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Durability aspects of additive manufactured parts for advanced requirements

Additive fabrication technology is predominantly used for prototyping applications up to now. One reason why these flexible technologies are not widely used for end user products is the restricted knowledge about the durability of the manufactured parts. This work provides detailed data on the long term behaviour of mechanical properties of stereolithography specimens after accelerated aging by thermal shock cycling according to automotive standards. One stereolithography resin is found, which shows high durability under repeated extreme thermal load.

Dauergebrauchseigenschaften additiv gefertigter Bauteile für hohe Anforderungen

Die Technologien der additiven Fertigung werden bis jetzt vorzugsweise zur Herstellung von Prototypen genutzt. Ein Grund, warum diese flexiblen Technologien keine weitere Verbreitung bei der Herstellung von Endprodukten finden, ist der Mangel an Wissen über die Dauergebrauchs-eigenschaften der hergestellten Bauteile. In diesem Beitrag werden Ergebnisse zum Langzeit-verhalten der mechanischen Eigenschaften von Stereolithographiebauteilen unter beschleunigter Alterung durch Temperaturschockbelastung nach einem Standard aus der Automobilindustrie vorgestellt. Dabei erweist sich ein Stereolithographieharz als besonders beständig unter wiederholter thermischer Belastung.

Durability aspects of additive manufactured parts for advanced requirements

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1 INTRODUCTION

Up to now additive fabrication technology is mainly used for prototyping, only a few examples are known which are used to fabricate end user products [1]. The applications of parts used in the field of additive manufacturing vary from individual parts for medical purposes to high loaded parts for fighter jets. Two of the main technologies are selective laser sintering (SLS) and stereolithography (SLA) [2]. However the stringent quality demands of several industries e. g. civil aviation or automotive prevent a wider usage of these flexible technologies. One of the strictest requirements among these quality demands are the accelarated aging tests like temperature shock cycling especially for polymer parts.

Whereas SLS parts are well known for their good mechanical properties and long term durability [2], SLA parts are considered to have better surface quality but degradable mechanical properties over time due to the UV curing nature of the resin [3].

According to their historic relevance for stereolithography acrylate based resins are intensively investigated [4]. Nowadays acrylate based resins seem to have a renaissance due to their biocompatibility compared to epoxy based resins [5]. Acrylate based resins are considered to be critical under dry temperature aging but also under moistly temperature aging. Under dry temperature aging a significant decrease of mechanical parameters like Young’s modulus, tensile strength and elongation of break is found. Under moistly temperature aging Young’s modulus and tensile strength decrease but elongation at break is increased. It is suspected that the decrease of mechanical parameters could be caused by thermal oxidative degradation and the softening of the material could be caused by inclusion of water [5]. This effect is confirmed for stereolithographic acrylate-epoxy combined systems. Here the magnitude of decrease of mechanical properties is found to be related directly to the magnitude of moisture up taken by the material [6]. Beside this also stereolithographic epoxy resins are investigated under aging conditions. Photo curing epoxy based systems used for stereolithography show a significant post built cure also without the presence of light, the so called “dark reaction” [7]. It is found that the degree of cure also under normal conditions (23 °C, 50 % relative humidity) is significantly increased and causes an embrittlement and not a softening of the material [8]. Change of the inner structure like the degree of curing causes not only alteration of the mechanical properties but also a change in glass transition temperature. An increase of glass transition temperature is directly related to an increase of the degree of cure. This is documented in literature for thermal curing and photo curing plastics [9, 10, 11]. As curing processes are enhanced at higher temperatures due to the better mobility of the polymer chains [12] the degree of cure and thus the change in mechanical properties is not easily predictable especially under time dependent temperature variations stereolithography parts for end user purposes suffer during use.

Thermal shock cycling is an introduced test standard in the automotive industry to shorten test time and to apply defined conditions. Further it states advanced requirements compared to prototyping especially for parts which properties are critical to temperature variations like epoxy based stereolithography parts [13].

To extend the knowledge about the durability of epoxy based stereolithography parts, this work provides detailed data on the time developing mechanical properties of stereolithography parts and the extend of embrittlement due to post built cure reinforced by thermal shock cycling according to automotive standards.

