

LONG-TERM DURABILITY OF SLS POLYMER COMPONENTS UNDER AUTOMOTIVE APPLICATION ENVIRONMENT

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REVIEWED, Accepted August 15, 2012

Abstract

Selective Laser Sintering (SLS) is close to be accepted as a genuine production technique (Additive Manufacturing). However, one problem restricting a more frequent specific use of SLS-parts is the limited or unknown long-term or functional behaviour under particular environmental conditions. In our specific case, for automotive applications, plastic materials can get in contact with brake fluid and coolant. The behaviour of commercial SLS materials in contact with these liquids must be qualified in advance for a successful implementation. This contribution investigates the resistance of Duraform[®] DF and Duraform[®] HST SLS made parts in contact with the cited automotive media. The testes were carried out for parts as of the machine and in a post processed coated state. Distinctive Epoxy-, Silicon- and PVC-based sealant was used. Gravimetric analyses and results of mechanical behaviour are presented with respect to material, type of coating and immersion time.

Introduction

Additive Manufacturing (AM) is a computerized method for direct conversion of 3D CAD data into physical objects by a variety of different approaches [1]. Selective Laser Sintering (SLS) of plastic powders is part of these ‘layer by layer’ based additive production techniques that are frequently considered as the next industrial revolution [2]. Solidifying plastic powders with laser radiation by means of digital data opens countless options for production of individualized parts with great freedom of complexity [3]. However, there are still some drawbacks hindering a wider acceptance of AM made plastic parts in many industries. Beyond the limited commercialised SLS suitable polymeric materials [4,5], only limited knowledge and data are available for an enduring use of parts under different industrial conditions. Only a few studies investigate long-term behavior of SLS materials so far, focusing on water contact [6,7] and mechanical alteration under load or different temperatures [8,9]. Moreover, the use of plastic parts can be very diverse and require precise information of the interaction between material and medium for each application. The interaction part/environment can occur with a wide variety of chemicals, gases, oxidative substances, vacuum, radiation (UV), living organism and much more [10]. Substances like brake fluid, coolant, gasoline, ethanol and diesel can be associated in the automotive sector. The most frequent applied commercial SLS powder materials to date are based on polyamide 12 (PA 12). Thus, it is apparent to investigate these types of polymers firstly (e.g. Duraform DF and HST). Additionally, functional coatings can be applied to those SLS parts in order to improve their resistance against specified chemicals. The paper describes a systematic investigation of SLS parts in long-term contact with typical automotive fluids (coolant and brake fluid) and explores the effectiveness of functional coatings as well.

Materials and Methods

Polymeric Materials: Commercial SLS polymers used in this investigation are Duraform[®] DF and Duraform[®] HST. The powders were used as purchased from supplier 3D Systems. The specimens were made by regular SLS processing (Equipment: DTM HiQ) the selected geometry was tensile specimens (DIN 527-2).

Automotive Fluids: Coolant and brake fluid (Type: DOT 4) were applied as purchased in a car accessory shop. The coolant mixture was used in 1:1 dilution with water (protection until -37°C). No further modifications or additives of the automotive fluids were introduced.

Coating chemicals (active component): Three different coating chemistries were applied: a) Epoxy (Araldit), b) Silicon (Elastosil), c) Polyvinylchloride PCV (Vinnol). The Epoxy coating is a 2 component coating system used as prescribed in the product instructions sheet. The Silicon and the PVC coatings were diluted with an organic solvent to a concentration of about 10% active component.

Coating procedure (dip coating): DIN 527-2 test specimens were immersed first for 2 minutes into the given coating solution (solvent and active component) and then dried overnight. In a second operation they were immersed once again for additional 2 minutes and dried again (double coating); The silicon coatings were dried at 60°C for 30 minutes as recommended by the manufacturer as to improve adhesion and film formation.

