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Investigation of the Matrix Influence on the Laminate Properties of Epoxy- and Polyurethane-based CFRPs manufactured with HP-RTM-Process

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Abstract. The high pressure resin transfer molding (HP-RTM) process has the potential for high-volume production of continuous fiber-reinforced components in the automotive industry. The development of robust equipment, new process variants and highly reactive matrix systems lead to significant reductions of the cycle time in recent years. The paper addresses the manufacturing of carbon fiber reinforced plastic (CFRP) laminates using different matrix systems. To evaluate the matrix influence on the material properties, matrix dominated test methods were selected for evaluation of the mechanical properties. The test plates were made with the HP-RTM process at constant process parameters using carbon fiber fabrics. Only the matrix-specific supplier instructions for processing of the matrix systems (mixing ratio, temperature of components in HP-RTM equipment and mold) were varied in the study. Three Polyurethane (PU) systems and one Epoxy (EP) system were used for the characterization of the matrix dominated properties. To identify the interlaminar shear properties, two test methods were selected and compared to each other: The Short-Beam Shear (SBS) Test and the Edge Shear Test (ESH). To obtain the damage tolerance under impact loading, the energy absorptions for each material combination during instrumented drop tower tests were investigated. The results show the impact of the different Epoxy and Polyurethane matrix systems on the laminate performance.

Keywords: CFRP, HP-RTM, ILSS, Short Beam Shear Test, Edge Shear Test, Impact test, Epoxy resin, Polyurethane
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INTRODUCTION

The HP-RTM process has been studied intensely in recent years [1–4]. During this time, different variants of the process were developed to fulfill the requirements of the industry for quick manufacturing of high-performance composites. The process variants, namely high-pressure injection resin transfer molding (HP-IRTM) and high-pressure compression transfer molding (HP-CRTM), were investigated with different epoxy resin systems. However, polyurethanes (PU) have gained high interest for the use in HP-RTM process due to a good adjustability of their processing behavior to the process and component requirements. PU resins furthermore promise comparable material properties with regard to epoxy resin systems. The co-authors investigated the quasi-static mechanical properties of epoxy and polyurethane based laminates. The results indicate that testing of quasi-static, fiber-dominated properties lead to no clear statement about the influence of different resin systems on the mechanical properties as the main load during testing is taken by the fiber [5]. The novel approach of this study is therefore to investigate matrix dominated test methods to gain a better understanding of matrix specific composite properties. Thus, in contrast to existing research efforts, the influence of PU and epoxy material on the laminate properties can be shown. The test plates were manufactured with constant and comparable process conditions to allow a direct comparison of the test results.

A widely used test method for determining the interlaminar shear strength is the Short Beam Shear (SBS) Test (figure 1a) according to the standard DIN EN ISO 14130 [6]. The test is similar to the three-point-bending test having a modified ratio of support distance L to sample thickness h (L/h) of 1/5 to obtain high shear stresses in the sample. The stresses are induced indirectly by the bending load and the resulting SBS values are therefore defined as the apparent interlaminar shear strength. The classical beam theory assumes a parabolic distribution of shear stresses in the cross section, having the maximum value in the middle of the sample thickness. At this point, the normal

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stresses theoretically disappear and a pure shear stress state is present. In the SBS test standard, an overview of approved types of failure and their interpretation is given. To obtain comparability between different samples a pure shear failure has to occur but even this does not guarantee a reliable value for the measured shear strength. Several publications indicate that the SBS theory does reflect the real stresses in the sample only partially and may lead to misinterpretations of the test results. The failure often occurred next to the loading or support rollers before a shear failure was observed [7, 8]. Finite Element Analysis (FEA) showed the appearance of shear and compressive stress concentrations near the force introduction and support areas which exceeded the theoretical stresses determined by the classical beam theory [9, 10].

