



Combined effects of multi-walled carbon nanotubes and lignin on polymer fiber-reinforced epoxy composites



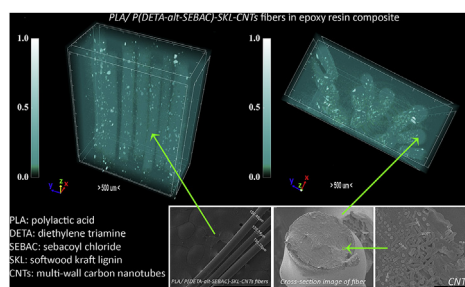
Panagiotis Goulis, Ioannis A. Kartsonakis, Konstantinos Mpalias, Costas Charitidis*

Research Unit of Advanced, Composite, Nano-Materials and Nanotechnology, School of Chemical Engineering, National Technical University of Athens, 9 Heroon Polytechniou St., Zographos, Athens, GR-15773, Greece

HIGHLIGHTS

- Synthesis of fibers including carbon nanotubes, lignin and nylon.
- Enhancement of the physical and thermal properties of the fibers and composites.
- Fiber reinforced epoxy composites demonstrated increased tolerance to stress.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Lignin
MWCNTs
Fibers
Polymers
Composites

ABSTRACT

This study is focused on the manufacturing of cost effective fibers that can be used as durable reinforcing materials. Nylon aliphatic polymer was synthesized and conjugated with softwood kraft lignin, multi-wall carbon nanotubes as well as with commercial polymers such as poly(lactic acid) and polypropylene. After the synthesis, the materials were melt spun producing fibers that were characterized in respect of their morphology, structural, chemical and elemental composition. In addition, epoxy composites were manufactured, incorporating the aforementioned fibers, in order to assess their mechanical behavior via tensile testing. The produced composites exhibited improved mechanical properties in respect of ultimate tensile strength and elastic modulus. The fiber composites were synthesized via a simple method, which combines chemistry and engineering in a multi-stage experimental process.

1. Introduction

One of the dominant reasons for the high price of fiber reinforced polymers is the costly fabrication of the conventional polyacrylonitrile fiber precursors. A potential low cost fiber component candidate is lignin, a naturally abundant polymer that can be easily extracted from the cell wall of plants [1]. Lignin has several aromatic groups and a three-dimensional complex structure, which is not yet fully defined [2,3].

Another fiber component candidate is nylon. Regarding nylon, the most common type is nylon-6,6 which can be synthesized by adding sebacoyl chloride in an hexamethylene diamine solution. In addition, it has been successfully melt spun into filaments after been mixed with cellulose, as presented by Zhu et al. [4]. Nylon-6,6 has been effectively electrospun in combination with butylene terephthalate composites and characterized by An et al. [5]. Furthermore, McHenry and Stachurski have manufactured composite materials based on nylon fibers [6].

Taking into consideration that the demand for advanced, durable

* Corresponding author.

E-mail address: charitidis@chemeng.ntua.gr (C. Charitidis).

<https://doi.org/10.1016/j.matchemphys.2018.07.025>

Received 1 April 2018; Received in revised form 30 June 2018; Accepted 11 July 2018

Available online 12 July 2018

0254-0584/ © 2018 Elsevier B.V. All rights reserved.

and robust materials is becoming increasingly higher, a combination of lignin and nylon type polymers is evidenced as a feasible way to form spinnable composites with tailored properties and desirable chemical and physical behavior [7]. However, it may be remarked that the intolerable cost of these materials has always been a significant impediment to their quality enhancement. Under this heading, contemporary composite materials have been developed containing relatively low cost polymers, such as poly(lactic acid) (PLA), enriched with reinforcing compounds, like multi-wall carbon nanotubes (MWCNTs) [8,9]. Furthermore, incorporation of natural and green substances into composites has been attempted and the manufacturing processes have been thoroughly investigated [10,11].

