Polymer Degradation and Stability 118 (2015) 137–146

Contents lists available at ScienceDirect

Polymer Degradation and Stability

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

Thermomechanical behavior of a novel biobased poly(furfurylalcohol)/silica nanocomposite elaborated by smart functionalization of silica nanoparticles

Nicolas Bosq, Nathanaël Guigo, Luc Vincent, Nicolas Sbirrazzuoli*

Université Nice Sophia Antipolis, CNRS, Laboratoire de Physique de la Matière Condensée – LPMC-UMR 7336, Parc Valrose, 06100 Nice, France

A R T I C L E I N F O

Article history:
Received 17 December 2014
Received in revised form
9 April 2015
Accepted 27 April 2015
Available online 6 May 2015

Keywords:
Silica nanoparticles
Biobased thermoset
Poly(furfuryl alcohol)
Nanocomposite
Thermal degradation
Glass transition

A B S T R A C T

The Polyfurfuryl Alcohol (PFA) is a biobased cross-linked polymer presenting high thermal performances. This work presents the processing of PFA/silica nanocomposite starting from pre-existing spherical silica nanoparticles obtained via the Stöber method. Prior to dispersion, silica nanoparticles were smartly decorated with furanic entities and such modification was analyzed by ThermoGravimetric Analysis (TGA), Fourier Transform InfraRed spectroscopy (FTIR) and solid state Nuclear Magnetic Resonance (NMR) spectroscopy. About 2/3 of surface Si–OH sites were grafted with furans and these modified silica nanoparticles were efficiently dispersed during polymerization of Furfuryl Alcohol (FA) as confirmed by Transmission Electronic Microscopy (TEM) observations. The thermo-mechanical performances of the PFA/silica nanocomposites were investigated by means of Dynamic Mechanical Analysis (DMA) and TGA. Unmodified nanoparticles do not change the final properties while the nanocomposite processed with functionalized nanoparticles presented improved properties. Strong interactions between cross-linked furanic matrix and the furfurylated nanoparticles resulted in a more rigid material whose thermal degradation processes were shifted to much higher temperature (+65 °C).

1. Introduction

Second generation biomass represents a sustainable and renewable source of biobased monomers (alcohols, terpenes, monosaccharides, etc), oligomers (hemicellulose, tannins), and polymers (lignin, cellulose, starch, etc.) [1]. Composites or nanocomposites made from biothermoplastics such as PolyLacticAcid (PLA) or PolyHydroxyAlkanoates (PHA) have been largely described in the past few years [2–4]. On the other hand, biobased thermosetting composites have been subject to much less attention. In the case of these thermosets, the matrix is mostly derived from modified vegetable oils [5] or from polycondensation of lignin derivatives [6].

Among the short list of biobased thermosetting resins, the PolyFurfurylAlcohol (PFA) is obtained under cationic polycondensation of Furfuryl Alcohol (FA) [7]. This biobased monomer is derived from the furfural, produced from hydrolysed biomass waste. The high carbon content, chemical inertness and thermal stability of PFA have led to several applications. The PFA can be used in the elaboration of foundry moulds [8,9] and fire resistant or corrosive resistant materials employed in the building [10,11]. FA impregnation and in-situ polymerization in wood increase significantly the wood durability [12]. Carbonaceous products such as mesoporous, microporous carbon and carbon nanocomposites derived from PFA pyrolysis have been also largely described in the literature [13,14]. Finally the PFA is a useful polymer for the preparation of carboneous and nanocomposite materials [15].

From a conceptual standpoint, the elaboration of organic-inorganic hybrids is particularly interesting because these materials combine characteristics of organic polymers with those of inorganic ceramics. Spange et al. [16–18] and Kawashima et al. [19] have initiated studies on PFA/SiO_2 hybrids. Since FA polycondensations and silane hydrolysis are both acid-induced, the authors successfully applied a sol–gel process to synthesize PFA/silica hybrids via simultaneous polymerization. After pyrolysis and silica network removal, the obtained mesoporous carbon nanostructures have shown potential applications for membrane engineering or solid catalysts. Turning to composite application, our group has recently prepared a PFA/SiO_2 hybrid nanocomposite

---

* Corresponding author.
E-mail address: sbirrazz@unice.fr (N. Sbirrazzuoli).

http://dx.doi.org/10.1016/j.polymdegradstab.2015.04.018
0141-3910/© 2015 Elsevier Ltd. All rights reserved.

whose properties were compared to those of neat PFA thermosetting [20]. As in the case of the above-mentioned studies, the silica network was prepared by sol–gel process from TEOS and was formed in-situ during FA polymerization. The nanoscale organization induced by the silica network improves significantly the thermo-mechanical performances of the PFA/SiO_2 hybrid compared to the neat matrix.

The so-called twin polymerization (TP) is an elegant method to obtain, in one single procedure, a nanometric combination of organic and inorganic polymeric systems without phase separation [21]. The TP implies that the two polymers are formed from one single source monomer called the twin monomer. The two polymerizable building blocks are bonded covalently in the twin monomer and are cleaved during polymerization. It is important to notice that the propagation reactions of the two polymers are mechanistically coupled. Interestingly, the FA was employed as building block in the discovery of TP [22]. The tetrafurfuryloxysilane (TFOS) was the first example of twin monomer that has generated hybrid interpenetrated network of PFA and SiO_2 [21,22]. On the other hand, the difurfuryloxydimethylsilane (DFOS) yield separation between cross-linked PFA and soluble cyclo-oligodimethylsilane phase. Similarly, TP was also used to prepare nanostructured organic/inorganic hybrids of PFA/TiO_2 and PFA/B_2O_3 [21,23].

