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Investigation of chemical ageing and its effect on static and fatigue strength of continuous fibre reinforced plastics

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ABSTRACT

The long term durability of continuous glass fibre reinforced thermosets with epoxy resin at high temperature and an oxygen-environment is investigated in detail. An extensive ageing-study is performed to detect the ageing effects on the residual strength in different laminate layups and to identify the corresponding damage mechanisms. Thermal degradation is found to be the dominant damage mechanism and the weight loss is found to be the most suitable measure of damage. A new phenomenological model that is based on the time-temperature-superposition principle and a master-relation between the residual strength and weight loss is presented to model the ageing effect on the residual strength. Fatigue experiments of pre-aged specimen are performed to verify the ageing effects on the fatigue strength. A simple methodology predicting the fatigue life of pre-aged specimen from the residual static strength is demonstrated and validated experimentally for several layups.

1. Introduction

The low specific weight and the high strength of continuous fibre reinforced plastics (FRP) offers light weight design opportunities. Therefore, the application of FRP materials in automotive engineering is increasing since 2000 [1,2]. If FRP parts are applied in power train systems these components must not only resist variable mechanical loadings but also ageing effects that are caused by aggressive media (e.g. oxygen, oil) and temperatures up to 160 °C. However the long-term properties of FRP exposed to environmental influences are still not well characterised [3].

The mechanical behaviour of FRP materials differs from metals since they are anisotropic and inhomogeneous in general [4]. Even though the fibre determines the mechanical properties like elastic modulus or strength, the matrix provides the physical and chemical durability by protecting the fibre from environmental influences [2]. The ageing affects mostly the matrix and also the fibre-matrix-interface, whereas this is the least known process [3]. As it can be seen from [5,6] the fibre is usually considered to be stable. Generally thermosets are more resistant against ageing than thermoplastic materials because of their chemical structure. Thermosets consist of polymer chains that are cross-linked by covalent bonds. On the other hand thermoplastics consist of polymer chains that are connected by weaker van-der-Waals linkages [7].

In this paper "ageing" is defined as the change of mechanical and physical properties caused by physical or chemical processes but not by mechanical loading. The exposure of several neat polymer resins to high-temperature ageing has been studied in literature (e.g. [8]) and generally two main mechanisms can be separated: physical and chemical ageing.

Physical ageing is a reversible process [9] and refers to the time-dependent volumetric shrinkage caused by a thermodynamic instable state after cooling down from the manufacturing temperature. Physical ageing is less important in thermosets than in thermoplastics since high temperatures cause cross-links that reduce a change in the free volume [10]. In [9] the finding that physical ageing is barely present in thermosets is confirmed.

Chemical ageing is an irreversible change of the chemical decomposition and the molecular structure [7,3]. Three different degradation mechanisms can be separated [7,9]: thermal degradation, thermo-oxidative degradation, hydrolytic degradation. Thermal degradation leads to chain-scission reactions caused by strong molecular oscillation at high temperature and/or additional crosslinking [7] while thermo-oxidative degradation refers to chain-scissions by oxidation [11,7,12]. The thermo-oxidative mechanism is therefore dominated by the diffusion and reaction

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Nomenclature

r	strength
σ	stress
b	fatigue factor
N	fatigue cycle
P	arbitrary mechanical property
T	temperature
p, q	material properties
D	damage measure
m	weight
E_a	activation energy
μ, σ	time-temperature-superposition parameter
α	time-temperature-shift factors
k	Boltzmann constant
t	time
t'	equivalent time
u, v	material properties strength degradation

Indexes

t	tension
c	compression
o	upper
min	minimum
0	initial state
r	residual
ref	reference
g	glass transition
11	longitudinal to fibre
22	transverse to fibre
12	in-plane shear
23	out of plane shear
13	out of plane shear

of oxygen. Changes in the glass transition temperature, weight or colour indicate thermal and/or thermo-oxidative ageing effects [9]. Which degradation mechanism is dominant depends on the temperature, environment and the resin type [13]. The hydrolytic degradation describes a chain reduction by water and goes along with an increasing weight since water is embedded in the polymer [13,14].

