Available online at www.sciencedirect.com

ScienceDirect

Journal of the European Ceramic Society 29 (2009) 3333–3339

www.elsevier.com/locate/jeurceramsoc

Burnout behavior of ceramic coated open cell polyurethane (PU) sponges

M. Dressler*, S. Reinsch, R. Schadrack, S. Benemann

BAM, Bundesanstalt für Materialforschung und –prüfung, 12230 Berlin, Germany

Received 24 March 2009; received in revised form 3 July 2009; accepted 22 July 2009
Available online 15 August 2009

Abstract

Open cell rigid foams made from polyurethane (PU) are frequently used in ceramic processing for preparation of porous ceramics by the so-called replica technique. This work presents data regarding the PU burnout, shrinkage characteristics as well as the morphology of the ceramic coated PU sponges during heating up. Shrinkage of the ceramic coated PU sponges closely follows the mass loss due to PU decomposition. Two temperatures (i) 267 °C and (ii) 380 °C were identified at which PU decomposition reaches local maxima. Shrinkage measurements on ceramic coated PU sponges reveal that both PU decomposition stages lead to similar extends of shrinkage in the ceramic coated PU sponge. Differential thermal analysis (DTA) showed that the two decomposition related temperatures (267 and 380 °C) differ concerning the energy release. While the low-temperature signal is endothermic, an exothermic signal was detected at 380 °C. The morphology of the ceramic coated PU sponges was investigated with scanning electron microscopy (SEM) which gave insight into the formation of hollow ceramic struts—a well known feature of ceramics being prepared by the replica technique.

Keywords: Polyurethane (PU); Porous ceramics; Mass spectrometry; Thermal analysis

1. Introduction

Porous ceramics are used in many different applications ranging from steel manufacturing to human implant materials. A process widely used to prepare such porous ceramics is the so-called replica technique which was patented by Schwartzwalder et al. in 1963.[1] According to this process an open cell rigid PU sponge is infiltrated with a ceramic slurry which is subsequently removed. In an ideal case the struts of the PU sponge are coated homogeneously with a uniform layer of ceramic slurry. The resulting ceramic coated PU sponge is heated up to appropriate temperatures which leads first to the decomposition of the polymer and at sufficiently high temperatures to the sintering of the ceramic particles. The resulting ceramic has the shape of the former PU sponge. Although this replica technique is a standard procedure in ceramic processing and PU is a widely used polymer only little systematic data is available regarding the PU burnout behavior in that particular application and especially the relationship between PU decomposition and shrinkage of the ceramic coated polymer. Furthermore, no report was found in the literature regarding the morphology of the ceramic coated PU in the transitional stage when the PU decomposition has started but is not yet completed.

Even ceramics whose sintering temperatures are as high as 1400 °C, e.g. alpha-Al_2O_3, do not collapse after burnout of the supporting polymer structure at temperatures well below 600 °C. Once the polymer is burned out the ceramic structure is not supported anymore by the PU sponge. Still the porous unsintered ceramic does not collapse after removal of the supporting PU sponge.

This work presents data regarding the thermal decomposition and shrinkage behavior of “pure” PU sponges and ceramic coated PU sponges in a temperature interval between room temperature and 1100 °C. This process was followed by differential thermal analysis (DTA), thermal gravimetry (TG), mass spectrometry (MS), dilatometric measurements and scanning electron microscopy (SEM).

2. Experimental

Open cell rigid PU sponges – which will in this work be addressed as PU sponges – with a pore content of 90 “pores per inch” (ppi) were purchased from Michael Zervos and used either in their as received state or after application of a ceramic

---

* Corresponding author.
E-mail address: martin.dressler@bam.de (M. Dressler).

0955-2219/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2009.07.025

coating. The sponges are prepared by the synthesis of polyoles and diisozyanates which are mixed with appropriate catalysts. It should be noted that 60 ppi sponges were analyzed as well but only marginal differences compared to 90 ppi PU sponges were observed. It appeared that the more coarse PU sponges with bigger pores (60 ppi) showed the same general behavior which was only shifted to slightly (up to 10 °C) higher temperatures. The ceramic used in this work for coating the PU sponges according to the replica technique was a resorbable biomaterial, namely $Ca_2KNa(PO_4)_2$.[2] The PU sponges were coated according to the following procedure. The ground ceramic powder ($d_{50} = 5\ \mu m$) was mixed with water without any further additives to give a suspension with 65 wt.% solids loading. PU sponges which had been cut to cubes with an approximate edge length of 5 mm were immersed into this suspension and put afterwards into a centrifuge in order to remove the excess ceramic suspension. After spinning for 1 min at 1000 rpm the wet ceramic coated sponges were allowed to dry at room temperature and ambient atmosphere for 24 h.