Coating layer thickness: The active medium layer thicknesses of the applied coatings was calculated by the weight difference before and after dip coating for each specimen divided by the theoretical surface area of a DIN 527-2 test bars (surface area (a): $a = 60 \text{ cm}^2$);

Immersion in the car fluids: Uncoated and coated test specimens were immersed for 1 week and 4 weeks respectively in coolant and brake fluid. The storing took place at room temperature (23°C).

Gravimetric evaluation: After immersion for the desired time (1 and 4 week) all specimens were removed from the fluid, dried with blotting paper and immediately weighted. From the weight difference compared to the uncoated specimen the barrier properties and behavior of each coating can be estimated qualitatively.

Mechanical evaluation: Tensile test according DIN 527-2 were performed for all combinations of exposure time and applied coating. E-modulus and tensile strength were used as parameter to estimate the influence of the automotive fluids, coating and time respectively on the long-term behavior.

Results and Discussion, Part 1: Coating of SLS Parts

Polymer parts show a different behavior exposed to different contact media. Some indication of behavior can be found in commonly used tables for chemical resistance of polymers [11]. Those tables for injected specimens help only in restricted manner for SLS parts as they are typically less dense as injection molded ones. This means that one has to count with higher permeation rate of gases and liquids into SLS parts, demonstrate porosity and therefore have a restricted chemical resistance. One way to improve SLS parts against (aggressive) contact media is a sealing of the surface with an adequate coating. The application of such coatings should be an easy going as it is the case for dip coating. Traditional coating like painting or varnishing is less suitable since 'real' SLS parts exhibit generally a high geometric complexity.

The aim of dip coating is an enduring sealing of the surface by a simple application process. Advantage of dip coating is that layer thicknesses can be easily controlled by the

residence time, concentration of the dip coating solution and the removal speed at withdrawal of dip solution. Moreover, the process is simple, economical and contamination of layers can be avoided without any effort. The dip coating solutions usually consists of an active component and an organic solvent. Both substances have to fulfil certain requirements. Figure 1 summarizes the main requests for active component and organic solvent in a dip coating solution.

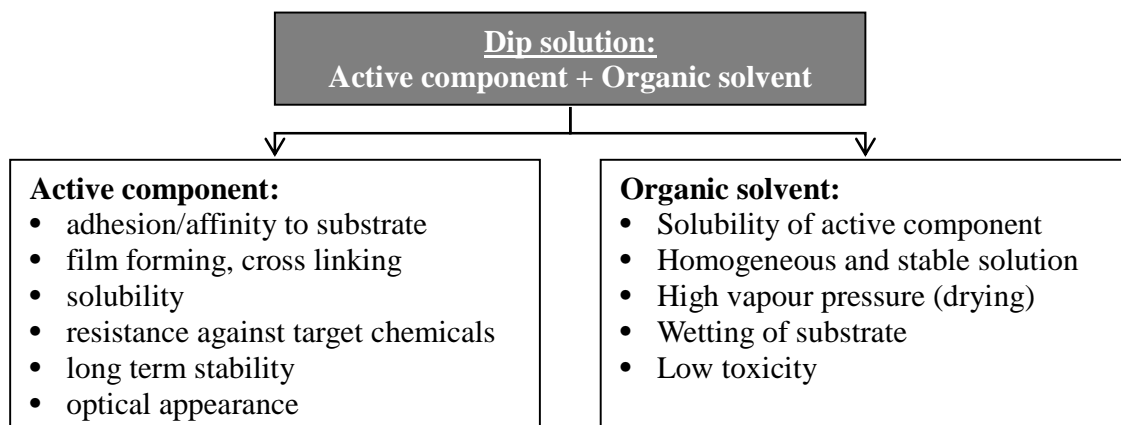


Figure 1: Main requirements for components for dip coating solutions

Especially the desired properties of the active component like film forming and resistance versus the target chemicals are very important for a successful sealing success. In our case a handful different chemical solutions (active component) are thinkable. Figure 2 recaps the chemical solutions suited in principle for our purpose and explore their advantage/disadvantage.

