INVESTIGATIONS ABOUT THE INFLUENCES OF TEMPERATURE AND OIL ON THE FATIGUE BEHAVIOR OF SHORT FIBER REINFORCED POLYAMIDE 6.6

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Abstract
Fiber reinforced polyamide (PA) plays a dominant role in lightweight automotive allocation. The interactions between vibration loading and the simultaneously effect of liquid media are not clear until now. Hence a study was carried out on flat specimens made of short glass fibre reinforced polyamide to determine the damage mechanism by effect of fatigue loading, temperature and automatic transmission fluid exposure. For the estimation different analytic methods such as infrared and polarized light microscopy, DMA in submersible configuration and sorption experiments were used to study the modification of the material by chemical or physical mechanisms. The findings were related to experimental results from fatigue tests.

1. Introduction

Fiber reinforced polyamide (PA) plays a pivotal role in lightweight automotive construction. As a result of its unique combination of excellent mechanical properties, paired with thermal stability and resistance against liquid media, especially lipophilic ones, they find increasing application in the engine compartment (e.g. under the hood applications).

Amongst other influences the components made of this material and used in automotive applications have to bear vibration loadings, temperature changes and liquid media contact. The influences of vibration loadings and simultaneous temperature changes on the mechanical material behavior can be estimated by standard tests. However, the interactions between vibration loading and the simultaneously effect of liquid media are not clear until now [1-3].

Hence a study was carried out on glass fibre reinforced PA to understand the mechanism of ageing and damage evolution due to fatigue loading and elevated temperature in the presence automatic transmission fluid. To elucidate the physicochemical mechanisms of vibrational loading and liquid media a range of characterization methods such as differential scanning calorimetry (DSC), infrared and optical light microscopy, dynamic-mechanical analysis in submersible configuration and sorption measurements were used. The findings from material characterization after exposure were related to the results from fatigue testing.

2. Experimental section

2.1. Specimens

For the following investigations two types of specimens were used, namely unnotched flat specimens and an inner pressure specimens, the so called “MultiTester” (MT), see Figure 1.

The specimens were made of the two materials an unreinforced PA66 and a short glass fiber reinforced PA 66 with a fiber content of 30 % (PA66-GF30). All specimens were produced by the injection molding process.

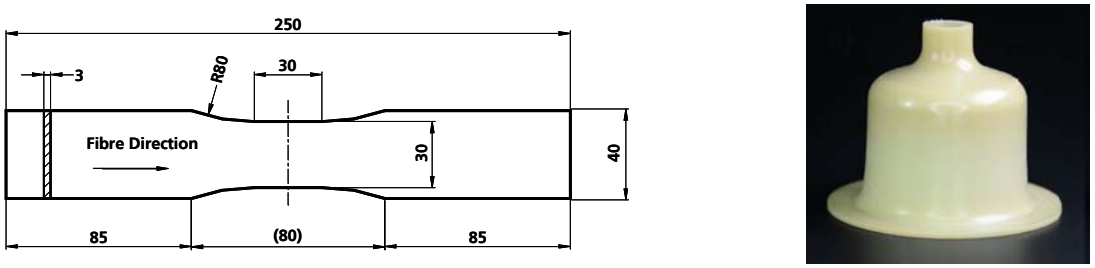

Figure 1. Unnotched flat specimen and inner pressure deformation specimen "MultiTester"

2.2. Analytical Methods

2.2.1 Differential Scanning Calorimetry

Microtome cuts over the cross-sectional area with a thickness of 400 µm (ca. 5 mg) were analyzed on a Mettler Toledo DSC 822e using a heating and cooling rate of 10 K/min under an inert atmosphere of nitrogen between 25 and 300 °C. The first heating cycle was used to calculate the degree of crystallinity (X_c).

2.2.2 Optical Light Microscopy

A microscope (BX50 F, Olympus) equipped with UPlan objectives was used for LM. A resin was used to fix the microtomed sections onto glass slides. Cuts of 40 µm thickness microtomed perpendicular to the direction of sample production were analyzed.

