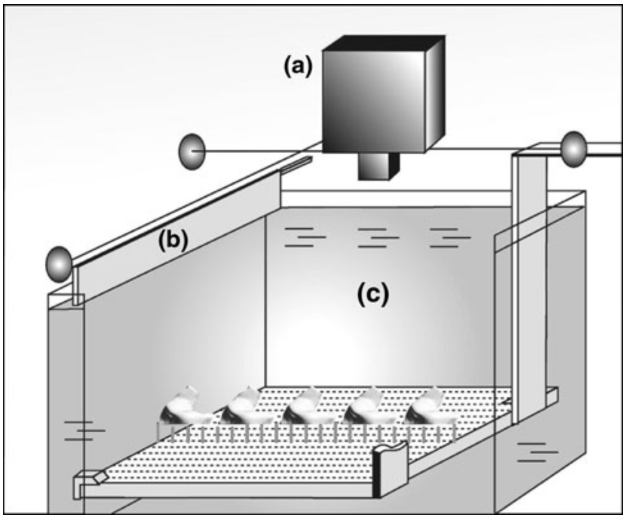

Fig. 1 Schematic view of a scan-LED device, (*a*) scan head, (*b*) coating system and (*c*) vat with photopolymerizable material

The choice of materials and processing conditions is essential to overcome the problems related to the scan-LED-technology such as shrinkage, warpage and brittleness due to the formation of highly crosslinked polymeric networks during the photopolymerization.

In addition to the requirements for resins used for technical applications such as low viscosities to obtain monomer layers with reproducible thickness on the building platform and linear shrinkage behavior of the resin to avoid curling and warpage, resins applied in dental processes must fulfill the following requirements: flexural strength above 80 MPa (according to DIN EN ISO 4049), low water absorption, high abrasion resistance, high transparency, and biocompatibility.

Urethandimethacrylate (UDMA) is well known as a monomer that combines relatively low viscosity and polymerization shrinkage with high flexibility, excellent mechanical values and transparency of the resulting polymer [3]. The performance of the monomer is usually improved by the addition of inorganic fillers. The development of nanoparticle-filled resins for applications in scan-LED-technology can be considered as a challenging possibility to improve the overall properties of the final products. It was shown that colloidal silica nanoparticles lead to reduced shrinkage and curling, resulting in an increased building accuracy and improved mechanical properties while the transparency of the produced parts could be maintained [4]. One crucial point of the application of silica nanoparticles for those resins is the silanization of the polar silica surface to enable dispersions on nanoscale and to avoid agglomeration.

The aim of this study was to examine the UV-LED initiated curing reaction of experimental resins for dental applications. UDMA was used as monomer and filled with silanized silica nanoparticles. To study the performance of the UV-LED as radiation source for the photopolymerization, a new type of UV-LED from Nichia Corp., Japan was used as a light source for photo-DSC measurements. Two LED were incorporated into a photo-DSC measuring cell. The advantage of the experimental setup was the possibility to measure and control the radiation intensity, i.e. the power of the electromagnetic radiation per surface area of the samples, which is an important parameter of the scan-LED-technology. The aim was to study the effect of changing radiation intensity on the double bond conversion during the curing reaction. Furthermore, the effects of the nanoparticle addition and of the silanization on the double bond conversions of the experimental resins will be discussed.

The aim of the study was also to identify and characterize other parameters of the nanoparticle-filled resins affecting the production process of scan-LED-technology. Residual solvent resulting from the preparation procedure of the resin from an organosol and the degree of silanization of the nanoparticles turned out to be such parameters. Therefore, photo-DSC measurements as well as thermogravimetric measurements (TGA) coupled with FTIR spectroscopy were used to examine the effect of the residual solvent on the double bound conversion and characterize the state of silanization of the silica nanoparticles.

2 Materials and methods

2.1 Materials and sample preparation

Materials used in this study are summarized in Table 1. All materials were used as received.

Experimental resins with varying amounts of silica nanoparticles as filler were synthesized. The surface of the nanoparticles was modified with different amounts of silane. The experimental resins were prepared in two steps.

At first, the modification of the inorganic filler surface with MPTMS was carried out. The amount of silane was varied between 2 and 22 wt% relative to the silica. The calculated amount of MPTMS was added to 150.00 g organosol in an airtight resin beaker. A pH of 2 was adjusted by addition of diluted HCl. The beakers were closed and the mixture stirred magnetically for at least 6 h at room temperature.

