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Abstract
One of the major challenges when preparing reliable hybrid structures is the adhesion between different components. Besides enduring the specific stress state, hybrid structures should maintain the required properties in the service environment without degradation. In this study, the environmental resistance of stainless steel/rubber/GFRP (glass fibre reinforced plastic) hybrid structures were tested by exposure to hot, moist and hot/moist environments and after the ageing by peel testing. Two different stainless steel surface finishes and two different rubber grades were investigated. The results were compared with the properties of a mild steel/rubber/GFRP structure. Both mild steel/rubber and composite/rubber structures are used in industrial applications, such as in vibration damping devices and in automotive components.

The peel tests showed that with right rubber compounds, stainless steel/rubber and GFRP/rubber interfaces can maintain their properties even in harsh hot/moist environments to such an extent that the interfacial strength of the joint is higher than the cohesive strength of the rubber. This enables the use of rubber's cohesive fracture properties instead of the substrate/rubber interfacial properties when estimating the strength of the steel/rubber/GFRP hybrid structure. In addition, based on the current study, time-consuming stainless steel pre-treatments are not needed but the stainless steel can be in the as-received stage. According to the chemical analysis even before and after the harsh hot/moist exposure used, none of the studied rubber grades had degraded. Thus, we conclude that it is possible to manufacture environmental resistant stainless steel/GFRP hybrid structures with the aid of EPDM rubbers.

Keywords: *Hybrid structure, Ageing, Adhesion, Degradation*

1. Introduction

Last decade has shown an increasing interest on polymer/metal hybrid materials and structures in different fields of industry [1]. The high specific properties, i.e. properties divided by the material density, of hybrids offer mainly benefits through weight savings [1]. However, other advantages, such as more beneficial manufacturing methods or improved damping properties, are achievable by these structures as well [2].

Commonly in adhesive bonded polymer/metal structures, different chemical or mechanical pre-treatments are required for the metal surface before joining the polymer by the adhesive [3, 4]. The pre-treatment steps are time-consuming and may require the use of hazardous chemicals. Thus the manufacturing method would be highly improved, if an adhesive enabling the use of the metal surface in an as-received stage would be available.

It would be tempting to integrate rubber in a hybrid structure for its good characteristics: rubbers can be compounded to be easily adhered to inorganic and organic materials [5, 6] and their damping properties can be tailored. However, the typical mechanical properties of rubbers, namely low modulus and high extensibility [7], do not favour their use as the main component in structural applications. Instead, rubbers can be used as adhesives in polymer/metal hybrid structures simultaneously improving, e.g., the vibration attenuation properties of the structure. The previous studies of the authors [8, 9] show, that a thin ethylene propylene diene (EPDM) based rubber layer between stainless steel and glass fibre reinforced epoxy (GFRP) composite enables the use of a simple manufacturing method without substrate pre-treatments and leads to a good contact and adhesion between the rubber and the substrates, as well as to improved damping properties. Thus, the studied stainless steel/rubber/GFRP hybrid structure has a simple manufacturing method and properties which could be utilized in several applications, such as in impact loaded stressed-skin constructions.

The durability of adhesive bonds is more dependent on the environmental resistance than on the fatigue resistance of the joint and in general the fatigue resistance of adhesive joints is superior when compared with mechanically fastened joints [10]. Thus the ageing performance of an adhesive joint is an important topic to be studied before the implementation of the structure in applications. Often when heat and humidity are present in the service atmosphere, rubber/metal interfaces tend to fail at the rubber/bonding agent interface, although they have shown cohesive failure in laboratory tests [11]. Within rubber/metal interfaces, the tyre cord/rubber adhesion and its resistance to different environments is widely studied (e.g. [12-14]) and interfaces are shown to degrade due to heat and moisture. Similarly, other polymer/metal interfaces are prone to moist environments and exhibit a significant decrease in interfacial strength after the ageing [15]. Thus, the suitability of the studied stainless steel/rubber/GFRP structures for real life applications has to be verified by environmental testing even though our adhesion studies [8] showed a good adhesion level for non-exposed samples.

Any established general practices for testing the environmental resistance of polymer/metal interfaces do not exist. Instead, it has been studied in various conditions depending on the material combination and application in question. Carbon fibre reinforced epoxy composite/EPDM rubber structure’s strength has been investigated after thermal ageing at 100 °C and after hot/moist ageing at 70 °C and 100 %RH [16]. Natural rubber/tyre cord strength has been studied after exposure to heat (70 °C), heat and moisture (70 °C, 96 %RH) and water immersion at the temperature of 70 °C [12]. Epoxy/copper strength has been tested after heat (85 °C) and four different levels of moisture: ambient atmospheric conditions, 50 %RH, 65 %RH and 85 %RH [17]. The combination of the 85 °C temperature and the 85

%RH humidity is also used in the steady state temperature humidity bias life tests for packaged devices [18]. Also the ASTM standard for the hydrolytic stability of rubbers [19] instructs the temperature of 85 °C above a water container, which is close to the humidity of 85 %RH. Thus, the 85 °C/85 %RH condition has been chosen for this study as well.

