European Polymer Journal 50 (2014) 78–86

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Macromolecular Nanotechnology

# Polystyrene/$TiO_2$ composite electrospun fibers as fillers for poly(butylene succinate-*co*-adipate): Structure, morphology and properties

Ramesh Neppalli [a,1], Valerio Causin [a,*], Edmondo Maria Benetti [b,c], Suprakas Sinha Ray [d], Antonella Esposito [e], Santosh Wanjale [f,2], Mallinath Birajdar [f,3], Jean-Marc Saiter [e], Antonio Marigo [a]

[a] *Dipartimento di Scienze Chimiche, Università di Padova, via Marzolo 1, 35131 Padova, Italy*
[b] *Laboratory for Surface Science and Technology, Department of Materials, ETH Zürich, Wolfgang Pauli Strasse 10, HCI G543, 8093 Zürich, Switzerland*
[c] *Materials Science and Technology of Polymers (MTP), Mesa+ Institute for Nanotechnology, University of Twente MTP CR 4241, PO Box 217 7500 AE Enschede, The Netherlands*
[d] *DST/CSIR Nanotechnology Innovation Centre, National Centre for Nano-Structured Materials, Council for Scientific and Industrial Research, 1-Meiring Naude Road, Brummeria, Pretoria 0001, South Africa*
[e] *AMME-LECAP International Laboratoire, EA4528, Institut des Matériaux, Université de Rouen, Faculté des Sciences, BP 12, 76801 Saint Etienne du Rouvray, France*
[f] *Polymer Science and Engineering Division, National Chemical Laboratory, Pashan Road, Pune 411008, Maharashtra, India*

A R T I C L E I N F O

*Article history:*
Received 12 July 2013
Received in revised form 30 October 2013
Accepted 3 November 2013
Available online 13 November 2013

*Keywords:*
Biodegradable polymers
Morphology
Degradation
Electrospinning
Polycaprolactone
Nanocomposites

A B S T R A C T

In this work, composite polystyrene/titanium dioxide (PS/$TiO_2$) electrospun fibers were used as a reinforcement for a poly(butylene succinate-*co*-adipate) (PBSA) matrix. The structure, morphology, mechanical properties and degradation behavior of such materials were investigated, finding that, as a function of their $TiO_2$ content, the fibers exerted different effects. The main mechanism through which the fibers modified the structure and morphology of the polymer matrix is by altering its crystallization kinetics. The presence of $TiO_2$ modified the roughness of the fibers and therefore affected the interfacial adhesion between the filler and the matrix. The modulus of PBSA was improved, even though the brittleness of the materials was increased by the presence of the fibers. Different amounts of $TiO_2$ within the fibers allowed to tune the hydrolytic degradation rate of the composites. This paper shows the potential of using composite electrospun fibers as effective fillers for the preparation of polymer-based composites.

## 1. Introduction

In the last few years, both the academic and industrial scientific community made considerable efforts in exploiting the potential of nanocomposites and nano-scaled materials. Even though in some cases the materials developed reached commercialization, the promise of ground-breaking improvements in properties has not yet been attained. This calls for the ideation of alternative strategies for the manufacturing of nanocomposites. One of these novel approaches consists in the reinforcement of polymeric matrices by electrospun nanofibers.

Among nano-scaled materials, nanofibers (especially polymeric nanofibers) are promising for diverse applications, such as drug delivery, tissue engineering and wound healing [1–3] due to their very large surface-area-to-volume

---

* Corresponding author. Tel.: +39 049 8275215; fax: +39 049 8275161.
*E-mail address:* valerio.causin@unipd.it (V. Causin).

[1] Present address: Division of Polymer Science, Department of Chemistry and Polymer Science, University of Stellenbosch, Private Bag X1, Matieland, South Africa.

[2] Present address: Aditya Birla Science and Technology centre, Taloja MIDC, Panvel, Raigad 410208, Maharashtra, India.

[3] Present address: Department of Chemical Engineering and Material Science, Chung-Ang University, 221 Heukseok-dong, Dongiak-gu, Seoul 15-756, South Korea.

0014-3057/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.eurpolymj.2013.11.002

ratio, flexibility in surface functionalities and superior mechanical performances.

Although they possess most of the ideal features required for a good nanofiller (i.e. good mechanical performances, tunable chemical and physical properties, low cost and low density), the use of electrospun fibers as fillers in composites is still surprisingly underrepresented in the literature. After the pioneering works of Kim and Reneker [4] and Bergshoef and Vancso [5], very few works were published on the use of such fibers as fillers in polymer-based composites [6–10]. However, it has been shown in a variety of systems that the addition of electrospun fibers increases the mechanical performances of the matrix and allows to tune its degradability, as it was observed in the case of polycaprolactone (PCL) [8] and poly(lactic acid) (PLA) [7].

