

Improving thermal and chemical stabilities of electronic epoxies using polysiloxane copolymers - Part I: core-shell particles

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ABSTRACT

In this paper the improvements of the thermal stability of cured epoxy resins in air as well as in various critical media like water, solvents, aerospace and automotive fluids are investigated. Upon modification with different addition levels of polysiloxane core-shell tougheners, the embrittlement upon thermo-oxidative ageing of the epoxy resin could be reduced significantly. Losses in strength and elongation caused by thermo-oxidative degradation of the polymer were minimized. The hygrothermal stability was increased significantly as well. It was found that the coefficient of thermal expansion (CTE) at temperatures above the glass transition temperature, increasing tremendously upon heat ageing, did not increase for a modified resin system. This enables the epoxy resin formulator to create systems for various electronic applications with a much better dimensional stability and an increased service life under harsh conditions.

KEYWORDS: epoxy, electronics, polysiloxane, core-shell, toughening, ageing, thermostability.

INTRODUCTION

For many years epoxy resin formulations have been used largely in electrical and electronic components. In 2020 in Europe approximately 30% of the epoxy resin sold was used in electrical and electronic applications [1]. In Asia the epoxy resin consumption

is 4-5 times larger and the share of electrical and electronic applications is even larger than in Europe. It is of utmost importance to avoid any failure of such electronic components; just think of applications in space satellites, aerospace, high speed trains, ship navigation or simply in terms of a failure-proof airbag system in a car. Often such electrical and electronic components are used in challenging environments, subjected to high temperatures, frequent temperature changes, contact with chemicals like oils, alcohols, skydrol or simply moisture. The ongoing miniaturization of electronic components combined with their continuously increasing power makes heat release and temperature management within the electronic parts an issue as well.

The investigations in thermal degradation of epoxy resins are nearly as old as epoxy resins themselves and the underlying mechanisms are fairly well understood. A brief overview of the mechanisms involved on molecular level will be given in this paper. It is important to know how thermal degradation works and what additional effects are created by harsh environments in order to predict the lifetime of epoxy formulations and to design failure-proof components. Figure 1 shows the undesirable case of crack formation in an epoxy potting caused by a temperature cycling between 25 °C and 120 °C [2]. The mismatch in thermal expansion of the various materials causes different material expansions upon temperature increase and creates stresses which cause crack formation. This crack formation is a major problem not only for

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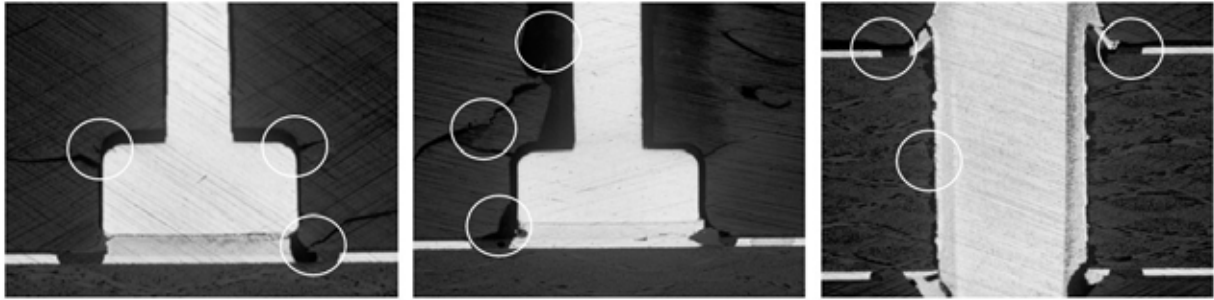


Figure 1. Microscopic image of the cross sections of cracks formed in an epoxy potting around the brass pin flange and the ripped copper barrels on a PCB mounting [2].

potting resins but also for underfills, encapsulations, masks or potted generators as well as for printed circuit boards based on epoxy resin formulations.

Similar problems with crack formation can occur in a printed circuit board (PCB) at the interface between glass fiber and epoxy resin upon thermal ageing [3]. Such cracks can form as a result of a mismatch in thermal expansion behavior of glass fiber and PCB matrix resin, especially at high temperatures. They enable the formation of the so-called conductive filaments which then cause a short circuit and are another major reason for the failure of electronic components.

It is obvious that the reliability of electronic components is of utmost importance for all aspects of modern life. Regarding space applications, especially satellite applications, the NASA Electronic Parts and Packaging Program (NEPP) is making many investigations publicly available [4].

Some investigations regarding the thermal ageing of epoxy formulations used for specific electronic applications have been published recently. Rmili *et al.* studied epoxy encapsulations treated by relatively short thermal cycles similar to those in the production of electronic components and reported an increase in modulus and glass transition temperature (T_g) [5]. They claimed that severe epoxy resin degradation starts above 220 °C.

Zhang and his coworkers investigated the changes in thermomechanical properties of epoxy molding compounds (MC) during high temperature storage [6]. The formation of an oxidative layer was observed, as well as considerable shrinkage during the first week, which may cause microcracks in the compound and a decrease in the coefficient of

thermal expansion (CTE). An increase in modulus and T_g over time was noted as well. Gromala *et al.* studied epoxy molding compounds used to protect electronic control units (ECU) for automotive applications [7]. They stored the test specimen at different temperatures for different storage times and investigated both the growth of the oxidized layer at the surface and the properties of the aged samples to develop a model capable to predict the reliability of electronic packages.

Transformer insulation materials were the subject of the research of Wang and his team [8]. They treated the samples with dry hot air at 130 °C and observed an increase of dielectric constant and dielectric loss factor caused by free radicals formed upon thermal aging. Furthermore they noted a severe increase in microcrack formation over time. If aged samples are subjected to partial discharge testing, the magnitude and phase of the discharge increase significantly compared to unaged material, a clear result of the degradation caused by the thermal treatment.

A recently published research paper recommends the addition of up to 2 wt% ZnO nanoparticles to the epoxy resin to increase thermal stability of a glass fiber-reinforced composite, taking into account a loss in strength [9]. Unfortunately, not much work has been published regarding the increase of thermal stability and the options available for an epoxy resin formulator to improve adhesives, pottings or encapsulations designed for electronic applications. The major reason is probably the very competitive nature of this market. Inorganic fillers can help to improve the thermostability of epoxy resins to a certain extent, but they affect other properties negatively and increase viscosity significantly,

which makes them not suitable for many applications in electronics where low viscosities are required. Studying the claims of the patent literature, a few hints can be found. In a patent application regarding electronic adhesives and encapsulants capable of withstanding operating temperatures up to 160 °C, the use of a core-shell toughener (CSR) with a polysiloxane core is mentioned [10].