Stereolithography

Like all other types of additive processes SLA enables the physical creation of a part from a designed CAD model. The digital data of this model has to be placed and orientated in the virtual building space of the stereolithographic machine. Further a filigree load carrying construction is generated automatically by the data pre-processing software. This construction supports the hardened and thus densified part in order to keep the position of the working piece on the building platform. As the building operation is performed layer wise the geometrical data of the part and the supporting construction has to be sliced in adequate digital layers with a height of typically 0.1 mm. One of these layers is fabricated by spreading a liquid photo-resin over the building platform with a spreading knife. Afterwards the radiation of an UV laser is used to cure the material on the surface of the resin bath according to the given layer information. Finally the building platform is lowered. By repeating this procedure the complete work piece is generated layer by layer. After the generative process is finished the part is cleaned from some adherent liquid resin and irradiated with artificial UV light in a post curing apparatus (PCA) for a predetermined time [14].

2 EXPERIMENTAL METHODS

Accelerated aging of stereolithography specimens is carried out by temperature shock tests with cycles between -40 °C and +125 °C according to DIN EN 60

068-2-14. The tests are conducted in a Weiss TS temperature shock chamber with a transition time of 15 s between the cold and the hot chamber. The dwell time at each temperature is 20 min. Beyond the standard procedure, where specimens are tested for pass or fail after 1000 cycles, three specimens are removed from the climatic chamber every 250 cycles and are qualified by tensile testing and dimensional measurement.

The specimens for tensile testing follow the geometrically proposal of CAMPUS Typ A, according EN ISO 3167, with a length of 170 mm, a width of 10 mm and a thickness of 3.5 mm. The tensile bars are orientated on the building platform in coating direction standing on the long edge, as shown in Figure 1.

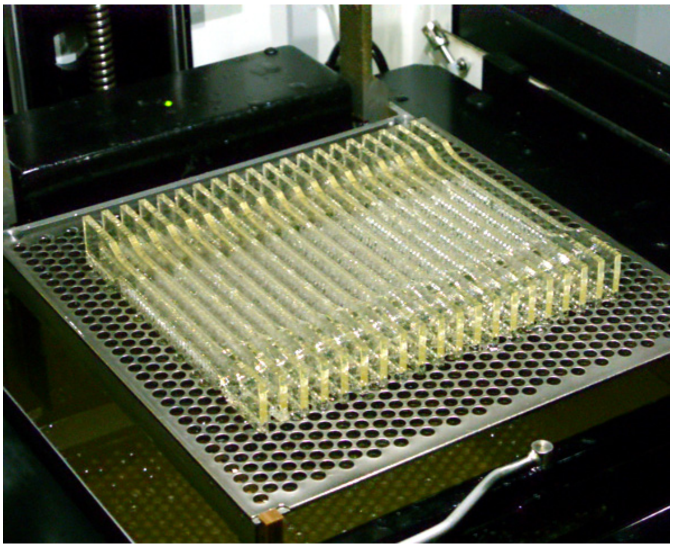

Figure 1: Tensile test bars on the building platform of a SLA 250/50

Tensile testing is performed by using universal test equipment (LFEM 300, Walter+Bai AG). The tensile force is measured with a 5 kN load cell at room temperature and a test velocity of 5 mm/min according to ISO 527. The diagrams in section 4 respectively show the average values and the measured standard deviation for three samples, due to the high number of specimens necessary for the complete test of 1000 cycles.

Glass transition temperature is determined as midpoint temperature by differential scanning calorimetry (DSC) according conditions described in ISO 11357-2:1999(E) by using a DSC 822 with intra cooler, Mettler-Toledo, Greifensee, Switzerland. Three samples are measured conditioned by the same number of temperature cycles.

For dimensional measurements a measuring gauge with a scale-reading precision of 0.05 mm is used. This scale-reading precision is equal to a relative length of 0.03 % for the used specimens.