PU sponges in their as received state were studied by TG and DTA which were recorded simultaneously in a thermobalance (TAG24, Setaram). It should be mentioned here, that not only uncoated PU sponges but also ceramic coated PU sponges were analyzed with TG and DTA. However, no significant differences between ceramic coated and uncoated PU sponges were found. Hence, in order to ease the comparability with the polymer literature, TG and DTA data are only reported for uncoated PU sponges in this work. The maximum weighing error during TG was $\Delta m = 0.01$ mg and the maximum error for temperature readings was $\Delta T = 5$ K. The test material was placed in an open Pt-crucible (100 μl). Samples were measured at a heating rate of 5 K/min in an argon plus air flow (volume flux ratio of argon and air was 3/4). The mass spectrometer (Quadstar 421, Balzers) for simultaneous analysis of evolved gases was coupled by a heated (150 °C) quartz glass capillary. Measurements were performed in bar graph modus ranging from $m/z = 12$ up to $m/z = 132$. Evaluation of DTA data was carried out using software (Setsoft, Setaram) delivered from the thermobalance supplier. In this work the reported DTA and DTG temperatures are peak temperatures unless otherwise stated.

The shrinkage behavior of both ceramic coated and as received PU sponges was investigated in a PC controlled hot stage microscope – occasionally also called optical dilatometer – combined with a picture analysis tool for optical dilatometers (Leitz, Hesse Instruments). The heating rate was 5 K/min in air. The data obtained with the hot stage microscope allowed for the quantification of sample shrinkage by the following technique. A beam of light was shed onto the sample which cast a shadow onto a camera (optical data acquisition, Hesse Instruments) which was placed behind the sample. The surface area of the detected shadow is proportional to the sample size. This setup is especially suited for determining the shrinkage of very porous and fragile samples like the ceramic coated PU sponges. The advantage is that the beam of light does not exert a force onto the sample. Especially in fragile samples even slight additional forces might erroneously change the shrinkage results. Furthermore, the unrestricted shrinkage during heating up in the hot stage microscope is in principal identical to the situation during heat treatment of bigger samples when preparing "real" samples according to the replica technique. An additional advantage can be seen in the following. As the lamp can shine through very porous structures the shrinkage measurement has a higher accuracy as not just the shrinkage of the outer contour is detected like in the case when a piston is used to detect the overall sample shrinkage. The detected surface area of the shadow on the camera allowed for the calculation of the ratio between the initial shadow size when the sample is at room temperature and the shadow size at any given increased temperature. This ratio will be termed "relative surface area" in this work. Shrinkage measurements were carried out up to 300 °C in the case of the uncoated PU sponges – a temperature at which PU degraded to a smoldering droplet – and up to 1100 °C in the case of the ceramic coated PU sponges.

In order to study the morphology evolution in ceramic coated PU sponges SEM micrographs were taken with a Zeiss SUPRA^{TM} 40 (Carl Zeiss SMT, Oberkochen, Germany) high-resolution microscope having a thermal field emitter. A comparatively low accelerating voltage of 5 kV was applied for acquiring surface sensitive micrographs. The specimens were coated with a very thin metal layer in order to improve the electrical conductivity of the sample surface. The best surface quality has been attained by using a nickel coating. Elemental analysis was also performed with an energy dispersive X-ray (EDS) system (NSS 2.1, Thermo Fisher Scientific, Waltham, MA, USA) coupled to the SEM. Two sample types were analyzed, namely ceramic coated PU sponges after heating to (i) 260 °C and (ii) 500 °C. Heat treatment was carried out in a muffle type furnace at ambient air for 6 min (260 °C) and 1 h (500 °C) accordingly. The heating rate in that particular experiment was set to 40 K/h and the samples were allowed to cool inside the furnace which cooled undisturbed by free convection.

3. Results

Fig. 1 shows the DTA result for an uncoated PU sponge. Two main features can be seen (i) a small endothermic signal at 270 °C and (ii) a much more pronounced exothermic signal at 380 °C. At both temperatures marked changes can also be found in the DTG signal (267 and 380 °C). The major exothermic DTA signal at 380 °C has two shoulders: one at 329 °C and the other one at 422 °C. Also these two shoulders are reflected in the DTG curve where slight changes are visible at these particular temperatures. The main exothermic signal has its offset temperature at 443 °C. This temperature also coincides with the end of the major mass loss signal. At 590 °C a minor exothermic signal was detected which corresponds with the decrease of the sample mass to zero. The three sections A, B and C will be discussed later (Fig. 2).