In the second step, the monomer was mixed with the silanized organosol. At first, 35.00 g UDMA and the respective amount of organosol were transferred in a glass flask and 0.0067 g TEMPO (dissolved in isopropanol) was added. The mixture was then stirred under vacuum at a temperature of 50°C to vaporize the isopropanol. The

Table 1 Materials

		Supplier
Monomer	1,6-*Bis*-[2-methacryloyloxyethoxy-carbonylamino]-2,4,4-trimethylhexane, urethandimethacrylate (UDMA): X-850-0000	Ess tech, Inc., Essington, PA, US
Organosol	SiO_2 nanoparticle with 13 nm average diameter and 200 m^2 g^{-1} specific surface area dispersed in propan-2-ol (isopropanole): Highlink NanOG 503-31	Clariant Int. Ltd., Mutterz, Switzerland
Silane	3-Methacryloyloxypropyltrimethoxy-silane (MPTMS) 97%	Alfa Aesar GmbH&Co. KG, Karlsruhe, Germany
Photoinitiator	2,4,6-Trimethylbenzoyldiphenyl-phosphineoxide: Genocure (TPO)	Rahn AG, Zürich, Switzerland
Anaerobic stabilizer	2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO), 0.1% in isopropanol	Sigma-Aldrich Chemie GmbH, Steinheim, Germany
Acid	0.5 mol l^{-1} hydrochloric acid (HCl)	Merk KGaA, Germany

isopropanol content was controlled by gas chromatography (GC Clarus 500 with FID, Fa. PerkinElmer, equipped with a Zebron Capillary Column, ZB-5). When the isopropanol content was less than 5%, the resin was diluted by the rest of the UDMA and the photoinitiator was added. The resin was then mixed under exclusion of UV-light for 10 min to become completely homogeneous and free of air bubbles. The ready-mixed resin still contained a small amount of ca. 1% isopropanol, which was determined by gas chromatography. The composition of the experimental resins is indicated in this paper as *R-x-y*, with *x* and *y* being the total content of SiO_2 in wt% and the MPTMS content with respect to the SiO_2 content in wt%, respectively.

Furthermore, samples of silanized organosols were prepared for thermogravimetric analysis, as described in step 1. The amount of MPTMS was varied between 2 and 22 wt% related to the SiO_2 solid content of the organosol. The composition of the samples is indicated as *O-y*.

2.2 Methods

2.2.1 *Photo-DSC measurements*

The DSC measurements were carried out with a Mettler Toledo 823^{e}700 instrument which was calibrated according to the standard procedures. The measuring cell was equipped with a home-made photo-DSC unit. Two UV-LED from Nichia Corp. Japan, Model NCSU033A(T), were used as radiation source. The UV-LED exhibit a small emission spectra between 360 and 370 nm with a maximum at 365 nm.

All DSC experiments were carried out at 30°C under 20 ml min^{-1} nitrogen flow. The LEDs were switched on 120 s after the start of the measurement. Both sample and reference crucible were exposed to UV-light for 4.00 min. Each measurement consisted of two scans. At first the curing reaction was carried out and the respective exothermic peak was registered. Then, the fully converted sample was exposed to the irradiation again under the same conditions. The second curve was used as a blank and subtracted from the first run. Mean values of at least three measurements were calculated. The average error range of the conversion data is ±1.7%.

The radiation intensity, i.e. the power of the electromagnetic radiation per surface area, of the LEDs used in this study was measured by a method proposed in [5]. The DSC crucible was filled with carbon black (Corax N660/45, Degussa-Hüls, Germany) to absorb the radiation. The heat flow difference between sample and empty reference crucible was detected at a constant temperature of 30°C with and without radiation. The radiation intensities were obtained as ratio of the step height of the DSC signal and the area of the crucible. The applied LED radiation unit allowed the variation of radiation intensity between 15 and 32 mW cm^{-2}.

2.2.2 *TGA measurements*

The degree of silanization of nanoparticles was studied by TGA coupled with FTIR spectroscopy (TGA/FTIR).

Dispersions of the silanized nanoparticles in isopropanol with varying amounts of MPTMS and nanoparticle filled resins were examined. A Mettler Toledo TGA/SDTA 851^{e} and a Thermo Scientific Nicolet 5700 instrument were used. Under a constant nitrogen flow of 50 ml min^{-1}, the isopropanol was allowed to evaporate at 100°C (heating from 25 to 100°C with 10 K min^{-1}; isothermal segment at 100°C for 15 min). Thereafter the sample was heated with 10 K min^{-1} to 900°C. FTIR spectra were continuously recorded by software OMNIC8.1.

3 Results and discussion

3.1 Radiation intensity and nanoparticle content

In order to discuss the effects of radiation intensity and nanoparticle content, the conversion and the rate of polymerization were evaluated from the DSC measurements. The conversion α was calculated by Eq. 1

$$\alpha = \frac{1}{\Delta H^0 \cdot [MA]} \int_0^t \left(\frac{dH_{\exp}}{dt}\right)_T dt \qquad (1)$$

with $\Delta H^0 = 55$ kJ mol^{-1} being the enthalpy of polymerization of methacrylate groups [6] and $[MA]$ the concentration of methacrylate groups of the respective resin, taking into account the methacrylate groups of the UDMA and the methacrylate groups of the silane as well.