2.2.3 Infrared Microscopy

Microtome cuts of 40 µm thickness parallel ($cut_{||}$) and perpendicular ($cut_{\perp}$) to the direction of extrusion were used. An IR microscope (Continuum, Thermo Nicolet (Madison, WI)) equipped with a MCT-A-detector coupled to a Nicolet-Nexus 670 FTIR spectrometer as beam source was used. 100 scans were accumulated per spectrum using an aperture of 40 x 40 μm^2. The step width of the line scans was 40 µm.

2.2.4 Dynamic mechanical analysis

Temperature and time dependent measurements of the complex Young's modulus ($E^* = E' + iE''$) at a frequency of 1 Hz were performed at rectangular specimens (10 mm x 1 mm x 20 mm) under controlled temperature (-50 to 270 °C) using a Q800 Dynamic Mechanical Analyzer (DMA, TA Instruments). For the modes of deformation tension and 3-point bend were used. For DMA experiments on samples embedded in the automatic transmission fluid the same setup in submersible configuration was used (≤ 80 °C).

2.2.5 Sorption experiments

The sorption measurements were performed at flakes (size of some millimeters) and flat plates (80 x 80 mm x 1.8 mm) stored under controlled humidity at room temperature (RT) or embedded in the automatic transmission fluid (RT or 130 °C). The samples were weighed after defined times of exposure.

2.3. Description of the carried out investigations

2.3.1. Experiments without mechanical loading

With the aim to estimate the influence of temperature and automatic transmission fluid some of the specimens were aged for 1000 h and accordingly for 2000 h at room temperature (RT), 130 °C and 140 °C in air and in automatic transmission fluid (ATF).

2.3.2. Experiments with mechanical loading

The investigated flat specimens were undergone uniaxial fatigue testing with constant amplitudes (Woehler). The stress ratio was R=0. The ambient was 130 °C and air and accordingly automatic transmission fluid (ATF). Because of the different material behavior of the pure polyamide and the short glass fiber reinforced polyamide two failure criteria had to be used, defined elongation of specimen and the rupture of the specimen.

The fatigue tests were performed with hydraulic test equipment and special test devices for fatigue testing under fluids. The set ups are describes in [4].

3. Results

3.1. Aging tests without mechanical loading

3.1.1. Effects of aging with temperature and automatic transmission fluid

With the "MultiTester" made of PA66-GF30 the influences of temperature and ATF were investigated. Therefore the specimens were aged at three different ambient conditions (2, 3, 4) and afterwards compared to the unaged specimens (1), see Figure 2.

