Material behaviour

The effect of the moisture content on the curing characteristics of an epoxy matrix in the presence of nanofibrous structures

Sam van der Heijden [a], Bert De Schoenmaker [a], Hubert Rahier [b], Guy Van Assche [b], Karen De Clerck [a, *]

[a] Ghent University, Department of Textiles, Technologiepark 907, B-9052 Gent, Belgium
[b] Vrije Universiteit Brussel, Department Materials and Chemistry, Pleinlaan 2, B-1050 Brussels, Belgium

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ABSTRACT

This paper investigates the effect of polyamide 6 (PA 6) nanofibres and microfibres, as well as the effect of moisture present in these structures, on the curing kinetics of a diglycidyl ether of bisphenol A (DGEBA)-methylenedianiline (MDA) system. Modulated temperature differential scanning calorimetry measurements show that the initial reaction rate follows a linearly increasing trend as a function of the moisture content present in the nanofibrous structures. Compared to PA 6 microfibrous structures, incorporating PA 6 nanofibrous structures exposed to the same humidity resulted in a higher initial reaction rate, which is in agreement with the higher water absorption of the nanofibrous structure, measured with differential vapour sorption. Overall, the nanofibres themselves affect the curing characteristics, and the moisture present in the structures enhances this effect.

1. Introduction

Incorporation of nanoparticles, such as carbon nanotubes, nanoclays and thermoplastic inclusions, can enhance the performance of a thermosetting epoxy matrix [1—5]. Depending on the incorporated particles, higher performance can be found in, for example, higher stiffness [3,6], increased toughness [7—9] or better electromagnetic properties [10,11].

Important disadvantages related to the use of nanoparticles are associated with safety issues [12] and dispersion problems [3,5,6]. Owing to their small dimensions, nanoparticles can easily be taken up by the human body, which is the main reason for health and safety problems. Furthermore, with the currently available techniques, it is still difficult to obtain homogeneous dispersion of nanoparticles in the resin. Homogeneous dispersion is required to take the full advantages of the nanoparticles in the composites.

The embedding of nanofibrous nonwoven structures in general, and polyamide nanofibrous structures in particular, offers an interesting alternative to tackle these problems [13—16]. Owing to the macroscale of the nanofibrous nonwoven structures, less health hazards are involved. Moreover, since these highly porous nonwoven structures are easily wetted by the epoxy resin, they can be incorporated in epoxy composites through a straightforward impregnation step, circumventing the dispersion issue. However, the effect of these fibrous structures on the curing behaviour of the epoxy matrix needs further attention. It is known that the incorporation of fibres in a matrix may alter the curing behaviour, and thus the final performance of the matrix [17,18]. It is also known that moisture can play an important role in the curing kinetics of a thermoset matrix [19—21].

* Corresponding author. Tel.: +32 9 264 57 40; fax: +32 9 264 58 46.
E-mail addresses: Karen.DeClerck@ugent.be, sam.vanderheijden@ugent.be (K. De Clerck).

Since nanofibrous nonwoven structures have high porosity combined with a high specific surface, they may very well interfere with the curing mechanism when incorporated in an epoxy matrix. In addition, the nanofibrous structures show a high moisture sorption capacity [22], thus the effect of moisture is also to be studied. Previous research showed that polyamide nanofibrous structures had a catalytic effect on the cure of an epoxy resin, and it was indicated that moisture may play an important role [22]. The effect of moisture present within the structures on the curing of epoxy resins has not yet been investigated.

This paper examines the influence of the moisture content in polyamide 6 (PA 6) nanofibrous nonwovens on the epoxy cure kinetics and on the glass transition temperature using modulated temperature differential scanning calorimetry (MTDSC). Moreover, a comparison with conventional polyamide fibre woven structures is made to fully understand the effect of the nanofibrous structures. The moisture absorbed by the epoxy resin and the PA 6 fibres is measured using dynamic vapour sorption (DVS).

2. Materials and methods

2.1. Materials

Epikote resin 828 LVEL (Hexion), which consists of the difunctional diglycidyl ether of bisphenol A (DGEBA) and the tetrafunctional hardener methylenedianiline (MDA) (Sigma-Aldrich), were used in stoichiometric quantities (molar ratio $r = [NH]/[Epoxy] = 1$).