Concomitantly to DTA and TG analysis MS signals for NO_2, H_2O and CO_2 were recorded as well. The two main mass loss temperatures which were given above (267 and 380 °C) can only partially be assigned to MS signals. The major mass loss signal at 380 °C (cf. Fig. 1) results in corresponding MS signals for $m/z = 46$, $m/z = 18$ and $m/z = 44$. An assignment of these mass

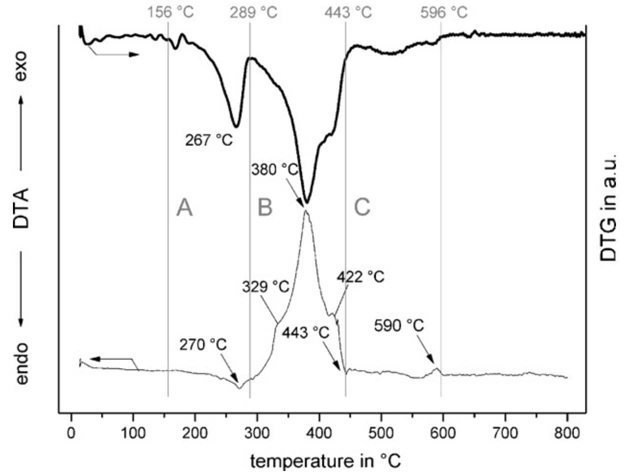

Fig. 1. DTA and DTG data of an uncoated PU sponge. The bold graph showing the DTG signal.

numbers to specific chemical compounds is arbitrary and especially complicated in the case of PU were a manifold of different compounds is released during thermal decomposition. However, these signals might be attributed to NO_2 ($m/z = 46$), H_2O ($m/z = 18$) and CO_2 ($m/z = 44$). Other marked MS signals apart from the three given here were not detected. The onset of the MS signals corresponds roughly with the start temperature (289 °C) of section B as indicated in Fig. 1. The peak temperatures at 380 °C ($m/z = 46$), 371 °C ($m/z = 18$) and 370 °C ($m/z = 44$) correspond well with the above mentioned major exothermic signal (380 °C). Also at the above mentioned shoulder temperatures at 329 and 422 °C corresponding changes in the MS signals for $m/z = 18$, 44 and 46 can be found. At the offset temperature (443 °C) of the main exothermic signal the MS signals tail off. Only for $m/z = 44$ and to a certain degree for $m/z = 18$ weak MS signals could be detected at temperatures higher than 443 °C, namely up to 596 °C. It should be noted, that the very small exothermic signal found at 590 °C corresponds well with a little hump in the MS signal for $m/z = 44$. After heating to ~600 °C the last remnants of the sample mass vanished and thus, no further MS signals were detected.

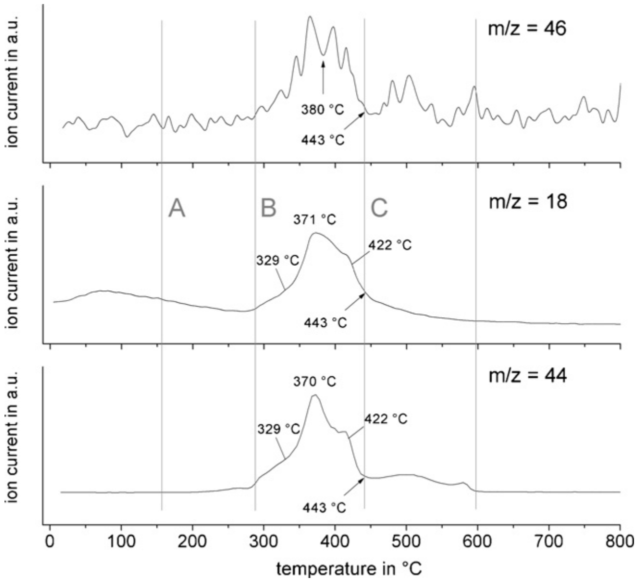

Fig. 2. Mass spectrometer signals of an uncoated PU sponge in air. The signal for $m/z = 46$ appears rather unsteady as this signal was very weak.

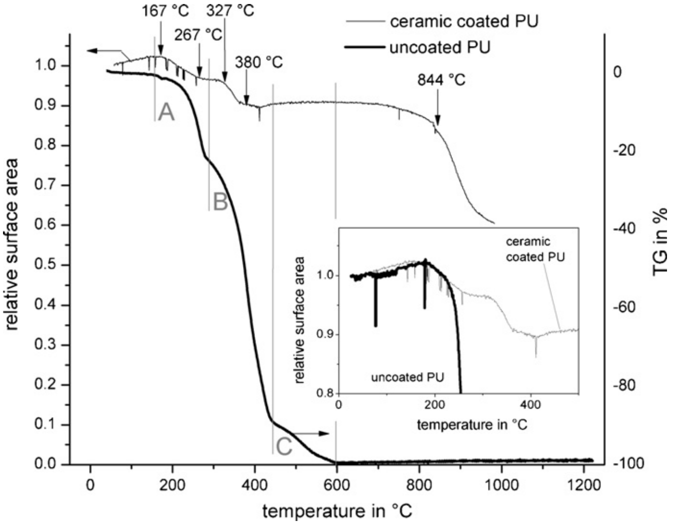

Fig. 3. Shrinkage of the ceramic coated PU sponge in comparison with the TG signal of the uncoated PU sponge. The inset shows the shrinkage of the coated and also the uncoated PU sponge.

