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STATIC AND THERMAL DYNAMIC MECHANICAL ANALYSIS OF AlOOH NANOPARTICLE REINFORCED FIBER COMPOSITES

Dilmurat Abliz[1,2(*)], Gerhard Ziegmann[1,2]

[1]Institute of Polymer Materials and Plastics Engineering, TU Clausthal, Clausthal-Zellerfeld, Germany
[2]Clausthal Center for Materials Technology, TU Clausthal, Clausthal-Zellerfeld, Germany
[(*)]*Email:* dilmurat.abliz@tu-clausthal.de

ABSTRACT

AlOOH - also called as boehmite - nanoparticle is a new and cost-effective alternative to modify and enhance the overall mechanical performance of fiber composites - especially those that are dominated by the matrix. This work investigates the static and thermal dynamic mechanical properties of AlOOH nanoparticle reinforced fiber composites, depending on the different nanoparticle concentrations and surface modifications. The results show that the AlOOH nanoparticle could remarkably increase the static and dynamic mechanical properties of the fiber composites at lower temperature, however, the high-temperature stability and dynamic mechanical properties are negatively influenced which is directly related to the binding intensity and characteristic of the nanoparticle with the epoxy depending on different modifications. The results provide a basis for the design and application of the nanoparticle reinforced fibre composites.

Keywords: fiber composites, nanoparticle, mechanical property, thermal dynamic property.

INTRODUCTION

The final properties of the FRPs are determined by both matrix and fibers, as well as the interphase. Between them, however, the potential of the fibers is remarkably compromised due to the comparably much lower properties of the matrix. According to related studies and reports, the weight-to-stiffness weight-to-strength of the carbon fiber will be compromised in the composite laminate by about 60% and 30% separately [1]. Therefore, the potential mechanical properties of fiber could be brought better into the play by enhancing the stiffness, strength and also the fracture toughness of the resin matrix. Especially, high-performance and temperature-stable resin systems tend to be brittle, and also show high reaction shrinkage after curing. This issue, especially, is critical for low-viscous resin systems which are suitable for cost-effective liquid composite molding (LCM) processes. A promising and potential way for the improvement of these issues is the introduction of nano-scale functional fillers -simply called nanoparticles, to fabricate a multi-scale hierarchical composite material - synergic integrated from nano to micro scale components - with tailored property profiles. The nano-scale functional fillers possess certain qualities that can change or adjust the overall properties of the composite part. By introducing effective nanoparticles into the composites, the critical properties of the fiber composites could be improved to exploit the fiber properties and enable more design freedom and light-weight potential.

In LCM processes by injecting the matrix filled with nanoparticle into the fiber preform, fibrous or sheet-structural carbon nanoparticles - CNT, GNP and etc. could face severe filtration which leads to poor impregnation of the preform [2, 3], due to the large size in length or width of these particles which are critical to the filter grain/particle diameter ratio. In the application in LCM processes, cake filtration is manifested by the partly volume capture due to the larger CNT or GNP length than the intra-fiber gaps of the textiles. As long as the particles are captured by the intra-fiber gaps, the permeability of the porous medium will greatly decrease, and at the same time the viscosity of the dispersion begins to rise due to the increased concentration of the particles. Therefore, the combined filtering and viscous resistance effect remarkably decrease the impregnation speed and quality. Gojny et al [4] tried a standard RTM technique to produce CNT/glass/epoxy multi-scale composite, and reported that it is a great challenge to manufacture a composite by resin with nanotube contents of more than 0.5 wt%, due to the enormous surface area of CNT/GNPs and the resulting increase in dispersion viscosity.

In comparison, quasi-spherical nanoparticles are much easier to be dispersed in matrix, and also could be much easier to be processed by impregnation techniques - due to the much lower D/d ratio. Among the different quasi-spherical ceramic nanoparticles, silica (SiO_2) nanoparticle is until now mostly investigated for application in FRPs [11, 12]. There are also some works that studied alumina (Al_2O_3) nanoparticle as functional fillers in epoxy[13, 14]. As a quasi-spherical ceramic nanoparticle, boehmite is an aluminum hydroxide (γ-AlOOH), which is often used as a precursor for many aluminum products. Boehmite particle is price-efficient and the hydroxyl groups on the surface could be directly used as functional groups, or easily be modified to different functional groups (amine, acetic acid, milk acid etc) to generate a good chemical stability and improved particle-matrix adhesion by possible covalent connection. In comparison, there are hardly any works found that investigate and describe the critical processing aspects and the influence on the FRP properties by application of boehmite nanoparticles. Therefore, in this paper, the matrix-dominated properties - interlaminar fracture toughness (G1C), three-point-bending (transverse to fiber direction) and thermal dynamic properties of the AlOOH nanoparticle reinforced fiber composites are investigated.