Active component	advantage	disadvantage
Silicone $\left[\begin{array}{c} R_1 \\ \\ -Si-O- \\ \\ R_2 \end{array} \right]_n$	- extremely water repellent - huge variations possible (R ₁ ,R ₂)	- inorganic (compatibility with organic solvents insufficient); - difficult further processing
Vinyl-Acrylate $\left[\begin{array}{c} R_1 \\ \\ -CH-CH- \\ \\ COOR_2 \end{array} \right]_n$	- very good soluble - good film-forming (lacquers) - huge variations possible	- affinity to water - poor UV stability (yellowing)
PVC-Basis $\left[\begin{array}{c} Cl \\ \\ -CH-CH- \\ \\ R_1 \end{array} \right]_n$	- long term resistance outdoor (UV stability) - water repellent	- Compatibility to PA poor (adhesion?) - chlorinated solvents
Epoxide $R_1-CH_2-\begin{array}{c} O \\ \diagup \quad \diagdown \\ CH-CH_2 \end{array} + \text{Aminhärter}$	- highly film-forming due to cross-linking - good substrate anchorage by 'insitu' chemical reaction	- 2 component systems (long term durability of solutions?); - water affinity by -OH groups
Poly-Urethane $\left[\begin{array}{c} H \\ \\ R_1-N-C-O-R_2 \\ \\ O \end{array} \right]_n$	- huge variation possibilities - chemically similar to PA's - good film-forming (lacquers)	- water absorption - long term stability at higher temperature reduced

Figure 2: Principal chemical coatings selection applicable as active components in dip solutions

From this assortment the epoxy, silicon and PVC coating chemicals were selected for this study. The motivations were some results of preliminary experiments and the commercial availability of the selected chemicals. The tensile test specimens were immersed in the three selected coating solutions and a medium layer thickness of the applied coatings was found to be: - Epoxy ca. 70 μm ; Silicon ca. 60 μm ; - PVC ca. 10 μm . These values have to be obviously considered in a final assembly design of real applications. The differences are due to the different viscosity of the dip coating solutions and the adhesion differences of the various coating chemicals. Bonding differences are not necessarily observed directly after the coating process, but only after a certain prolonged contact with the desired automotive media. We observed some drastic effects in the case of the epoxy coating, that was completely delaminated from the Duraform[®] DF specimens after 4 week immersion in the brake fluid (see Figure 3). In contradiction the epoxy coating demonstrate no delamination in case of Duraform[®] HST.

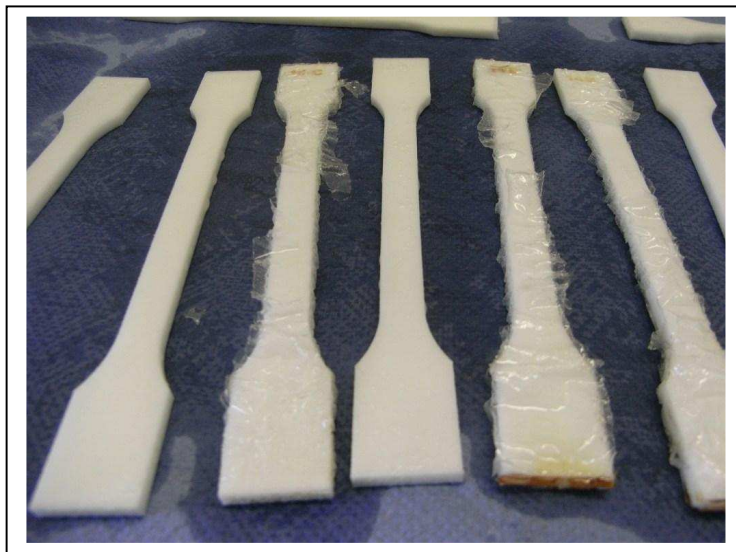


Figure 3: Epoxy coating on DF after 4 weeks in brake fluid

A complete overview of the behaviour of the different coatings immersed in brake fluid (B) and coolant (C) is summarized in Table 1.