3 MATERIAL SELECTION AND MECHANICAL CHARACTERISATION

Epoxies do normally not show ductile behaviour, they are brittle with few percents of elongation at break. SLA epoxies are developed in order to show more ductility or even a homogenous deformation. Despite the stereolithographic resins not reaching the high elongation at break of the most thermoplastics or even elastomers the characteristic behaviour with few percents of elongation at break is given. The selection of investigated materials was done by considering epoxy-based SLA resins, which represent different typical mechanical behaviours of polymers, which are ductile behaviour, ductile behaviour with drawing and homogeneous deformation [15]. Due to the specific mechanical behaviour the selected resins are designed for specific applications or to imitate the mechanical properties of technical thermoplastics. The epoxy based Accura SI45HC (3D Systems, Rock Hill, USA) is chosen as a ductile thermoset. Nevertheless, it is rather brittle compared to thermoplastics. Accura SI45HC is typically used for thermally loaded, functional parts [16]. Somos 11110 (DSM, Elgin, USA) as well as an epoxy based resin shows a ductile behaviour with some drawing, which imitates ABS [17]. The also epoxy based resin Somos 8110 is a material with high impact strength, which shows some extend of homogeneous deformation [18].

For the Purpose of characterizing the materials before aging test a tensile test is conducted. The specimens for this test are manufactured under typical conditions for manufacturing of additive parts. This includes the use of resin, which is stored and in dependency from the volume of former parts partially renewed in the stereolithography apparatus. Figure 2 shows a comparison of the measured tensile stress-strain-curves of not preloaded stereolithography specimens and the data-sheet values of elongation at break as well as of maximum tensile strength.

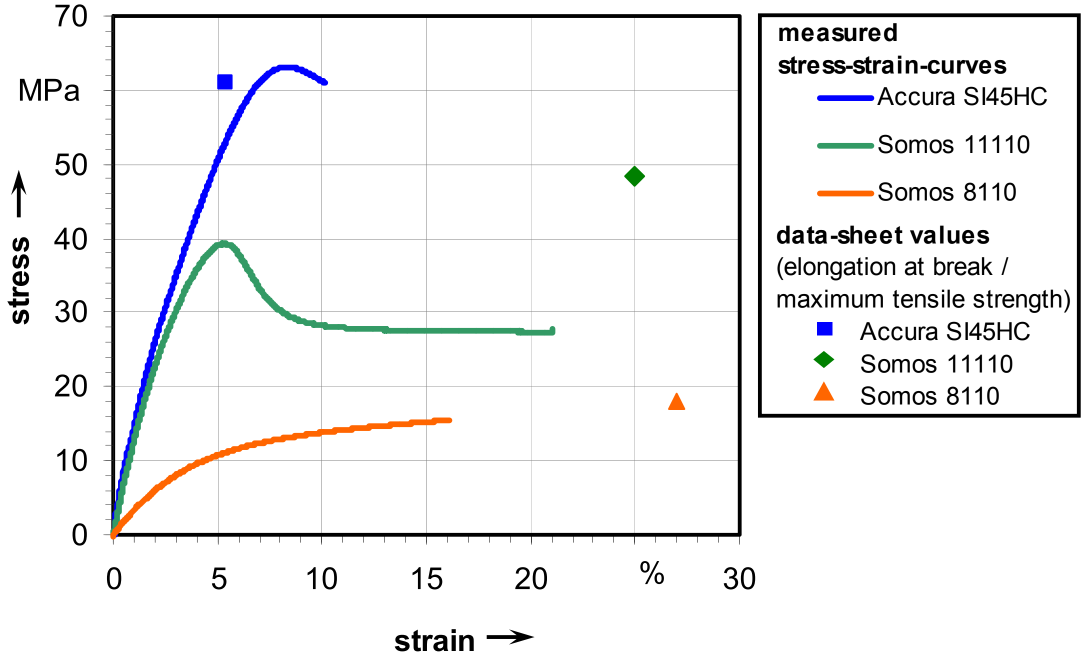

Figure 2: Typical tensile stress-strain-curves of the selected SLA resins;

Accura SI45HC: brittle/ductile without stretching behaviour;
Somos 11110: ductile behaviour with stretching;
Somos 8110: material with homogeneous deformation

For Accura SI45HC elongation at break is approximately two times higher than the data-sheet value. The maximum tensile strength can be reproduced. For Somos 11110 a distinct lower maximum tensile strength as in the data-sheet was detected but the elongation of break comes close to the data-sheet value. For Somos 8110 the high specified elongation of break in the data-sheet could not be confirmed but the maximum tensile strength matches the data-sheet value. According to material supplier the datasheet values are taken immediately after optimal manufacturing of the samples. This procedure neglects pre-aged liquid resin, uncontrolled manufacturing conditions, dark reaction of the cured resin and thermal load during shipment. Despite the used samples show not the optimum mechanical properties they represent a more realistic state of the art.