In the present study, the environmental resistance of stainless steel/EPDM rubber/GFRP structures is tested after the exposure of the samples for hot, moist and hot/moist environments. In practice, this is done by testing the two interfaces of the structure separately. Two different stainless steel surface finishes, an industrial surface finish and a sand blasted one, as well as two different EPDM based rubbers are used in the studies for the stainless steel and GFRP substrates. The results are compared with the results of a mild steel/EPDM rubber/GFRP system since such structures are used in industrial applications, e.g., in vibration damping devices [20] and in automotive components [2]. The effects of the ageing environments on the interfaces of the hybrids are investigated by peel tests, microscopy, Fourier transform infrared analysis and thermogravimetric analysis.

2. Experimental

In the present study, the environmental resistance of steel/rubber and GFRP/rubber interfaces were investigated. Two steel grades, stainless steel AISI 304 (Outokumpu Stainless Oy, Finland) and cold rolled mild steel EN 10130 DC01 (Rautaruukki Oyj, Finland) were studied. The mild steel was passivation treated as is customary for grades used as industrially coated. The aim of the passivation treatment is to enhance the adhesion properties of the steel but the procedure is not public. For the stainless steel grade, two different surface finishes were used, namely the as-received cold rolled, heat treated and pickled (2D) industrial surface finish and the same surface with an additional sand blasting step (SB). The surface finish 2D is defined in the standard EN 10088-2. The 2D surface was chosen for the as-received surface finish, because it showed the best adhesion strength among the different as-received surface finishes in preliminary tests [8]. The thickness of the steel sheets was 0.5 mm, but a thicker metal stiffener was glued on the back side of the metal component to prevent its bending during peel testing. The material combinations used in this study are summarized in the Table 1. The sand blasting media was aluminium oxide (grit 36, average particle size 483 μm). A more detailed study of these steel surfaces can be found in [8].

Table 1: *The used substrates, their average profile roughness parameters (R_a) measured with laser profilometer [8] and the studied material combinations.*

Substrate			
Code	***Surface treatment***	***R_a [μm] [8]***	***Rubber***
2D	*Cold rolled, heat treated, pickled AISI 304*	*0.38*	*A*
SB	*Sand blasted 2D surface of AISI 304*	*2.46*	*A*
GFRP	*HexForce® T470 peel ply*	*23.51*	*A*
2D	*Cold rolled, heat treated, pickled AISI 304*	*0.38*	*B*
SB	*Sand blasted 2D surface of AISI 304*	*2.46*	*B*
GFRP	*HexForce® T470 peel ply*	*23.51*	*B*
CR	*Cold rolled, passivation treated EN 10130 DC01*	*0.43*	*C*
GFRP	*HexForce® T470 peel ply*	*23.51*	*C*

The glass fibre reinforced plastic (GFRP) composite was manufactured in-house by vacuum infusion from stitched 0/90 E-glass fibre fabrics (682 g/m^2, Ahlstrom Oyj, Finland) and Sicomin SR 1660 / SD 7820 epoxy. The thickness of the GFRP sheets was 3.5 mm and its fibre content was about 45 vol-%. A metal stiffener was glued on the back side of the GFRP sheets to prevent its bending during peel testing. The heat resistant epoxy was chosen to provide the resistance of the GFRP sheet to the vulcanising temperature of the rubber (varying between 130-160°C for the different rubber grades). From the adhered GFRP surface, a HexForce® T470 (Hexcel Co., USA) peel ply was removed prior rubber attachment.

The EPDM based rubbers adhered to the steel and composite surfaces were manufactured by Teknikum Oy, Finland (grade A) and by Kraiburg GmbH, Germany (grades B and C). The grade A has a trade name Teknikum TRA10 and its ingredients are EPDM rubber, ZnO, stearic acid, polyethylene wax, carbon black, paraffin oil, internal adhesion promoter and peroxide. The grade B is also designed for stainless steel whereas the grade C is designed for mild steels. The main components of the rubbers B and C are EPDM rubber, silica (rubber B) or carbon black (rubber C), paraffin oil, internal adhesion promoters, silane, curing promoters, and peroxide.