Table 1: Visual appraisal of behaviour of coatings in contact with brake fluid (B) and coolant (C);

	Duraform[®] DF	Duraform[®] HST
Epoxy coating	C: discolouring; B: delamination;	C: good adhesion – slight discolouring; B: no delamination;
Silicon coating	C: coating stable; B: delamination;	C: good adhesion – slight discolouring; B: delamination by mechanical forces;
PVC coating	C&B: coating stable; neutral behaviour	C&B: coating stable; neutral behaviour

With this table it is observable that different coatings perform different on Duraform[®] DF and Duraform[®] HST. Duraform[®] HST contains mineral fibers as reinforcement components. By this, the polarity of the surfaces changes necessarily and the adhesion capability as well. The

different behavior of coatings on Duraform[®] DF and HST is not unexpected and explainable. This different performance must be kept in mind for the review and quantification of the following gravimetric evaluation and the results of mechanical testing.

Results and Discussion, Part 2: Gravimetry

Gravimetric evaluation of the different coated specimen with respect to immersion time provides a good indication about the ability of the applied coatings regarding their sealing properties. If the weight change of a coated sample is less than for uncoated specimen after the same ambient exposure a certain sealing capability can be implied. Figure 4 and Figure 5 illustrates the weight change findings in percentage for Duraform[®] DF and Duraform[®] HST with the various applied coatings. Taking the uncoated test specimen (grey bars in Figure 4 and 5) as reference it can be seen clearly that the silicon and PVC coating exhibit a certain sealing ability for Duraform[®] DF in case of contact with coolant (Figure 4, left diagram). Definitely, no effect or even a negative effect was established for all coating combinations of Duraform[®] DF in contact with the brake fluid (Figure 4, right diagram). The weight increase in case of Epoxy and Silicon coating is dramatic and means that these coatings even support absorption of brake fluid. This shows that Duraform[®] DF cannot be protected from brake fluid with the chosen coatings at all.

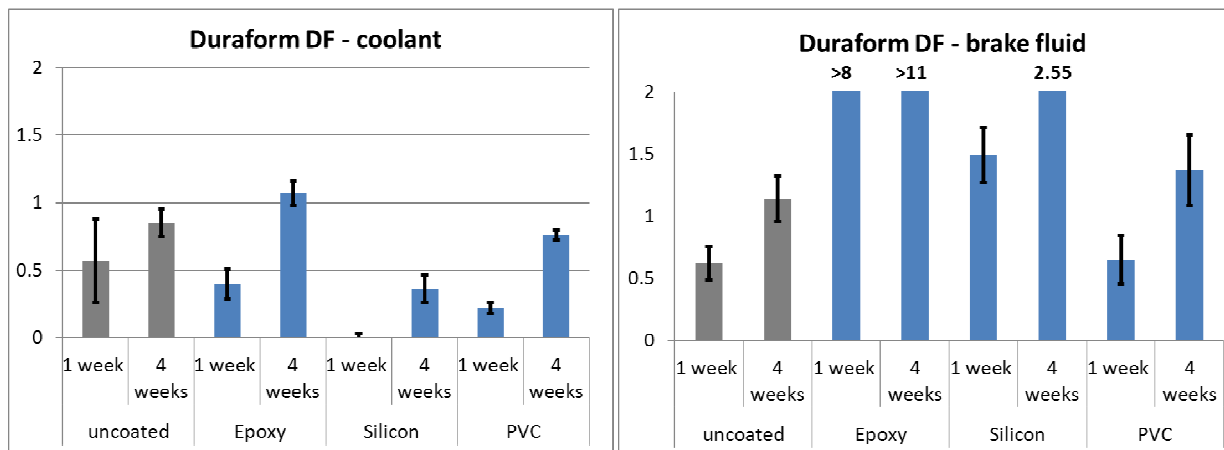


Figure 4: Weight change (%) of DF specimen with different coatings and immersion time