Core-shell tougheners have been developed several decades ago as tougheners for epoxy resins to overcome the disadvantages of classic rubber toughening using CTBN adducts, especially loss in modulus and glass transition temperature as well as high formulation viscosities [11]. Another important aspect for electronic formulations is the very high chlorine content of CTBN tougheners compared to polysiloxane core-shell particles. Another benefit is the very low T_g of the polysiloxane, making them suitable as tougheners even at cryogenic temperatures, whereas CTBN-modified epoxies become very brittle at temperatures below -40 °C. Additionally the polysiloxane elastomers exhibit excellent stability at high temperatures as well. The improvement of mechanical properties and especially fracture toughness of epoxy resins using core-shell tougheners as well

as the mechanisms involved are well understood [12]. Due to the very low T_g of the polysiloxane core significant toughness increases are found even at cryogenic temperatures [13]. This makes polysiloxane core-shell particles special, as other core materials like polybutadienes or polymethacrylates become brittle below -40 °C as well and cannot provide the excellent stability at high temperatures. Figure 2 shows a scanning electron microscopy (SEM) image of the fracture surface of an anhydride-cured DGEBA modified with the polysiloxane core-shell particles. The spherical shape is clearly visible. Upon impact the particles form a dilatated void with the polymer of the former particle lining the void (one of the most important mechanisms of rubber-toughening). As a consequence, a fracture surface as shown in Figure 2 typically shows voids only. It has to be noted that the average particle size is around 0.16 μm . Pictures of fracture surfaces obtained from amine-cured epoxy resins look very similar [14]. In many epoxy resin formulations such core-shell particles are combined with silica nanoparticles to optimize performance further [14, 15].

The aim of this paper is to study the improvements in thermostability under dry and wet conditions of epoxy resins achieved by modification with polysiloxane core-shell elastomers.

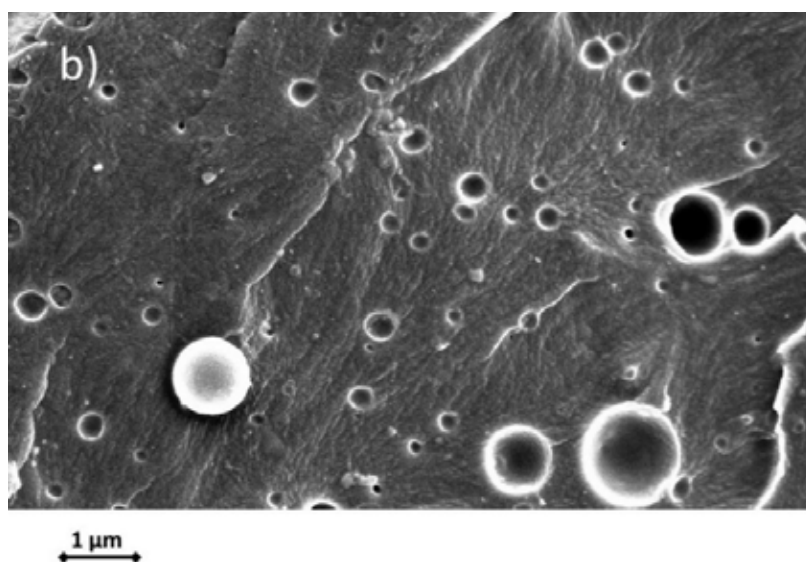


Figure 2. SEM picture of the fracture surface of an anhydride-cured DGEBA epoxy resin, modified with polysiloxane core-shell particles.

MATERIALS AND METHODS

Materials

A standard grade DGEBA (comparable to Epikote[®] 828) was blended with various amounts of Albidur[®] EP 2240 A obtained from Evonik Operations GmbH (Germany) and cured with the stoichiometric amount of accelerated methyl hexahydrophthalic acid anhydride (Albidur[®] HE 600 from Evonik Operations GmbH, Germany). As the Albidur[®] EP 2240 A is a 40 wt% concentrate of a polysiloxane core-shell toughener, an addition level of 5 wt% core shell requires a replacement of 12.5 wt% of the DGEBA by the Albidur. Cure schedule was 4 hours at 90 °C followed by 8 hours at 160 °C in order to obtain a complete cure.

The cured samples were aged under air at 180 °C in an oven type ED 53 from Binder (Germany). The test specimens were analyzed after 0, 1, 2 and 4 weeks of aging. Hygrothermal ageing was performed according to DIN EN ISO 9142 using a climate chamber LH 114 from ESPEC (Japan). Half of the test specimens were stored for 500 hours in a climate chamber at 85 °C and 85% relative humidity, and the other half for 1000 hours. Before testing the samples were conditioned for 72 hours at room temperature with a relative humidity below 35%.

Ageing in media was performed according to DIN EN ISO 175. Test media selection was done by using the VW 8000 (LV 124) guideline. Flasks with the test specimen immersed in the test fluid were stored at a temperature of 60 °C for 7 days or for 24 hours at room temperature. Then the test specimen were cleaned, dried and conditioned for 48 hours at room temperature before testing. Materials used: engine oil Synthoil Energy 0W-40, differential oil Hypoid LS SAE 75W-140, gear box oil Dexron ATF III, hydraulic fluid I HVLP 46; all supplied by Liqui Moly (Germany). As antifreeze a 1:1 blend of water and ethylene glycol was used. Kerosene was supplied by Carl Roth (Germany). Hydraulic fluid II Aeroshell Fluid 41 was provided by Shell (Germany). Acetic acid, acetone, ethanol and isopropanol were all provided by Carl Roth (Germany).

Testing procedures

Dynamical mechanical analysis (DMA) was performed as required by ISO 6721-11 using a

DMA 1 equipment from Mettler Toledo (Switzerland). Elastic modulus was determined according to ISO 6721-4:2019-05. Glass transition temperature (T_g) was determined according to ISO 6721-11:2019-06. Thermomechanical analysis (TMA) was performed using a TMA/SDTA 2+ from Mettler Toledo (Switzerland) according to ISO 11359-2. Testing was performed from 0 °C-250 °C with a ramp of 1 K/min and a constant force of 0.02 N. The coefficient of thermal expansion was determined below and above T_g . 3-Point-bending testing was performed using a Universal Testing Machine AllroundLine Z020 from ZwickRoell (Germany). Bending strength and bending modulus were determined according to ISO 178:2019-04. Impact testing was done as described in DIN EN ISO 179 using the HIT5P test equipment from ZwickRoell (Germany).

RESULTS AND DISCUSSION

Thermal ageing of polymers under air as well as in various media was the subject of numerous investigations in the last decades. In this context epoxy resins have been researched intensively as well. Many scientists reported that cured epoxy resins being exposed to elevated temperatures over a period of time show a loss in mechanical, electrical and other properties and exhibit shrinkage – as expected [16-19]. The formation of oxidized surface layers serving as crack initiators was observed already at relatively low temperatures below 100 °C [16]. Celina *et al.* reported significant oxidation rates around and above 100 °C [17]. Celina *et al.* pointed out that the exposure conditions of a polymer have an influence on the degradation of the polymer and that they are interdependent from each other [20]. For different polymers the effects will be different.

Depending on the epoxy resin and the hardener used, the three-dimensional network formed upon cure is different. It exhibits different properties (i.e. strength, modulus, T_g , CTE – just to name a few) and therefore will be affected differently by thermal ageing in air or other media. This makes general lifetime predictions for a specific electronic application very difficult.