It is interesting to note that in general only the major mass loss signal at ~380 °C has corresponding MS signals whereas the first somewhat smaller mass loss at 270 °C does not observe any corresponding MS signals albeit MS signals up to $m/z = 132$ were scanned. This is unusual as any mass loss detected in the TG should result in a MS signal. It might be surmised that some volatile species condensed at the MS capillary rendering them undetected. Condensation of decomposing PU species was already addressed by Woolley in 1972.[3]

Fig. 3 shows the shrinkage of the ceramic coated PU sponge expressed in relative surface area. As can be seen, three relevant temperature intervals (A: 156–289 °C, B: 289–443 °C and C: 443–596 °C) were defined. The expansion up to 167 °C can be attributed to the expansion of both the PU and the ceramic material due to the mere temperature increase. In sections A and B marked shrinkages occur. No such shrinkage was found in section C. At temperatures above 844 °C the ceramic material starts sintering which is accompanied with a pronounced decline in relative surface area.

The inset in Fig. 3 shows the shrinkage of the uncoated PU sponge up to 300 °C. For comparison the shrinkage curve of the already presented coated PU is shown as well. It can be seen that not just the ceramic coated PU but also the uncoated PU exhibits the small but significant expansion up to 167 °C. Already in section A the uncoated PU sponge shrinks rapidly due to decomposition. The shrinkage experiment for the uncoated PU sponge was aborted at 300 °C as the sample had collapsed to a droplet and started smoldering heavily. Hence, the camera in the hot stage microscope could not detect any further sensible readings.

Fig. 4 shows a SEM micrograph of a ceramic coated PU sponge after heating to 500 °C. After heating to this tempera-

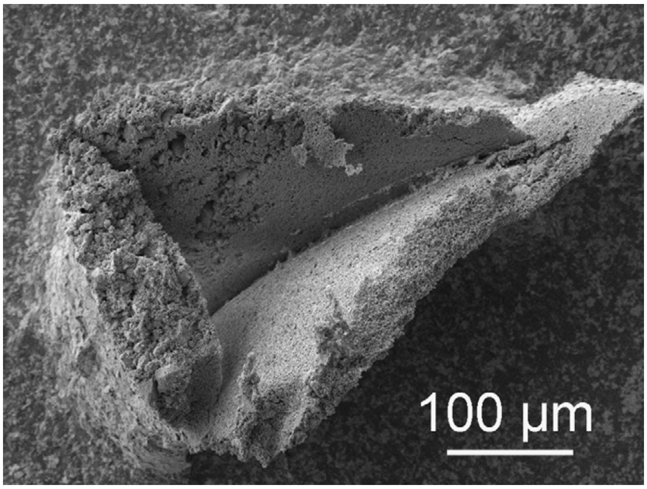

Fig. 4. SEM micrograph of a ceramic coated PU sponge after heating to 500 °C in air. Clearly the hollow nature of the strut which is caused by the burn out of the supporting PU sponge can be seen.

ture the ceramic sponges had a light grey appearance whereas the samples were bright white after heating to 1100 °C. The observation of the naked eye whereas the sponges were light grey after heating to 500 °C corresponds with the SEM micrograph shown in Fig. 4. No obvious remnants of the PU sponge were detectable, which might have provoked a more pronounced color change of the ceramic body. The hollow nature of the strut is a well known feature in the replica technique.

After heating to 260 °C, i.e. the temperature which according to Fig. 3 corresponds to a marked shrinkage of the uncoated PU sponge and at which the first marked mass loss can be detected (cf. Fig. 1), the struts of the porous ceramic body are already quite hollow. This implies that at this temperature a majority of the PU has vanished from inside the PU sponge. However, as can be seen in Fig. 5 a small film was found at the inner wall of the ceramic strut as indicated by arrows in Fig. 5. It was confirmed with EDS that this thin film contains carbon. Hence, it can be concluded that this film is the residue of the PU decomposition after heating to 260 °C. It is an interesting finding that the hollow strut does not have a structure like a hollow tube but should rather be seen as an array of three elliptically shaped laths. These three laths are separated by a thin PU residue film (indicated by arrows) as can clearly be seen in Fig. 5.