The modification of composites using CNTs is widely investigated, due to their highly desired properties. The characteristics of these composites have been assessed and defined [12,13]. A combination of CNTs with other compounds has also been conducted in order to achieve even better properties and thermal stability [14,15]. Additionally, taking into consideration that the final goal of the synthesis and development of such materials is to produce fibers which can then be processed into carbon fibers with minimum cost, electro-spun [16], dry-spun and melt-spun fibers [17] have been also used towards that direction. Nevertheless, the mere blending of different compounds in order to produce a functional final product is not adequate [18]. Therefore, the optimization of all the included parameters is a factor of paramount importance [19] for the synthesis of a durable composite. Subsequently, the final material undergoes several characterization techniques, mechanical and physical trials in order to determine its durability, morphology, structure and potential [20–22].

The aim of this study was to design and produce cost effective polymeric fibers [23], with a diameter of micrometers, that can be used as durable reinforcing materials, via repeatable and applicable methods [24,25]. Therefore, melt-spun fibers containing nylon, MWCNTs, softwood kraft lignin (SKL) together with commercial polymers, either PLA or polypropylene (PP), were synthesized and characterized in respect of their morphology, structural, chemical and elemental composition. An evaluation of the MWCNTs addition into these blends was conducted with respect to fiber alignment. Moreover, an investigation of further SKL addition in the precursor blends was carried out with respect to the fibers surface texture, their total porosity, thickness and density. Finally, experiments were performed on composites based on epoxy resin including the aforementioned fibers regarding their total stress and strain tolerance. The motivation of this work was highlighted by the processes which lead to the exploitation of SKL, MWCNTs and nylon aliphatic polymer [1,26,27] in the view of producing cost-effective and usable products such as fibers, which can function as reinforcing materials in composites, [28,29].

2. Materials and methods

2.1. Materials

All chemicals were of analytical reagent grade. Polypropylene (PP, $M_n \sim 67,000$, Aldrich, St. Louis, USA), polylactic acid (PLA, $M_w \sim 60,000$, Aldrich, St. Louis, USA), hydrochloric acid (HCl 37%, Fisher Chemicals, Waltham, Massachusetts, USA), sebacoyl chloride (SEBAC, Acros Organics, Geel, Belgium), diethylene triamine (DETA, Fisher Chemicals, Waltham, Massachusetts, USA), acetylene (Air Liquide), Fe $(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Aldrich, St. Louis, USA), zeolite Y (Alfa Aesar; particle size $\sim 1 \mu\text{m}$; specific surface area $975 \text{ m}^2/\text{g}$), bisphenol-A/F mono-functional RD (ER 1042–7, IpoX Chemicals GmbH, Laupheim, Germany) and modified cycloaliphatic amine (EH 2117, IpoX Chemicals GmbH, Laupheim, Germany) were used as received without further purification. Softwood kraft lignin (SKL, Westvaco Corp., Indulin AT, MWV, Norcross, Georgia, USA) was treated with HCl 0.1 M prior to its use. All melt-spinning blends were dried in a vacuum oven for 24 h prior to their extrusion.

2.2. Experimental process

Synthesis of MWCNTs was performed according to our previous work [30] via chemical vapor deposition (CVD) method using a thermal reactor that consists of a horizontal quartz tube housed in a three-zone cylindrical furnace. Firstly, the catalyst particles [Fe/zeolite particles, Fe content (20 wt%)] were synthesized by dissolving appropriate amounts of zeolite and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in water. The obtained slurry was placed into tubes at 95°C for 24 h. After that, the resulting dispersion was centrifuged at 2.0×10^3 rpm for 10 min, the supernatant solution was discarded and the obtained particles were dried at 120°C for 4 h. Finally, the received material was calcinated at 550°C under nitrogen flow for 1 h.