Many years ago differences in thermal degradation behavior under air were observed for different curing agents used for the crosslinking of the

epoxy resin [16]. Rose and her group investigated the degradation of a tetrafunctional aromatic epoxy resin (tetraglycidyl ether methylene dianiline (TGMDA)), cured with two different amine hardeners, dicyandiamide (Dicy) and 4,4' diamino diphenyl sulfone (DDS) [21]. As expected, the aromatic diamine cured epoxy showed a better thermostability and a higher activation energy for thermo-oxidative degradation. Shanahan and Buch evaluated the same epoxy resin systems and differentiated two stages of degradation [22]. In the first stage chain scission caused by thermolysis occurs – and the presence or absence of oxygen seems to have no or little influence. The second stage of degradation occurs only in the presence of oxygen and leads to the total degradation of the organic material.

Richaud *et al.* attributed the embrittlement of thermally oxidized epoxy (DGEBA, cured with DDS) to a preferred oxidation of the hydroxypropyl ether group which formed upon cure from the epoxy group [23]. They conducted their trials at temperatures below and above T_g . Ageing amine-cured epoxy resins at relatively mild conditions (70 °C), below the glass transition temperature of the triethylene tetramine (TETA)-cured DGEBA, was studied by Morsch and her team [24]. They reported an oxidization of the amine to occur first, the DGEBA part being affected only after 38 days of ageing. The discoloration always observed upon the thermal ageing of aromatic epoxy resins can be attributed to the formation of quinone methide structures. Their formation has no negative influence on mechanical properties, however [25]. Colin *et al.* did an extensive study on the ageing of diamine-cured DGEBA at temperatures around the glass transition temperatures [26]. They found the molecular mobility above and below the T_g has a great influence on the propagation of the oxidation which of course is responsible for mechanical properties and durability.

Delor-Jestin *et al.* tested a standard bisphenole A epoxy resin (DGEBA) cured with diethylene triamine (DETA) as well as methyl nadic anhydride (MNA) and reported a better thermostability of the anhydride-cured epoxy [27]. This could be one of the reasons why anhydride curing agents are preferred in electronic formulations.

NMA-cured DGEBA, flexibilized with a dimeric fatty acid, was the subject of the early studies of Verdu *et al.* [28]. They defined three stages of different thermo-oxidative behavior: below the glass transition temperature, between T_g and 200–220 °C and above 220 °C. They postulated that for temperatures below T_g mainly stress relaxation occurs, whereas above T_g radical chain oxidation is dominant. Weight loss, macroscopic shrinkage and the formation of an oxidized layer prone to crack formation also occur. No reduction in strength, but a significant reduction in elongation was reported upon increased duration of the ageing process. Above 220 °C they believed only thermolytic processes to be relevant.

Xian and his team performed thermal ageing of an anhydride-cured DGEBA at 130 °C and 160 °C [29]. They reported an increase in T_g (unaged 138 °C), followed by a smaller decrease over time. Furthermore a second T_g at higher temperature develops and increases – this is associated to the occurrence of molecular chain rearrangements. At an ageing temperature of 130 °C (below T_g), these rearrangements seem to be of minor relevance. Flexural tests showed no loss in strength upon thermal ageing, but a reduction of break strain (or flexibility).

According to Zhao *et al.* the aromatic rings of an epoxy resin are thermally quite stable; the dominant mechanism of ageing is oxidative chain scission resulting in degradation and the formation of water molecules [18]. Those affect electrical properties negatively. Zhang and Tao simulated the decomposition of anhydride-cured DGEBA and determined the cleavage of an ester bond formed upon cure as initiation reaction for the decomposition [30, 31]. In many electrical and electronic applications anhydrides are used as curing agents, as they enable low viscosities, high filler loading levels and well controlled cure as well as long open times at ambient temperatures which are extremely important in the production environment. The need for formulation ingredients capable to improve thermo-oxidative stability becomes more than obvious. Unfortunately typical antioxidants, used in abundance in thermoplastic materials like polypropylene, do not work in thermosets [16].

An overview of the change in mechanical properties as consequence of physical aging by elevated temperatures was provided by Odegard *et al.* in their review for various amine-cured and anhydride-cured epoxy resin systems [32].

Thermal ageing under air (thermo-oxidative ageing)

The glass transition temperature of the anhydride-cured DGEBA investigated was determined by DMA to be 156 °C. The temperature for the ageing tests under air was chosen to be reasonably above T_g , at 180 °C. Taking into account the curing regime applied and the relatively high ageing temperature, it is no surprise that no further increase of the glass transition temperature was found. Figure 3 shows the change in T_g over the duration of the ageing tests for various addition levels of core-shell toughener. The addition of the polysiloxane modification decreases the initial T_g minimal by 1-2 °C at addition levels of 2.5 wt% and 5 wt%. The reduction in T_g observed over time is identical for all systems investigated and can be attributed to chain scission followed by oxidative degradation of the DGEBA/anhydride matrix.

Interestingly, Xian and his team reported no loss in bending strength upon ageing at 160 °C for an anhydride-cured DGEBA [29], whereas we observed losses in bending strength for the control

as well as for the epoxy resin containing 10 wt% of polysiloxane toughener. The systems with 2.5 wt% as well as 5 wt% core-shell toughener showed no reduction in bending strength, as can be seen in Figure 4. It has to be noted that the bending strength of the unaged systems is reduced by approximately 10% for each 2.5 wt% core-shell toughener added (compare Table 1). After the thermal treatment, the system modified with 2.5 wt% polysiloxane particles outperforms the unmodified control in showing a higher bending strength.

A reduction in flexibility (compare [28]), clearly the result of embrittlement caused by the molecular deterioration upon high temperature storage, was found for all systems investigated. As shown in Figure 5, the loss in elongation was worst for the control (-42%), followed by the 10 wt% modification (-38%), medium for the 2.5 wt% modification (-26%) and best for the 5 wt% modification (-14%). It is evident that the epoxy resins containing 2.5 wt% and 5 wt% of polysiloxane core-shell toughener maintain a significantly higher flexibility after the thermal treatment.

As can be seen in Table 1, an increase in modulus was found for the control (+12%), whereas the modified epoxy resins with 2.5 wt% and 5 wt% modification showed a minor increase of 2-3% and the system containing 10 wt% of toughener exhibited a loss in modulus of 5%. Looking at the

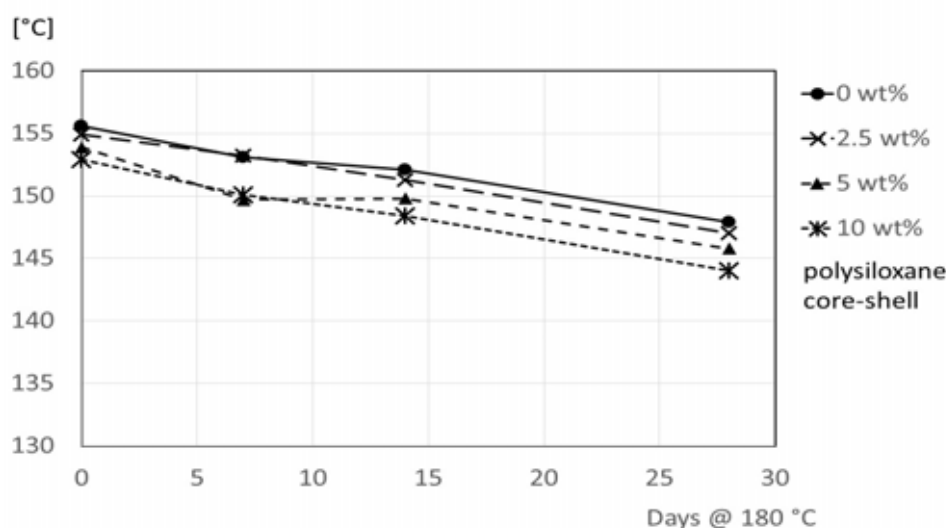


Figure 3. Glass transition temperature upon ageing under air for various contents of polysiloxane core-shell toughener.