Radiation intensities are crucial parameters for the scan-LED-technology since they influence conversion and consequently the final properties of parts produced. It is essential to examine the relations between radiation intensity and conversion. The applied LED radiation unit allowed the variation of radiation intensity between 15 and 32 mW cm^{-2}.

The effect of radiation intensity on conversion is shown in Fig. 2 for the resins without nanoparticles. As expected, one can see that increasing radiation intensity results in remarkable higher conversions for the unfilled resin. Furthermore, the conversion increases with increasing nanoparticle content at constant radiation intensity. As an example, the dependence of conversion on nanoparticle content is shown for samples with SiO_2 nanoparticles modified with 10 wt% MPTMS in Fig. 3. It can be seen that higher radiation intensities lead to a more pronounced conversion increase. Similar effects have also been observed for the resins filled with unmodified nanoparticles. At low radiation intensities, only a small difference in conversion with increasing filler content could be observed. But, as higher the intensities became the conversion increase with increasing filler content was more apparent.

There are controversial data reported in literature concerning the dependence of conversion on the filler content. For nanosilica in a dimethacrylate matrix [7] or in an cationically photopolymerized epoxy photoresist [8] it was found that for small filler loadings the conversions increased and the polymerization reactions were accelerated. The activation energies of the acrylate or epoxy polymerization were lowered. Synergistic effects of the silica nanoparticles as effective flow or diffusion-aid agent and a site for scattering or reflecting the UV-light were claimed to be the explanations for the findings. At higher filler loadings, the conversion was decreasing again, which was attributed to the formation of filler aggregates due to their high surface energy [7, 8]. On the contrary, a decreasing conversion with increasing content of microfillers was found for Bis-GMA/TEGDMA composites in [9] and [10] for filler loadings up to 75%.

The discussion of the nanoparticle effect on stereolithography parameters is also controversial: Increasing

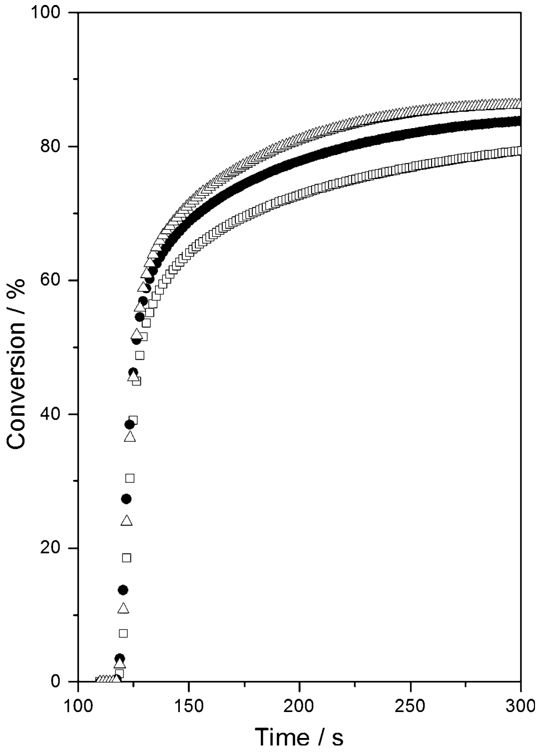

Fig. 2 Conversion as function of radiation intensity for a resin without nanoparticles, radiation intensities: *open square* 15 mW cm^{-2}, *filled circle* 24 mW cm^{-2}, *open triangle* 32 mW cm^{-2}

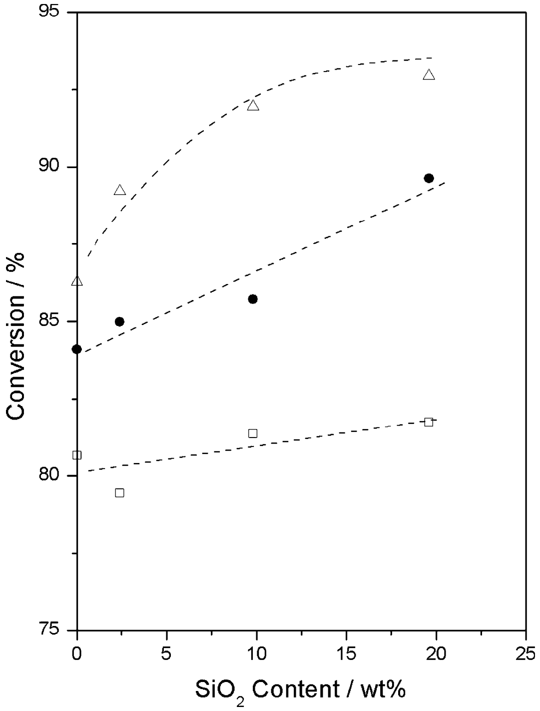

Fig. 3 Conversion as function of radiation intensity and nanoparticle content, nanoparticles modified with 10 wt% (related to the SiO_2 fraction) MPTMS, radiation intensities: *open square* 15 mW cm^{-2}, *filled circle* 24 mW cm^{-2}, *open triangle* 32 mW cm^{-2}