Weidenmann et al. proposed the Edge Shear Test (ESH) as an alternative test method to obtain the interlaminar strength of fiber reinforced plastics which is schematically illustrated in figure 1b. This test uses a direct force introduction (F_p) on the laminate cross-section to apply shear load between two fabric layers of the sample. No overlap between the upper and lower force introducing areas should be present to transfer the load by interlaminar shearing to adjacent laminate layers. During the test, fixing jaws (F_{Fix}) support the sample to prevent tilting and thin specimens may be equipped with caps to achieve homogeneous force introduction and to avoid peeling of the specimens near the load. Weidenmann et al showed that the EST provides a reliable shear failure of the specimens [7]. The distribution of the load stresses in the sample can be predicted with a numerical analysis of the Compression Shear Test (CST) which has the identical force introduction principle. Comparing ESH and CST, the main difference is the sample geometry which is slightly curved for the CST test. The shear stress showed homogeneous distribution along the sample and small stress concentrations near the force application areas were identified [8].

The characterization of the damage behavior under dynamic impact load was carried out in accordance to the standard DIN EN ISO 6038 [11], which is also known as Compression After Impact (CAI) test. Firstly a sample is pre-damaged by an impactor in a drop tower (see also figure 1c). Subsequently, the residual compressive strength of the damaged sample is measured with a compression test rig. Having an instrumented drop tower, the absorbed energy in the specimen during the impact can be evaluated. This study is confined to the analysis of the energy absorption / time relation during the impact tests of specimens with different matrix systems at various energy levels. Delfosse and Poursartip evaluated an energy-based approach for investigating impact damage behavior. A full penetration of the sample by the impactor lead to approximately 30 % energy absorption by matrix damage and 70 % by fiber damage [12].

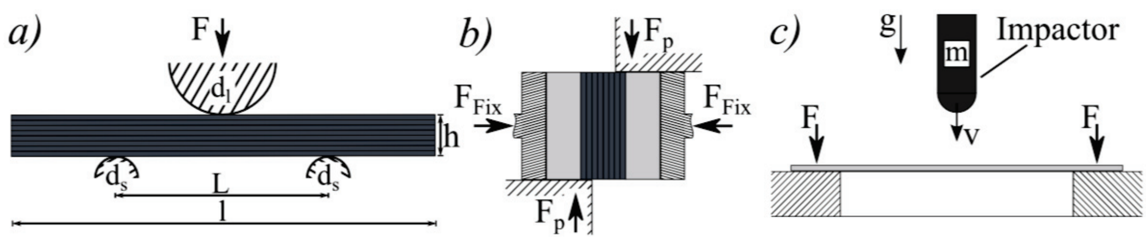

FIGURE 1. Test methods used in the study: a) Short Beam Shear Test; b) Edge Shear Test; c) Impact Test in drop tower

EXPERIMENTAL

The carbon fiber (CF) reinforcement used consists of 8 layers biaxial non-woven fabric from Zoltek (type MD300) with a symmetrical layup of $[0/90]_{4s}$. Each layer of the fabric is made of 150 g/m² carbon fibers in 0° direction and 150 g/m² in 90° direction. The biaxial layers are stitched with a polyester yarn having 4 g/m². The fabric is based on the 50 K heavy tow carbon fiber roving type Panex 35. Four different matrix systems were used for the investigations - one epoxy resin (EP1) and three polyurethane systems (PU1, PU2 and PU3). The resins were processed following the technical specifications of the respective supplier.

Manufacturing of the test samples with the HP-RTM process

The resin specific process parameters are given in table 1. The laminates were manufactured with the HP-RTM process using constant process parameters to ensure the direct comparability of the samples. A highly precise hydraulic press from Dieffenbacher type Compress Plus DCP G 3600/3200 AS with parallel holding system and a maximum press force of 36,000 kN was used. The oil tempered RTM plate mold has a central film gate, two vacuum blocks and a cavity size of 900 x 550 mm^2. Two HP-RTM machines from KraussMaffei were used for the infiltration, a KraussMaffei 8/3,2K for processing of the EP system and a KraussMaffei RimStar 8-4 for the processing of the PU systems. The machines are equipped with separate circulation units for the single components of the resins which are then mixed under high pressure of 120 bar in the mixing head during the injection step. The injection was carried out with constant process parameters for all matrix systems used. After placing the fabric layup in the cavity, the mold was closed by the press and vacuum was applied for 60 s. The press force for the injection was set to 500 kN and a resin amount of 710 g was injected with a constant flow rate of 40 g/s. After the mixing head had closed, the press force was increased with a press force increase rate of 750 kN/s to 5000 kN achieving the desired laminate thickness and to cure the resin. After demolding and post-curing of the plates the test samples were obtained by water-jet cutting. The epoxy resin system was processed with an additional component, an internal mold release agent (IMR) with a content of 2 % w/w. The manufactured CFRP laminates have a fiber volume content of 52.4 ± 3.7 Vol.-% and a thickness of 2.3 mm.

