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Fatigue and Izod impact performance of carbon plain weave textile reinforced epoxy modified with cellulose microfibrils and rubber nanoparticles

Valter Carvelli [a,*], Andrea Betti [a], Toru Fujii [b]

[a] Department of Architecture, Built Environment and Construction Engineering, Politecnico di Milano, Piazza Leonardo Da Vinci 32, 20133 Milan, Italy
[b] Department of Mechanical Engineering and Systems, Doshisha University, Tatara Kyotanabe, Kyoto, Japan

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ABSTRACT

This work details an experimental investigation on understanding the effects of hybrid epoxy resins, filled with micro-fibrillated cellulose (MFC) and carboxylated nitrile-butadiene rubber nanoparticles (XNBR), on the tensile–tensile fatigue performance of carbon plain weave textile reinforced composites. Twelve combinations of MFC and XNBR weight contents in the epoxy resin (from 0% to 0.5% MFC and from 0% to 3% XNBR) were considered for preliminary quasi-static tests and five of them were selected to study the fatigue behaviour considering different loading levels. Moreover, the effect of the twelve fillers contents was observed on the Izod impact strength. The investigation finds that the best fatigue performance, for the considered weight contents of fillers, is of the composite enhanced with the maximum content of MFC. The SEM observations of the fracture surfaces indicate the extensive "plastic" deformation of the matrix and the improved fibre and matrix adhesion.

1. Introduction

Despite the extensive theoretical and experimental knowledge, detailed in the literature, the mechanical performance of fibre reinforced polymer composite materials needs to be improved in some aspects to be really competitive with metallic materials such as super aluminium alloys.

Structures made of advanced epoxy reinforced composites suffer the potential risk of propagation the internal defects under fatigue and impact loadings, due to the brittle nature of epoxy resins. Therefore, improvement of those mechanical performances is on a high demand by industries. In practical applications, most advanced composites adopt 2D laminate configurations. The main issue in damage tolerance of laminated composite structures is the delamination. Over the past decades, research efforts were dedicated to the development of toughened fibre–matrix composites, with basically two distinct approaches [1]. The first approach is based on 3D fibre reinforcement using advanced textile techniques [2], e.g. stitching, z-pinning, weaving, braiding, knitting, etc. It could not be an effective way to fabricate toughened composites, the reduction of the in-plane effective fibre volume fraction and local damage imparted in manufacturing (e.g. in stitching) could lead to decrease of in-plane stiffness and strength [3]. But efficient modern technologies of low-cost manufacturing of 3D single-layer preforms can improve the damage tolerance and the mechanical performance of composites ([4,5]). The second approach is to develop modified epoxy resins with improved toughness. Modified thermosetting matrix resins for fibre reinforced composites have evolved greatly over the past three decades in overcoming the brittle nature of thermosetting polymers by dispersion of a second phase that normally consists of nano- or micro- sized fillers (such as nanotubes, nano-fibres, nano-particles, rubber, etc) (see e.g. [6–10]). Fillers are expected to provide extrinsic toughening mechanisms [11] and, as consequence, to positively affect the mechanical response of fibre reinforced composite materials.

The identification of nano-sized cellulose microfibrils, named micro-fibrillated cellulose (MFC) [12], increased the family of hybrid nano-enhanced composite materials [13]. Cellulose is the most abundant natural homo-polymer and one of the most promising renewable and environmentally friendly resources [14]. MFC is obtained through a homogenization process, at high shear, producing microfibrils with a diameter range of 10–100 nm and a web-like structure. Plant derived cellulose were adopted as either composite reinforcement [14], or biodegradable natural polymer matrix [13], and even as all-cellulose composites [15]. The effect on tensile mechanical properties and fracture toughness of micro-fibrillated cellulose-based epoxy reinforced

* Corresponding author. Tel.: +39 0223994354.
E-mail address: valter.carvelli@polimi.it (V. Carvelli).

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carbon plain woven was investigated in [16]. Results in [16] reveal a major role of MFC to improve the interlaminar fracture toughness in mode I, which could be attribute to strong adhesion between filled epoxy and carbon fibre. The mentioned and other results available in literature show the important improvement of the damage tolerance of composite materials enhanced with the proper content of MFC for quasi-static loading.

Several studies involved the chemical modification of epoxy resin with reactive liquid rubber, particularly carboxyl-terminated butadiene acrylonitrile (CTBN), see e.g. [17]. The micro-structure consists of an elastomeric phase dispersed in the epoxy matrix with the elastomeric particle diameter of few micro-meters. Epoxy matrix modified with micro-fibrillated cellulose and carboxyl-terminated butadiene acrylonitrile as liquid rubber was adopted to improve the interfacial adhesion in plain woven carbon fibre composites in [18]. This hybrid epoxy resin significantly increased the interlaminar fracture toughness in mode I, as discussed in [19].

The present work gives a contribution on understanding the effects of hybrid epoxy resins, filled with micro-fibrillated cellulose (MFC) and carboxylated nitrile–butadiene rubber nanoparticles (XNBR), on the tensile-tensile cyclic loading and impact response of carbon fibre composites. Both loading conditions are not extensively investigated despite are of high interest in industrial applications. The adopted hybrid epoxy system intends to couple the effect of both fillers. Namely, the improvement of interfacial adhesion observed with MFC and the resin ductility attributed to the rubber nanoparticles. The experimental results, presented in this paper, show initially the effects of twelve different combinations of MFC and XNBR weight contents in the epoxy resin (from 0% to 0.5% MFC and from 0% to 3% XNBR) on quasi-static tensile and interlaminar shear strength, as previously detailed in [20] by the authors. Five of twelve contents have been selected and the effects on the fatigue behaviour are detailed considering different loading levels, damage monitoring by digital image correlation and scanning electron microscope observation of the failure mechanisms. Finally, the Izod impact response is presented for the complete set (twelve) of fillers combinations.