nanoparticle content of a resin led to increased penetration depth D_p and increased critical exposure E_c [4]. E_c describes the minimal value of radiation energy per surface area that is necessary to initiate the polymerization. D_p is the penetration depth and depends on the radiation absorption. Increasing D_p means less absorption of radiation due to the initiation reaction. Klare et al. [1] found the contrary. The critical exposure E_c was decreasing with increasing nanoparticle content.

The explanation for the increasing values of E_c and D_c given in [4] is that the initiator concentration per volume decreased with increasing addition of nanoparticles and therefore higher intensities are necessary to start the polymerization. In our case, the initiator concentration was kept constant with respect to the total composition of the samples. The consequence is that the molar ratio of initiator to double bounds is increasing with increasing filler content, e.g. from 1.028 to 1.283 for sample *R-0-0* and *R-19.6-0*, respectively. The molar ratio of initiator to double bonds is not changing significantly at constant nanoparticle content and increasing MPTMS content. This has to be taken into account while discussing the effect of nanoparticles on conversion. Alternating concentrations of initiator or/and reactive groups as a consequence of variation of nanoparticle and silane content have not been discussed in most of the papers published [1, 7–10] and can be considered as one source for the contradictory results published. The conversion of the curing reaction may be influenced by both, the alternating concentrations of initiator and/or double bonds as well as the presence of nanoparticles which may act as a site for scattering and reflection of the UV-light.

Our results also suggest that the radiation intensity is another parameter influencing the correlation between filler content and double bond conversion. At smaller intensities, the conversion was increasing only slightly with increasing filler content, although the initiator/double bond ratio was increasing. The effect of the nanoparticle filler on the conversion is more distinct at higher radiation intensities.

The rate of polymerization, R_p, was calculated from the conversion according to Eq. 2

$$R_p = \frac{d\alpha}{dt} \tag{2}$$

The rate of polymerization depends on the radiation intensity for the unfilled resin. Smaller radiation intensities resulted in lower polymerization rates. This is depicted in Fig. 4. The shape of the curves of polymerization rate versus conversion resembles that of an autocatalytic reaction. Polymerization of dimethacrylates is characterized by a very fast onset of autoacceleration. The reason is, compared to monomethacrylate monomers, the restriction of the mobility of the macroradicals by network formation at the very beginning of the reaction [11]. The polymerization rate reaches its maximum between 20 and 40% of conversion as it can be seen in Fig. 4. The gel point can occur at 1–2% of conversion [11]. Higher light intensity will result in higher initiation rates of the polymerization and consequently in higher propagation rates. The propagation rate can surpass the volume shrinkage rate which leads to an excess of free volume and increasing mobility in the polymerization system. Therefore, higher conversions can be reached at higher light intensities [11]. The final conversion depends on the reaction rate, the higher the reaction rate the higher the conversion [11]. Our results for the unfilled resin are in good agreement with the theoretical approach that the reaction rate is proportional to the square root of the light intensity [12, 13].

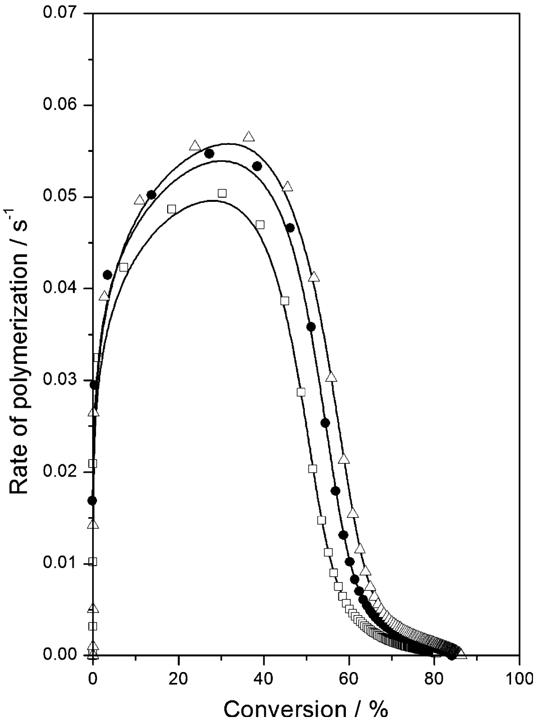

Fig. 4 Rate of polymerization of unfilled resins, radiation intensities: *open square* 15 mW cm^{-2}, *filled circle* 24 mW cm^{-2}, *open triangle* 32 mW cm^{-2}

If one considers the effect of the nanoparticles on the polymerization rate one can see in Fig. 5 for a radiation intensity of 24 mW cm^{-2} that there is no significant difference with respect to filler content. This result was also observed for the other radiation intensities studied. Furthermore, it turned out that at constant filler content the rate of polymerization did not systematically change with changing radiation intensity. An acceleration of the polymerization, as it was reported in [7, 8], could not be found in our experiments.