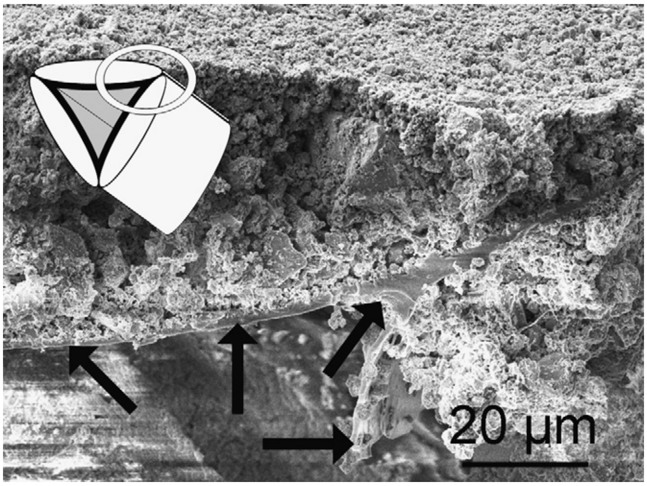

Fig. 5. SEM micrograph showing the PU residues after heating a ceramic coated PU sponge to 260 °C in air. Encircled region illustrating the location of the depicted sample point in a hollow ceramic strut. Arrows marking PU residues.

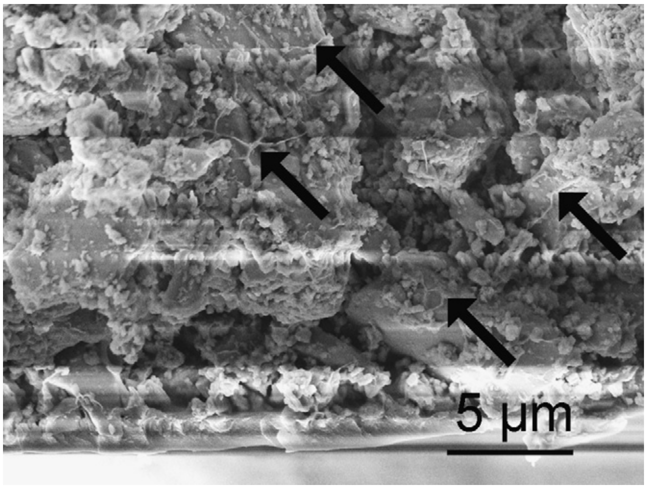

Fig. 6. SEM micrograph of a ceramic coated PU sponge after heating to 260 °C in air. Arrows marking string-like artefacts perhaps being traces of vaporized and subsequently condensed PU. *Note*: horizontal contrast changes are artefacts due to electric charging effects during SEM acquisition.

Another interesting feature of the PU decomposition after heating to 260 °C is the discovery of string-like features at a fracture surface of a ceramic strut. Such strings are depicted in Fig. 6. Attempts were made to analyze these strings with EDS. However, as these strings are apparently very thin no clear separation of X-ray signals originating from the underlying ceramic and the string material was possible. Still, spot scans on these strings (not shown) revealed not only the presence of Ca, K, Na and P which were expected constituents of the base ceramic, but also a pronounced carbon related signal was found. When EDS spectra were normalized to the height of the Ni–L peak, i.e. the coating metal which should be present in similar amounts in all samples, the carbon signal decreased when spots other than the strings were analyzed. In other words it might be concluded that these strings are some carbon containing PU decomposition residues. Their presence in the ceramic coating implies that these PU decomposition products condensed at the ceramic particles.

4. Discussion

The term polyurethane stands for a huge number of many different compounds. PU is characterized by a urethane group which links an aliphatic, aromatic or alicyclic derived isocyanate monomer and a polyol component such as a polyether or polyester.[4] The isocyanate monomer chain is usually called the *hard* building block whereas the polyether/polyester segment is addressed as the *soft* building block.[4] The thermal decomposition behavior of PU is mostly seen as a three step process.[5] It is generally accepted that (i) the decomposition starts predominantly within the hard segments[6] and (ii) a higher content of soft segments leads to PU with an increased thermal stability.[7]

4.1. PU decomposition in sections A, B and C—relation to literature data

Many very differing thermal decomposition reports can be found in the literature which cannot only be attributed to the high number of differing PU compositions but also to the variety of different testing conditions, like, e.g. heating rates and atmosphere. Some authors use a nitrogen atmosphere[7] while others also apply air.[8] However, according to Mequanint et al.[8] who investigated the behavior of phosphate containing PU, no marked difference results when thermogravimetric analyses are run in nitrogen or air.

