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Semi-continuous flow recycling method for carbon fibre reinforced thermoset polymers by near- and supercritical solvolysis

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ABSTRACT

This paper presents an innovative fibre-matrix separation method applied to carbon fibre reinforced thermosets with two different media (water and a water/ethanol mixture) under sub- and supercritical conditions. The influence of different experimental conditions, nature of solvents and temperature on the properties of the recycled carbon fibres (rCFs),[1] is studied. This is performed with regard to the efficiency of the removal of the thermoset resin from the fibres as well as the surface and mechanical properties of the rCFs. It is shown that the recycling with both media provides rCFs with promising qualities for reuse in carbon fibre reinforced polymers (CFRPs)[2] of second generation. Besides, the water/ethanol mixture tends to achieve better results than pure water and creates rCFs with mechanical and surface properties comparable to that of virgin carbon fibres (vCFs).[3] Finally, the mechanism of polymer degradation is discussed regarding the nature of chemicals dissolved in the reactive media.

1. Introduction

As they are lightweight and demonstrate high strength properties, high fatigue and oxidation resistance, CFRPs are suitable for high-performance applications. Hence, there is an increasing demand of CFRP components which leads to the generation of high quantity of wastes, from their production to their end-of-life [1]. CFRPs are energy intensive materials and should be recycled with regard to resource efficiency. Due to economic reasons and environmental legislations, efficient and scalable recycling processes are developed to separate the polymer matrix and fibres [2,3] and re-integrate the CFs into second generation of CFRP materials for new applications. However, their recycling is challenging due to the three-dimensional linking of the thermoset matrix, the large variety of fibre-resin compositions and the mixture of different materials e.g. metal/CFRP hybrid components [4]. Thus, thermal, chemical and mechanical processes are widely discussed in the literature as recycling methods [1,5–7]. Mechanical processes appear to be the greenest as they do not involve any solvents and toxic gas emissions. However, the recycled carbon fibres are highly degraded [8] and present an unstructured architecture [9]. Pyrolysis and chemical recycling processes allow a high retention of the fibre mechanical properties but induce a modification of the fibre surface [10,11]. Here, we present a chemical process based on the sub- and supercritical solvolysis technology as it was claimed to be a sustainable and eco-friendly method for recycling CFRPs [12,13]. As the chemical recycling was performed at lower temperature than the pyrolysis process, the physico-chemical properties of the regained fibres are expected to be different. Moreover, it was revealed that supercritical solvolysis allowed an efficient recycling of CFRPs. Different research groups succeeded in the recovery of carbon fibres from an epoxy/resin composite under supercritical conditions by the use of different solvents (n-propanol, methanol) in a continuous-flow reactor [3,14,15]. The best tensile strength retention and highest fibre purity were obtained by performing subcritical water treatments at 260 °C under 6 MPa [16] and 340 °C under 155 MPa [17] or by using n-propanol at 350 °C and 15 MPa in a semi-continuous flow reactor [18]. Additionally, the degradation rate of a thermoset matrix was successfully improved by adding phenol and potassium hydroxide (KOH) to water [19]. Apparently,

List of abbreviations: CF, carbon fibre; CFRP, carbon fibre reinforced polymer; rCF, recycled carbon fibre; SCW, supercritical water; vCF, virgin carbon fibre.

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[1] rCFs means recycled carbon fibres.
[2] CFRPs means carbon fibre reinforced polymers.
[3] vCFs means virgin carbon fibres.

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the two major factors to optimize the efficiency and selectivity of the fibre-matrix separation process are the nature of solvent and temperature. This was further confirmed by a recent study on the near critical solvolysis of phenolic-based CFRPs. Indeed, highest degradation efficiency and mechanical retention were achieved by processing a mixture of water and ethylene glycol in subcritical conditions (400 °C, 4.2 MPa). The resin removal raised 97.6% in a batch reactor process for an optimized molar ratio of 1:5. Moreover, the addition of ethylene glycol, in comparison with pure water, allowed to remove a high quantity of resin without mechanical losses [20]. However, the authors faced repolymerisation and char formation issues during their recycling process which were responsible for the surface pollution of the recovered fibres. This study revealed that the resin removal efficiency decreased with several operating parameters such as time, temperature and quantity of water. In order to improve the purity and cleanliness of the rCFs, we focused on the study of a promising semi-continuous flow solvolysis method.

In this paper, we investigated different processing parameters on the efficiency of the fibre-matrix separation and, so, on the mechanical properties of the rCFs. Water and a water/ethanol mixture were used as solvents to vary the selectivity of the process and the surface properties of the fibres. The final goal is to understand the degradation mechanism of the resin in order to be able to tune the physico-chemical properties of the fibre surface *in situ* in the recycling process.