Functional composite nanofibers, can be processed by electrospinning polymer solutions containing nanoparticles, carbon nanotubes, catalysts, enzymes, ceramics and so on [11–14]. Nanofibers can therefore be electrospun ad hoc for a given purpose and used for various applications, ranging from biotechnology to advanced microelectronics.

Poly(butylene succinate)-*co*-adipate] (PBSA) is an aliphatic polyester synthesized by the polycondensation of butane-1,4-diol in the presence of succinic and adipic acids with a relatively low production cost and mechanical properties equivalent to those of polyolefins [15–20]. As compared to poly(butylene succinate), PBSA is more susceptible to biodegradation by virtue of its lower crystallinity and higher flexibility of the polymer chains [21,22]. Moreover, it benefits from an excellent processability; it can be processed into any form of yarns (melt blown, multifilament or monofilament, tape or split) for textile purposes, in addition to the fabrication of the more common injection molded items. However the mechanical, barrier and thermal properties of neat PBSA are still not sufficient for a wide-range of end-use applications.

So far, PBSA has been mostly reinforced with fillers such as layered silicates (mostly montmorillonite) and carbon nanotubes [21,23–28]. In few cases, traditional fibers were used as reinforcing agents in PBSA [29,30]; as for electrospun fibers, nothing has yet been reported in the literature. The advantage of electrospun nanofibers over traditional fibers is their diameter (reduced of at least one order of magnitude); with respect to other fibrillar fillers (e.g. carbon nanotubes), electrospun nanofibers are much cheaper and, most of all, can be obtained with different chemical compositions and morphologies by adjusting the processing steps of their fabrication.

The main aim of this paper was to prove that composite electrospun nanofibers can actually be used to fill PBSA matrices with the purpose of improving their properties. The first part of the study focused on the possibility of considering composite electrospun nanofibers as effective fillers for polymer matrices; in fact, the potential of electrospun fibers themselves has already been adequately shown, but their behavior as a filler has not yet. Polystyrene nanofibers containing different amounts of $TiO_2$ nanoparticles were therefore electrospun and characterized. The second part of the study aimed to investigate the structure and the mechanical, thermal and functional properties of the composite materials obtained by embedding the previously electrospun PS–$TiO_2$ nanofibers into a PBSA matrix.

## 2. Experimental

### 2.1. Materials

Poly(butylene succinate-*co*-adipate) (PBSA) with commercial designation BIONOLLE #3001 ($M_w$ = 190 kg/mol, density 1.24 g/cm$^3$) was purchased from Showa Denko (Japan). PBSA was dried under vacuum at 50 °C for 36 h prior to use. Polystyrene (PS) ($M_w$ = 280 kg/mol) and anatase nanopowder (titanium(IV) oxide, size <25 nm, 99.70%, metal basis) were purchased from Sigma–Aldrich. Dimethyl formamide (DMF) was purchased from Merck Ltd. (Mumbai). Aqueous solutions were prepared with de-ionized water. All the chemicals were used as received without further purification.

### 2.2. Electrospinning of PS/$TiO_2$ nanofibers

PS was dissolved in DMF (10% (w/w) solution) by magnetic stirring. After complete dissolution, a weighed amount of $TiO_2$ powder was added to the PS solution at room temperature. The mixture was stirred for 2 h and then used for electrospinning. Electrospun nanofibers with different chemical compositions could be processed by varying the atanase-to-polystyrene mass ratio in the DMF/PS/$TiO_2$ solutions; mass ratios of 0, 5, 15 and 25% $TiO_2$/PS were used.

8 ml of each DMF/PS/$TiO_2$ solution were introduced in a 10 ml syringe equipped with a stainless steel hypodermic needle; the inner surface of the needle (pore diameter 0.8 mm) acted as the electrode for the subsequent electrospinning process. The syringe needle was connected to a high voltage generator [GAMMA High RR40 3.75/DDPM, voltage regulated DC power supply; Ormond Beach, USA] operated in positive DC mode with an applied voltage of 15 kV. The syringe filled with the solution was then loaded in a syringe pump [Model 351, SAGE Instruments, Division of Orion Research Development] capable of accurately controlling the injection flow rate as compared to the spinning rate; the flow rate was set at 0.015 ml/min for the size of the droplet at the tip of the needle to stay constant during the process. An aluminum plate placed in a closed chamber was used as the grounded collector for the fibers; the needle-to-collector distance was fixed at 15 cm. Electrospinning was performed at room temperature.

### 2.3. Preparation of PBSA–PS/$TiO_2$ composites

Composites with 1.5% (w/w) of each type of electrospun PS/$TiO_2$ nanofibers were prepared as in our previous work [8,9]. The mat of nanofibers was interposed between two PBSA films and then pressure and heat were applied (Carver press). The temperatures of the top and bottom plates of the press were set at 120 °C and 80 °C respectively, high enough to melt the PBSA matrix without melting the PS