Supplementary Materials

High-performance epoxy vitrimer from commercial epoxy-anhydride system with reprocessable and chemical degradable properties

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Materials and methods

1． Materials.

Diglycidyl ester of aliphatic cyclo (DGEAC, Tianjin Jindong Chem), methyl tetrahydrophthalic anhydride (MTHPA, Energy Chemical), carbon fiber woven T300 (GW3011, Weihai Tuozhan), 1,5,7-triazabicyclo [4.4.0] dec-5-ene (TBD), and monoethanolamine (MEA, Energy Chemical) were used directly without undergoing any purification.

2． Preparation of DGEAC/MTHPA-TBD networks.

Firstly, TBD (with a molar ratio of 1% relative to all the epoxy groups, i.e., TBD/epoxy group = 0.01/1) was added into liquid DGEAC in a beaker at 80°C. Subsequently, the liquid hardener MTHPA was added into the solution at 50°C to obtain a homogeneous resin solution. Upon addition of MTHPA, the mixture was vacuumed at 60°C and further poured into a stainless mold with a dimension of 80 mm × 10 mm × 4 mm. Then the stainless mold was placed in a vacuum drying oven. Finally, after curing at 80°C for 1 hour, 150°C for 3 hours, and 180°C for 2 hours, the cross-linked networks formed by DGEAC and MTHPA were obtained. The stoichiometric ratio of anhydride to epoxy group was 0.9/1.

3． Preparation of CF/DGEAC/MTHPA composite laminates.

Initially, TBD was introduced into liquid DGEAC at a molar ratio of 1% relative to all the epoxy groups (TBD/epoxy group = 0.01/1) using a beaker at 80°C. Subsequently, the liquid hardener MTHPA was added into the solution at 50°C to ensure the formation of a homogeneous resin solution. Following this, four slices of T300 woven carbon fibers were dip-coated with the DGEAC/MTHPA mixture, utilizing a manual paste application method. The impregnation process was conducted layer by layer, with the weight fraction of resins being approximately 30%. After impregnation, the carbon fibers were arranged in layers within a stainless steel mold of dimensions 100 mm × 80 mm × 1 mm. These arranged fibers were then subjected to a curing process in a press vulcanizer. The curing process involved heating the samples at 80°C for 1 hour, followed by 150°C for 3 hours, and finally 180°C for 2 hours under a pressure of 5 MPa for CF/DGEAC/MTHPA composites.

4． Characterization.

Differential scanning calorimeter (DSC) test: Differential scanning calorimeter (DSC, TA250) was used to investigate the curing behavior and glass transition of DGEAC/MTHPA networks and DGEAC/MTHPA-TBD networks. The pre-cured samples were scanned from 20 to 250°C at a heating rate of 5°C/min, whereas the fully cured samples were scanned at a heating rate of 20°C/min. Both sets of scans were performed under a nitrogen atmosphere.

Fourier transform infrared spectroscopy (FTIR) test: Fourier transform infrared spectroscopy (FTIR) analysis was performed using a spectrophotometer (Nicolet 6700). Each sample powder (approximately 100 mg) was mixed and ground with potassium bromide (KBr) in a mortar. The resultant mixture was then compressed into a disk. The samples were scanned in the range of 4000 to 400 cm−1.

Gel content test: The dry sample (∼30 mg, m0) was immersed in 5 ml of acetone, dichloromethane (DCM), ethyl acetate (EA), ethanol (EtOH), and methanol (MeOH) at room temperature for 24 h. Following this immersion period, the samples were dried in a vacuum oven at 90°C for 10 h and then weighed (m1). The gel content was calculated according to Eq. 1

(1)

Thermal stability test: Thermal stability was evaluated using a thermogravimetric analyzer (TGA, TA-Q600). Samples (~5 mg) were scanned from 30 to 700°C at a heating rate of 10°C /min under a nitrogen atmosphere.

Dynamic thermomechanical analysis test: Dynamic thermomechanical properties were assessed using a dynamic thermomechanical analyzer (Mettler DMA1) in Three-Point Bending mode. Each sample with a dimension of 15 mm × 10 mm × 4 mm was scanned from 50 to 250°C at a heating rate of 10°C/min. The test conditions were set with an amplitude of 10 micrometers and a frequency of 1 Hz.

Tensile properties test: Tensile properties were evaluated using a universal testing machine (MTS-CMT4304) adhering to ASTM D882 at a stretch rate of 5 mm/min. The same vitrimer system underwent testing at least 5 times to obtain an average value.

Stress relaxation test: Stress relaxation was evaluated using a dynamic mechanical analyzer (Mettler DMA1) in three-point bending mode. Each sample, measuring 30 mm × 10 mm × 4 mm, was heated to a specified temperature and maintained for 10 minutes. Subsequently, an instantaneous strain of 1% (40 μm) was applied to the material. The stress and modulus were continuously monitored over several hours until equilibrium was attained.

Remodeling test: The remodeling of vitrimers was performed in a vacuum oven. The preheated sample, with dimensions of 80 mm × 10 mm × 4 mm, was bent and secured onto a mold. The mold was then inserted into a vacuum oven at 200°C for 2 hours.

The chemical degradable test: The chemical degradable property was assessed using vials containing MEA (~5 mL) at 160°C. A block sample (~60 mg, m0) was immersed in MEA at 160°C. The DGEAC/MTHPA samples were retrieved from the vial at time intervals of 5, 10, and up to 45 minutes, whereas the DGEAC/MTHPA-TBD samples were filtered out at intervals of 10, 20, and up to 65 minutes. After retrieval, they were dried at 100°C for 10 hours and weighed (m1). The relative weight was calculated using Eq. 2. To ensure accuracy, the same vitrimer system was repeated at least 3 times to obtain an average value.

(2)

Degradation component test: the component was analyzed by high-performance liquid chromatography-mass spectrometry (HPLC-MS, Agilent 1260 Infinity II, G6465B). Ethyl alcohol was served as a solvent. Data were acquired in positive-ion mode and negative-ion mode. Chromatographic conditions were meticulously set as follows: the column was Agilent Eclipseplus C18 (1.8 μm, 2.1×100 mm), the mobile phase A for gradient elution was 5 mmol/L ammonium acetate, while mobile phase B was methyl alcohol, the flow rate was 0.3 ml/min, and the injection volume was 10 μL. Conditions for electrospray mass spectrometry were as follows: dry gas temperature of 300°C, nebulizer pressure of 15 Psig, capillary voltage of 4 kV, and m/z range of 100-1400.

Raman test: Raman spectra of virgin and recycled carbon fibers were measured using a Raman spectrometer (HORIBA HR Evolution) with a laser wavelength of 532 nm and a Raman shift range of 0-3000 cm-1.