4 EXPERIMENTAL RESULTS

Figures 3 to 5 show the development of the characteristic mechanical values under accelerated aging activated by thermal shock cycling. Additionally, data-sheet values are outlined on the ordinate. For maximum tensile strengths, see Figure 3, different types of developing are visible. Whereas the Accura SI45HC shows no significant alteration over time, the Somos 11110 and the Somos 8110 show a significant increase of maximum tensile strength.

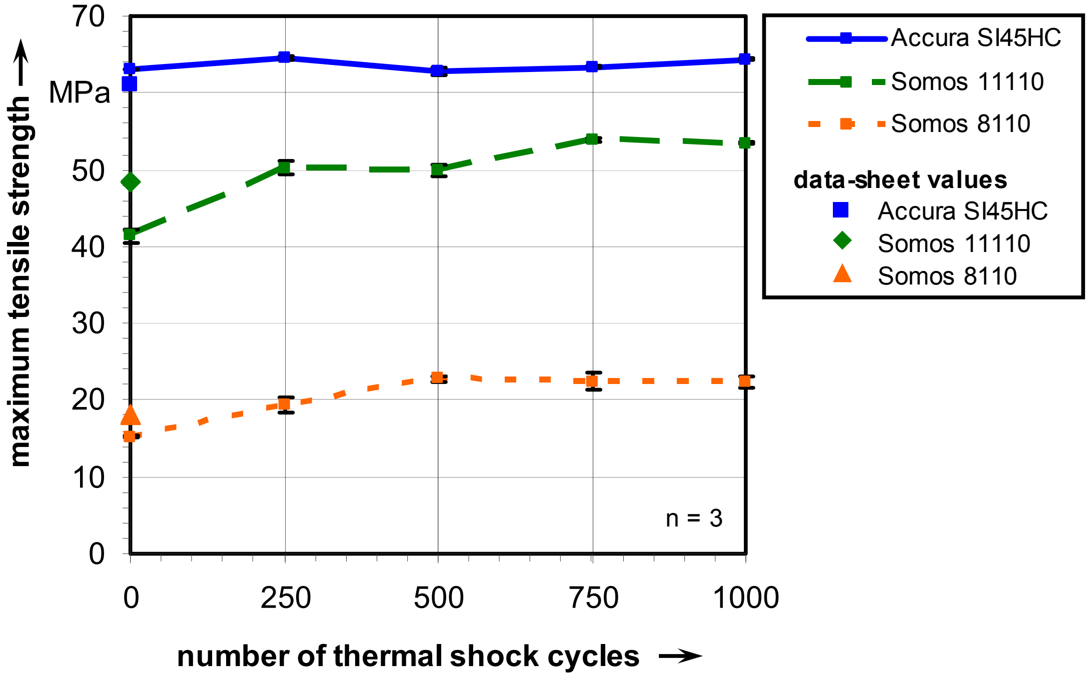

Figure 3: Maximum tensile strength versus number of thermal shock cycles

According to this, the elongation at break is reduced for these materials as shown in Figure 4. This can be understood as an embrittlement of the material. This is also confirmed by regarding the modulus of elasticity, see Figure 5. For Somos 11110 the modulus of elasticity is already increased after 250 cycles as well as the elongation at break. For the Somos 8110 material the modulus of elasticity reaches an upper level approximately after 500 cycles. A similar behaviour can be observed for the elongation at break. For the elongation at break and the modulus of elasticity of Accura SI45HC no significant alteration is investigated.