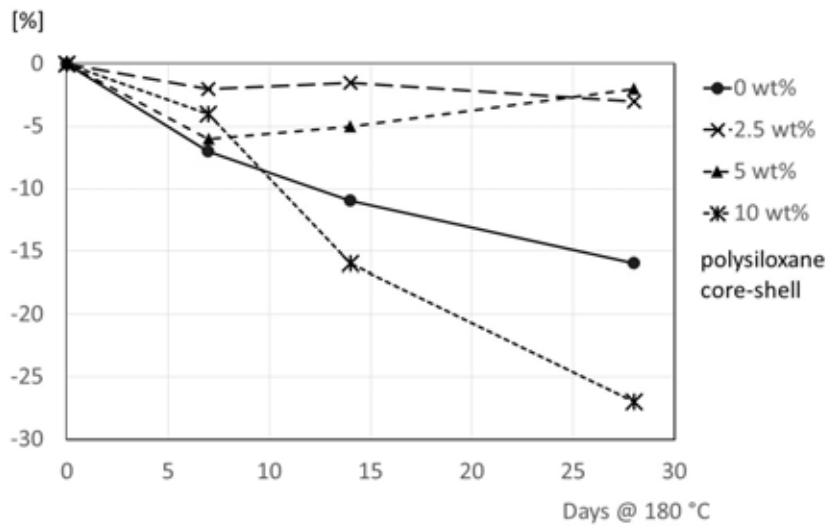


Figure 4. Loss in bending strength upon ageing under air for various contents of core-shell toughener.

Table 1. Thermomechanical data of anhydride-cured DGEBA with various contents of polysiloxane core-shell toughener.

	Polysiloxane core-shell [%]	0 days 180 °C	7 days 180 °C	14 days 180 °C	28 days 180 °C
Glass transition temperature [°C]	0	155.6	153.1	152.1	147.9
	2.5	154.9	153.2	151.3	147.0
	5	153.9	149.7	149.8	145.8
	10	152.9	150.1	148.4	144.0
Bending strength [MPa]	0	149 ± 3.0	138 ± 5.9	133 ± 7.3	125 ± 43
	2.5	138 ± 2.1	132 ± 1.4	133 ± 2.8	131 ± 2.0
	5	123 ± 3.9	116 ± 2.2	117 ± 1.4	121 ± 7.0
	10	111 ± 23	107 ± 15	93 ± 8.9	81 ± 18
Bending modulus [GPa]	0	3.07 ± 0.14	3.19 ± 0.07	3.02 ± 0.49	3.44 ± 0.79
	2.5	2.96 ± 0.05	2.95 ± 0.05	2.98 ± 0.03	3.04 ± 0.04
	5	2.73 ± 0.08	2.74 ± 0.05	2.80 ± 0.05	2.81 ± 0.14
	10	2.73 ± 0.73	2.66 ± 0.67	2.46 ± 0.12	2.59 ± 0.02
Elongation at break [%]	0	7.3 ± 0.9	6.7 ± 0.9	5.3 ± 0.6	4.2 ± 1.1
	2.5	8.5 ± 0.7	8.7 ± 0.8	7.5 ± 1.0	6.3 ± 0.2
	5	7.9 ± 0.9	8.6 ± 1.0	8.7 ± 0.8	6.0 ± 0.8
	10	6.1 ± 2.0	6.1 ± 1.5	4.8 ± 1.1	3.8 ± 1.5

coefficient of thermal expansion (above T_g) given in Figure 6, the improvements achieved by the modification with a polysiloxane core-shell toughener becomes evident. The modified systems show no substantial change in CTE upon thermal ageing, whereas the control shows an enormous increase –

probably linked to the formation of an oxidized layer and the molecular deterioration. The significant increase in dimensional stability by the modification is of enormous importance for electronic applications in order to minimize the buildup of inner tensions caused by heat ageing.

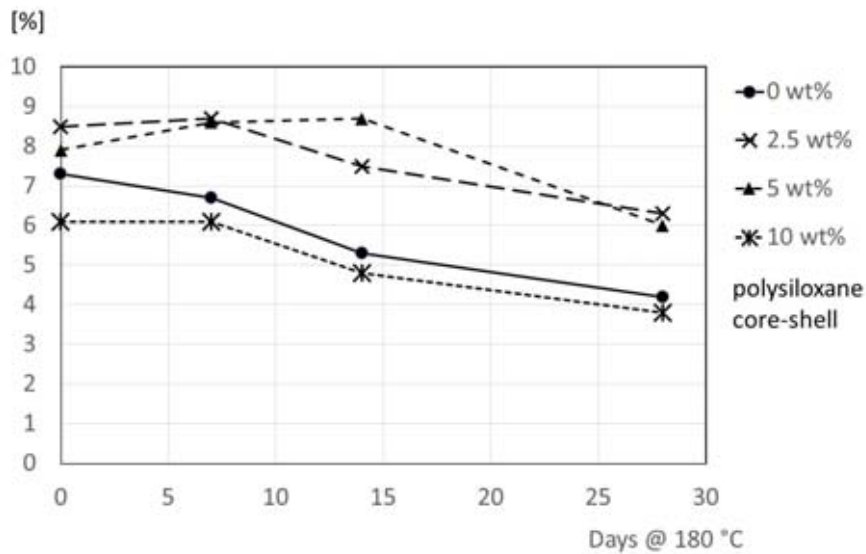


Figure 5. Elongation upon ageing under air for various contents of core-shell toughener.

