Polymer Testing 32 (2013) 1495–1501

Contents lists available at ScienceDirect

Polymer Testing

journal homepage: www.elsevier.com/locate/polytest

Material properties

Effect of electrospun polyamide 6 nanofibres on the mechanical properties of a glass fibre/epoxy composite

Bert De Schoenmaker [a], Sam Van der Heijden [a], Ives De Baere [b], Wim Van Paepegem [b], Karen De Clerck [a,*]

[a] Ghent University, Department of Textiles, Technologiepark 907, 9052 Zwijnaarde, Belgium
[b] Ghent University, Materials Science and Engineering, Technologiepark 903, 9052 Zwijnaarde, Belgium

ARTICLE INFO

Article history:
Received 7 August 2013
Accepted 23 September 2013

Keywords:
Structural composites
Polyamide 6 nanofibres
Matrix cracking
Stress-strain curves
Optical microscopy

ABSTRACT

Recently, several types of nanoparticles are frequently incorporated in reinforced epoxy resin composites. A homogeneous dispersion of these nanoparticles is still a problem. Thermoplastic nanofibrous structures can tackle this dispersion issue. Therefore, this paper investigated the effect of electrospun polyamide 6 nanofibrous structures on the mechanical properties of a glass fibre/epoxy composite. The nanofibres were incorporated in the glass fibre/epoxy composite as stand-alone interlayered structures and directly spun on the glass fibre reinforcement. Both ways of nanofibre incorporation have no negative effect on the impregnation of the epoxy. Moreover, the nanofibres remain well dispersed within the matrix. Incorporation of nanofibres increases the stress at failure in the 0°-direction, the best results are obtained when the nanofibres are directly electrospun onto the glass fibres. Optical microscopic images also demonstrate that nanofibres prevent delamination when a 90° crack reaches a neighbouring 0° ply. Furthermore, mode I tests showed a small improvement when a thin nanofibrous structure is deposited directly onto the glass fibres. When the composites are loaded under 45°, it is proven that, for an identical stress, the glass fibre composite with deposited nanofibres has less cracks than when interlayered nanofibrous structures are incorporated. Generally, it can be concluded that the addition of polyamide 6 nanofibres improves some mechanical characteristics of a glass fibre/epoxy composite.

1. Introduction

Owing to their light weight and high stiffness and strength, fibre reinforced epoxy resin composites are widely used in industry [1,2]. However, an epoxy matrix is a brittle material, which could lead to unexpected failure of the composite. Thus, an improvement of the resin rich region between two plies with a different fibre orientation is recommended. Therefore, secondary (sub)micron reinforcements are often incorporated in the matrix.

Nanoparticles such as carbon nanotubes (CNT) and nanoclays can be added to the epoxy matrix to improve the mechanical properties of the matrix [3–6]. Due to their theoretical high stiffness and strength, CNT might improve the matrix characteristics [7–9]. However the overall improvement in mechanical properties such as stiffness and fracture toughness of the epoxy matrix is mostly very moderate [3,10,11]. The main disadvantage with these CNT's and nanoclays, besides the safety issues due to the small dimensions [12], is the difficulty in obtaining a homogeneous dispersion of the nanoparticles in the resin [7,13]. Moreover, the viscosity of the resin increases significantly when nanoparticles are added. The toughness of a matrix can also be improved by incorporation of rubber

* Corresponding author. Tel.: +32 9 264 57 40.
E-mail addresses: bert.deschoenmaker@ugent.be, Karen.DeClerck@ugent.be (K. De Clerck).

0142-9418/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.polymertesting.2013.09.015

particles or embedding thermoplastic inclusions [13,14]. But again, a homogeneous dispersion of the particles in the matrix is hard to obtain.

Thermoplastic nanofibrous structures offer a solution for the dispersion issue, since they can be readily embedded in the resin and incorporate a nanosized phase in the composite. These nanofibres also do not increase the viscosity of the resin. Moreover, due to their macro scale length, no health hazards are involved in the production and use of these nanofibres. Recent literature indicates that nanofibres may contribute substantially to the ductility and fracture toughness of the composites [15–18]. This is related to the hypothesis that a secondary fibrous structure with a pronounced lower fibre diameter in addition to a primary fibre structure may increase several mechanical properties of composite materials [19].