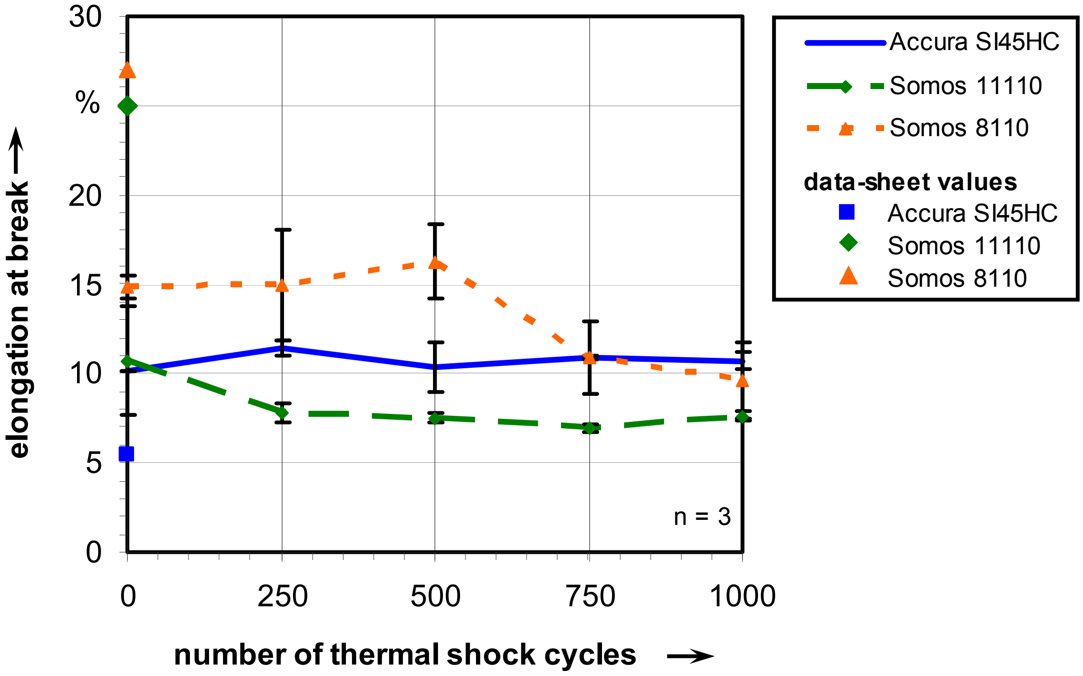

Figure 4: Elongation at break versus number of thermal shock cycles

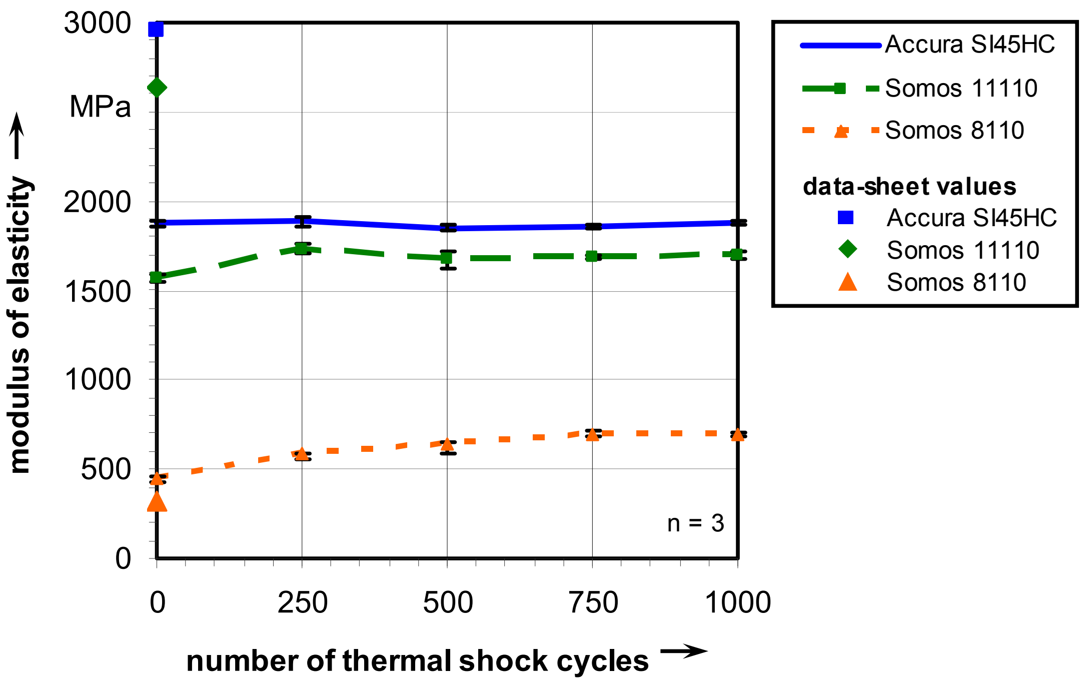

Figure 5: Modulus of elasticity versus number of thermal shock cycles

The embrittlement of the materials can be explained by proceeding cross linking due to thermal activation during the thermal shock cycles as reported for thermosetting polymers in general and epoxy resins in particular. Proceeding cross linking is proven by increasing glass transition temperature of the investigated materials, see Figure 6.