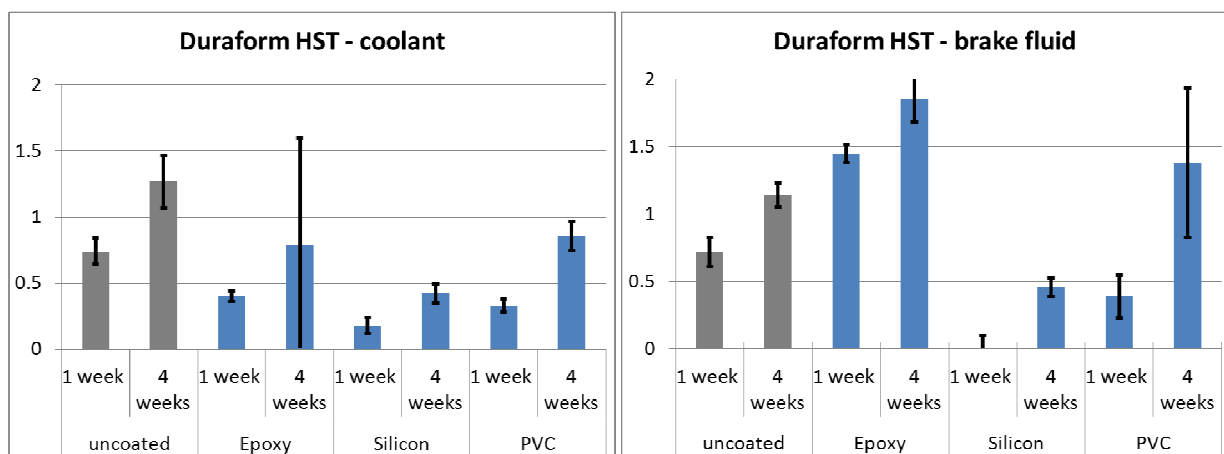


Figure 5: Weight change (%) of HST specimen with different coatings and immersion time

A different behaviour was found for Duraform[®] HST and brake fluid (Figure 5, right diagram). A positive effect of sealing can be clearly seen for Silicon coating. A reduced absorption of brake fluid (less than 0.5% after 4 weeks) is designated. But there is no significant effect for epoxy and PVC coating in case of brake fluid. For coolant in combination with Duraform[®] HST all sealing chemical seems to have a certain positive effect, whereas the silicon coating seems to be most effective option from the chosen solutions (Figure 5, left diagram). In summary the effect of the various coatings can be summarized as following:

- **Epoxy coating:**
 - massive weight increase especially for brake fluid → no sealing effect
 - negative enhancement (absorption of fluids); → additional severe delamination;
- **Silicon coating:**
 - less weight increase than uncoated (exception: DF/brake fluid - with delamination);
 - certain protection capability seems to be present; adhesion to be enhanced;
- **PVC coating:**
 - positive sealing effect for coolant but hardly no effect for brake fluid; → Optimisation possibly due to increase of coating layer thickness and the substrate/ coating anchorage;

Results and Discussion, Part 3: Mechanical Properties Testing

In addition to gravimetric evaluation, also mechanical testing was performed as an indication of the inherent properties changes. Variation of E-modulus and tensile strength were measured as representative values. Figure 6 and 7 illustrates the findings.