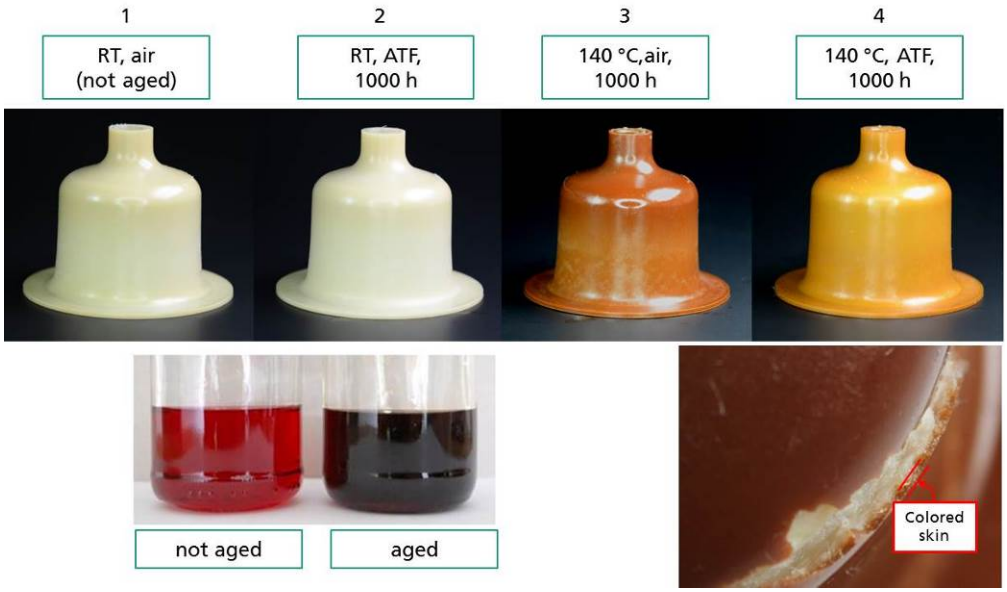

Figure 2. Test series with different aging conditions

The specimens aged in ATF at room temperature (2) do not show any visible change of their skin appearance compared to the unaged ones (1) while the specimens which were aged at 140 °C show a strong discoloration. It is worth to mention, that the discoloration is most intense for those specimen aged in air at 140 °C. The yellowing of the specimen aged at 140 °C in ATF is less and more homogeneous than that for the sample aged in air which can be explained by theromo-oxidative degradation as a result of the exposure to air. The inhomogeneous coloring after aging at 140 °C in ATF seems to reflect an inhomogeneous morphology (crystalline structure or GF distribution) due to injection molding. The different amount of ATF soluble components after aging is indicated by the dark color of the extract.

The optical images of PA66 test bars after different exposure are shown in Figure 3.

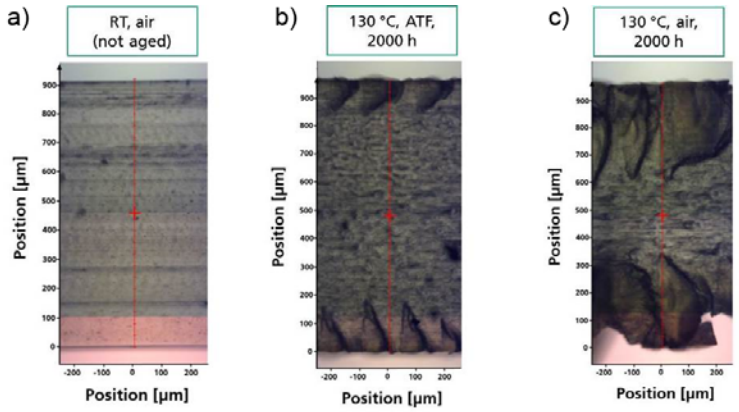

Figure 3. Optical images of test specimen a) unaged, b) 2000 h in ATF at 130 °C and c) 2000 h in air at 130 °C

The degradation starts from the outer edges in both media air and ATF. In case of ATF the degradation occurs much slower than in air, since only a layer of 150 µm seems to be brittle. In contrast, the exposure to air in combination with heat causes a rapid oxidation of the material and after 2000 h almost 80 % of the specimen is destroyed. Figure 3c indicates a degradation reaching to a depth of of 400 µm from the outer surface.

DSC heating curves for PA66 samples aged ATF (a) and air (b) are shown in Figure .

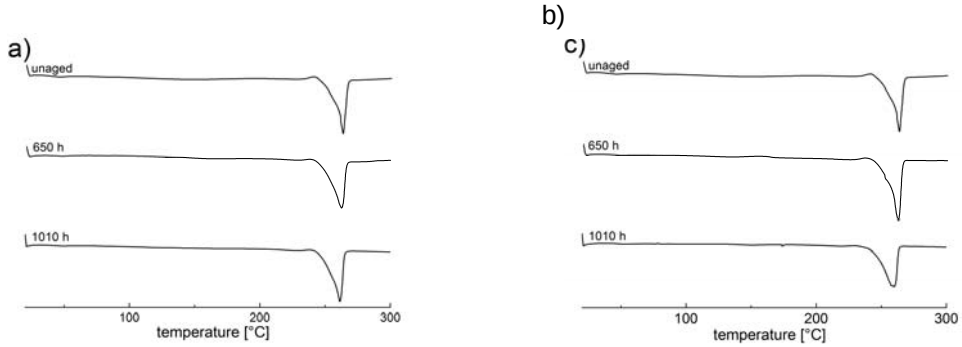

Figure 4. Melting endotherms of PA66 microtome slices taken across the bar thickness. a) 1st heating in ATF and b) 1st heating in air.

For the first heating cycle (
Figure 4a and c) only one melting peak is observed at 262 °C, which remains constant during aging for both conditions (air and ATF). The DSC experiments indicate only a minor effect of aging on crystalline structure and melting temperature.