Against this background of differing testing conditions found in the literature the overall outline of the detected mass loss in this work agrees with literature values. The shape of the mass loss curve with its three distinct steps in sections A, B and C corresponds well with data published by Nangrejo et al.[9]

It also agrees with literature reports, that the major mass loss (90 wt.%) in the present work was achieved after heating to 443 °C. This temperature (443 °C) is in reasonable accord with reports by Coutinho and Delpech,[7] Mequanint et al.,[8] Herrera et al.[10] and Coutinho et al.[6] According to these authors the majority of PU decomposes at ∼400 °C (nitrogen, 10 K/min),[7] ∼410–460 °C (nitrogen, 2.5–10 K/min),[8] ∼420 °C (nitrogen, 10 K/min)[10] and 355–455 °C (nitrogen, 10 K/min).[6] As is indicated, the decomposition studies of the above mentioned authors were carried out under nitrogen atmosphere in which PU decomposition produces a char residue. A complete burnout of the char residue takes place in air. In the present study were an air atmosphere was used the burning of char possibly takes place in section C in Fig. 1, i.e. between 443 and 590 °C. This assumption is in line with Herrera et al.[10] which report the char burnout to take place between 500 and 600 °C in air. Furthermore, the char burnout can be concluded as during the temperature interval 443 and 590 °C a much lower mass loss rate compared to section B was detected (cf. Figs. 1 and 3). In addition, MS measurements (cf. Fig. 2) show a constant release of CO_2 in section C which adds to the conclusion whereas section C is related to char burnout. Furthermore, the small exothermic peak found at 590 °C corresponds with a little MS signal for $m/z = 44$. The end temperature of the possibly char burnout related section C (596 °C) is in good accord with data published by Mamleev et al.[11] who studied the decomposition of PU in air at differing heating rates—among them also a rate of 5.3 K/min which is comparable to the heating rate in this work (5 K/min). According to these authors, the char residue from PU decomposition vanished completely after heating to 600 °C. The temperature of 600 °C corresponds also with experimental details found in Refs. 12, 13. These authors report their ceramic coated PU sponges to be heated up to 600 °C in order to burn off the PU.

Although there are many reports about the weight loss behavior only little data was found regarding the energy release during thermal decomposition. Herrera et al.[10] report a DTA peak maxima (heating rate 10 K/min) at a temperature of 377 and 555 °C when using synthetic air as atmosphere and 384 °C when running their DTA analysis under nitrogen. Unfortunately, these authors did not specify whether their peaks are exo- or endothermic. However, the temperature of their unspecified DTA peak (377 °C) corresponds well with the exothermic signal found in this work at 380 °C. The major exothermic signal found in this work exhibits two distinct shoulders at 329 and 422 °C. At these temperatures also (i) changes in the mass loss behavior and (ii) in the mass spectrometer signals ($m/z = 18$ and 44) can be detected.

Apart from the exothermic signal at 380 °C a small endothermic peak was detected at 270 °C which corresponds with the marked mass loss signal in section A, namely at 267 °C. One might surmise that this endothermic signal was caused by PU pyrolysis and partial melting.

4.2. Relationship between shrinkage and PU decomposition

When comparing the mass loss curve of the uncoated PU with the shrinkage of the ceramic coated PU sponge it becomes obvious that the shrinkage of the ceramic coated PU is closely connected to the decomposition of the PU sponge (cf. Fig. 3). As can be seen in Fig. 3 PU decomposition takes place in three distinct temperature intervals, namely A, B and C. While sections A and B resulted in a marked shrinkage of the ceramic coated PU sponge section C did not result in any marked shrinkage. Based on the discussion of PU decomposition the following stages during heating up of ceramic coated PU sponges can be assigned. At low temperatures, i.e. up to 167 °C in this work, the ceramic coated PU expands due to the thermal expansion of both the PU and the ceramic. When further increasing temperature the initial sample expansion comes to an end because PU starts to decompose which causes the ceramic coated PU sponge to shrink. When the mass loss in section A reaches its maximum (267 °C) a small endothermic DTA peak appears and the shrinkage of the ceramic coated PU stops. From the end of section A (289 °C) until 327 °C no shrinkage occurs although mass loss measurements indicate that the PU is loosing mass during this temperature interval. At 327 °C the ceramic coated PU sponge starts shrinking again. This newly onset of shrinkage is accompanied with (i) a marked increase in mass loss rate of the PU and (ii) a marked exothermic shoulder. The maximum mass loss rate and maximum exothermic signal during PU decomposition (both at 380 °C) coincide roughly with yet another stop in shrinkage of the ceramic coated PU sponge (367 °C). The char burnout in section C did not result in any noticeable shrinkage which picks up again only until the shrinkage caused by sintering of the ceramic particles sets in at 844 °C. The following general pattern for PU decomposition related shrinkage is hypothesized. (i) After the first expansion of the ceramic coated PU due to thermal expansion, shrinkage processes set in in the ceramic coated PU sponges when the supporting PU starts loosing mass due to beginning decomposition. The shrinkage of the ceramic coated PU sponge does not reach its maximum when the PU decomposition reaches its maximum but the shrinkage of the ceramic coated PU already comes to an end when the mass loss of the supporting PU sponge reaches its maximum. (ii) Further shrinkage will only start again when another marked mass loss during PU decomposition occurs. During the second PU decomposition related shrinkage of the ceramic coated PU –which was observed for the PU used in this work – the same pattern as during the first shrinkage is being followed. The ceramic coated PU sponge starts to shrink when the residues of the supporting PU structure starts to loose mass again. When the PU mass loss reaches its maximum the shrinkage of the ceramic coated PU sponge has again already come to an end. Char burnout does not result in any noticeable shrinkage. After these PU decomposition related shrinkage steps the ceramic will only shrink again when temperature is high enough to trigger sintering of the ceramic particles.