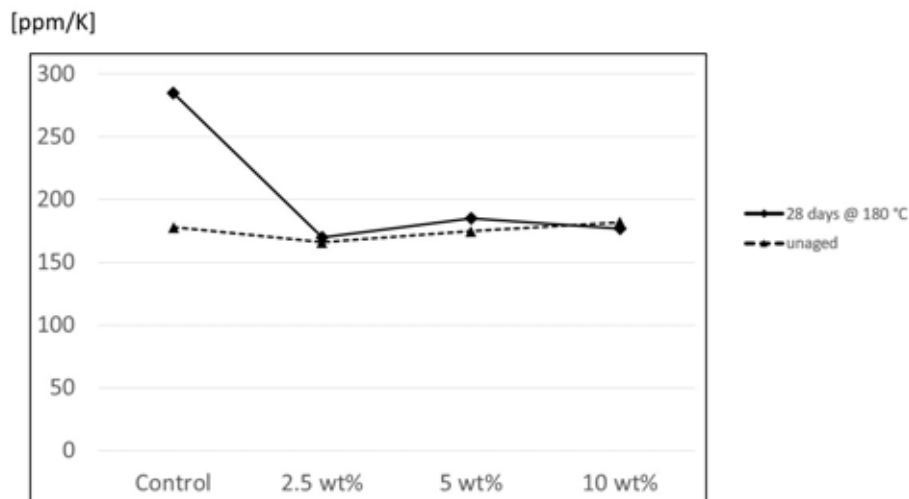


Figure 6. CTE (above T_g) for various contents of polysiloxane core-shell toughener unaged and after 4 weeks @ 180 °C.

Of course the CTE as such can be reduced much further by using fillers in the formulation, and by using a combination of fillers and toughener particles, best performance regarding CTE can be achieved. A low CTE is very important for electronic potting and encapsulation formulations in order to achieve a good dimensional stability over a broad temperature range. Further optimization can be achieved by combining standard fillers with nanoscaled fillers. All previously cited work agrees upon the fact

that very often crack failure of electronic devices is caused by crack formation due to tensions created by a mismatch of thermal expansion of the different materials combined in an electronic component. Metals like copper, silver or complex alloys are combined with various polymers, mounted on printed circuit boards (PCBs) consisting of glass fibers and epoxy resins. These material combinations are then embedded in an epoxy resin potting. Most electronic adhesives have to join various substrates

and act as an encapsulating sealant as well. It is obvious that for applications where dimensional stability over the whole lifecycle and under rough conditions like elevated temperature exposure the modification of the epoxy resin with a polysiloxane core-shell toughener is extremely helpful. Although the toughness of an epoxy resin is increased nearly linear with increasing addition level of toughener [13], our results indicate that the best addition level of core-shell particles for the improvement of the thermooxidative stability of an epoxy resin is between 2.5 and 5 wt% addition level.

Looking at the relatively low addition levels and the distribution of the core-shell particles in the polymer (compare Figure 7) it is evident that a barrier mechanism with the particles prohibiting or significantly slowing down the diffusion of oxygen into the epoxy resin at a temperature well above the glass transition temperature does not apply. The reduction of glass transition temperature by the thermo-oxidative ageing is identical (- 5 %) for the unmodified epoxy resin and the epoxy resins containing core-shell particles. Hence the molecular chain degradation (chain scission followed by oxidation) is the same. This confirms the findings of Verdu and his group, claiming that at temperatures between T_g and 200-220 °C, radical chain scission and oxidation become dominant over stress relaxation [28].

The reduction of losses in bending strength and flexibility by the addition of polysiloxane core-shell

particles can be attributed to the capability of the elastomeric particles to compensate inner tensions of the molecular network. Inner tensions resulting from the cure process do cause relaxation processes upon thermal ageing (compare Shanahan and Buch [22]) as well as ruptures of the molecular network which are followed by a microcrack formation. Like relaxation processes the microcrack formation is accelerated by thermo-oxidative ageing (compare [8]). In the modified epoxy resins the inner tensions of the molecular network are compensated by the core-shell particles – as a consequence the microcrack formation is reduced significantly. The big differences in changes in CTE between unmodified and modified epoxy resin are explained by this as well.

An important aspect regarding testing conditions and lifetime predictions based on the test results for epoxy resins designed for space applications was discovered by Causse *et al.* [33]. They investigated an amine-cured epoxy adhesive in bulk and in a bonded assembly configuration and found that in the absence of oxygen it seems to make no difference if the thermal ageing occurs under atmospheric pressure or under vacuum.

Hygrothermal ageing – the 85/85 test

Another challenge for electronic components is the contact with humidity, especially at elevated temperatures – just think about machines in an

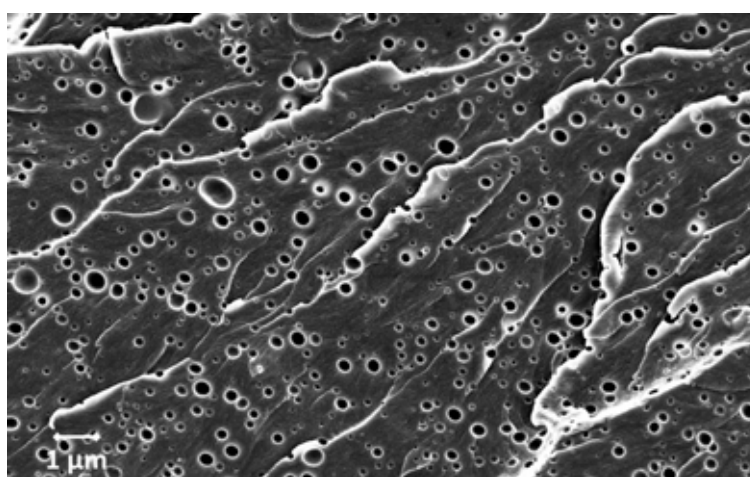


Figure 7. SEM picture of the fracture surface of an anhydride-cured DGEBA modified with 5.5 wt% polysiloxane core shell toughener.

industrial environment, about aerospace or marine electronics or simply mobile devices. Mallarino and her group investigated the hygrothermal ageing of an amine-cured DGEBA at temperatures from 30 °C-60 °C [34]. After 6 weeks immersion in deionized water they observed the water absorption of the polymer causing a plasticization, which decreased stiffness and T_g . However, this process was completely reversible, when the samples were dried for 2 weeks under vacuum. Krauklis *et al.* studied the irreversible discoloration of amine-cured epoxy resins during hygrothermal ageing [35]. After 8 weeks in deionized water at 60 °C the samples showed a uniform yellowing. Cross-sections showed that the yellowing was throughout; not just a surface effect. No chain scission due to hydrolysis and no changes in morphology could be observed. The yellowing was attributed to a carbonyl formation in the aliphatic epoxy resin and in the aliphatic amine hardener used. The aromatic DGEBA seemed not to be affected.

The changes in electrical properties of an anhydride-cured epoxy resin upon storage at 95% relative humidity and 80 °C for 2 weeks were tested by Liu *et al.* [36]. They observed an increase in crack formation with increase in exposure time. The dielectric constant changes and the original electrical properties cannot be restored upon drying. They attributed the loss in electrical properties to irreversible chemisorption of water molecules. Le Guen-Geffroy *et al.* used amine-cured epoxy resin blends which were stored at 40 °C and 50% relative humidity, at 40 °C and 75% relative humidity and were immersed in sea water at 40 °C [37]. They distinguished between two reversible processes: plasticization, which reduces both tensile strength and T_g , and physical ageing, which increases tensile strength. The physical aging, which was observed without plasticization by storing the test specimen at 40 °C in an inert atmosphere, was extremely accelerated by the presence of water. They attributed this to the increased mobility of molecular chains in the presence of water. Aamir and his team tested the ageing behavior of amine-cured DGEBA-based glass fiber-reinforced laminates when stored in sea water at room temperature [38]. They reported a reduction in fracture toughness of 30% after 24 days and of 55% after 35 days of

immersion in sea water. Manalo and his team suggested the use of fillers to improve the performance of an amine-cured DGEBA after hygrothermal aging [39]. The test specimens were stored at 98% relative humidity at temperatures up to 60 °C for 18 weeks. The water absorption was significantly reduced by the addition of fillers, especially for high loading levels (40 wt% respectively 60 wt%) and 60 °C aging temperature. Although the losses in flexural strength and compressive strength after hygrothermal aging were slightly inferior, the overall performance of the filled epoxy resins before and after aging was much lower due to the significantly increased brittleness.