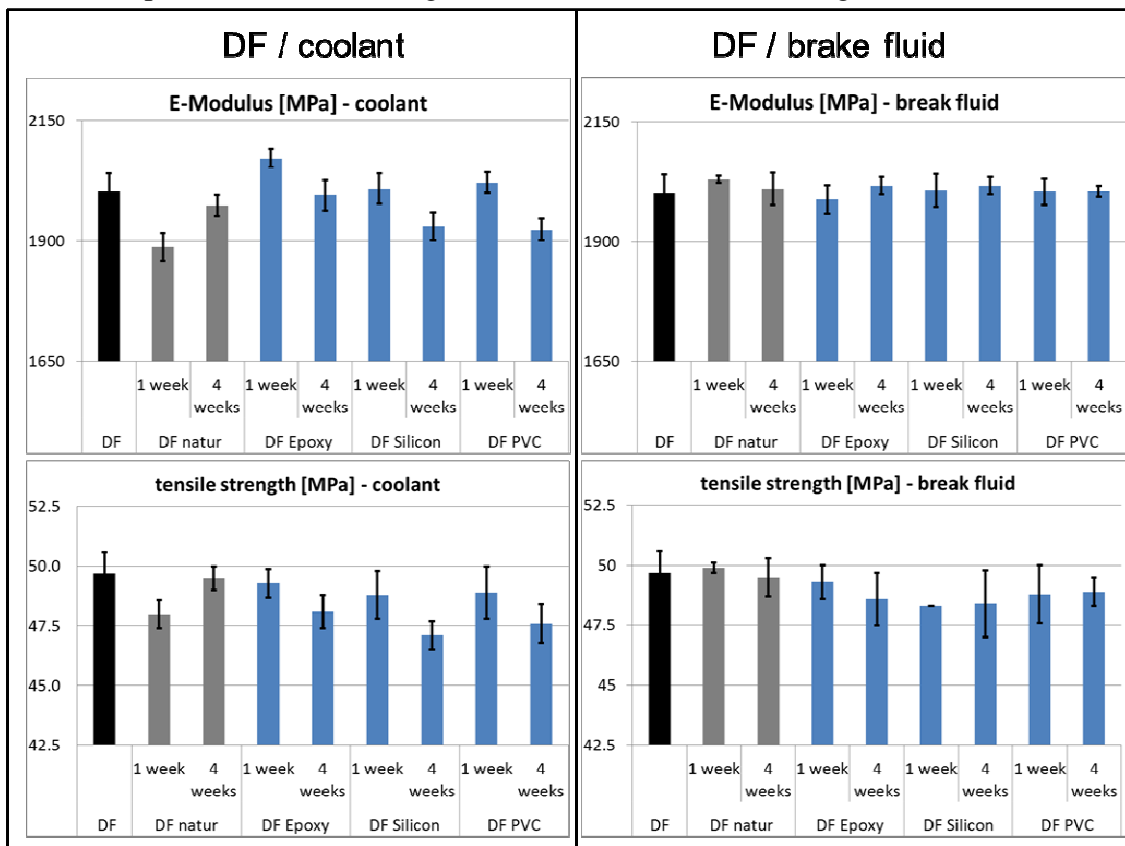


Figure 6: Change of E-mod. and tensile strength for DF in dependence of store time and coatings;

Referring to Figure 6 it is evident that the mechanical properties of Duraform® DF will not be influenced severely under the chosen conditions. Neither coolant nor the brake fluid show particular drastic alteration of the mechanical properties. An effect of coatings cannot be documented.

Somewhat different were the findings for the Duraform® HST. Figure 7 (left side) illustrates a noticeably reduction of E-modulus and the tensile strength for Duraform® HST in contact with the coolant emulsion. Regarding the brake fluid the influence is marginal (Figure 7, right side) and not at the same rate as for coolant exposure.