MATERIALS AND METHODOLOGY

1) Fiber reinforcement: a quasi-unidirectional carbon-fiber (CF) textile (Style 796) from Fa. ECC is used. The textile has an average areal weight of 270 g/m^2 (warp/0° direction: 400 tex carbon fiber, weft/90° direction: 34 tex glass fiber for stabilization). The unidirectional fiber textile is selected as the fibers are mostly aligned in just one direction which is optimal to differentiate the influence of the fiber direction on the critical process parameters and final properties.

2) Epoxy matrix: The commercial epoxy resin system LY 556 (DGEBA-type epoxy) with corresponding hardener HY917 (methyltetrahydrophthalic anhydride) and accelerator DY070 (1-methyl imidazole) from Huntsman Advanced Materials (Switzerland) GmbH is used. The resin, curing agent and accelerator are mixed at the recommended mass ratio of 100:90:1. In order to assure a homogeneous mixture of the reactants, they are mixed using a Thinky Mixer ARV-310 planetary mixing machine at 1500 rpm under vacuum of 0.3 bar absolute pressure for 1.5 minutes, then at 2000 rpm under vacuum of 0.1 bar absolute pressure for another 1.5 minutes at room temperature.

3) Boehmite nanoparticle: In this paper boehmite nanoparticles functionalized with acetic acid (CH_3COOH), as shown in the following Figure 1, are investigated. The special functionalized boehmit nanoparticle are called as KE later for the simplification. The boehmite nanoparticles that are used in the study are provided by SASOL (DISPERAL®. HP 14).

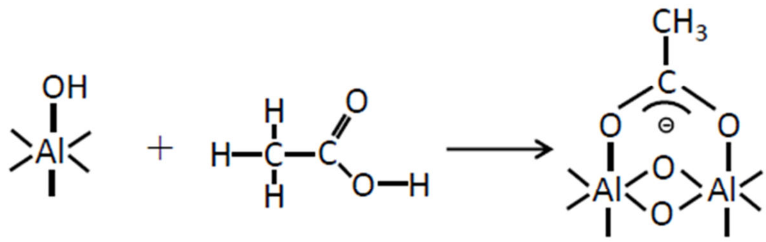

Fig. 1 - Schematic illustration of boehmite nanoparticle functionalized with Acetic acid (CH_3COOH)

4) Boehmite-epoxy suspension: as the basic nanoparticle-epoxy system, boehmite-epoxy masterbatches with boehmite nanoparticles (primary particle size of 20nm) are dispersed into the epoxy matrix by 40 wt%, at the Institute for Particle Technology (IPAT)-TU Braunschweig. The x10%, x50% and x90% values of dispersed particle size within the produced masterbatch are separately 81 nm, 104 nm and 134 nm. For the experiments, the masterbatch is diluted with the epoxy matrix to the desired particle concentration with a planetary mixing machine (Thinky Mixer ARV-310) twice with the same parameters as describe before for the preparation of neat resin matrix.

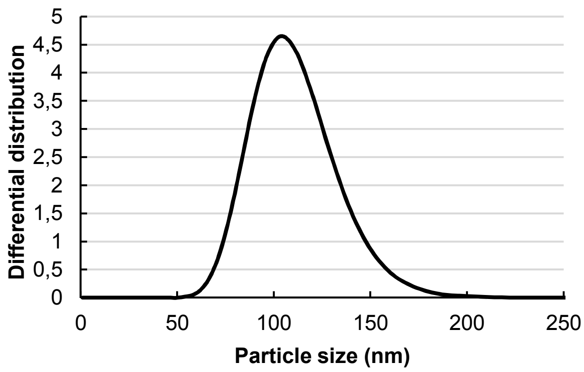

Fig. 2 - Particle size distribution of boehmite nanosuspension

5) FRP laminate manufacturing

Considering the increased viscosity of the particle-filled matrix and possible retention behavior of the nanoparticles, an out-of-plane impregnation method is applied, as shown in Figure 3. A high permeable flow medium is adjusted under the textile, by which the fluid will quickly flow through the flow media and impregnate the laminate in the thickness direction due to the high permeability difference between the compacted textiles and the flow media. By the applied out-of-plane impregnation strategies, a quick impregnation with homogenous particle distribution in the laminate could be achieved.