This paper describes the effect of electrospun polyamide 6 (PA 6) nanofibrous structures on the mechanical properties of a glass fibre/epoxy composite. Therefore, the mechanical properties of a pure glass fibre composite are compared to glass fibre composites with added nanofibres. These nanofibrous structures are, on one hand, incorporated between the glass fabrics as stand-alone structures and, on the other hand, directly deposited onto the glass fabrics. In addition to the tensile tests, dynamic mechanical analysis and mode I tests using a double cantilever beam are used to examine the properties of the investigated composites. The crack propagation in the loaded sample is studied through optical microscopy.

2. Materials and methods

2.1. Materials

All composite plates were reinforced with unidirectional E-glass fabric (Roviglas R17/475). The reinforcement was 475 g/m^2 in the fibre direction, while in the perpendicular direction the reinforcement was 17 g/m^2. The matrix was EPIKOTE resin MGS RIMR 135 with EPIKURE curing agent MGS RIMH 137, both purchased from Hexion (Currently Momentive).

The composite plates were manufactured by vacuum assisted resin transfer moulding (VARTM) using a closed steel mould. The epoxy was first cured at room temperature for 24 hours and, thereafter, post cured for 15 hours at 80 °C, as described by the supplier. For all composite plates the stacking sequence was $[0°,90°]_{2S}$. The samples were cut to dimensions on a water-cooled diamond saw. All specimens had a thickness of 3.0 mm and a nominal width of 30 mm, as described in ISO 527-5:2009. End tabs were used to avoid failure at the clamps.

The nanofibres were incorporated in the glass fibre/epoxy composites in two different ways. On one hand, they were inserted in between the various glass fibre mats as a stand-alone structure. On the other hand, they were directly deposited onto one side of the glass fibre reinforcement. Reference composites without nanofibres were also manufactured, to be able to investigate the improvement of the nanofibre addition.

For the fabrication of the nanofibres, 16 wt% PA 6 was dissolved in a 1:1 solution of 98–100 v% formic acid and 98 v% acetic acid. Both the polymer and solvents were obtained from Sigma-Aldrich and used as received. To obtain large uniform nanofibrous structures, the nanofibres were produced using a multi-nozzle electrospinning set-up. This multi-nozzle method, an in house developed technology [20], diverged from a mono-nozzle set-up only by the number of nozzles, the general methodology itself is identical. Ten nozzles, each fed by a syringe, were placed in two alternating rows in a plate which had movement in the transverse direction. In the meantime, a grounded collector was moving in the longitudinal or production direction.

All nanofibrous nonwovens were spun in a conditioned room at 23 ± 2 °C and 50 ± 5% RH. The tip-to-collector distance was 7 cm and the flow rate was set at 1.5 mL/h. The voltage was adapted until a stable process was achieved, this was between 25 and 30 kV. The stand-alone structures were electrospun directly onto an aluminium foil, and afterwards released using water. For the deposited version, the nanofibres were directly electrospun onto the glass fibre mats. The fibre diameter of the interlayered nanofibrous structures was 150 ± 19 nm, while for the deposited nanofibrous structures it was 230 ± 26 nm.

2.2. Methods

Scanning electron microscopy (SEM), a FEI QUANTA 200F system, was used to investigate the cross sections of the composite plates. Prior to the SEM-measurements, the specimens were gold sputter coated (Balzers Union SCD 030). An optical microscope, a Olympus BX51 with an Olympus UC30 camera, was used to visualize cracks on the polished edges of the composites.

The tensile tests on the composites were performed on an electromechanical Instron 5800R machine with a load cell of 100 kN following the ISO 527-5:2009-standard. The tests were displacement controlled with a speed of 2 mm/min and both displacement and load were recorded. All specimens were instrumented with two strain gauges to measure the longitudinal and transversal strain, ε_{xx} and ε_{yy}, respectively. Not all samples were loaded until failure, since some were needed for other experiments.

On the same Instron 5800R, mode I tests were executed following the ISO 25217:2009-standard, the double cantilever beam (DCB) test. Two different thicknesses of the deposited nanofibres were used: 5 and 10 g/m^2. The dimensions of the mode I samples were 20 × 160 × 3 mm^3 and the initial delamination length was 50 mm.

The dynamic mechanic analysis (DMA) was executed on a Q800 from TA Instruments. Before the start of the DMA experiments, a complete calibration was carried out, the temperature calibration being performed using an indium standard. Owing to the high modulus of the samples, the experiments were carried out with a single cantilever clamp. The frequency was kept constant at 1 Hz and the displacement amplitude was set to 20 μm. The experiments started with bringing the DMA-temperature to 30 °C followed by an equilibration time of 15 min, after which the temperature was raised at 2.5 °C/min to 150 °C.