Since ageing is a thermally activated process the testing time can be reduced by increasing the test temperature. For chemical ageing accelerated testing can also be achieved by increasing the concentration of the reactive component (e.g. oxygen, water, acid) [15]. In [9] it is found that the time temperature superposition principle is valid for polymer and for polymer composites.

Both ageing mechanisms, chemical and physical, can cause microcracks and lead to a degradation of the material's strength and stiffness [3]. An exception is the initial increase in strength and stiffness by post curing that is described in [13]. However according to [9] ageing-studies and models capable of predicting the long-term changes due to chemical ageing are rare.

2. State of the art

Generally there are two approaches to capture the ageing behaviour. The first one is to make model-based predictions with mechanism based models that try to model the actual chemical and physical processes causing the ageing degradation (e.g. [12]). The second one relies on experimental ageing tests of residual strength or stiffness which is described in [16].

Mechanism-based models are very common. In [16] a mechanism-based model for thermo-oxidative degradation is presented. It also includes the modelling of oxygen-diffusion and reaction whereas the temperature-dependency is an Arrhenius relation. Based on a closed-loop reaction scheme the concentration-dependency of the reaction is derived. The weight loss is then correlated to the reaction rate. This model is only valid for low conversion rates.

Therefore the model is extended by [11,17] towards high conversion rates by using a minimum residual weight fraction Φ_{ox} that defines the reaction end. Practically this means that the oxidation front can move towards the core of the specimen. The oxidation level is separated into three different stages: (fully) oxidized zone, active zone (oxidation is still ongoing), unoxidized zone. The model is validated by measurements of the oxidation-layer growth and the weight loss. In [16] the detection of the oxidation zone and the active zone is done using IR spectroscopy and interferential contrast. It is said that the oxidized zone is characterised by a high roughness while the active zone is smoother but brighter than the unoxidized core. In [18] the oxidation layer is measured using dark-field microscopy. However the measurement of the active zone is not described.

While the model was used in [16,11] to describe the oxidation in neat resin only, it is extended in [6] to simulate the movement of oxidation front in unidirectional composites. The application of the model to woven composites in shown in [19].

The model is enhanced by Liang and Pochiraju in [20,21] where they introduce an oxidation induced chemical strain that is caused by a mismatch of shrinkage of un-oxidized and the oxidized material. The different shrinkage degrees of un-oxidized and oxidized result from molecular degradation by ageing processes. The chemical strain leads to substantial stresses in the oxidized zones. The damage initiation is modelled by the use of a failure criterion that is similar to the one of Hashin. However the model is only validated to experimental crack length but not validated to experimental residual strength data.

Considering all these cited models it can be noted that they are very similar especially the thermo-oxidative ageing models. Furthermore all of these models are validated to only two materials: PMR-15 [6,11,17,19–21] and Epoxy/Amine + 30% PES [16,22,23].

One of the first experimental investigations concerning the residual strength can be found in [24]. The results show that the ultimate tensile strength in fibre direction of Graphite/Epoxy reduces by 20% after 10.000 h of ageing at 177 °C. When exposed to 10.000 h of ageing at 121 °C the strength is not reduced at all.

In [25] the ageing influence on the compressive strength of T650-35/PMR-15 is tested at temperatures between 204 and 343 °C. Additionally the thickness of the specimen is varied. An enormous weight loss 6% after 1.2 h of ageing at 316 °C is found in the 4-ply-specimen. By increasing the ply number to 20 the weight loss can be reduced to 2% which means that the surface-dependent thermo-oxidative degradation is the main mechanism. This finding correlates with [11,17].

Since thermo-oxidative degradation is the main mechanism the oxidation front (in the paper called "surface layer thickness") is tracked and correlated to the compressive strength. The more the oxidation front and therefore the mircocracks are grown into the core of the specimen the lower the compressive strength. The experimental data shows that the residual compressive strength and the surface layer thickness follow a linear relationship independently from the ageing temperature.

The influence of chemical ageing on the fracture toughness of carbon/epoxy specimen was investigated in [26]. Interestingly the fracture toughness is increased by ageing effects. Further