In Figure 5 the relative change of sample mass ($\Delta m/m_0$) of PA 66 plates (80 mm x 80 mm x 1.8 mm) with different GF content is shown as a function of exposure time in water at 85 °C (a), in air at 130 °C (b) and in ATF at 130 °C (c), where $\Delta m = m(t) - m_0$ with the initial value m_0. The samples before the sorption experiments were dry (stored under nitrogen atmosphere after injection molding).

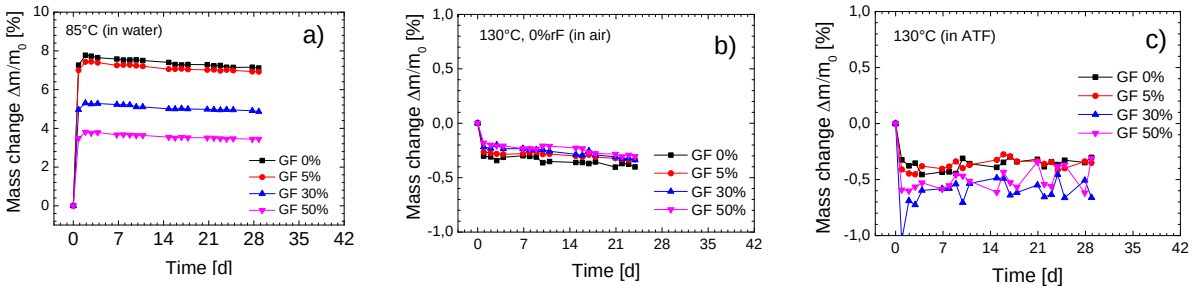

Figure 5. Sorption experiments of dry PA 66 samples with different GF content immersed in water at 85 °C (a), air at 130 °C (b) and in ATF at 130 °C (c).

These experiments were performed to differentiate between uptake of water and ATF and weight loss by degradation or extraction by water, air and ATF. Water exposure was included, since the PA properties strongly depend on water content. Figure 5a shows a fast water uptake in the first two days followed by a continuous mass loss. Both processes are independent of the GF content and can be explained by fast water sorption of the matrix and slow extraction of soluble components. The diffusion coefficients of the first and second process are about $3 \cdot 10^{-13}$ m²/s and $9 \cdot 10^{-13}$ m²/s independent of the GF content. The mass loss of the PA at 130 °C in air (Figure 5b) accounts for roughly 0.4 wt. % and seems to be related to oxygen induced degradation. A similar behavior is found for the sample immersed in ATF as shown in Figure 5c. Here the oxygen induced degradation can almost be excluded and thermal degradation and/or extraction of ATF soluble components is expected.

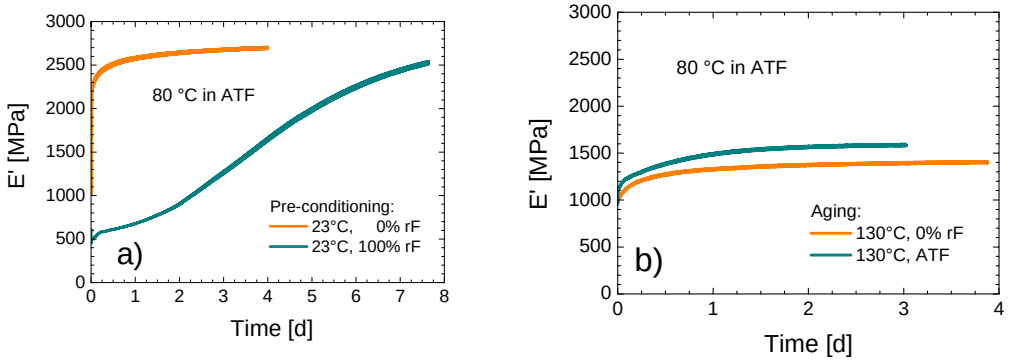

Figure 6. Time dependence of the storage modulus E' of PA 66 measured at 80°C in ATF after different pre-conditioning/aging. a) Initially dried and water saturated specimen (at room temperature). b) Aged at 130 °C in air and ATF for 1000 h.