The steel/rubber and composite/rubber hybrids were manufactured by vulcanising the rubber to the substrates. The steel surfaces were rinsed with ethanol and acetone and the peel-ply was removed from the composite surfaces just before the rubber bonding but no other pre-treatments for the composite surface were done. A uniform rubber thickness of 2 mm was ensured during the manufacturing of the laminates. A more detailed description of the manufacturing steps of the hybrids can be found in [8]. The peel test samples (size 100 x 12 mm) were cut from larger steel/rubber and GFRP/rubber laminates by water jet cutting.

The environmental resistance of the structures was tested by exposure to isohume (25 °C, 85 %RH), isothermal (85 °C, ambient atmospheric conditions) and hygrothermal (85 °C, 85 %RH) environments and after the ageing by peel testing. The running time of the exposure tests was 500 hours. The EPDM rubber should endure the aforementioned environments without degradation [21]. Between ageing and testing, the samples were stabilised for 72 hours in 23 °C and 50 %RH.

The adhesion of the steel/rubber and GFRP/rubber interfaces were studied by a floating roller peel test configuration (Fig. 1). The floating roller peel test geometry introduces a constant peel angle of 45 degrees which is shown to be the most convenient to study the adhesion between steel and rubber [22]. The peel tests were done with a universal mechanical testing machine with 1 kN load cell (Messphysik, Austria). A cross head rate of 100 mm/min was used according to the [23].

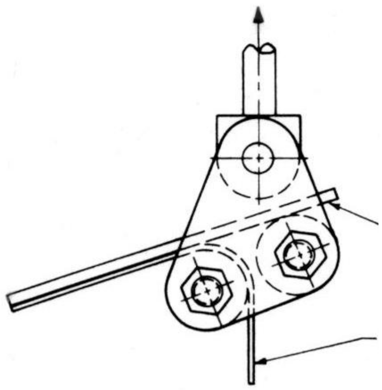


Figure 1: *The floating roller peel test configuration. Modified from* [24].

To determine the possible changes in the chemical structure or composition of the rubbers after ageing, Fourier transform infrared (FT-IR) and thermogravimetric analysis (TGA) were performed. The FT-IR spectra were measured with Tensor 27 from Bruker Optics, equipped with germanium attenuated total reflection (ATR) accessory. For each spectrum 64 scans were collected with resolution of 4 cm^{-1}. A Perkin Elmer STA 6000 equipment was used for the TGA studies. For the TGA analysis 10-20 mg specimens of the rubber grades were heated from 30 to 950 °C at a rate of 10 °K/min under nitrogen flow of 20 ml/min. In addition, the Shore D hardness of different rubber grades was measured according to the ASTM D2240 standard [25] before and after each environmental test. The peeled steel and rubber surfaces were also investigated with a Field Emission Gun Scanning Electron Microscope FEG-SEM, Zeiss ULTRAplus, Germany.

3. Results and discussion

3.1 Adhesion of aged samples

The floating roller peel test results are summarised in Table 2. The reported peel strength values are averages of 5-7 peel tests. The non-exposed, the isothermal and the isohume exposed mild steel (CR)/rubber C samples exhibited cohesive fracture of rubber before the interfacial peeling started, meaning that the cohesive strength of rubber C is less than its peel strength to the mild steel. The peel force at which the non-exposed rubber C fractured was 70

N ± 15 N and it remained at the same level after the exposure to hot or moist environments. Only in the case of hygrothermal ageing, adhesive fracture between the mild steel and the rubber C was observed together with a distinct decrease in the peel force. The GFRP/rubber samples showed a cohesive fracture after all ageing procedures. Since the mild steel/rubber combinations are widely used in industrial applications, such as in vibration damping devices [20], we set the results of the mild steel/rubber C and GFRP/rubber C peel tests as a point of comparison to the corresponding stainless steel/GFRP hybrids.

Table 2: *Summary of the floating roller peel test results. The adhesive peel force could not be determined for the samples in which the interfacial peel strength exceeded the cohesive strength of rubber (referred in the table as "Cohesive" cases).*

	Sample		***Interfacial peel strength [N/mm]***			
Steel	***Surface***	***Rubber***	***Non-exposed***	***Isothermal***	***Isohume***	***Hygrothermal***
AISI 304	*2D*	*A*	*Cohesive*	*Cohesive*	*Cohesive*	*Cohesive*
	SB	*A*	*Cohesive*	*Cohesive*	*Cohesive*	*Cohesive*
AISI 304	*2D*	*B*	*0.90*	*0.87*	*0.70*	*0.21*
	SB	*B*	*26.88*	*Cohesive*	*2.99*	*1.52*
EN 10130 DC01	*CR*	*C*	*Cohesive*	*Cohesive*	*Cohesive*	*0.66*
GFRP	*Peel ply*	*A*	*Cohesive*	*Cohesive*	*Cohesive*	*Cohesive*
	Peel ply	*B*	*Cohesive*	*Cohesive*	*Cohesive*	*2.60*
	Peel ply	*C*	*Cohesive*	*Cohesive*	*Cohesive*	*Cohesive*