For our investigations we have chosen an addition level of 5 wt% core-shell toughener, as this is a very typical addition level in many electronic epoxy formulations like pottings, underfills, adhesives... As can be seen in Figure 8, the bending strength was reduced for the control by 11%, whereas the modified systems showed no change at all. This confirms the absence of relaxation effects caused by inner tensions, which are predominant for ageing phenomena at temperatures below T_g .

In Figure 9 the modulus is shown – it did not change upon the hygrothermal ageing neither for the control nor for the modified system. This was found for 3 weeks and for 6 weeks of ageing. No reversible plasticization was detectable. The glass transition points remained unchanged as well (compare Table 2), which clearly indicates that no irreversible changes occurred to the molecular network. It has to be noted that the presence of microcracks cannot be detected by DMA. A detailed microscopic investigation is currently performed.

However, very similar to the thermo-oxidative ageing, a significant embrittlement of the unmodified epoxy resin could be observed – the elongation was reduced by more than 30%, as can be seen in Figure 10. The loss in flexibility upon ageing for the core-shell-modified epoxy was much smaller (-11%). A similar behavior was found for the impact resistance (see Figure 11); the control lost 12% in toughness, the polysiloxane-modified system only 7%.

A summary of the property changes after the hygrothermal ageing is provided in Table 2.

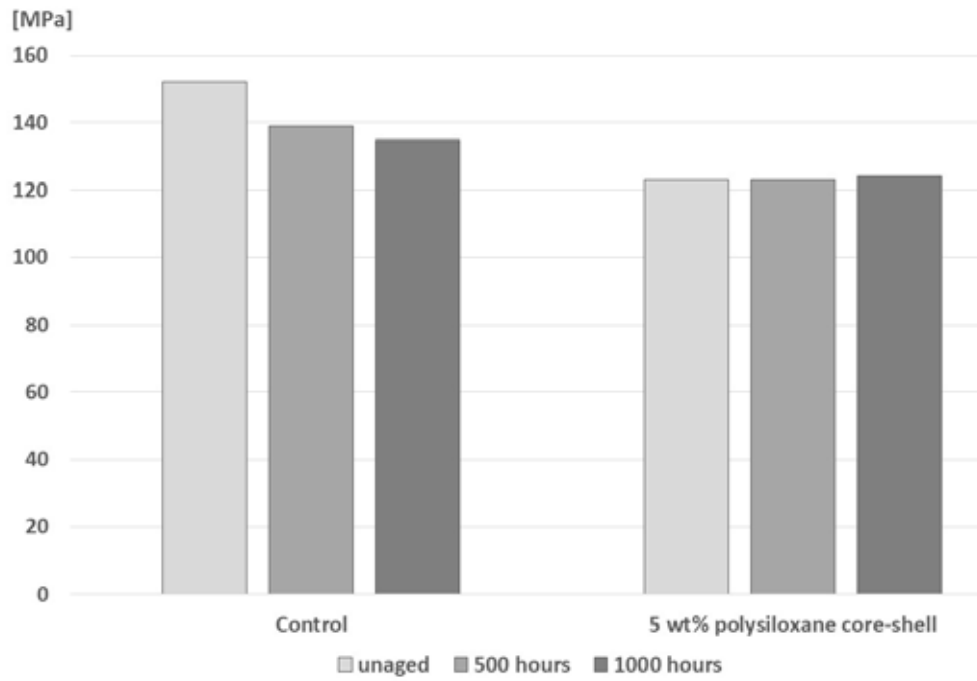


Figure 8. Bending strength upon hygrothermal ageing for epoxy resin unmodified and modified with 5 wt% polysiloxane core-shell particles.

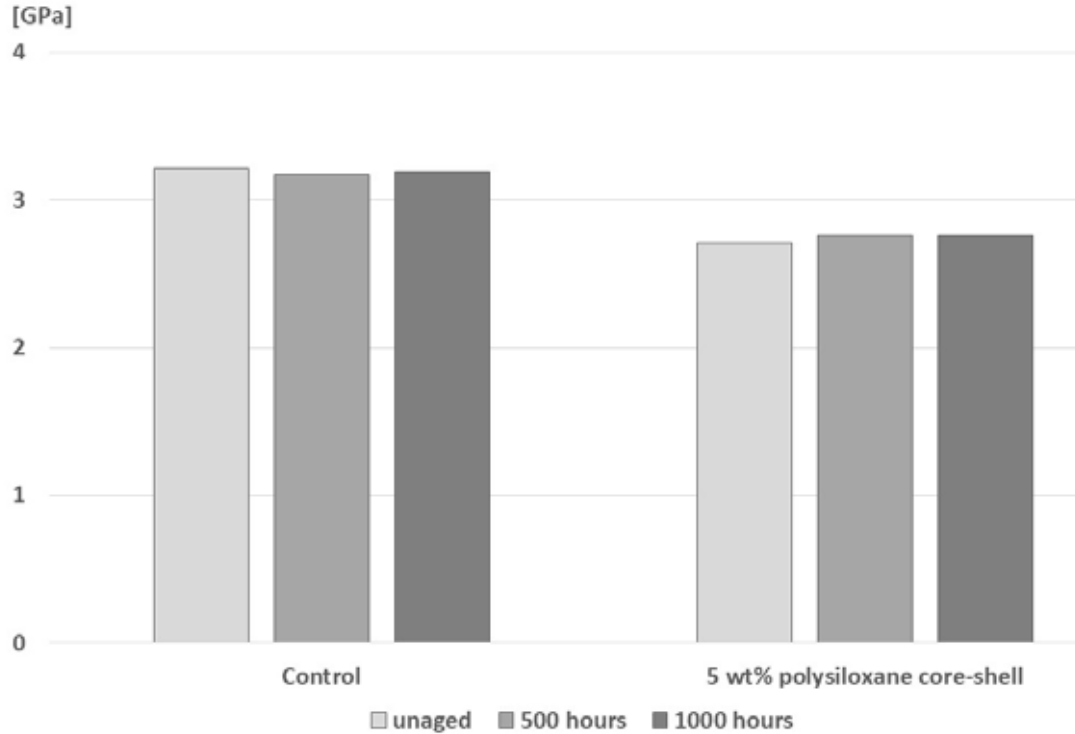
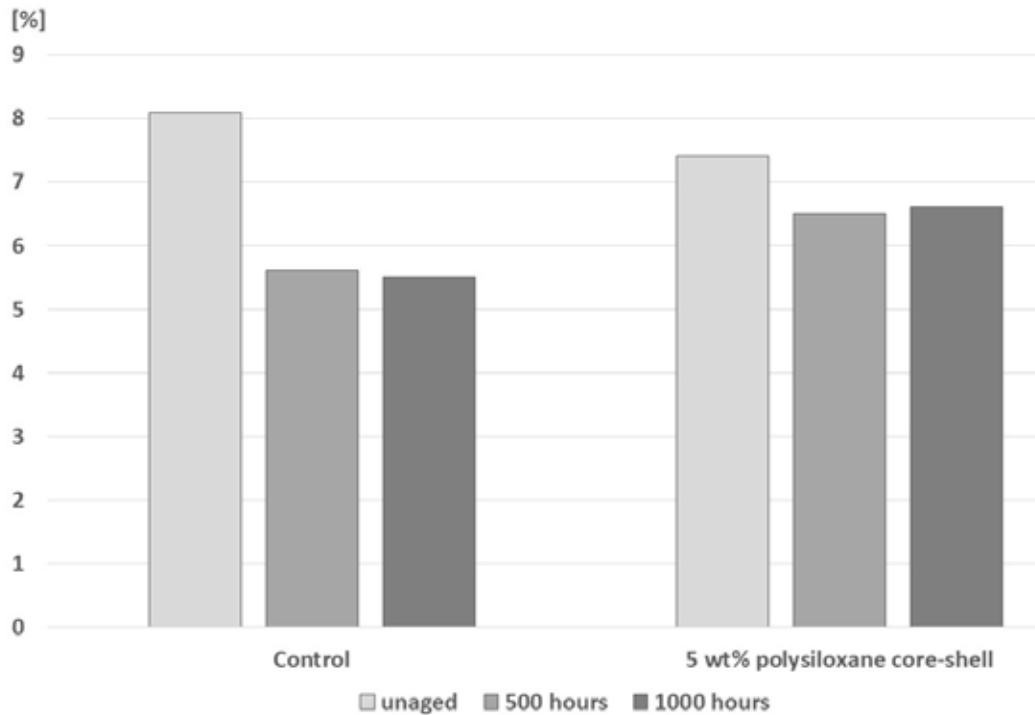