2. Materials and manufacturing

The composite material under investigation is an epoxy matrix reinforced with a carbon fabric. The matrix properties were enhanced with two fillers: (1) micro-fibrillated cellulose (MFC) (Celish KY100G, Daicel Chemical Industries, Ltd., Japan) whose transverse dimensions and longitudinal length are 5–20 nm and from 10 nm to several mm, respectively; (2) nanoparticles of carboxylated nitrile-butadiene rubber (XNBR) (JSR Corporation Ltd., Japan) whose diameter is in the range 80–200 nm.

The reinforcement is a balanced carbon fibres plain weave textile (Pyrofil TR-3110-MS, Mitsubishi Rayon Co. Ltd., Japan, areal density 200 g/m^2, warp and weft count 4.87 ends-picks/cm). Warp and weft yarns have 3 thousand fibres (Pyrofil TR30S3L Mitsubishi Rayon Co. Ltd., Japan). The tensile strength of carbon fibres is higher than 4 GPa and the Young's modulus is 240 GPa. The textile reinforcement is selected to have an important influence of the matrix on the mechanical behaviour of the composites with a higher fibres and matrix adhesion surface than for a unidirectional reinforcement.

Epoxy resin is used as matrix (E-828, Japan Epoxy Resins Co. Ltd., Japan). The curing agent is modified aliphatic polyamine (JER cure-113, Japan Epoxy Resins Co. Ltd., Japan).

The water slurry containing 10% MFC nano fibres is treated by solvent exchange with pure ethanol to remove water (100 g of ethanol for 10 g of water slurry). MFC containing ethanol is filtered by Büchner funnel to obtain a sheet of MFC. Then, the filtered sheet is stirred with additional ethanol and 300 g of epoxy resin. They are mixed together for 15 min in a high speed homogenizer at 15,000 rpm. In this phase, ethanol is used to decrease the epoxy viscosity and to have uniformly dispersed MFC. The ethanol is completely removed maintaining the mixture at 80 °C for 120 h. The appearance and distribution of MFC in the epoxy was observed by transmission electron microscopy (see Fig. 1a).

XNBR nanoparticles are mixed with methyl ethyl ketone (MEK) using 100 g of solvent for 1 g of rubber. The mixture is then placed on a magnetic stirrer at 80 °C for 24 h to dissolve the rubber into MEK, and then added to MFC containing epoxy resin previously prepared. Transmission electron microscopy observations of the XNBR in the epoxy show a fairly good distribution (see Fig. 1b).

The mixture of epoxy, XNBR and MFC is blended again in a homogenizer for 30 min to have good dispersion. It is finally kept in an oven at 80 °C for 120 h to remove the solvents. Next, the correct amount (32%) of curing agent is added to the hybrid resin. The

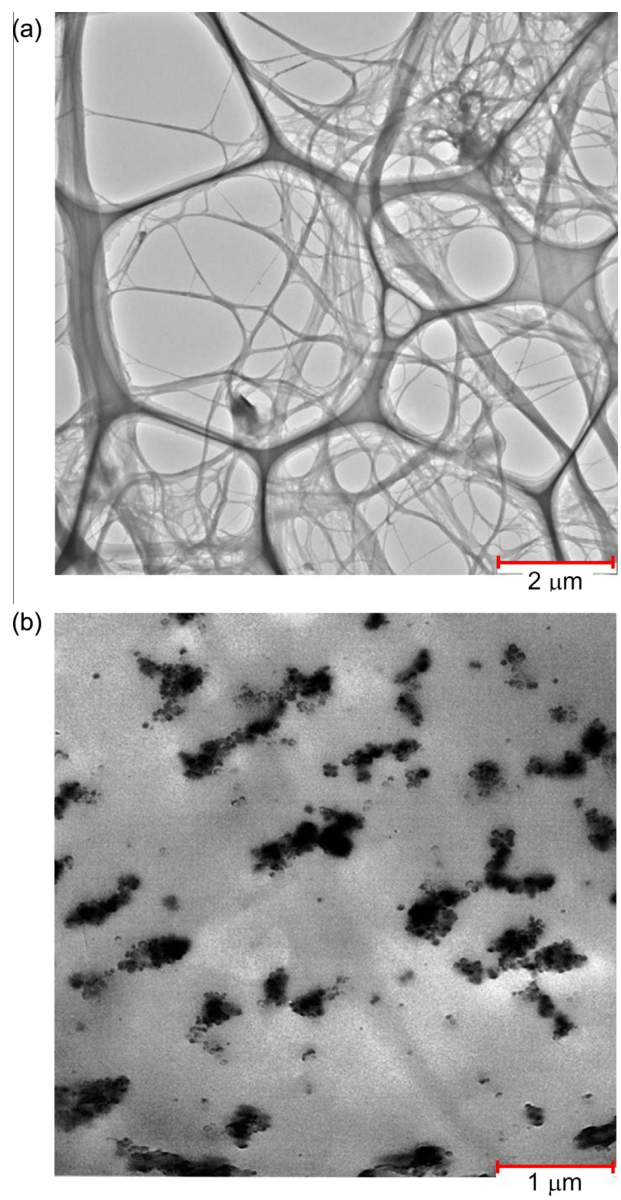

Fig. 1. Transmission electron microscopy (TEM) image of (a) MFC and (b) XNBR in the epoxy matrix. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)