All GFRP/rubber A and stainless steel/rubber A samples showed a cohesive fracture after all ageing procedures. Thus, stainless steel/rubber and GFRP/rubber interfaces resistant to degradation in harsh environments can be manufactured. Also, no additional surface treatments of the stainless steel substrate are needed which simplifies the manufacturing process substantially. Further, during the mechanical evaluation of such steel/rubber or GFRP/rubber components, the strength of the interface, which otherwise is difficult to define, can be considered higher than the cohesive strength of the rubber. For the non-exposed samples the peel force at the rubber failure was 382 N ± 97 N but the force decreased to 42-45 N for the exposed samples.

The rubber grade B did not show as good adhesion to the stainless steel properties as the grade A. However, at the sand blasted stainless steel surface (SB) the adhesion strength of the non-exposed and the isothermally exposed samples exceed clearly the values of non-aged mild steel and natural rubber [22] and stainless steel and thermoplastic urethane [26] samples. The change of the fracture mode from adhesive to cohesive after the isothermal ageing also indicates that elevated temperatures enhance the interfacial strength of the stainless steel/rubber B structure. From the GFRP substrate, the interfacial peel strength exceeded the rubber's cohesive strength in all cases except for the hygrothermally exposed samples. Like to rubber A, a decrease in the peel force at which the rubber B fractured cohesively was observed from 268 N (non-exposed) to around 55 N (hot or moist exposure).

According to our peel studies, EPDM rubbers can be bonded to both stainless steel and GFRP substrates so that its interfacial strength under peel loading in both cases is higher than rubber's cohesive strength. In general, EPDM rubbers are known to have good mechanical properties when compared with other rubber grades [27]. Also, the interfacial strength of these EPDM/substrate joints withstands harsh environments. This makes the manufacturing of stainless steel/rubber/composite hybrids reasonable: First, stainless steel and epoxy which are difficult to adhere can be joined without time-consuming pre-treatments with the aid of a thin EPDM layer. Second, the strength of the joint can be estimated by the cohesive properties of the rubber.

3.2 Characterisation of substrates after peel tests

Due to the cohesive fracture, most substrates did not have peeled substrate surfaces suitable to being analysed. Fig. 2 shows two examples of the samples after peeling: cohesively and adhesively fractured ones. When studied with FEG-SEM, the adhesively fractured samples showed a partial adhesive/cohesive fracture. In the sand blasted surface, the rubber residues were distributed quite uniformly to the asperities of the surface (Fig. 3.a) whereas at the as-received stainless steel 2D substrates, the cohesive fracture was found mainly at the grain boundaries (Fig. 3.b-f). These results emphasise the importance of the mechanical interlocking. However, some rubber residues were observed also outside the grain boundaries where the 2D surface was smooth, which suggests that other adhesion mechanisms are present as well. No remarkable difference was observed between the non-exposed samples and those exposed in isohume environments, as seen in Fig. 3.b-d. However, when comparing the Fig. 3.c of the isothermally aged stainless steel 2D/rubber B sample with the peel test results of the 2D/B and SB/B peel test results, it can be seen that thermal ageing has an improving effect on the strength of the stainless steel/rubber B interface.