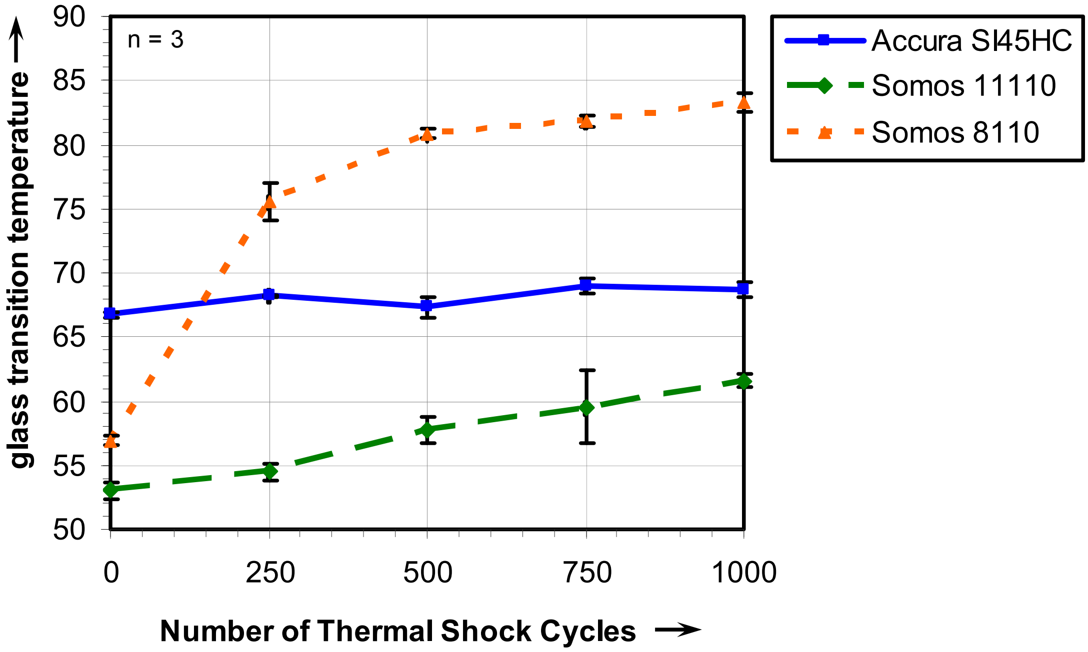

Figure 6: Change of glass transition temperature versus number of thermal shock cycles

The glass transition temperature versus number of thermal shock cycles develops differently. The Accura SI45HC shows only 2 K average increase of glass transition temperature, the Somos 11110 shows 9 K and the Somos 8110 shows 26 K after 1000 cycles. Despite the dependency between increasing glass transition temperature and proceeding cross linking is not linearly and material dependent a correlation of increasing glass transition temperature and increasing embrittlement can be stated.

A further effect of proceeding cross linking is the shrinkage of the parts. To correlate investigated embrittlement with shrinkage the development of the relative length of the specimens is shown over the number of load cycles in Figure 7.