Subsequently, the produced catalyst was placed on a silicon substrate, located inside the quartz tube, in the middle of the reactor's isothermal zone. The system was purged from atmospheric air via argon flow through the quartz tube (flow rate 2.0×10^2 ml/min). Then, the reactor was heated at 800°C . Afterwards, the argon was replaced with a mixture of gases (acetylene/argon 40:60) with a flow rate of 3.5×10^2 ml/min. The synthesis was carried out at the same temperature for 1 h, where pyrolysis of the acetylene took place and carbonaceous materials were deposited on the silicon substrate. The produced MWCNTs were cooled down to room temperature in inert atmosphere. Then, they were milled and exposed to atmospheric air flow at 400°C for 1 h, in order to remove the amorphous carbon.

The obtained MWCNTs were purified from the catalyst metal particles via constant boiling with 5M HCl solution, in a Soxhlet extractor. Afterwards, the surface of the produced MWCNTs was functionalized with $-\text{COOH}$ groups by using an acid solution mixture of nitric acid and sulfuric acid ($\text{HNO}_3:\text{H}_2\text{SO}_4$ 1:3). The MWCNT/acid mixture (1.5×10^{-1} g MWCNTs/ 1.0×10^1 ml acid solution) was stirred for 5 h at room temperature. The treatment was followed by ice quenching and neutralization with an aquatic solution of NaOH. The suspension was filtered and the deposited on the filter black powder, was rinsed with distilled water, ethanol, acetone and distilled water. Finally, it was dried in an oven. The surface functionalization of the aforementioned MWCNTs with carboxylic groups was carried out in order to enhance their chemical affinity properties with diethylene triamine (DETA) and sebacoyl chloride (SEBAC).

The polymerization of DETA and SEBAC results to the synthesis of a nylon aliphatic type polymer, entitled *P(DETA-alt-SEBAC)*. Samples of nylon and nylon-SKL such as *P(DETA-alt-SEBAC)* and *P(DETA-alt-SEBAC)-SKL* were synthesized in order to investigate the differences between the nylon type polymer and the SKL enriched polymer. The SKL was purified prior its use with HCl 0.1 M. Afterwards, 2.0×10^1 ml of DETA and 1.0×10^1 ml of SEBAC were mixed into a glass spherical flask so as to produce the nylon type polymer *P(DETA-alt-SEBAC)*. The aforementioned chemical reactions are depicted in equations (1)–(3) (Fig. 1). Then, the produced material was oven dried at 80°C . Furthermore, in another spherical glass flask, 2.0×10^1 ml of DETA and 2.0 g of SKL were mixed under stirring until the full dissolution of SKL. Subsequently, 1.0×10^1 ml of SEBAC was added to the reaction mixture and the SKL enriched nylon type polymer was formed, entitled *P(DETA-alt-SEBAC)-SKL*. The fabricated nylon type polymer was dried in an oven at 80°C for 24 h. The mechanism of the esterification reaction (alcoholysis) between SKL and *P(DETA-alt-SEBAC)* is illustrated in the chemical reactions (4), (5) and (6) (Fig. 2). The esterification process comprises the formation of a tetrahedral intermediate due to an addition of oxygen (nucleophile) to the carbonyl group. Then, an electron pair from oxygen displaces the chloride (leaving group), yielding a new carbonyl compound as a product.

Moreover, *P(DETA-alt-SEBAC)-CNTs* and *P(DETA-alt-SEBAC)-SKL-CNTs* samples were also synthesized. Therefore, in a spherical glass flask, 5.0×10^{-1} g of MWCNTs were dissolved in 3.0×10^1 ml of DETA under stirring at room temperature. After that, 1.0×10^1 ml of SEBAC was added to the mixture so as to produce *P(DETA-alt-SEBAC)*

Download English Version:

<https://daneshyari.com/en/article/7921159>

Download Persian Version:

<https://daneshyari.com/article/7921159>

[Daneshyari.com](https://daneshyari.com)