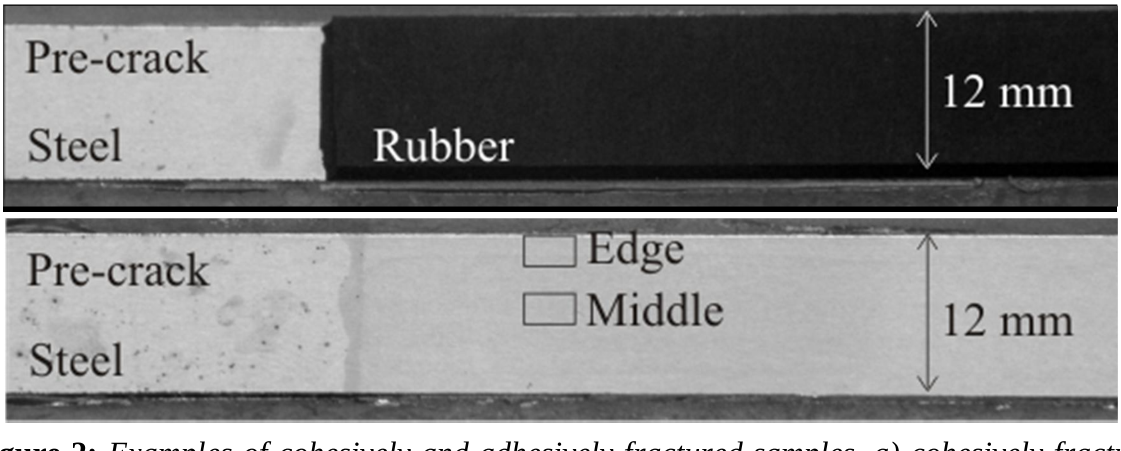


Figure 2: *Examples of cohesively and adhesively fractured samples. a) cohesively fractured non-exposed stainless steel 2D/rubber A sample and b) adhesively fractured hygrothermally exposed stainless steel 2D/rubber B sample. The pre crack and the studied middle area and edge area are also shown.*

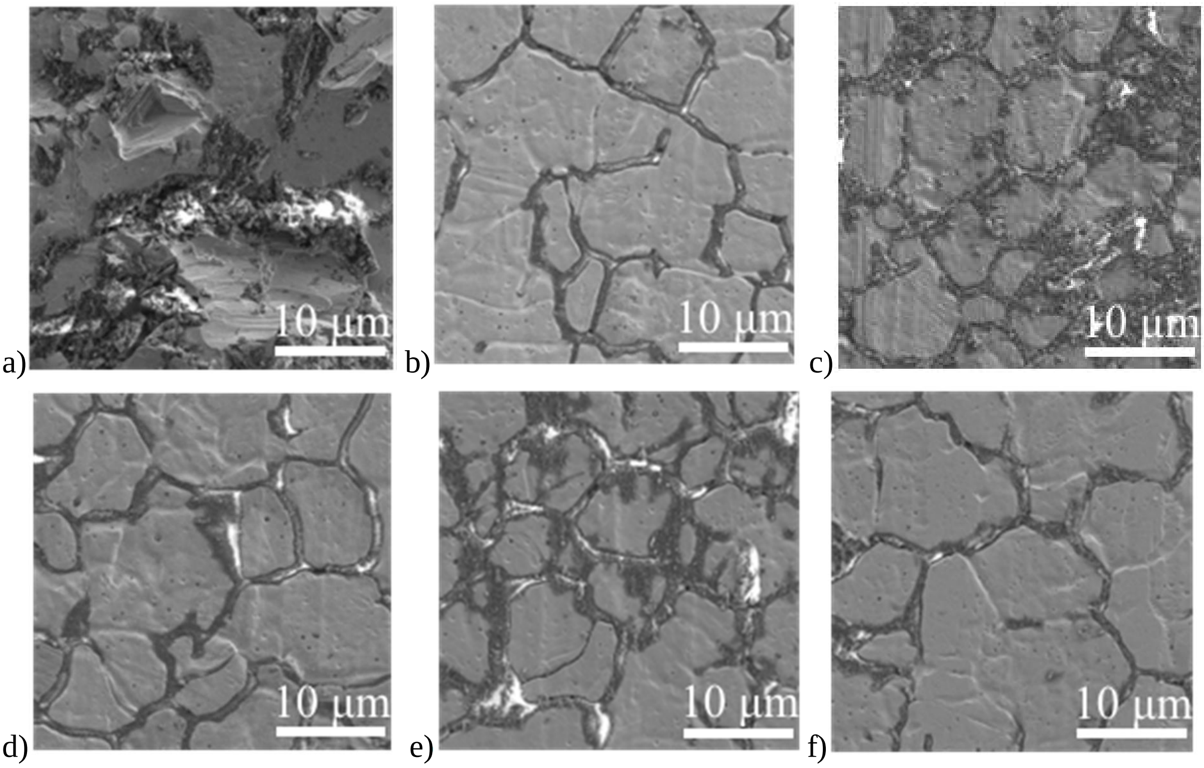


Figure 3: *FEG-SEM images from the peeled stainless steel substrate of a) non-exposed SB/rubber B sample, b) non-exposed 2D/rubber B sample c) isothermally aged 2D/ rubber B sample and d) isohume exposed 2D/rubber B sample. These images are taken from the middle area (see Fig. 3) of the samples. In e-f) is the hygrothermally exposed and peeled substrate of 2D/rubber B samples from e) the middle area f) the edge area of the sample.*

The steel substrates of the hygrothermally aged samples showed less rubber residues, i.e. less cohesive fracture, after adhesive fracture in the edge areas of the peel test samples when compared with the middle areas of the samples (Fig. 2 and 3.f). According to this, the effect of high humidity and temperature cause the degradation of the interface starting from the sample edges. The degraded, less tightly bound area was roughly 2 mm wide on the both sides of the 12 mm wide 2D/rubber B and SB/rubber B samples. This explains the clearly decreased peel force of the hygrothermally aged samples. The other sample types did not show this kind of degradation of the interface at the sample edges.