2. Materials and methods

2.1. Carbon fibre composite material

The investigated samples are CFRP plates manufactured via the vacuum assisted resin infusion (VARI) process. The resin used is the tetra-functional epoxy resin HexFlow® RTM6 which is a mono-component epoxy resin system [21]. The starting material consists of the tetra-functional epoxy resin tetraglycidyl methylene dianiline (Fig. 1a)) and the hardeners 4,4′-methylenebis(2-isopropyl-6-methylaniline) and 4,4′-methylenebis(2,6-diethylaniline) (Fig. 1b) and c)). The reinforcing fibres are arranged as plain weave fabric layers of Hexcel 48192 C 1270 ST carbon fibre [22]. These vCFs possess a thin polymer film at their surface, known as sizing agent. Hence, a thermal desizing was performed at 1100 °C for 1 h under a constant nitrogen flow to produce a reference desized vCF.

2.2. Semi-continuous flow reactor

For convenience, the recycling experiments were performed in a 200 mL capacity reactor under continuous flow of the reactive medium (water and a water/ethanol mixture 50/50 vol.%). The recycling set-up consists of different units: high pressure pump, heating and cooling down systems, filter and back pressure control valve as shown in Fig. 2.

First, the composite materials (20 mm × 50 mm × 2.2 mm) were loaded into the reactor. Then, the reactor was sealed, the experimental circuit was closed and the back pressure valve was opened. At ambient temperature, the pump flow-rate was set to 1 L/h and the pressure was adjusted by closing the back pressure valve. Once the pressure stabilizes at 25 MPa, the heating system of the pre-heater part and the reactor was turned on to achieve the set temperature inside the reactor (350 °C, 375 °C or 400 °C). The heating took up to 40 min and the treatment time (plateau) was 1 or 2 h under a constant pressure of 25 MPa. At the end, after the heating system was turned off, the cooling down took about 1 h. Finally, the system was depressurized and the samples were removed from the reactor. The rCFs were dried for 12 h at 120 °C before characterization.

2.3. Scanning electron microscopy

Scanning electron microscopy (SEM) was used for the surface analysis of the rCFs (JEOL, JSM-6360A). The SE mode and a 15 kV acceleration voltage were selected to acquire images. Fibres were metallized with a thin gold layer to improve conductivity. The double side conductive adhesive carbon tape allows to glue them to the support.

2.4. Raman spectroscopy

Raman spectroscopy (DXR Confocale Raman apparatus from *Thermofischer* at a wavelength of 633 nm) was used to investigate possible changes of the chemical nature of the fibre surface after treatment. For this purpose the relative intensity of G and D bands of desized vCF and rCFs was investigated.

2.5. Atomic force microscopy

All atomic force microscopy (AFM) measurements were performed in tapping mode with a Dimension Icon® (Bruker) and a measuring tip with a tip radius of about 8 nm. The fibre samples to be tested were mounted on a twin-sided adhesive carbon tape. For each sample three different positions on three individual fibres were tested. The scan direction was perpendicular to the fibre axis with a scan size of 5 μm and a scan rate of 0.5 Hz (512 samples per line). To evaluate the fibril roughness, the raw data was corrected by a background subtracting according to [23]. The fibril roughness was dominated by the fibrils which are oriented parallel to the fibre axes based on their manufacturing process. The mathematical evaluation was performed using Matlab® R2012b.

2.6. X-ray photoelectron spectroscopy

The surface composition of rCFs and desized vCFs was investigated by X-ray photoelectron spectroscopy (XPS). The analysis provides information about the elemental composition as well as the nature of functional groups at the surface. The samples were mounted on an electrically grounded sample holder. The XPS measurement was conducted using monochromatic Al-X-ray

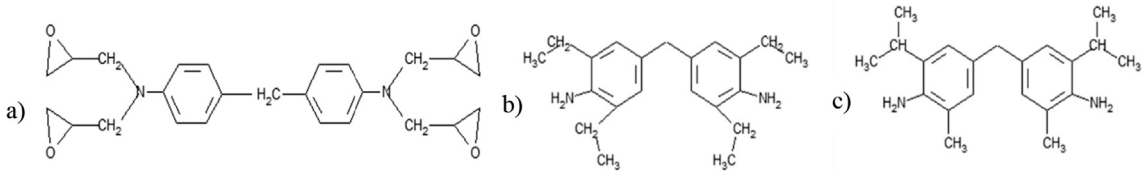

Fig. 1. Chemical structure of a) the epoxy resin tetraglycidyl methylene dianiline and the hardeners, b) the 4,4′-methylenebis(2-isopropyl-6-methylaniline) and c) the 4,4′-methylenebis(2,6-diethylaniline).