4.3. Hollow strut formation

It was shown above that ceramics prepared by the replica technique have hollow struts. This is a well known feature which had been documented before by many authors.[13–18] The SEM micrographs shown in this work illustrate not only the hollow struts in the sintered ceramic but also the intermediate stage during PU decomposition. As was shown in Fig. 5 heating to 260 °C, hence the temperature of the first marked PU mass loss (cf. Fig. 1), already led to the formation of struts which were almost completely void of any PU residue. It is an interesting finding that already after heating to this comparatively low temperature a huge portion of the PU seemed to have vanished. Based on the mass loss data shown in Fig. 3 heating to 260 °C resulted in a mass loss of 13%. Thus, the major mass loss is still to come which arouses the question why a mass loss of 13% already resulted in the formation of almost completely hollow struts. One explanation might be seen in the carbon rich string-like features observed with SEM/EDS (cf. Fig. 6). It could be surmised that after heating to 260 °C a huge portion of the PU becomes mobile, e.g. by melting or vaporization, which would be in line with the small endothermic DTA signal. It could furthermore be speculated that these mobile species penetrate the ceramic coating which surrounds the PU sponge and condense at ceramic particles thus resulting in the formation of the observed string-like features. As a result, the PU has been transferred from the interior of the ceramic coated PU sponge to the surrounding ceramic coating. The PU matter however is still there. This hypothesis would reconcile the observed formation of almost completely hollow struts and the only small mass loss after heating to 260 °C as the PU has not vanished but is still there—within the ceramic coating. The penetration of PU into the surrounding ceramic material is supported by the color change of the ceramic coated PU sponges during heating up. While the as prepared ceramic coated PU sponges have a white appearance heating to 260 °C resulted in a brownish color which again turned to a light grey color after heating to 500 °C. The brownish color might be ascribed to condensed species within the ceramic material. The outlined stages in PU burnout are summarized in Fig. 7.

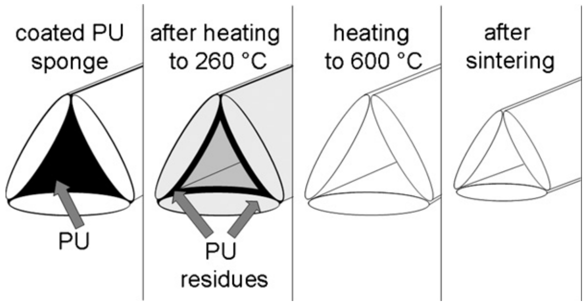

Fig. 7. Schematic drawing illustrating the stages while PU burnout in ceramic coated PU sponges.

It could even be assumed that the penetration of PU decomposition products – either as melt or vapor – does play a role in providing enough mechanical strength to the ceramic body during PU burnout. In general it is fascinating that ceramic parts do not collapse once the supporting PU sponge has vanished. This becomes even more interesting if taking into account the low temperatures of 260 °C when according to SEM micrographs already a huge portion of the supporting PU has vanished from the PU interior. One might object that it is well known that ceramic particles being much smaller than the majority of the ceramic particles might facilitate the formation of small necks between these bigger particles. Indeed, such particle related contact formation gives even merely room temperature dried ceramic bodies a certain mechanical strength. However, the observed penetration of PU decomposition products into the whole ceramic structure might add to the mechanisms giving the ceramic green part enough strength in order to support its own weight until ceramic particle sintering leads to the creation of firm particle-particle contacts.

5. Conclusion

The present work reports about the relation between PU decomposition and resulting shrinkage of ceramic coated rigid open cell PU sponges—a process called replica technique which is being widely used in ceramic processing. It was found that below 167 °C the ceramic coated PU sponges expand due to thermal expansion. Afterwards the shrinkage of the ceramic coated PU sponges closely follows the PU decomposition. When the PU sponge begins to loose mass the ceramic coated PU sponge also starts shrinking. Once the mass loss of the PU reaches its maximum rate the shrinkage of the ceramic coated PU sponge comes to an end. As the PU investigated in this work showed two distinct mass loss peaks this pattern was repeated two times at different temperatures, i.e. between 167 and 267 °C and between 327 and 367 °C. The burnout of the char residue does not lead to a shrinkage of the ceramic body containing these char residues. It was furthermore found that heating to 260 °C already led to the formation of almost completely hollow struts in the ceramic body. Decomposition products of the PU burnout seemed have condensed within the ceramic material.