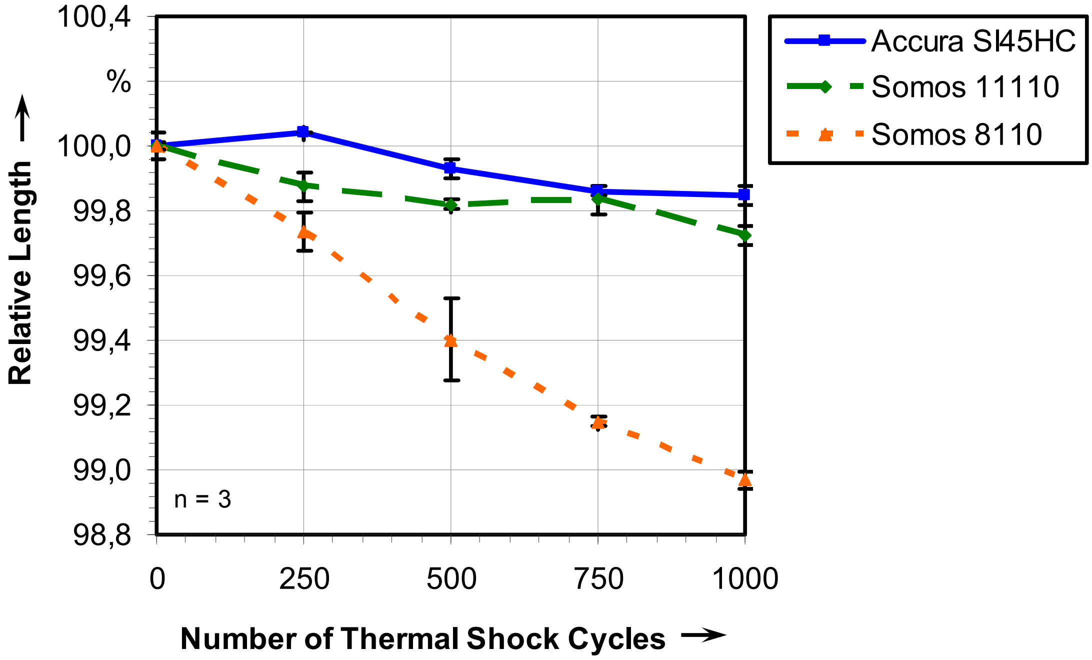

Figure 7: Relative length of specimens versus number of thermal shock cycles

The investigated materials show significant differences in shrinkage. The Accura SI45HC shows only 0.15 % the Somos 11110 shows 0.30 % and the Somos 8110 shows 1.0 % after 1000 cycles. This corresponds well with the investigated amount of embrittlement of the materials. For the Accura SI45HC a relative increase of maximum tensile strength of 2.0 %, a relative increase of modulus of elasticity of 0.4 % and a relative decrease of elongation at break of 5.6 % compared with the unloaded specimens is found. The Somos 11110 shows a relative increase of maximum tensile strength of 29 %, a relative increase of modulus of elasticity of 7,8 % and a relative decrease of elongation at break of 29 % compared with the unloaded specimens. For the Somos 8110 the highest shrinkage corresponds to the most prominent relative increase of maximum tensile strength of 47 % and modulus of elasticity of 56 % as well as to the highest relative decrease of elongation at break of 35 % compared with the unloaded specimens.

5 SUMMARY

Additive fabrication technologies especially stereolithography is not widely used for end user products. One reason is the restricted knowledge about the durability of the manufactured parts. In order to overcome this deficit long term behaviour of mechanical properties after accelerated aging according to automotive standards are determined. As mechanical properties of stereolithography parts are critical under variation of temperature thermal shock cycling is selected as test procedure. By the results of this test the knowledge about the durability of epoxy based stereolithography parts is extended and detailed data on the time developing mechanical properties of stereolithography parts as well as the extend of embrittlement is provided.

The lack of reproducible part properties could be tolerated so far in terms of prototyping but not for additive manufacturing. The difference of mechanical properties which is obvious by the comparison of the mechanical values in the data-sheets and the measured values points out one of the basic issues stereolithography and other additive processes suffer so far.

The presumed degradation of mechanical properties of SLA parts under accelerated aging could be confirmed only partially. The SLA resin with ductile behaviour (Accura SI45HC) shows a quite durable behaviour. Maximum tensile strength and modulus of elasticity does not change significantly versus the number of thermal shock cycles. Only elongation at break increases by 5.6 %. Besides this, the SLA resin with the ductile behaviour and drawing (Somos 11110) shows a significant increase of about 30 % in maximum tensile strength and the same range of decrease in elongation at break. The modulus of elasticity increases only by 8 %. The SLA resin with the homogeneous deformation (Somos 8110) shows 45 % increase in maximum tensile strength, 35 % decrease in elongation at break and 55 % increase in modulus of elasticity.