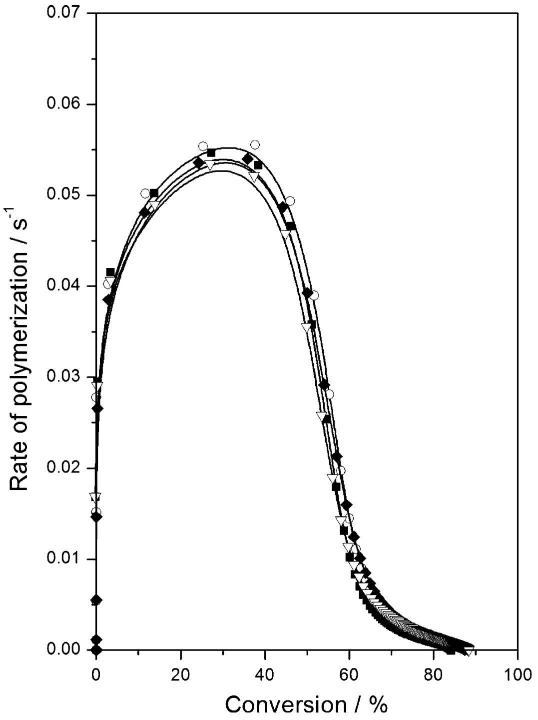

Fig. 5 Rate of polymerization of resins filled with unmodified nanoparticles, SiO_2 content: *filled square* 0 wt%, *open circle* 2.4 wt%, *filled diamond* 9.8 wt%, *open triangle* 19.6 wt%, radiation intensity: 24 mW cm^{-2}

Furthermore, the effect of varying amounts of the silane MPTMS on conversion and rate of reaction was examined. It turned out that changing the degree of silanization did not result in significant differences of reaction rate and conversion.

3.2 Residual isopropanol

Since silica nanoparticle exhibit strong interactions due to hydrogen bridges between silanol groups and the formation of siloxane linkages, they show strong tendency to agglomerate in the dried state. Therefore nanosilica particles are often supplied in form of dispersions in a solvent. In our study, organosols of silica in isopropanol were used for the preparation of the nanoparticle filled resins. It is therefore essential to investigate the effect of residual solvent on the double bond conversion. It is shown in Fig. 6 that a linear relationship exists between the conversion and the isopropanol content. This can be explained by the decrease in viscosity, which is also depicted in Fig. 6, and the resulting improved mobility of reactive chain ends. Figure 7 displays the rate of polymerization as function of residual isopropanol content. It can be seen that the rate of polymerization increases linearly with the isopropanol content.

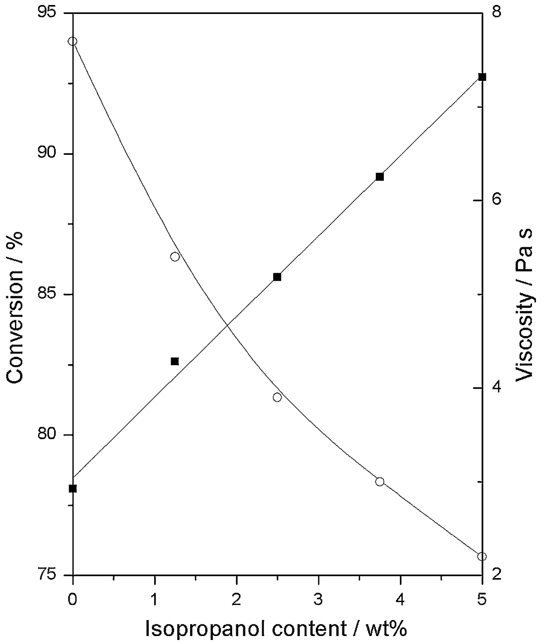

Fig. 6 Conversion (*filled square*) and viscosity (*open circle*) of unfilled resins as function of isopropanol content, radiation intensity: 19.2 mW cm^{-2}