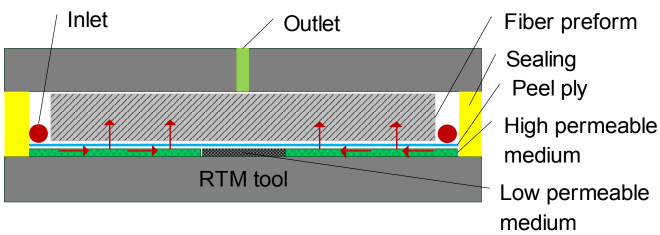

Fig. 3 - Illustration of out-of-plane impregnation process

6) Interlaminar fracture toughness

Interlaminar fracture is a critical failure mode for laminated composite structures which occurs due to high out of plane loads where no fibers are present to resist loading. Delamination can occur due to tensile (mode I, G1c), shear load condition (mode II, G2c), or a combination of the both (mode III, G3c). In this research, the interlaminar fracture toughness of functional FRPs is investigated under mode I deformation. The tests are conducted by a Double Cantilever Beam (DCB) specimen according to the Airbus Industry Test Methods (AITM) “AITM 1-0005 / EN 6033 Fibre reinforced plastics - Determination of interlaminar fracture toughness energy - Mode I - GIc [15]”. The initial crack formed in the middle plane of the laminate is made by inserting a Teflon film with a thickness of 25 μm into the stacking process of the laminate. The universal material testing machine is also applied for the test.

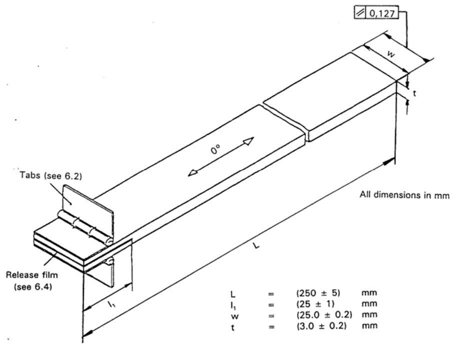

Fig. 4 - Schematic illustration of DCB specimens for G1c test

The fracture surface after fracture tests is analyzed by high-resolution SEM to investigate the fracture mechanism of crack propagation in the functional FRPs. Samples are cut from the fracture surface in size of 10 mm × 5 mm. After cleaning with pressure air the samples are mounted on aluminum stubs. The fracture surfaces of the samples are then sputter coated with a thin layer of gold to avoid electrical charging. The micro-graphs are taken at various magnifications using a Field Emission Scanning Electron Microscope (FESEM) CamScan CS4. The effect of nanoparticle content and gradient on fracture properties under mode I deformation mode are studied.

7) Three-Point-Bending

The bending properties of the multi-scale FRPs are measured by three-point-bending. The test samples are prepared transverse to fiber direction, in order to differentiate the effect of nanoparticle on the matrix. The test is conducted according to the standard DIN EN ISO 14125 [16]: “Fibre-reinforced plastic composites: Determination of flexural properties”. The tests are carried out with a velocity of 1 mm/min.

8) Dynamical mechanical properties (DMA)

DMA tests are selected as they could provide a further information about how the material behaves under dynamic load - even combination with thermal (temperature) load. It could be seen as an important property criterion for application in a structure level in complex combination. DMA measurements are performed on DMA Q800 device from TA Instrument. Experiments are run with samples which have a size of about 35 mm × 10 mm × 3 mm (single cantilever). The aim of the measurements is to study the effect of the nanoparticles on the dynamic mechanical properties of functional FRPs. The samples are subjected to a temperature scan from 30 °C to 180 °C with a ramp of 2 °C /min. A fixed strain of 10 μm and frequency of 1 Hz are used in the measurement.