The PA 6 nanofibres were in-house produced on a multinozzle set-up [23]. Polyamide 6 pellets (16 wt%) were dissolved in a 1:1 formic acid/acetic acid solution. All chemicals were purchased from Sigma-Aldrich. The tip-to-collector distance and flow rate were set at 7 cm and 2 mL/h, respectively, while the applied voltage was adapted, between 25 and 30 kV, to obtain a stable electro-spinning process. The conventional woven fabric of PA 6 microfibres was obtained from Concordia Textiles (Waregem, Belgium). All fabrics were desized and washed. The average fibre diameter of both the nanofibres and conventional microfibres was measured using Cell^D-software from Olympus (Table 1). The specific surface area was calculated based on a circular cross section and a PA 6 density of 1.14 kg/m^3.

2.2. Methods

The moisture sorption of the resin, the PA 6 microfibrous woven and nanofibrous nonwoven structures was

Table 1
Characteristics of PA 6 nanofibres and microfibres.

	Fibre diameter [nm]	Specific surface area [10^6 m^2/kg]
Nanofibres	180 ± 20	19.5
Conventional micro fibres	10428 ± 140	0.35

evaluated using a TA Instruments Q5000 dynamic vapour sorption (DVS) analyser. All samples were analysed in TA instruments DVS quartz pans at 23 ± 1 °C. For the fibrous structures, a full sorption and desorption isotherm was measured. The method started with drying the fibres at 0 % relative humidity until the weight change of the sample was less than 0.01 % for 15 min. The sorption isotherm was measured by increasing the relative humidity in steps of 10 %, in the range of 5 to 95 %RH. Next, the desorption was measured by decreasing the relative humidity, with the same step size. For both the sorption and desorption steps, the sample was allowed to equilibrate until the weight change was less than 0.01 % during the last 15 min of the measurement. For the DGEBA-MDA resin, the maximum sorption at 95 %RH was determined as an indication of the moisture sorption of an uncured resin. A drying step was not necessary since the resin was heated to 160 °C during preparation.

Modulated temperature differential scanning calorimetry (MTDSC) measurements were performed using a TA Instruments Q2000 Tzero™ DSC, purged with a constant nitrogen flow of 50 mL/min. The instrument was calibrated using sapphire (Tzero calibration) and indium (heat flow rate and temperature). The modulation amplitude for the MTDSC measurements was chosen at 0.5 °C with a period of 60 seconds, as used in previous work [22,24]. The samples were analysed in aluminium Tzero hermetic DSC pans (TA Instruments), which were loaded with 3.50 ± 0.05 mg fibres and 10.0 ± 1 mg resin, which implies a fibre content of 26 ± 2 wt%. The epoxy resin was heated to 160 °C for 15 minutes, followed by the addition of the ground hardener and a quick stir for a few seconds. Immediately after mixing, the hot mixture was quickly poured into a syringe and quenched in liquid nitrogen (the reactive mixture was less than 10 s at 160 °C). After keeping the (quenched) syringe at room temperature until the resin was sufficiently liquid, about 3 min, a drop of resin mixture was injected into the DSC pan. The resin penetrates immediately into the PA6 nanofibre web. All samples were cured quasi-isothermally at 80 °C for 250 min. For the determination of the glass transition temperature and the residual reactivity, non-isothermal heating from 0 °C to 195 °C at 2.5 °C/min was performed after the quasi-isothermal cure. The glass transition temperature of the fully cured system was obtained by a second identical heating ramp.

To compare the heat flow signal profiles, which relate to variations of the reaction rate as the conversion progresses, it is necessary to have a good definition of time zero, the time at which the reaction is considered to start. In this paper, time zero is defined as the moment when 79 °C was reached. The choice of 79 °C was prompted by the fact that the (average) heating rate decreases significantly when approaching the final isothermal temperature of 80 °C. Therefore, it may take a few minutes before 80 °C is reached exactly.

A statistical analysis of variance (ANOVA), was performed in SPSS to investigate the different kinetic parameters at the different relative humidity levels. Prior to the ANOVA analysis, the normality of the distribution was tested by a Shapiro-Wilk test.