



Composite materials from fully bio-based thermosetting resins and recycled waste poly(ethylene terephthalate)

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ARTICLE INFO

Keywords:

Recycling
Thermosetting resin
Mechanical properties
Moulding compounds

ABSTRACT

During the last two decades, interest in bio-based polymers, especially in bio-based composite materials, has grown as a result of environmental concerns. In this paper new composites obtained from fully bio-based unsaturated polyester resin (UPR) and waste poly(ethylene terephthalate) (PET) were studied for the first time. The composites were prepared by crosslinking the UPR in the presence of functionalized PET particles (3, 6 and 9 wt %), using dimethyl itaconate as reactive diluent. The results showed that the incorporation of the PET particles led to the increase in mechanical properties. However, higher PET loading caused a decrease in the mechanical properties of the composites because of the PET particle agglomeration.

1. Introduction

Due to a good balance between mechanical properties, cost, processability and adaptability to the various industries, unsaturated polyester resins (UPR) are widely used among the thermoset polymer materials [1]. Almost exclusively commercial UPRs have a petrochemical origin which could be seen as a serious disadvantage from both economic and environmental perspective [1]. Furthermore, recent studies showed that UPRs pose health risk due to the use of styrene as almost the exclusive reactive diluent of choice for UPRs. Namely, styrene is classified as a suspected carcinogen, neurotoxin, and respiratory tract irritant and poses a health risk for employees who are exposed to either vapours or physical contact with the styrene monomer [2]. To overcome or mitigate such disadvantages, in the last years, several UPRs based on 'green' monomers, i.e. derived from biomass, have been synthesized. The majority of studies investigated fatty acid-based monomers as bio-based alternative to petrochemical UPRs [3–6]. Although these resins showed low volatility, their moderately high viscosity limited their usage. Also, UPRs from this group showed elastomeric properties as a consequence of lower crosslinking density and higher content of aliphatic chains i.e. the lack of stiff aromatic groups from styrene. Aromatic bio-based monomers, mostly lignin derivative, were investigated as a promising way to increase UPR stiffness

[7,8]. These resins showed high values of storage moduli (over 3 GPa), still relatively high viscosity of aromatic monomers limited their usage due to the processing issue. In order to lower viscosity of bio-based UPRs, some authors designed systems composed of oligomers and/or monomers [9–12]. These UPRs also possessed elastomeric behaviour (low storage moduli and glass transition temperature and high elongation at break). Unsaturated cyclocarbonates were investigated as low viscosity styrene replacement. They have been proven as less harmful compounds but their lower reactivity has made them unsuitable as reactive diluents for UPRs. Cousinet et al. achieved promising results using vinyl levulinate as reactive diluent [13]. This UPR exhibited lower α relaxation temperature, elastic moduli at the rubbery plateau and mechanical properties determined by the three points bending test. UPRs with good mechanical properties were prepared using various bio-based methacrylates as styrene replacement [14]. Bearing in mind that there is no industrial production of bio-based methacrylates, the usage of these monomers will lower the bio-based content of the resin.

As presented, a variety of UPRs derived from bio-based monomers have been investigated, still these materials cannot keep appropriate features of ones with styrene. An increase in resin viscosities, low glass transition temperature, low elastic and storage modulus were the main problems which can be attributed to unusual reactivity of the pre-polymer fumarate groups with other kinds of the double bonds on the

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bio-based reactive diluent [14]. To overcome this issue, in our previous studies, we synthesized several UPRs where prepolymer and reactive diluent were both based on itaconic acid [15,16]. The UPR where prepolymer was prepared from itaconic acid, succinic acid and propylene glycol, while dimethyl itaconate was used as reactive diluent exhibited good applicative properties. We showed that this resin could be used for the preparation of gel coat. In order to be used for other applications, the mechanical properties of these resins should be further improved.

The development of novel composites has attracted the attention of material scientists as efficient, easy and cost-effective method to improve bio-based UPRs properties. Various fillers have been used for this purpose such as glass fibre [1], natural fibre [17], nano clay [18], lignin [19], etc. In the recent years, there has been increased interest in the preparation of UPR composites using waste materials because of their availability, low cost, and low carbon footprint. The use of waste paper [20,21], agricultural wastes [22,23], waste printed circuit board [24], scrap tire [25], waste Tetra Pak [26], waste fabric [27], waste grass broom fibre [28], etc have been investigated. These studies indicate a wide variety of pathways that have unfortunately not yet led to widespread application and use of effective filler for bio-based UPRs. Factors such as high viscosity, low mechanical properties, and/or application issues have limited their use to many applications.

As a ductile material, PET has been used as filler in various composites to enhance material properties [29–33]. It has excellent mechanical strength, inertness to many chemical reactions, and good thermal resistance [29]. Additionally, similarity of PET and UPR chemical structure will ensure good miscibility and moderate interface adhesion leading to improved physical–chemical properties. Furthermore, waste PET is present in abundant amount worldwide because of its widely usage for bottles, containers, woven sacks, and food packaging [34]. Nowadays, around a million of PET bottles per minute are discarded worldwide and it is expected to increase by 20% by the 2021 [35]. Unfortunately, the discard rate of PET bottles is greater than its recycling rate [36], and can lead to serious environmental problems due to littering, illegal landfilling, and incinerating [37]. One of the best ways to lower the environmental risk is to reduce PET waste by recycling. This research paper focuses on the investigation of waste PET as a suitable reinforcement for bio-based UPRs. The aim of this paper is particularly targeted at the establishing structural/properties relationship using mechanical, dynamic mechanical and thermomechanical analysis.