The peeled rubber surfaces of adhesively fractured samples were also studied with FEG-SEM. To ensure the conductivity of these SEM samples, gold coating was applied before the examination. Similarly to the stainless steel surfaces, the rubbers from non-exposed and from the samples aged in isothermal or isohume environments did not show any remarkable difference. However, in the edge areas of the hygrothermally exposed samples small asperities on the surface were observed more often than in the middle areas (shown by arrows in Fig. 4). In addition, in visual inspection a colour change from bright orange to brown was observed for the rubber grade B after isothermal and hygrothermal ageing. To characterise the possible chemical or physical degradation in the rubbers due to the hygrothermal ageing, FT-IR, TGA, and hardness studies were also performed.

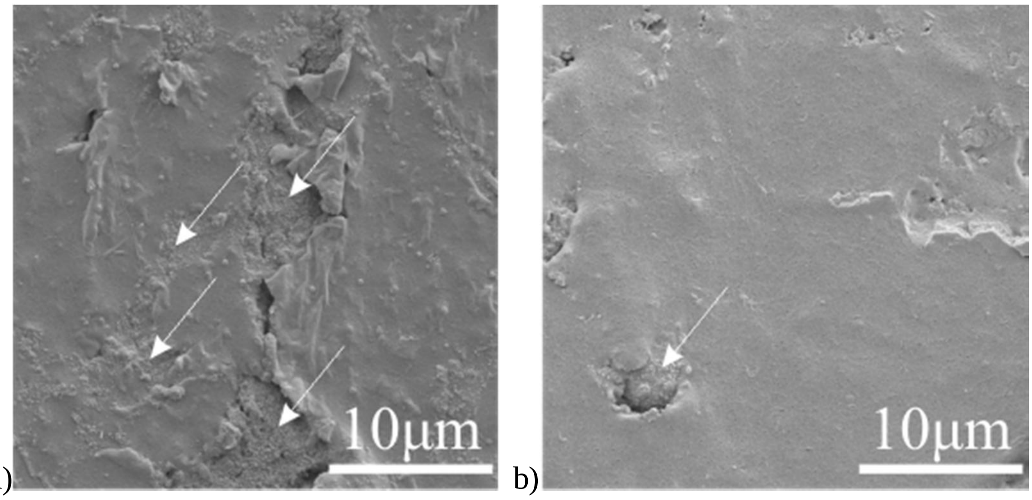
a) b)


Figure 4: *The peeled rubber surface of a) a non-exposed and b) a hygrothermally exposed stainless steel (surface finish 2D)/rubber B samples from the edge of the sample.*

3.3 Changes in rubbers due to ageing

The adhesively fractured rubber B surfaces were studied by FT-IR to study the possible changes of the peeled rubber surfaces before and after hygrothermal ageing. Other rubber grades did not allow studies of the peeled rubber surface due to the cohesive fracture occurring in them. The spectra for the non-exposed and for the hygrothermally exposed 2D/B samples were similar, as seen from Fig. 5. There was a small difference in the area of hydrogen bonded OH groups (3200-3600 cm^{-1} [28]) shown in insert A of Fig. 5. This suggests that the fraction of hydrogen bonded water has increased during the exposure at the interface and it remains in the interfacial area also after 72 hours stabilisation at 23 °C and 50 %RH. However, the change is minor. Although no chemical changes in the polymer structure were observed, the absorbed water may have decreased the peel strengths through plasticization effects [29].

Recently, it has been shown in other studies that an increased temperature and humidity lead to an increased oxygen content in a brass/natural rubber (NR) interface: Ozawa et al. assume that in humid environment, water decomposes upon infiltration into rubber increasing the oxygen density in the rubber and in the brass/rubber interface [12]. Increased oxygen density promotes such changes in the oxide structure of the brass surface, which weaken the interfacial adhesion strength [12]. EPDM rubbers are typically impermeable to water and they are used widely in different sealing applications [21]. Thus, it can be assumed that the infiltration of water through the rubber is minimal. However, depending on the exact composition of the rubber compound, the permeability coefficient values of EPDM rubbers vary remarkably up to the values reported for natural rubber [30, 31]. Therefore, the detailed mechanisms of the chemical changes at the stainless steel/rubber interface in hot/moist environment should be studied further.