By correlating these amounts of embrittlement with the amount of shrinkage for the investigated stereolithographic resins it seems that thermal shock cycling is enhancing post built cure due to the better mobility of the polymer chains at higher temperatures. Like it is known for other epoxy based resins a higher degree of cure cause significant embrittlement. But this influence on the mechanical properties clearly depends on the considered stereolithographic resin. The findings indicate that the higher the elasticity of a resin is the more embrittlement occurs under thermal shock cycling. Beyond that phenomenological statement the detailed correlations between shrinkage and post cure effect as well as between post cure effect and mechanical behaviour are not yet completely explained and should be addressed by future work. But for the use of stereolithography parts as end user parts important information can be provided.

The found alteration in mechanical properties of the ductile resin with drawings and the resin with homogeneous deformation has to be taken into account by using these materials in applications with advanced thermal load. In contrast to this the SLA resin with ductile behaviour (Accura SI45HC) has shown the potential to pass an accelerated aging test according to automotive standards.

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References

[1] Gebhardt, A. Rapid Prototyping. Carl Hanser Verlag, Munich, 2003

[2] Kruth, J. P. et. al. Lasers and materials in selective laser sintering. Assembly Automation, 4, 2003, pp. 357-371

[3] Wohlers, T. Wohlers Report 2009 Rapid Prototyping, Tooling & Manufacturing State of the Industry. Wohlers Associates, Inc., Fort Collins, Colorado, USA, 2009

[4] Corcione, C. E., Greco, A., Maffezzoli, A. Photopolymerization kinietics of an Epoxy based resin for stereolithography. Journal of Thermal Analysis and Calorimetry, 72, 2003, pp 687-693

[5] Tröger, C. et. al. Ageing of acrylate-based resins for stereolithography: thermal and humidity ageing behaviour studies. Rapid Prototyping Journal, 14, 5, 2008, pp. 305–317

[6] Ottemer, X., Colton, J. S. Effects of aging on epoxy-based rapid tooling materials. Rapid Prototyping Journal, 8, 4, 2002, pp. 215–223

[7] Decker, C., Moussa, K. Kinetic study of the cationic photopolymerization of epoxy monomers. Journal of Polymer Science Part A: Polymer Chemistry, 28, 12, 1990, pp. 3429-3443

[8]	Mansour, S. Gilbert, M. Haguec, R.	A study of the impact of short-term ageing on the mechanical properties of a stereolithography resin Materials Science and Engineering Part A, 447, 2007, pp. 277-284
[9]	Di Benedetto, A.T.	Prediction of the Glass Transition Temperature of Polymers: A Model Based on the Principle of Corresponding States Journal of Polymer Science: Part B: Polymer Physics, 25, 1987, pp. 1949-1969
[10]	Venditti, R. A. Gillham, J. K.	A Relationship Between the Glass Transition Temperature (T_g) and Fractional Conversion for Thermosetting Systems Journal of Applied Polymer Science, 64 (1998) 1, pp.3-14
[11]	Kannurpatti, A. R. Andersond, K. J. Anseth, J. W. Bowman, C. N.	Use of ‘‘Living’’ Radical Polymerizations to Study the Structural Evolution and Properties of Highly Crosslinked Polymer Networks Journal of Polymer Science Part B: Polymer Physics 35 (1998) 14, pp. 2297-2301
[12]	Sourour, S. Kamala, M.R.	Differential scanning calorimetry of epoxy cure: isothermal cure kinetics Thermochimica Acta, 14, 1-2, 1976, pp. 41-59
[13]	Lee, H. Neville, K.	Handbook of epoxy resins. McGraw-Hill, 1967
[14]	Jacobs, P. F. Reid, D. T.	Rapid prototyping & manufacturing: Fundamentals of stereolithograph Society of Manufacturing Engineers, 1992
[15]	Ward, I. M. Sweeney, J.	An introduction to the mechanical properties of solid polymers John Wiley and Sons Ltd., 2004
[16]	3DSystems	Stereolithography (SL)-Materialf: Accura® si 45HC. 2004, pp. 2, www.3dsystems.com, 09.11.2009
[17]	DSM-Somos	Technical Datasheet Watershed 11110, 2005, pp. 2, www.dsm.com, 09.11.2009
[18]	DSM-Somos	Technical Datasheet Somos 8110 Epoxy Photopolymer, 2005, pp. 2, www.dsm.com, 09.11.2009

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