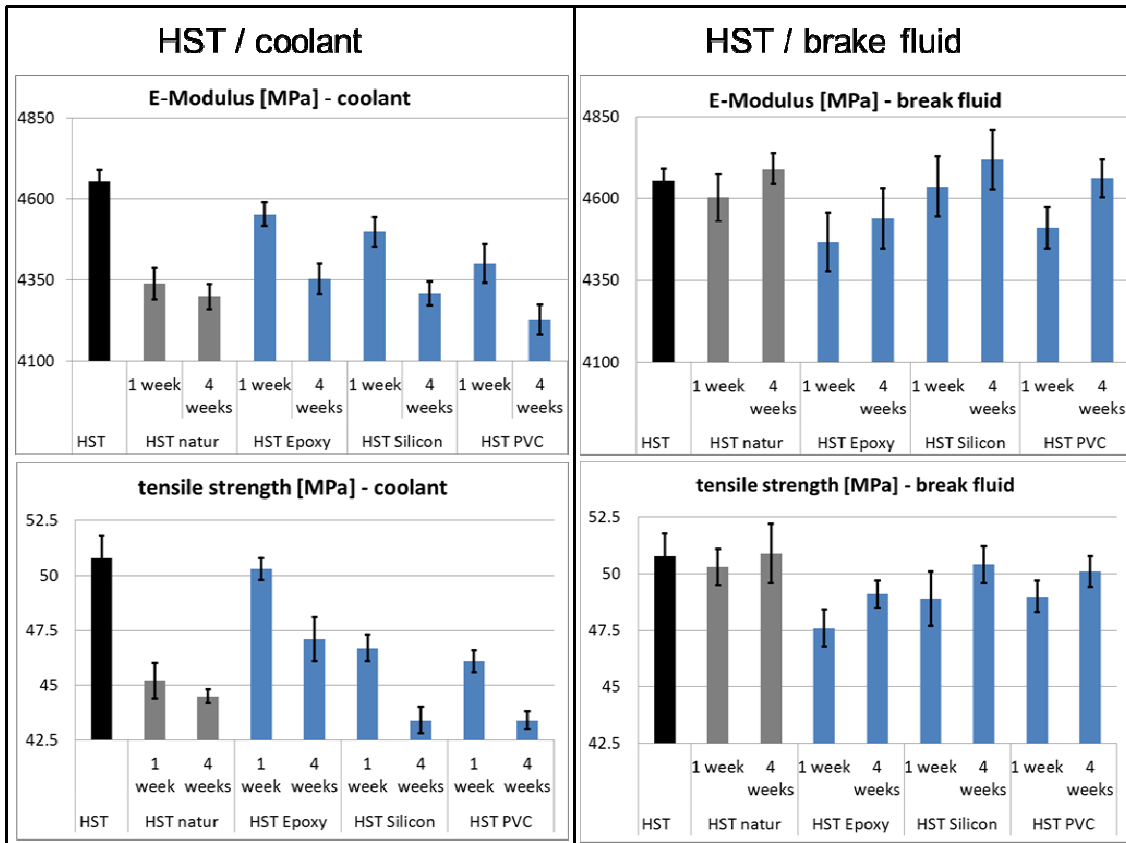


Figure 7: Change of E-mod. and tensile strength for HST depending on store time and coatings

Conclusion and Outlook

The presented work launches for the first time a systematic investigation of changes of SLS parts made from Duraform® DF and Duraform® HST in contact with car media (coolant and brake fluid). Moreover, the influence of certain sealing chemicals was evaluated as well. Overall, it can be specified that coatings on epoxy-, silicon- and PVC-basis could be successfully applied by means of dip coating. Coatings layer thicknesses between (10 µm and 70 µm) were obtained. It turned out that epoxy coatings are inadequate. A massive weight increase and delamination can be observed. Overall, silicon coatings illustrates a positive sealing effect regarding gravimetry but the adhesion to the Duraform substrates is somehow insufficient and must be improved in case of further implementation for existent car applications. PVC coatings have a marginally positive sealing effect regarding coolant. Possible improvement with increased layer thicknesses and substrate anchorage can be predicted. The overall mechanical properties investigations provide

no clear indication regarding practicality of the different applied coatings. However, it is clearly recognized that coolant weakens the mechanical properties of Duraform[®] HST substantially.

Further investigations as to understand and improve the coating systems are necessary. The coating chemistry options can be extended to polyurethanes, fluorinated polymers and many more. In a different direction it might be also of high necessity to work on improved adhesion principles of the coatings to the substrate and film formation by cross-linking. Other car fluids used regularly (gasoline, diesel fuel, motor oils) should be investigated in similar research programs.

Acknowledgements

The authors are grateful to the whole laboratory staff of irpd institute who supported this work, especially Pirmin Rutishauser who carried out all gravimetric analyses.

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