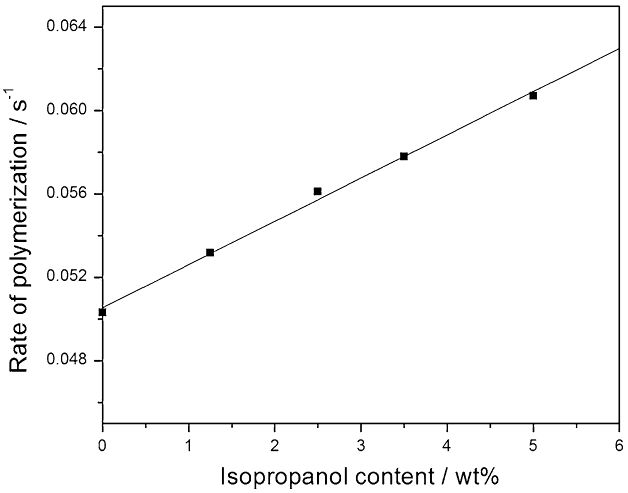

Fig. 7 Rate of polymerization of unfilled resins with increasing isopropanol content: *solid line* linear fit of experimental date with correlation coefficient of $r = 0.998$, radiation intensity: 19.2 mW cm^{-2}

3.3 Silanization of nanoparticles

Thermogravimetric (TGA) together with FTIR measurements were carried out to examine the silanization of the nanoparticles. Figure 8 shows the TGA curve of the resin *R-19.6-22* containing 19.6 wt% nanoparticles that are modified with 22 wt% MPTMS. The first derivative of the weight loss curve and the Gram-Schmidt plot from FTIR measurements are also included in Fig. 8.

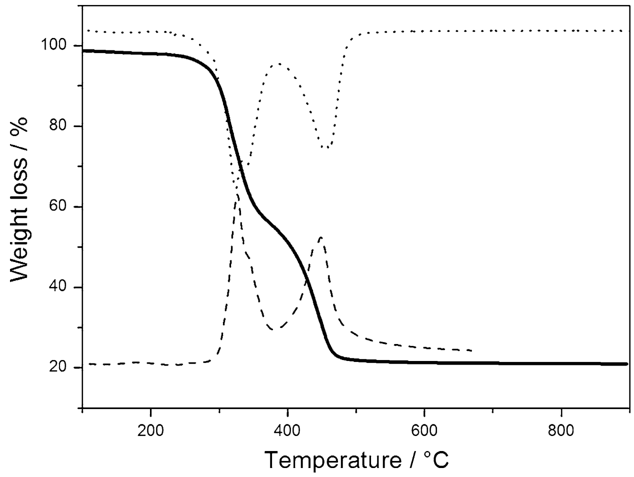

Fig. 8 TGA curve of sample *R-19.6-22* (*solid line*), first derivative of weight loss curve (*dotted line*) and Gram-Schmidt plot of the FTIR measurement (*dashed line*), heating from 100 to 900°C with 10 K min^{-1}

After the small amount of isopropanol remaining from the synthesis was evaporated during heating to and annealing at 100°C, the sample shows two main degradation areas that are indicated by the first derivative of the weight loss curve in Fig. 8. The simultaneously detected SDTA signal (not shown in Fig. 8) indicated an exothermic event in the temperature range 170–220°C with a peak temperature at 197°C which is not accompanied by a weight loss and is interpreted as the thermally initiated curing reaction of the resin. Furthermore, the SDTA signal showed two endothermic effects which occurred in the range of temperatures where the first derivative curve exhibits the two minima. The two weight loss steps in the temperature range of 290–340 and 420–465°C are due to the disintegration of the cured urethandimethacrylate matrix. FTIR spectra collected around the first maximum of the Gram-Schmidt plot exhibited signals of methacrylic acid esters, whereas the spectra from the second maxima indicated volatile organic compounds as heptanes, methylhexanes and other. The methacrylic acid esters emerge from the cross linking points of the matrix whereas the aliphatic hydrocarbons are fragments of the middle part of the UDMA molecule, as it might be seen from the chemical structure shown in Fig. 9.

The decomposition of the organic part of the silane also occurs in the temperature range indicated by the second minima of the first derivative shown in Fig. 8. This was proved by TGA experiments carried out under the same conditions with the silanized organosols. Results are shown in Fig. 10. The weight loss of the MPTMS modified organosols after the evaporation of the isopropanol at 100°C is displayed.