Acknowledgements

The authors would like to thank U. Braun and D. Hodoroaba for critical reviewing the manuscript. Furthermore the staff of BAM, Federal Institute for Materials Research and Testing, division V.41 “biomaterials and implants” is to be thanked for preparation of the ceramic powder.

References

1. Schwartzwalder, K., Somers, A. V., US Patent No. 3,090,094, 1963.
2. Berger, G., Spitzer, A., Jäger, C., Pauli, J. and Gildenhaar, R., German Patent DE 102 49 627 B4, 2005.;
   Berger, G., Spitzer, A., Jäger, C., Pauli, J. and Gildenhaar, R., US Patent 7,547,448, 2009.
3. Woolley, W. D., Nitrogen-containing products from the thermal decomposition of flexible polyurethane foams. *Br. Polym. J.*, 1972, **4**(1), 27–43.
4. Krol, P., Synthesis methods, chemical structures and phase structures of linear polyurethanes. Properties and applications of linear polyurethanes in polyurethane elastomers, copolymers and ionomers. *Prog. Mater. Sci.*, 2007, **52**(6), 915–1015.
5. Lefebvre, J., Mamleev, V., Le Bras, M. and Bourbigot, S., Kinetic analysis of pyrolysis of cross-linked polymers. *Polym. Degrad. Stab.*, 2005, **88**(1), 85–91.
6. Coutinho, F. M. B., Delpech, M. C., Alves, T. L. and Ferreira, A. A., Degradation profiles of cast films of polyurethane and poly(urethane-urea) aqueous dispersions based on hydroxy-terminated polybutadiene and different diisocyanates. *Polym. Degrad. Stab.*, 2003, **81**(1), 19–27.
7. Coutinho, F. M. B. and Delpech, M. C., Degradation profile of films cast from aqueous polyurethane dispersions. *Polym. Degrad. Stab.*, 2000, **70**(1), 49–57.
8. Mequanint, K., Sanderson, R. and Pasch, H., Thermogravimetric study of phosphated polyurethane ionomers. *Polym. Degrad. Stab.*, 2002, **77**(1), 121–128.
9. Nangrejo, M. R., Bao, X. and Edirisinghe, M. J., Preparation of silicon carbide–silicon nitride composite foams from pre-ceramic polymers. *J. Eur. Ceram. Soc.*, 2000, **20**(11), 1777–1785.
10. Herrera, M., Matuschek, G. and Kettrup, A., Thermal degradation of thermoplastic polyurethane elastomers (TPU) based on MDI. *Polym. Degrad. Stab.*, 2002, **78**(2), 323–331.
11. Mamleev, V., Bourbigot, S., Le Bras, M., Duquesne, S. and Šesták, J., Thermogravimetric analysis of multistage decomposition of materials. *Phys. Chem. Chem. Phys.*, 2000, **2**(20), 4796–4803.
12. Noudem, J. G., Lemonnier, S., Prevel, M., Reddy, E. S., Guilmeau, E. and Goupil, C., Thermoelectric ceramics for generators. *J. Eur. Ceram. Soc.*, 2008, **28**(1), 41–48.
13. Callcut, S. and Knowles, J. C., Correlation between structure and compressive strength in a reticulated glass-reinforced hydroxyapatite foam. *J. Mater. Sci.: Mater. Med.*, 2002, **13**(5), 485–489.
14. Haugen, H., Will, J., Köhler, A., Hopfner, U., Aigner, J. and Wintermantel, E., Ceramic TiO2-foams: characterisation of a potential scaffold. *J. Eur. Ceram. Soc.*, 2004, **24**(4), 661–668.
15. Oliveira, F. A. C., Dias, S., Vaz, M. F. and Fernandes, J. C., Behaviour of open-cell cordierite foams under compression. *J. Eur. Ceram. Soc.*, 2006, **26**(1/2), 179–186.
16. Luyten, J., Mullens, S., Cooymans, J., De Wilde, A. M. and Thijs, I., New processing techniques of ceramic foams. *Adv. Eng. Mater.*, 2003, **5**(10), 715–718.
17. Hagiwara, H. and Green, D. J., Elastic behaviour of open-cell alumina. *J. Am. Ceram. Soc.*, 1987, **70**(11), 811–815.
18. Goretta, K. C., Brezny, R., Dam, C. Q., Green, D. J., De Lopéz, A. R. A. and Rodriguez, A. D., High temperature mechanical behavior of porous open-cell Al_2O_3. *Mater. Sci. Eng. A*, 1990, **124**(2), 151–158.