The works mentioned above show that a homogeneous interpenetrated silica network is created with PFA either employing simultaneous polymerization through sol–gel process [17–20] or the TP process [21–23]. In addition, the dispersion of pre-existing silica nanoparticles during FA polymerization to prepare PFA/SiO_2 nanocomposites could be an alternative method to those approaches. Indeed, pre-existing silica nanoparticles with different sizes and morphologies are nowadays commercially available. Then, the pre-existence of the inorganic nanoparticle would not require the use of specific initiator/silica precursor as in the case of sol–gel process or the preliminary synthesis of twin monomers. However, the major drawback of the dispersion of pre-existing nanoparticles is that the hydrophilic nature of silica surface (hydroxyl groups) will restrain their use to hydrophilic or highly polar media. In order to widen their use to non-polar systems, a surface modification is necessary. It has been shown that surface modification allows to create strong or weak interactions with the polymer matrix. Besides, the surface modification leads to the reduction of the filler agglomeration and improves the dispersion of the filler within the polymer matrix.

The present study aims consequently to elaborate and characterize a PFA/SiO_2 hybrid network starting from pre-existing silica nanoparticles with the objective to obtain biobased thermosetting materials with high thermal stability. The inorganic nanofillers are synthesized beforehand in order to control their size and morphology. Dispersion of silica nanoparticles within the matrix and the final macroscopic properties are governed by the interaction between the two systems. Then, the nanoparticle surface was chemically modified with the aim to enhance the interactions with the FA monomer before polymerization. For this purpose, the silica nanoparticles were modified with furan entities onto surface and such chemical modifications were verified by Fourier Transform InfraRed spectroscopy (FTIR), ThermoGravimetric Analysis (TGA) and solid state Nuclear Magnetic Resonance spectroscopy (NMR). Three thermosetting materials were elaborated i.e. the neat PFA material and PFA nanocomposites containing unmodified or modified silica nanoparticles. The thermomechanical properties and the thermal stability of each material were investigated by Dynamic Mechanical Analysis (DMA) and TGA while the inorganic network dispersion was analyzed by Transmission Electronic Microscopy (TEM). The results aim then to highlight the intrinsic role played either by the silica network and the preliminary nanoparticle chemical modification.

2. Experimental

2.1. Materials

All the products were purchased from Aldrich Chemical Co. and were used as received. Furfuryl Alcohol (M_w = 98.10 g mol^{-1}, b.p. = 170 °C, purity >99%), and Maleic Anhydride (MA) (M_w = 98.06 g mol^{-1}, m.p. = 51–56 °C, purity >99%) were used for PFA synthesis. TetraEthoxyOrthoSilicate (TEOS, M_w = 208.33 g mol^{-1}, b.p. = 166–169 °C, purity >99%), Ethanol (M_w = 46.07 g mol^{-1}, b.p. = 78 °C, purity = 96% and ammoniac (M_w = 17.03 g mol^{-1}, b.p. = −33.34 °C, concentration = 28%) were used to prepare silica nanoparticles. Epichlorohydrin (M_w = 92.52 g mol^{-1}, b.p. = 115–117 °C, purity >99%), furfurylamine (M_w = 97.12 g mol^{-1}, b.p. = 145–146 °C, purity >99%), toluene (M_w = 92.14 g mol^{-1}, b.p. = 110–111 °C, purity >98%), Potassium Iodide (M_w = 166.00 g mol^{-1}, purity > 99%), ether crown (M_w = 264.32 g mol^{-1}, m.p. = 42–45 °C, purity >99%) were used to functionalize the silica nanoparticle with furan functions.

2.2. Synthesis of silica nanoparticles (SiNP)

Neat (i.e. non functionalized) SiO_2 nanoparticles with a theoretical diameter of ~100 nm were prepared via the well-known Stöber method, which was first reported in 1968 [24]. The Stöber method is a simple route to obtain silica nanoparticles with a smooth surface and spherical shape. Hydrolysis of tetraethylorthosilicate (TEOS) catalysed by ammonia forms silicic acid that condenses with each other to create Si–O–Si bonds. The first solution contains 15.6 g (0.916 mol) of NH_4OH (i.e. 47.25 g of 33% w/w NH_4OH aqueous solution) that was diluted in technical ethanol (96%) to obtain 1 L of solution. Then, the blend was vigorously stirred (1000 rpm) with a magnetic stirrer during 15 min at room temperature until a homogenous solution formed. A second solution was prepared by diluting 208.33 g of TEOS (0.98 mol) in technical ethanol 96% to reach a final volume of 1 L. This second solution was magnetically stirred for a few minutes and was added over 1 min to the NH_4OH solution. The mixture was stirred at 500 rpm over 72 h at room temperature. The nanoparticles were kept in the reaction medium. The mass of nanoparticles per volume of solution was determined after evaporation to dryness of a defined volume of solution.

2.3. Surface modification of silica nanoparticles by furfurylamination (SiNP-Furan)

Previously synthesized silica nanoparticles exhibit silanol groups on their surface. The objective is to obtain nanoparticles functionalized with furan rings on the surface. The strategy of surface functionalization is depicted on Scheme 1 and occurs in two main steps. The first step allows to form epoxy groups onto surface by reaction of silanol with epichlorohydrin. In the second step the epoxidized silica nanospheres react with furfurylamine to graft the furan rings onto the silica surface.

Fresh solution of SiNP were washed 5 times with dry toluene and recovered by centrifugation (3500 rounds min^{-1}). Epoxidation was carried out in excess of epichlorohydrin. The epichlorohydrin/dry silica weight ratio was ~8. KI and 18-crown-6 ether were used as epoxidation catalysts. The blend was refluxed at 130 °C for 24 h under vigorous mechanical stirring [25]. The epoxidized silica nanoparticles were recovered by centrifugation and thoroughly washed several times with ethanol and acetone to remove catalysts