RESULTS AND CONCLUSIONS

The results of the three-point bending and G1c properties are provided below separately in Figures 5 and 6, and it could be seen from the interlaminar fracture toughness and flexural properties that the influence of the boehmite nanoparticles are quite remarkable: there are about 32.61 % in the G1C fracture toughness properties. Moreover, the flexural modulus and strength increased about 38.14 % and 47.66%.

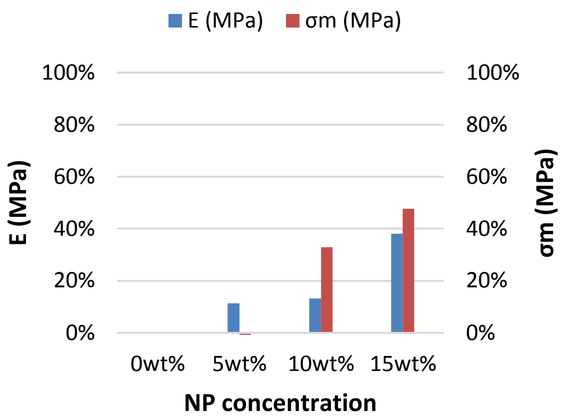

Fig. 5 - Flexural properties versus boehmite nanoparticle concentration

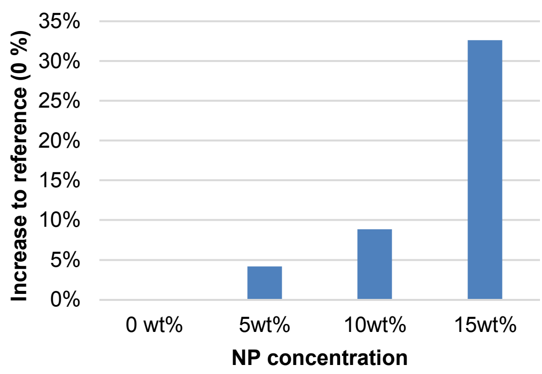

Fig. 6 - Interlaminar fracture toughness G1C versus boehmite nanoparticle concentration

The acting mechanism of the nanoparticles can be revealed combining the microstructure of the fracture surfaces. The following Figure 7 shows the morphology of fracture surface from G1C test. It could be observed that matrix fracture surface between the two samples are totally different. The matrix by the unmodified CFRP system is rather smooth without much observable micro deformations or fractures. Nevertheless, the fracture surface of the boehmite nanoparticle modified CFRP structure showed an extreme rough microstructure with quite large area of debonding between the nanoparticle-matrix interface and plastic cavity growth. Therefore, it is reasonable to believe that main fracture mechanism by the boehmite nanoparticle modified CFRP structure is the debonding between the nanoparticle-epoxy interface and the crack pinning/bridging by the nanoparticles.

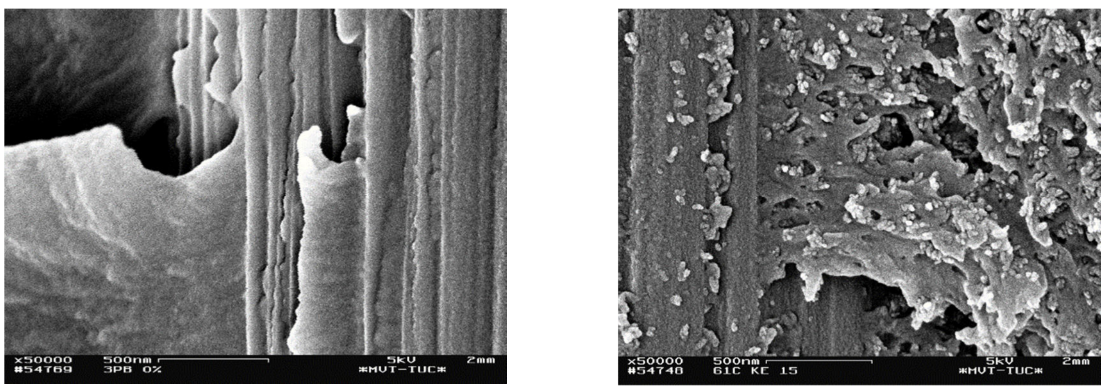

Fig. 7 - CFRP G1c fracture surface by FESEM. Left: unmodified sample; Right: modified with 15wt% boehmite

Besides the static properties at room temperature, the dynamic mechanical properties under combined mechanical and thermal loading could provide further information about the nanoparticle-modified FRP structures under complex load conditions. At the same time, it is also possible by the DMA analysis to obtain some further information about the fiber-matrix, nanoparticle-matrix interfacial properties and temperature stability.