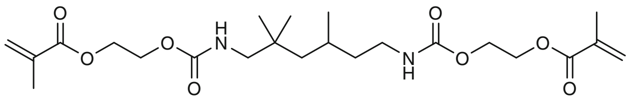

Fig. 9 Chemical structure of UDMA

We note that the weight loss is increasing with increasing MPTMS content. Furthermore, we observed that even the pure organosol exhibits a weight loss in the respective temperature area. The results of the TGA measurements of organosols are summarized in Table 2. In

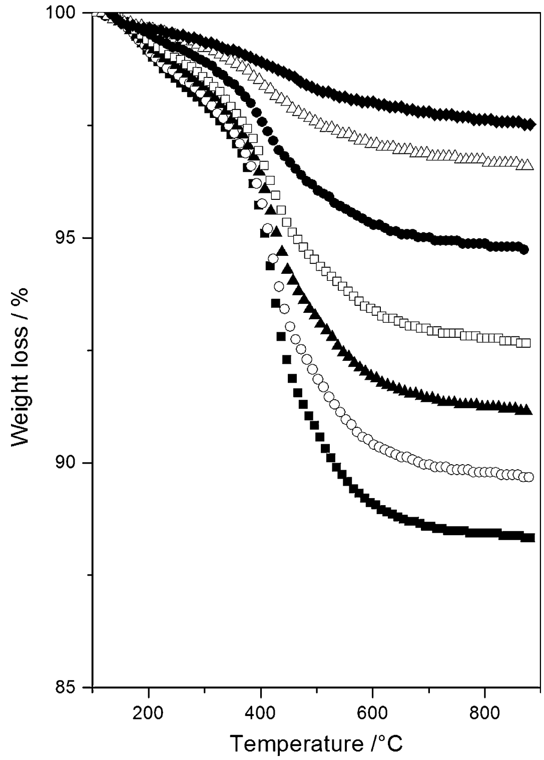

Fig. 10 Weight loss as function of temperature for MPTMS modified organosols (the solvent isopropanol was allowed to evaporate before), MPTMS content given as weight fractions related to the nanoparticle content from the *bottom* to the *top*: 22 (*filled square*), 18 (*open circle*), 14 (*filled triangle*), 10 (*open square*), 6 (*filled circle*), 2 (*open triangle*), 0 (*filled diamond*)

Table 2 Results of TGA measurements of organosol

Sample	Silane content (wt%)	Weight loss between 100 and 900°C (wt%)	Inflection points of weight loss curves (°C)	Silane layer thickness (nm)
O–0	0	2.48	455.3	–
O–2	2	3.41	412.1	0.16
O–6	6	5.27	412.4	0.25
O–10	10	7.34	416.9	0.36
O–14	14	8.85	417.0	0.43
O–18	18	10.32	418.9	0.51
O–22	22	11.67	422.3	0.60

[14] it was shown that the TGA weight loss measured in air is only slightly higher than that measured under nitrogen flow. A differentiation between physically absorbed and chemically linked silane due to two different weight loss ranges during the TGA scan was discussed in [15]. It was claimed that the physically absorbed silane was removed at lower temperatures (50–150°C). The boiling point of MPTMS is 190°C and physical absorption would certainly result in higher weight loss temperatures. Careful inspection of our weight loss curves, Fig. 10, revealed that there is a small weight loss of ca. 0.5–1.5 wt% at about 200°C. But the simultaneously recorded FTIR spectra do not allow the conclusion that this is due to vaporized silanes. Rather, we believe that the evaporation of the physically absorbed silane under the conditions of the measurement is prevented by intermolecular silanol condensation leading to layers of siloxane on the filler surface and the thermally induced polymerization of the methacrylate groups. Since we cannot distinguish between the different processes, we consider the total weight loss in the temperature range between 100 and 900°C. A plot of the weight loss versus the silane weight fraction should therefore reveal a linear relationship having a slope that is resulting from the amount of the decomposing organic fraction of MPTMS. Therefore, the weight loss data of Table 2 have been plotted in Fig. 11 as function of inserted MPTMS. The slope of the linear fit is 0.44 which is in good agreement with the fact that about 51% of the MPTMS molecule represents the organic part that is going to be decomposed during the measurement. This is in good agreement with previous studies [16].

Figure 12 shows the inflection points of the weight loss curve of the TGA measurements. The inflection points characterize the temperature exhibiting the highest rate of decomposition, i.e. the minimum of the first derivative. A slightly increasing trend of the inflection points can be observed for the MPTMS modified nanoparticles with increasing MPTMS content. This could be an indication of changes in the bonding and orientation of the silane molecules at the silica surface. It was found in [14] that at low silane concentrations the MPTMS molecules are oriented parallel to the silica surface and linked by silanol linkages as well as hydrogen bridges between the carbonyl group of MPTMS and hydroxyl groups of the silica. With increasing silane concentration the parallel orientation is gradually replaced by a perpendicular orientation and therefore, the fraction of less strong hydrogen bridges is declining in favor of formation of more silanol linkages.