Figure 6a shows the time dependent changes of the real part of Young's modulus *E*' of an initially dry and an initially water saturated sample immersed in ATF at 80 °C. *E*'(*t*) of the wet sample shows the typical shape for drying of a hydroplasticized sample (here in hot ATF). The sample changes from an initially rubber-like material with a modulus of about 500 MPa to a glassy polymer with about 2.5 GPa. In other words, the glass transition temperature increases due to the loss of water. The changes of the storage modulus (*E*') of the dry sample from about 2.2 to 2.6 GPa can be explained by changes of crystalline morphology, embrittlement or extraction of soluble components. For samples aged in air or ATF at 130 °C for 1000 h (Figure 6b) the storage modulus shows a similar shape as the dry sample in Figure 6a. The main difference is that the initial modulus of about 1.0 GPa is only about half of that of the unaged dry sample (23 °C and 0 % RH in Figure 6a). This indicates degradation during high temperature exposure at 130 °C.

3.2. Experiments with mechanical loading

3.2.1. Fatigue testing of flat specimens made of PA66 and PA66-GF30

In Figure 8 the single results of the Woehler-tests with flat specimens are shown in a S/N-diagram. The ambient temperature was 130 °C for all tests.

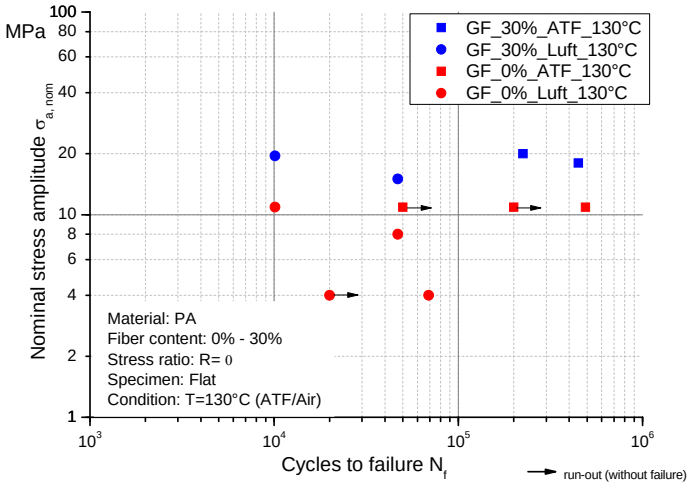

Figure 7. Woehler-Tests under different ambient conditions with flat specimens made of unreinforced polyamide 66 and short glass fiber reinforced polyamide with 30 % fiber content

For the specimens, which were tested in automatic transmission oil, was determined a higher fatigue life than for the specimens, which were tested in air. This effect was found for the specimens made of PA66 and for the specimens made of PA66-GF30.

According to the material and the ambient condition different criterion of failure had to be determined. For the glass fiber reinforced polyamide 66 the criterion of failure was the rupture of specimens in all cases. The cyclic creeping was in the range of 1.5 – 2 mm elongation of the specimen.

For the polyamide 66 without fibres two kind of failure had to be defined. For the tests in air the failure criterion was also the rupture of specimen. The elongation of the specimens was about 6 mm. For the tests in ATF no rupture of specimen could be realized because of the high elongation of the material. Therefore the criterion of failure was the elongation of the specimen with 11 mm (~ 14 %).

The behavior of X_c during the mechanical load in air of PA66 and PA66-GF30 according to loading cycles is shown in Figure .

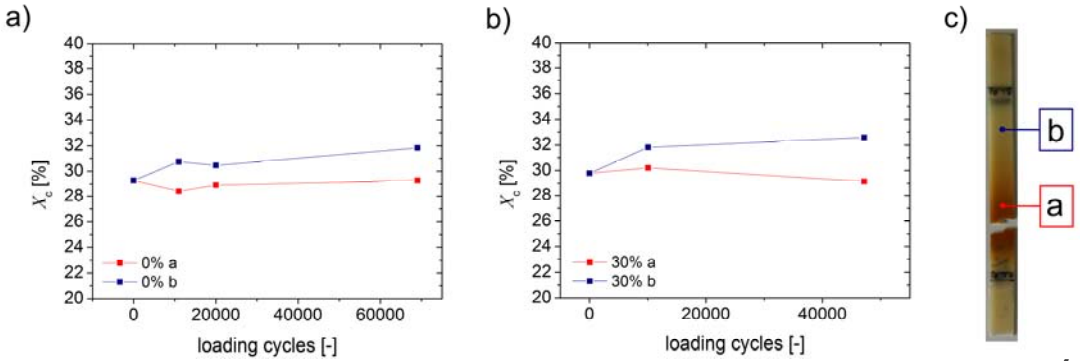

Figure 8. X_c for a) PA66 and b) PA66-GF30 according to loading cycles and c) Test bar PA66 at $2*10^5$ cycles.