TABLE 1: Matrix specific process parameters

	EP1	**PU1**	**PU2**	**PU3**
Resin/Polyol temperature in equipment	80 °C	80 °C	70 °C	45 °C
Hardener/Isocyanate temperature in equipment	30 °C	35 °C	50 °C	45 °C
Mold temperature	120 °C	110 °C	90 °C	90 °C
Mixing ratio Resin:Hardener:IMR and Polyol:Isocyanate [% w/w]	100:24:2	100:132	100:121	100:178

Testing parameters

The rectangular specimens for the SBS test had a length (l) to thickness (h) ratio of l/h = 10 and a thickness (h) to width (w) ratio of w/h = 5. The diameter of the loading roller (d_l) was 5 mm and the support rollers had a diameter (d_s) of 2 mm. For each matrix system at least five tests at a test speed of 1 mm/min were conducted using a 50 kN testing machine type Inspect table 5 kN from Hegewald & Peschke and the shear strength was calculated at the maximum force following the test standard: $\tau_{SBS} = ¾ \cdot F_{max} \cdot (w \cdot h)^{-1}$. The ESH specimens (length = 8 mm; width = 9 mm) were prepared with force introduction caps made of a 2 mm thick aluminum plate on each side to prevent the sample of pressure failure near the force introduction. At least eight samples of each matrix system showing pure shearing failure were considered for the evaluation of the ESH properties. The failure of the samples was well observed during the ESH tests in form of a significant drop of the force and the test was stopped subsequently. The interlaminar shear strength was then calculated using the maximum force during the test (F_{max}), relative to the shear area (l x w) of the sample: $\tau_{ESH} = F_{max} \cdot (l \cdot w)^{-1}$.

The energy absorption of the specimens during the instrumented impact was analyzed at nine impact energy (E_I) levels: 10, 15, 20, 24, 27, 32, 37, 42, 45 Joule. The impactor was a cylinder with a spherical head diameter of 19 mm and a mass of 4.84 kg. The sample size was 150 x 100 mm² (length x width). The tests were carried out on an Instron Dynatup® 9250HV drop tower at KIT. The force-time data and impact speed were recorded and the energy-time relation for each test was calculated by the integrated Instron Dynatup® Impulse Data Acquisition Software. Figure 2 shows a representative curve of the absorbed energy by time for an impact test. At maximum energy (E_{max}) the complete kinetic energy of the impactor is transferred to the sample having the maximum deflection at this point. The elastically stored energy (E_{el}) in the specimen is then returned to the impactor in form of kinetic energy. The remaining difference is the energy absorbed by damage mechanisms: $E_D = E_{max} - E_{el}$.

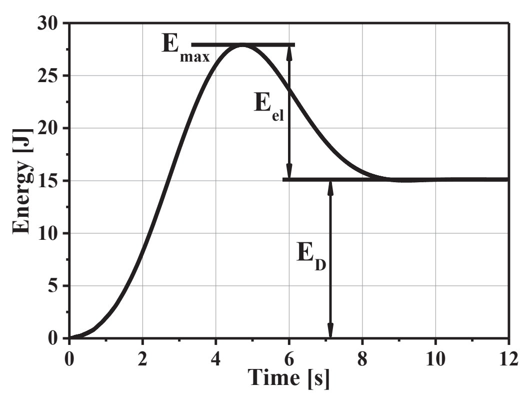

FIGURE 2. Schematic energy-time-plot for an impact test with maximum energy E_{max}, elastic energy E_{el} and damage energy E_D