According to the dynamic mechanical properties (transverse to fiber direction), as shown in the following Figure 8, it is obvious that the storage modulus of the FRP structures at lower temperature are increased depending on the increase of boehmite concentration, similar to that of statistic mechanical properties. However, the high temperature stability of the FRP structures is decreased with increasing nanoparticle concentration: the higher the concentration of the boehmite nanoparticle, the earlier begin to drop the storage modulus (Figure 8left), similarly, the peak of the tangent delta also showed an decreasing trend (Figure 8 right) - indicating a decrease in the T_g of the structure. The similar decreasing trend in T_g was also shown in the curing kinetics investigation of the boehmite-epoxy suspensions. It is clear that the boehmite nanoparticle that are used for the investigation showed an adverse effect on the high-temperature stability of the FRP structures.

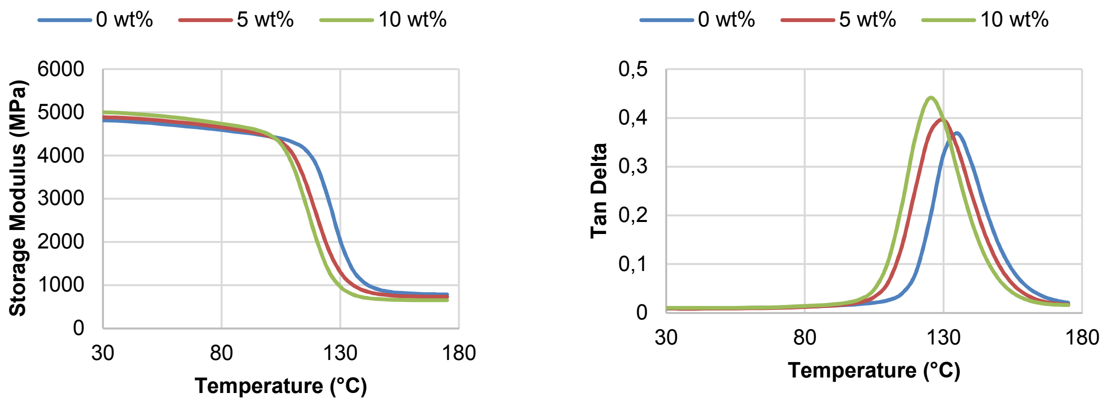

Fig. 8 - Dynamic mechanical properties of the boehmite-nanoparticle modified FRPs; left: storage modulus vs. temperature, right: Tangent delta vs. temperature

It was already previously shown by the investigation of curing kinetics that the boehmite nanoparticles could react with the epoxy to build covalent chemical connections. However, it needs to be noticed that the high-temperature stability is decided by the intensity and density of the chemical connections after full cure. It seems that, even if the boehmite-nanoparticle could build covalent chemical connections with the epoxy, but the intensity and the density of the polymerization is weaker than that from the epoxy and anhydrite curing agent, which leads to a decreased stability at high temperatures. Nevertheless, combining the results on the statistic mechanical properties and observations on the fracture surface, the weak chemical bonding between the nanoparticle and the epoxy, in a certain degree, seems to provide positive influence on the fracture toughness and other similar mechanical properties of the FRP structures. As the introduced weak interphase provide potential path where the crack propagation could be deviated very effectively, to transform the possible brittle failure to more ductile failure - higher fracture toughness. Therefore, it is reasonable to believe that the main mechanism by the boehmite nanoparticle modified CFRP structure is the energy distribution and consumption due to the weaker nanoparticle-epoxy interfacial strength where the cracks could be deviated and bridged due to the nanoparticle-epoxy debonding. Therefore, the matrix showed an increased ductile behavior which could absorb and consume extra fracture energies. Therefore, the stress concentration on the fiber-matrix interface is remarkably reduced, showing much lower fiber-matrix debonding failure. The increase in the interlaminar fracture toughness could be well explained by these effects, as the increased interface and interphases with the nanoparticles could provide potential path for crack propagation by pinning, bridging effects, showing a ductile fracture behavior with increased fracture toughness compared to the brittle failure in the neat matrix samples.

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