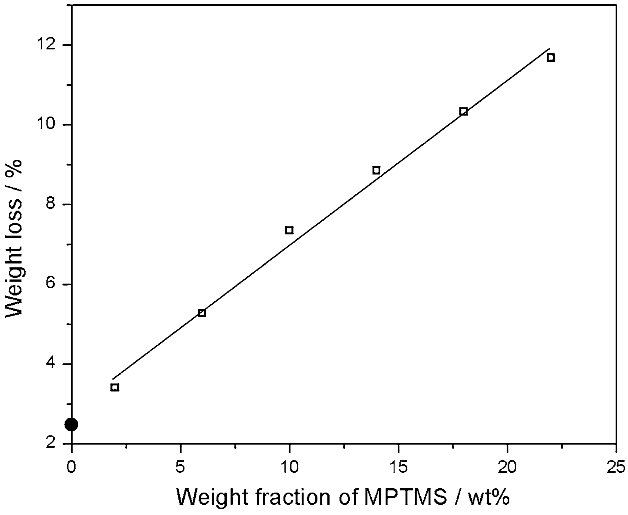

Fig. 11 Weight loss during TGA measurements. The curve was obtained by linear fit of the data points, correlation coefficient: 0.997

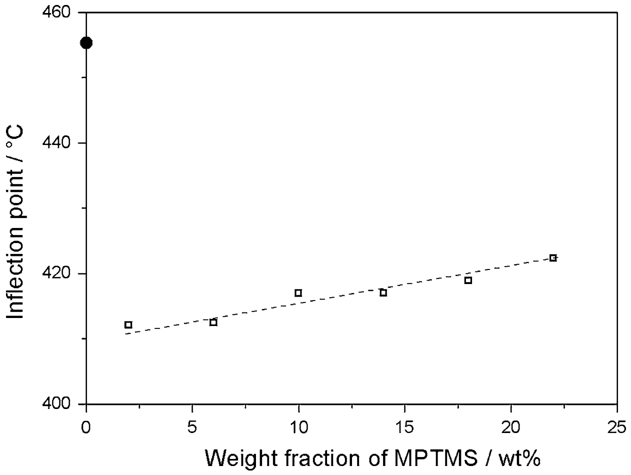

Fig. 12 Inflection points of weight loss curves shown in Fig. 10

Furthermore it can be seen that the inflection point corresponding to the weight loss of the pure organosol sample is remarkably higher than for the other samples. That might be an evidence for a chemical difference in the bonding of the decomposing species on the silica surface. The weight loss of the unsilanized organosol might be caused by the condensation of surface silanole groups. A similar interpretation was given in [15] for a TGA weight loss at about 500°C.

The TGA data can be used to approximate the surface layer thickness of the silane, $\delta = R - r$, in accordance to [17] by Eq. 3

$$\Delta m = \frac{[R^3 - r^3] \cdot \rho_{\mathrm{MPTMS}}}{[R^3 - r^3] \cdot \rho_{\mathrm{MPTMS}} + r^3 \cdot \rho_{\mathrm{Silica}}} \tag{3}$$

where Δm is the TGA weight loss and R and r are the radii of the silica particles with and without silane layer, respectively. The densities, ρ, of silica and MPTMS were approximated as 2.3 and 1.0 g cm^{-3}, respectively. The results are shown in Table 2. The dimension of a MPTMS molecule can be approximated by structure calculations to be ca. 1.1 nm in length and 0.39 nm in diameter. It can be concluded from the TGA data that the silica surface is not sufficiently covered if the silane content is less than 10%.

This is in agreement with [18] where the complete coverage of the surface was calculated under the assumption that one silane molecule covers 1.11 nm^2. It can also be assumed from the calculated silane layer thicknesses that for silane concentrations higher than 10% the MPTMS forms a layer in which the MPTMS molecules have a random orientation, perpendicular and parallel, to the filler surface, as it was proposed in [14].

4 Conclusions

By photo-DSC measurements using UV-LED as radiation source, which will be the central part of the upcoming new scan-LED-technology, the effect of radiation intensity on conversion and rate of reaction of experimental nanoparticle-filled UDMA resins for dental applications was analysed. An increase of double bond conversion was caused by increasing radiation intensities. The observed increase of conversion of nanoparticle-filled resins could have been caused by a combination of increasing nanoparticle content, increasing initiator/double bond ratio and increasing radiation intensity. A significant dependence of the rate of curing reaction on radiation intensity could only be observed for the unfilled resin. No significant effect of increasing nanoparticle content and of variations of the MPTMS surface modification on the rate of conversion could be seen irrespective of the applied radiation intensity.

Residual solvent such as isopropanol can be present in the nanoparticle-filled resins resulting from the preparation of the materials. Double bond conversion and rate of reaction are increasing linearly with isopropanol content in the resin.

From the TGA/FTIR measurements it can be concluded that it is not possible to distinguish between physically absorbed and chemically linked silane on the nanoparticle surface. However, the silane layer thickness on the nanoparticle surface can be determined by the measurements.

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