RESULTS AND DISCUSSION

The interlaminar shear strength results (SBS and ESH) are given in figure 3a. The results of the SBS test show an average shear strength of > 60 MPa for each of the investigated materials whereas the PU1 has the highest average value of 69 MPa. The EP resin shows the highest standard deviation compared to the PU systems. In contrast the ESH test results are consistently lower compared to the SBS test results with an average deviation of 27 % (PU3) to 42 % (PU2). The measured average ESH shear strength values are in a range of 37 to 48 MPa. Comparing ESH and

SBS test for the EP resin system the standard deviation is consistently higher compared the PU systems. The shear strength measured for PU2 in ESH test shows a decrease in its average value compared to the SBS test result and the standard deviation is significantly higher for the EHS.

Figure 3b shows the results of the impact tests at different impact energy levels. The ratio of energy absorbed by deformation (E_D) to the impact energy (E_I) is drawn as solid line and increases at lower impact energy levels. For the EP resin the maximum is reached at 27 J impact energy and for the PU resins the maximum appears in a range of 27 to 32 J. At impact energy levels > 27 J the EP resin samples drop significantly compared to the PU systems. The E_D energy has exceeded a critical value in failure behavior of the laminates (see also figure 4). The second relationship shown in figure 3b (dashed lines) is the ratio of the elastic energy (E_{el}) to the impact energy (E_I) which represents the elastic energy stored in deflection of the samples during the impact considering that the impactor will be rebounded. As the impact energy increases the elastic share reaches 0 % at 27 J for the EP samples which indicates that a critical value of a total material failure (see figure 4) is reached. The PU samples show a low amount of 5 to 12 % elastic energy absorption at 27 J which reaches the critical value of 0 % at 32 J impact energy.

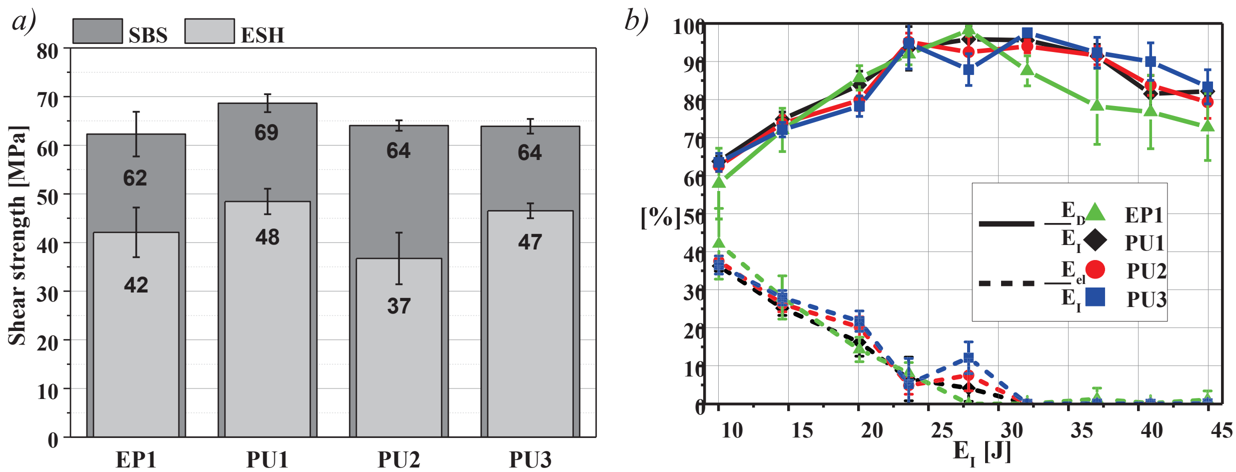

FIGURE 3. a) Comparison of interlaminar shear strength results of SBS and ESH test method; b) Result of the impact tests, ratio of the maximum energy E_{max} to the impact energy E_I at different impact energy levels