2. Experimental

2.1. Materials

The itaconic acid, succinic acid, 1,2-propanediol, hydroquinone, and dimethyl itaconate were supplied by Sigma Aldrich and are used as received. Methyl ethyl ketone peroxide (MEKPO) was used as the initiator. Recycled PET flakes were purchased from Jugoplastic recycling, RS (transparent, whit dimension of flakes 8×12 mm) and were used as received.

2.2. Extrusion of recycled PET fibers

The small laboratorial vertical extruder was used to homogenize and even recycled PET flakes. The inlet temperature of extruder was 265°C while the output temperature was 165°C . The extruder was set at those temperatures for 30 min before the initial feeding and continuously monitored during operating time. Extrusions process was carried out under atmospheric pressure. The raw material was fed using one batch charge of 100 g. Recycled PET fibers were automatically hauled on the coil. The obtained fibers had diameter of $50 \pm 10\ \mu\text{m}$. After cooling the recycled PET fibers were chopped to a length of 3 ± 0.2 mm.

2.3. Chemical surfaced activation of recycled PET fibers - aminolysis reactions

The aminolysis reactions were carried out according to Bech et al. [38]. PET (1.5 g) was added in a round-bottom flask containing 25 mL of the corresponding diamine (1,6-diaminohexane or 3,6-dioxo-1,8-diaminooctane), which was previously thermostated at 50°C in an oil bath. The reaction mixture was moderately stirred for 20 min. The PET particles were then carefully removed from the liquid phase, washed successively with methanol and water, and dried in vacuum at room temperature for ca. 8 h. The weight loss was around 5% for both methods. The aminated PET particles (1.0 g) were dispersed in 20 mL of dichloromethane and itaconyl chloride (0.055 mL) and triethylamine (0.65 mL) were added. The reaction mixture was moderately stirred for 1 h at room temperature. The particles were then separated from the solution, washed successively with aqueous solution of NaHCO_3 and water, and dried in vacuum at room temperature for ca. 8 h.

2.4. Synthesis of UPRs reinforced with recycled PET

The prepolymer was synthesized by melt polycondensation with diacids and 1,2-propanediol as described in detail by Fidanovski et al. [16]. The synthesized UPR was mixed with MEKPO (2.5% w/w) and with functionalized recycled PET particles in amounts of 3, 6 and 9 wt %, homogenized and poured into Teflon molds. The samples were cured at 60°C for 24 h and at 120°C for additional hour.

2.5. Functionalized PET particles characterization

Functionalized PET particles size and size distribution were determined by optical microscope (Olympus CX41RF, Tokyo, Japan) using ImageJ software.

2.6. Characterization of composite materials

The cross-section morphology of composite materials was studied by JEOL JSM–6610L scanning electron microscope (SEM). All the SEM samples were coated with platinum using LEICA SCD005 nebulizer. The dynamic mechanical properties of prepared composites were examined by Discovery Hybrid Rheometer HR2 (TA Instruments, New Castle, DE, USA) in the torsion deformation mode. Dimensions of tested samples were: $58\ \text{mm} \times 12\ \text{mm} \times 2\ \text{mm}$. The experiments were performed in the temperature range from 25°C to 150°C , at fixed strain amplitude of 0.1% and a single angular frequency of 1 Hz. The storage modulus (G' /GPa), loss modulus (G'' /MPa) and damping factor ($\tan \delta$) were determined. The mechanical properties of the composites were tested through both uniaxial tensile testing and dynamic mechanical testing (DMA). Tensile testing was performed with the Shimadzu Servopulser according to ASTM D638. Five specimens of each sample were tested at a rate of $0.5\ \text{mm min}^{-1}$. The elastic moduli, tensile strength and elongation at break were calculated and analyzed. DMA testing was conducted with the Discovery Hybrid Rheometer HR2 (TA Instruments), in which the thin rectangular samples ($58\ \text{mm} \times 12\ \text{mm} \times 2\ \text{mm}$) were loaded into a tension fixture and subjected to a test at fixed strain amplitude of 0.1% and a single angular frequency of 1 Hz at a temperature range from 25°C to 150°C . The values of storage modulus (G' /GPa), loss modulus (G'' /MPa) and damping factor ($\tan \delta$) were obtained. The glass transition temperature ($T_g/^\circ\text{C}$) was obtained as the temperature at which $\tan \delta$ had a maximum value. The coefficients of thermal expansion of the prepared samples were determined by thermal-mechanical analysis (TMA) in the expansion mode by Q400 (TA Instrument). The experiments were performed at constant load of 10 mN under argon atmosphere ($100\ \text{mL min}^{-1}$). The temperature range was from 0°C to 115°C and a heating rate was $10^\circ\text{C min}^{-1}$.

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