The mechanical load of the test bars in air caused a highly colored zone around the place of fracture (Figure c). Based from that zone the brownish color vanishes with increasing

distance. Therefore X_c was determined at two different positions. Position (a) was set close to the place of fracture and position (b) close to the clamps. X_c decreases slightly with increasing loading cycles at position (a), while an increase is observed at position (b). The brown color at position (a) indicates the degradation of the material as a matter of mechanical stress and oxidation. As a consequence less material is left which could crystalize and X_c decreases. The increase of X_c at position (b) can be explained by post-crystallization of the amorphous phase, which is cause by the elevated temperature. Figure 9 shows the temperature dependence of storage (E') and loss modulus (E'') of PA 66 after different cycles of uniaxial fatigue testing at 130 °C and in air and ATF in 3-point bending mode at a frequency of 1 Hz.

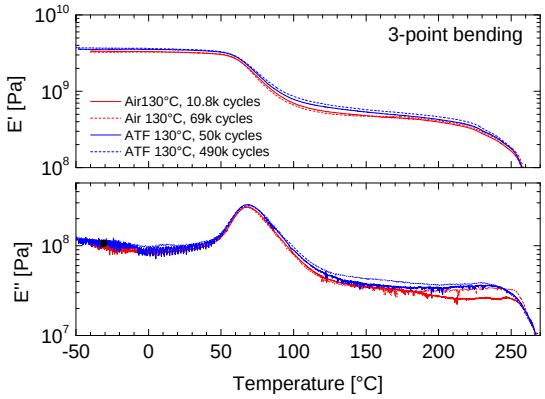

Figure 9. Temperature dependence of storage (E') and loss modulus (E'') at 1 Hz after different loading cycles in the uniaxial fatigue test at 130 °C in air and ATF.

The glass transition temperature T_g is indicated by a step in E' and by the E'' maximum. Because T_g is related to molecular relaxations of the polymer chains it is expected to be influenced by chemical degradation. However, no significant influence of fatigue testing at 130 °C in air and ATF be identified. The same is the case for the melting temperature T_m indicated by the decrease in E' above 250 °C. The mass difference in the rubber-like plateau modulus (logarithmic scale) between air and ATF aged samples might be caused by small changes in crystalline structure and or reduction of molar mass in amorphous phase due to aging in air. Such changes are also indicated by more detailed DSC investigation on the aged samples.

4. Conclusion

As a result of the unique combination of good mechanical properties, thermal stability and resistance against lipophilic liquids, fiber reinforced polyamide 66 (PA 66) is of large importance for lightweight automotive construction.

The interactions between vibration loading and lipophilic liquids has been investigated in this study by comparison of different characterization methods such as differential calorimetry, dynamic mechanical analysis in submersible configuration, infrared and optical light microscopy, sorption measurements and fatigue tests on specimen aged thermally in air and an automatic transmission fluid (ATF).

It has been found that

(i) there is no significant influence of the glass fibres on sorption and aging behavior,

(ii) aging in air is more pronounced than aging in a lipophilic automatic transmission fluid. The former starts at the sample surface and can be explained by oxygen

induced degradation. The lipophilic liquid prevents oxygen induced degradation and leads to a more homogeneous aging due to better heat transfer.

(iii) oxygen induced degradation and heat transfer between different regions of the sample explains the different failure mechanisms in fatigue testing in air and automatic transmission fluid. Inhomogeneous degradation and "hot spots" due to viscoelastic heating are suppressed.

(iv) In addition to the influence of temperature, mechanical load and organic liquids the strong influence of water uptake which leads to acceleration of chemical and physical processes by hydroplastification has to be taken into account for polyamide.

Further experiments with different loads, in different organic liquids and with more complex test programs (e.g. combination of air and lipophilic liquid exposure) are needed.

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