Figure 9. Bending modulus upon hygrothermal ageing for epoxy resin unmodified and modified with 5 wt% polysiloxane core-shell particles.

Table 2. Thermomechanical data of anhydride-cured DGEBA (unmodified and modified with 5 wt% polysiloxane core-shell toughener) after ageing at 85 °C/85 % relative humidity.

Ageing @ 85 °C, 85 % rel. humidity	5 wt% polysiloxane core-shell particles			Unmodified control		
	0 hours	500 hours	1000 hours	0 hours	500 hours	1000 hours
Bending strength [MPa]	123 ± 2.6	123 ± 3.6	124 ± 3.4	152 ± 1.8	139 ± 9.0	135 ± 15.5
Bending modulus [GPa]	2.71 ± 0.05	2.76 ± 0.04	2.76 ± 0.07	3.21 ± 0.03	3.17 ± 0.04	3.19 ± 0.05
Elongation at break [%]	7.4 ± 0.9	6.5 ± 0.7	6.6 ± 0.5	8.1 ± 0.5	5.6 ± 0.9	5.5 ± 1.3
Impact strength [kJ/m ²]	23.1 ± 3.0	20.3 ± 3.0	21.5 ± 2.7	13.6 ± 2.4	12.7 ± 1.6	12.0 ± 1.6
Glass transition temp. [°C]	155.3	154.6	154.7	155.4	154.4	153.6

**Figure 10.** Elongation at break upon hygrothermal ageing for epoxy resin unmodified and modified with 5 wt% polysiloxane core-shell particles.

Ageing in various media

Akderya *et al.* investigated the changes in performance of glass fiber-reinforced epoxy composites after thermal ageing in a heat transfer oil for 3 weeks [40]. The amine-cured DGEBA-

based laminates showed a strong discoloration when stored in the oil at temperatures above T_g (which was approx. 80 °C). They reported a significant brittleness increase with increasing ageing time as well as a loss in strength and modulus.

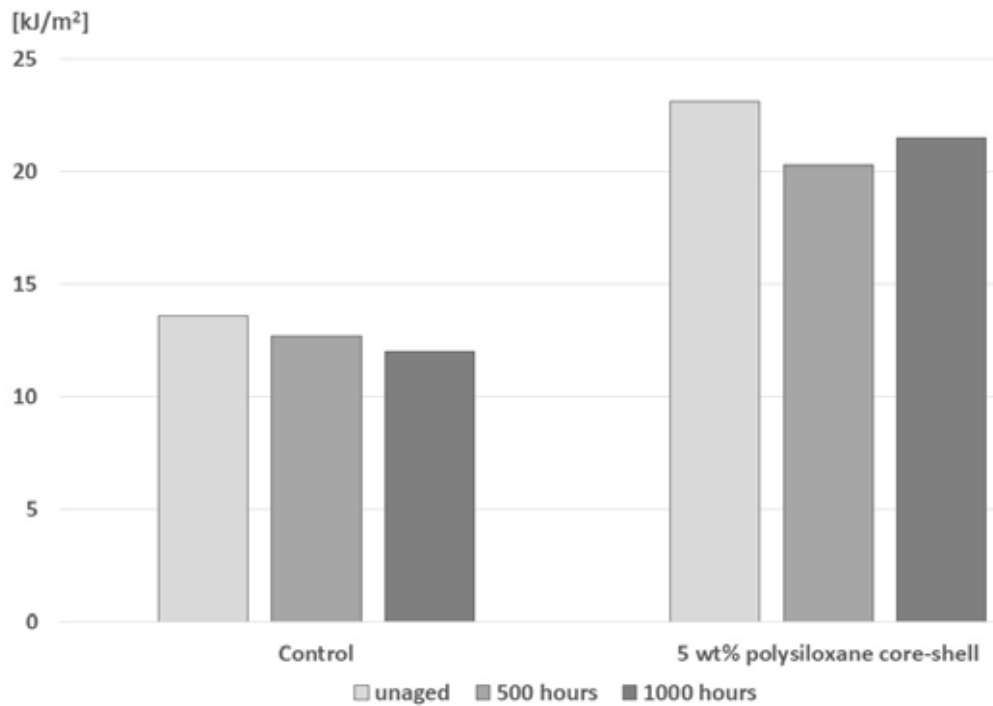


Figure 11. Impact resistance upon hygrothermal ageing for epoxy resin unmodified and modified with 5 wt% polysiloxane core-shell particles.

Table 3. Thermomechanical data of anhydride-cured DGEBA (unmodified and modified with 5 wt% polysiloxane core-shell toughener) after ageing in media.