Comparing SBS to ESH test a significant drop of the shear strength can be observed in a range of 27 % (PU3) to 42 % (PU2). It has to be noted that a direct comparison of the results is only possible if a clear shear failure of the samples can be observed [6]. In this study, all SBS samples showed consistently complex failure modes. As already mentioned in the introduction, several publications have investigated this test method demonstrating, that a pure shear failure may not be realized with the SBS test. The indirect force introduction by the rollers causes significant high compression and shear stresses which lead to interferences of failure modes in the load introduction area [9, 10]. Thus, the results of the SBS test indicate that a realistic value of the interlaminar shear strength can hardly be obtained by using this method. In contrast the results of the ESH tests show a consistent interlaminar shear failure between two layers of the sample. The force-displacement-curves are characterized by a significant drop of the force during the test which is accompanied by an abrupt failure. The stress distribution and the influence of possible stress concentrations in the force introduction area are not precisely known and the determined values may not represent the real interlaminar shear strength. However, the reproducible sample failure in ESH test allows a more reliable comparative statement of interlaminar shear behavior with respect to the SBS test. Both test methods indicate that the PU1 specimens tend to have the highest interlaminar shear strength, although this statement has no absolute validity considering the standard variations. The drop of the PU2 shear strength in ESH test can be explained by the existence of many small micropores, which were identified in SEM. These voids are imperfections and act as starting points for sample failure which causes a decrease of the pure shear strength obtained by ESH test. Generally the PU based samples have a lower standard deviation than the EP and tend to have slightly higher average shear

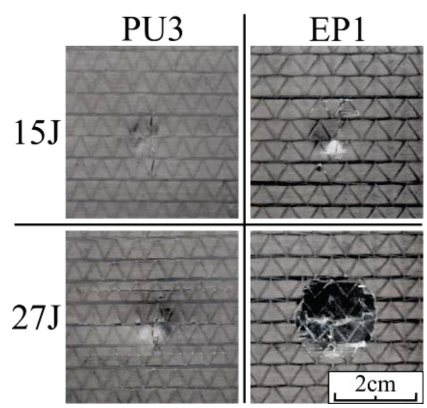

FIGURE 4. Comparison of the EP1 and PU3 samples at 15 and 27 J impact energy

strength values with exception of PU2 in ESH test. The elongations at break of the PU materials (> 9 %) are higher compared to the EP system (< 6.6 %). This indicates that the higher PU ductility might lead to a better compensation of peak stresses on microscopic level.

The dynamic impact test curves at energies < 27 J indicate a quasi-linear and comparable behavior of the tested materials. Until this point, the impactor is prevented to punch trough the specimens of all materials and a significant content of elastic energy is present. The critical impact energy for the EP is reached at 27 J. At this energy the impactor punches through the samples and the elastic energy decreases to 0 % which indicates that the impactor is not rebounded anymore. This critical impact energy is higher for the PU materials (32 J). At energies > 32 J no elastic energy could be measured for all materials, the energy absorption caused by damage decreases and the impactor punches through the samples. It was clearly seen, that the PU based samples were able to absorb higher level of impact energy compared to the EP samples. Nevertheless, the real extend of damage could not be determined quantitatively. Possible delaminations, fiber and matrix cracks within the laminate layers are not visible on the specimen's surface. For a comprehensive assessment of the damage, additional testing methods like computer tomography have to be considered.

CONCLUSIONS

In this study laminates with different resin systems were manufactured using the HP-RTM process to investigate the matrix influence on the interlaminar shear strength and the materials behavior under dynamic load. Two test methods, SBS and ESH were used and compared to each other to obtain the shear strength. The results show that the SBS causes complex failure modes in contrast to the ESH test having a high reproducible interlaminar shear failure of all tested samples. The ESH values were consistently lower compared to the SBS and the negative influence of micropores could be observed with the ESH test method. The results indicate that the ESH test is more reliable than the SBS test to obtain comparable shear properties. More tests and simulations of the stresses in the sample are needed to evaluate and establish the ESH test method for composite characterization. The impacts tests indicate a higher energy absorption of PU materials compared to EP if the impact energy exceeds a critical value. Below that critical value the impact data is characterized by a comparable behavior but the visual analysis of the damage patterns shows that PU has a higher damage tolerance than EP based material. Further evaluations are necessary to gain a better understanding of the dynamic behavior regarding the investigated materials.

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