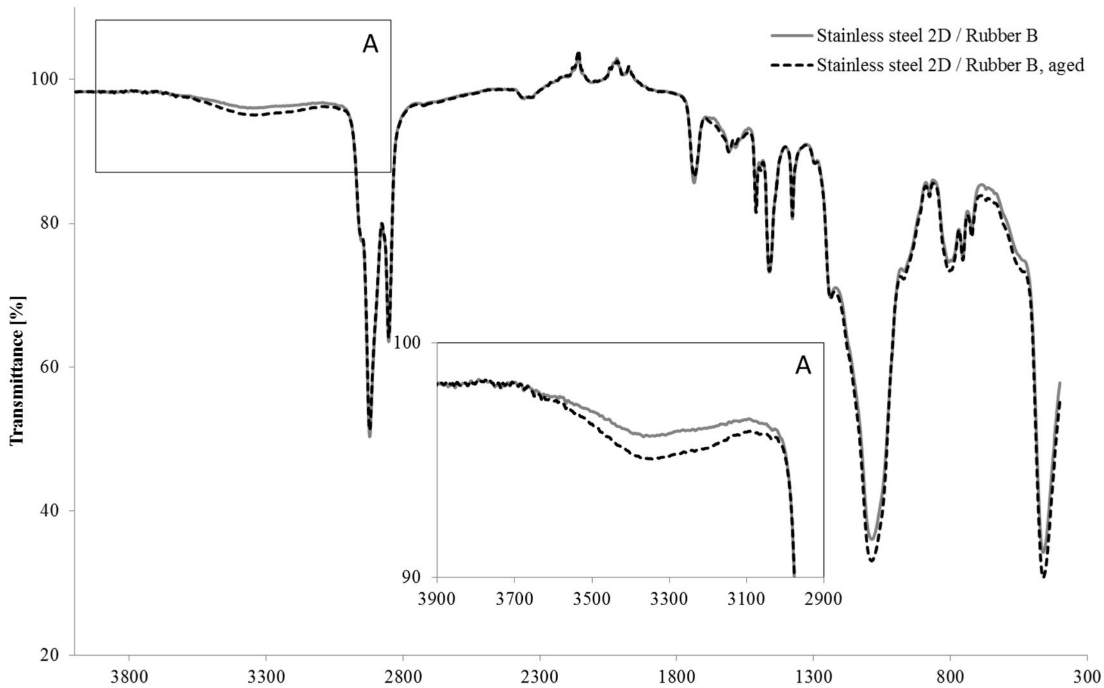


Figure 5: *FT-IR spectra of peeled stainless steel surface 2D before and after hygrothermal ageing. The spectrum of the aged rubber is measured from the edge area of the sample (see Fig. 2).*

To study further the possible changes in the different rubber grades due to the hygrothermal exposure, TGA curves were measured (Fig. 6). The aged rubber grade A did not show changes due to the ageing, whereas the elastomer degradation of the aged B and C samples was observed. In the latter case, the TGA curves (the main step at 400-500 °C) shifted in minor extent when compared with the non-exposed ones. In rubber B, the degradation of the aged sample begins slightly earlier while the temperature at which the degradation takes place and the amount of inert residue remain unaltered. On the other hand, the degradation of the aged rubber C is delayed, the degradation temperature is increased and the apparent elastomer fraction decreased more significantly than for other rubber grades (15% vs. 8%). These changes may indicate an increase in cross-link density due to hygrothermal exposure.