Ageing medium ^a 7 days/60 °C ^b 24 hours/ 25 °C	5 wt% polysiloxane core-shell particles				Unmodified control			
	Bending strength [MPa]	Bending modulus [GPa]	Elongation at break [%]	T _g [°C]	Bending strength [MPa]	Bending modulus [GPa]	Elongation at break [%]	T _g [°C]
Unaged/none	126 ± 4.4	2.76 ± 0.09	8.9 ± 1.6	157.4	151 ± 3.9	3.13 ± 0.09	7.6 ± 1.2	158.0
None (air) ^a	128 ± 1.1	2.82 ± 0.03	7.8 ± 1.3	157.0	150 ± 8.8	3.05 ± 0.17	7.8 ± 1.0	156.1
Engine oil ^a	129 ± 1.0	2.84 ± 0.03	7.8 ± 0.8	156.6	144 ± 7.0	3.12 ± 0.10	7.2 ± 1.3	156.7
Differential oil ^a	125 ± 3.6	2.76 ± 0.13	7.8 ± 1.4	157.6	140 ± 14.8	3.16 ± 0.04	7.2 ± 1.7	156.4
Gear box oil ^a	128 ± 2.8	2.85 ± 0.04	8.0 ± 1.5	157.2	145 ± 4.4	3.15 ± 0.03	7.4 ± 1.1	152.6
Hydraulic fluid I ^a	127 ± 3.4	2.80 ± 0.13	8.0 ± 1.1	156.5	142 ± 12.5	3.13 ± 0.08	7.3 ± 1.5	156.0
Anti freeze ^a	127 ± 1.0	2.81 ± 0.04	8.1 ± 0.7	154.5	146 ± 3.5	3.13 ± 0.11	7.5 ± 0.6	155.6
Kerosene ^a	132 ± 1.8	2.84 ± 0.03	8.0 ± 1.4	156.6	153 ± 4.4	3.18 ± 0.11	7.4 ± 0.9	156.9
Hydraulic fluid II ^a	127 ± 4.1	2.75 ± 0.15	8.6 ± 1.1	157.1	145 ± 0.7	3.15 ± 0.03	7.7 ± 0.6	156.6
Acetone ^b	115 ± 1.6	2.61 ± 0.03	11.0 ± 1.2	156.0	143 ± 3.5	3.00 ± 0.08	11.4 ± 1.0	155.5
Isopropanol ^b	131 ± 4.8	2.77 ± 0.09	8.7 ± 1.0	156.7	153 ± 3.3	3.13 ± 0.07	7.9 ± 1.0	157.2
Ethanol ^b	128 ± 4.3	2.79 ± 0.05	8.5 ± 1.7	156.8	152 ± 3.6	3.10 ± 0.12	7.7 ± 0.8	156.7
Acetic acid 10 % ^b	129 ± 1.8	2.82 ± 0.06	8.6 ± 1.2	156.8	155 ± 3.6	3.16 ± 0.07	8.0 ± 0.7	155.6

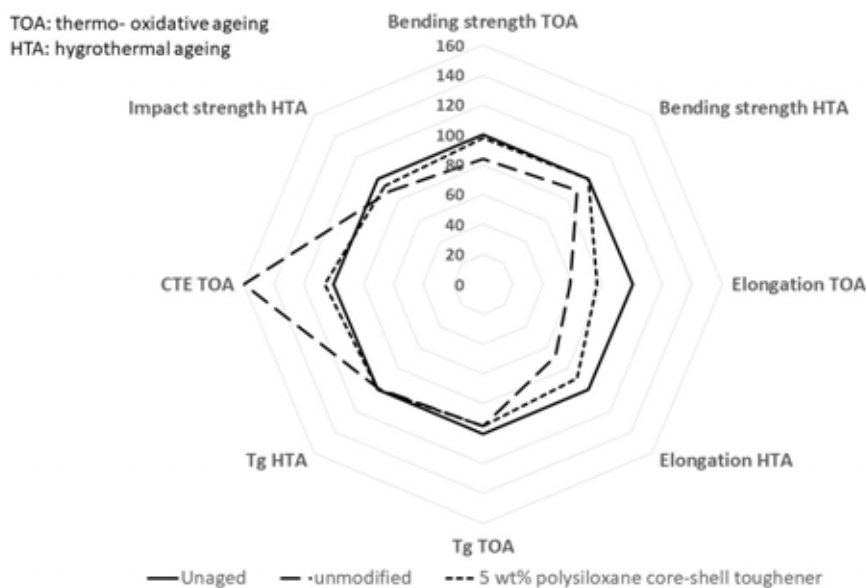


Figure 12. Overview of property changes of an anhydride-cured epoxy, unmodified and modified with 5 wt% polysiloxane core-shell particles.

Our investigation with various different oils and other media showed no loss in strength or modulus, no discoloration and no changes in elongation at break – except for acetone (compare Table 3). The test specimen did not change in weight, except for those immersed in antifreeze and acetone. Both the unmodified and the modified system showed a weight increase of 0.45% after the ageing in antifreeze. However no significant change in mechanical properties was found. T_g 's remained unchanged as well. Epoxy resins are well known to be sensitive regarding the contact with acetone. This was confirmed again for both systems; the loss in strength and modulus was accompanied by a significant increase in elongation. The unmodified control showed a weight increase of 1%; the polysiloxane-modified system exhibited a weight increase of 1.6%. Strength was reduced slightly, but elongation was increased significantly, which indicates a chemical ageing. Interestingly enough the glass transition temperature was not lowered by the irreversible absorption of acetone (see Table 3). This phenomenon needs further investigation.

It can be concluded that the modification with the core-shell particles does not affect the excellent stability of epoxy resins against operating fluids typical for aerospace or automotive applications.

As we performed the media ageing at 60 °C, this conclusion is of course only valid for temperatures below T_g , however.

SUMMARY AND OUTLOOK

It is well known that the modification with polysiloxane core-shell particles significantly improves the toughness of epoxy resins over a broad temperature range [13]. The results provided in this research paper highlight the improvements achievable in thermo-oxidative stability and hygrothermal stability. Figure 12 shows an overview of the percentual changes of the control and a modified epoxy resin upon ageing.

It is evident that the modified system shows no losses in strength upon thermo-oxidative or hygrothermal ageing, whereas the unmodified control loses strength upon ageing. Worse yet, a tremendous loss in flexibility can be observed for both dry and wet ageing for the control. This indicates a significant embrittlement. The enormous increase in the coefficient of thermal expansion of the control is striking. The improvement in dimensional stability and the avoidance of embrittlement by the modification of the epoxy with polysiloxane core-shell particles is extremely important for electrical and electronic applications.

Another option in improving the properties of epoxy formulations for electronic and electrical applications is the use of polysiloxane epoxy block copolymers, which will be evaluated in Part II of this research work. They form interpenetrating networks with the epoxy matrix, therefore providing a transparent formulation (whereas the polysiloxane core-shell particles yield white formulations). As a consequence, they are used very often in sensor embedding applications. Depending on the addition level of block copolymer, materials with more “epoxy-like” or more “silicone-like” properties can be formulated. First trials indicate that such copolymer exhibits synergistic performance improvements when used together with nanosilica as well.

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CONFLICT OF INTEREST STATEMENT

The authors declare no conflict of interest.

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