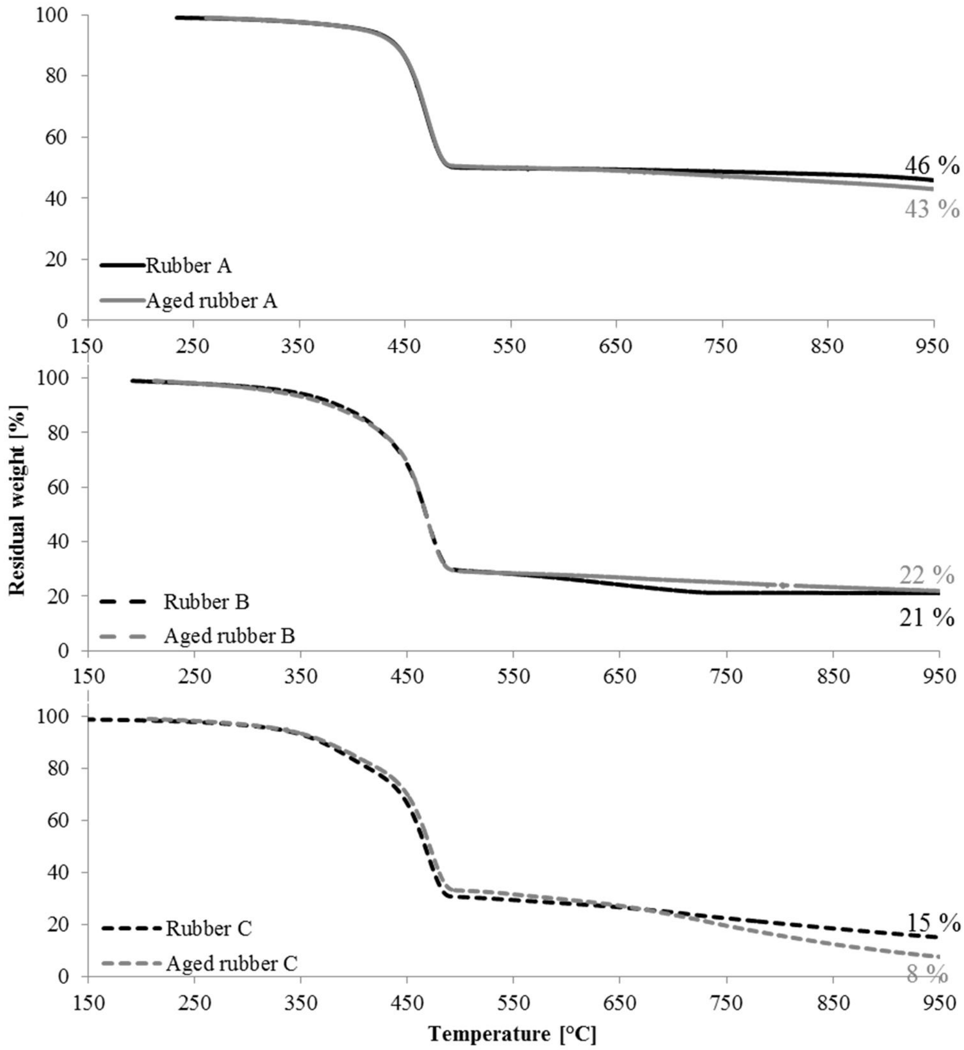


Figure 6: *The TGA spectra of the non-exposed and hygrothermally exposed rubbers A-C. The curves are plotted starting from the point where the mass has decreased one percentage unit (weight 99%). In addition, the weight of the inert residue is reported.*

The Shore D hardness before ageing for rubbers A, B and C was 41 ± 1.2, 43 ± 0.9, and 44 ± 0.8, respectively. Changes in hardness due to hot, moist or hot/moist environment were not observed for rubbers A and B but the Shore D values stayed within the standard deviation limits. A slight increase in hardness was observed for rubber C (47 ± 0.9 after hygrothermal ageing). This supports the assumption that hygrothermal exposure has caused an increase in the cross-link density in rubber C.

Based on the results of the FT-IR, TGA and Shore D hardness measurements, significant changes in the rubbers were not observed. However, further studies about the degradation mechanisms of the stainless steel/rubber interface would offer interesting information which could be utilized to develop more reliable stainless steel/rubber components. In addition, it is possible that the current tests procedure has ignored some ageing processes that are reversible in nature. Such changes can vanish during the stabilisation period. However, the available test equipment did not allow environmental peel testing, which would be an interesting topic for a study in itself.

Conclusions

The environmental resistance of stainless steel/EPDM rubber/GFRP composite structures was investigated by ageing steel/rubber and GFRP/rubber interfaces in hot, moist and hot/moist environments prior to peel testing. The main interest was in two different rubber grades and in two different stainless steel surface finishes, in which the used steel/rubber/GFRP hybrids were based. The results of these structures were compared with the peel strength values measured for the non-exposed samples and with a mild steel/EPDM rubber/GFRP system. After peel testing, the substrate and rubber interfaces were characterised by scanning electron microscopy and chemical analyses.

Our studies showed that with proper compounding, EPDM based rubbers have high adhesion strength to both stainless steel and epoxy. The adhesion strength exceeds the cohesive strength of the rubber even after ageing in harsh hot/moist environments. In addition, no need for substrate pre-treatments prior rubber bonding was observed, even the stainless steel can be in the as-received state. This makes possible the use of EPDM rubber in stainless steel/polymer hybrid systems to replace adhesives. These stainless steel/rubber/composite hybrids combine the good properties of steel (mechanical properties and corrosion resistance), rubber (adhesion and vibration damping properties) and composite (light weight) in a simple manner by vulcanising the rubber between the steel and the composite.

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