Applied Surface Science xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Applied Surface Science

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

Full length article

Formation of polymer nanoparticles by UV pulsed laser ablation of poly (bisphenol A carbonate) in liquid environment

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ARTICLE INFO

Article history:
Received 15 June 2016
Received in revised form 31 October 2016
Accepted 23 November 2016
Available online xxx

Keywords:
Pulsed laser ablation in liquids
Polymer ablation
Polymer nanoparticles

ABSTRACT

Suspensions of poly(bisphenol A carbonate) (PBAC) nanoparticles of varying size and shape have been produced by ablation of a PBAC target in liquid media with the fourth harmonic of a Q-switched Nd:YAG laser (wavelength 266 nm, full width at half maximum 4 ns, repetition rate 10 Hz). The polymer target was placed at the bottom of a rotating glass vessel filled with around a 10 mm column of liquid. Laser ablation in water leads to spherical nanoparticles with diameters of several tens of nanometers for fluences close to 1 J/cm^2. Ablation at lower fluences, around 0.1 J/cm^2, results in the production of nanoparticles of smaller diameters and also of non-spherical nanoparticles. Additional irradiations at the fluence of 0.1 J/cm^2 were performed in several liquid media with different properties, in terms of density, viscosity, thermal conductivity, boiling temperature, isothermal compressibility and polarity. The different size distributions observed were related to the thermal conductivity of the systems, while their viscosity seems to be responsible for the development of nanostructures with different morphologies.

1. Introduction

Interest in the properties of polymers confined into the nanometer scale is increasing in recent years [1]. Polymers are widely used in nanofabrication processes like wires of nanometer-scale diameters [2], nanoscale polymeric particles [3,4] and nanoimprinting [1].

Polymer nanoparticles have found use in a number of applications like coating and functionalization of surfaces [5], adhesives [6], drug delivery systems [7], enhanced polymer blends preparations [8], organic photovoltaic systems [9] and smart/stimuli-responsive materials [10]. The applications of polymer nanoparticles are significantly affected by their physical properties as well as their surface morphology. Both factors can be controlled by the preparation method used to generate such particles.

Different methods for preparing polymer nanoparticles have been proposed [11–13]. In-situ polymerization can be carried out so that from a monomer it is possible to obtain a nanostructured polymer in the form of a particle [12]. A different approach consists of the use of a previously synthesized polymer in solution and the subsequent processing of the material to generate the nanostructures [4,13,14].

Pulsed laser ablation has evolved as one of the most efficient physical methods for nanofabrication [15,16]. In particular, pulsed laser ablation of solids in liquid environment (PLAL) was reported for the first time in 1987 [17]. In that work, a metastable phase of iron oxide was synthesized by ablating an iron target in water. Since then, this technique has been extensively investigated for the fabrication of nanoparticles of a large variety of materials, including metals, alloys, ceramics and semiconductors [17–25]. More recently such approach has also been proposed to process insoluble organic compounds, like phtallocyanines [26,27], aromatic hydrocarbons [27] and polymers [28]. Remarkable advantages of this method over chemical synthesis rely on the simplicity of the procedure, the weak aggregation effects, and the lack of impurities caused by chemical precursors. The nanoparticle concentration, size, polydispersity, shape and solid phase (amorphous or crystalline) can be controlled by the adequate choice of laser wavelength, pulse duration and fluence [18,23,29,30].

In the case of PLAL of polymeric materials, nanoparticles of several polymers such as poly(ethylene terephthalate) (PET), polycarbonate (PC), polyimide (PI) and polystyrene (PS) have been obtained in water [28] upon ablation at 248 nm. However the role of the liquid media on the characteristics of the particles obtained

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http://dx.doi.org/10.1016/j.apsusc.2016.11.186
0169-4332/

Table 1
Density (ρ), boiling temperature (T_b), thermal conductivity (*k*), viscosity, isothermal compressibility, polarity (normalized E_T^N values) and solubility of PBAC on the different liquids employed. Size of the PBAC particles obtained upon irradiation at 0.1 J/cm^2 is also listed.

Liquid	n-hexane	Heptane	Distilled water	Carbon tetrachloride	2-propanol	Ethylene glycol
ρ (g/cm^3)	0.66	0.68	1	1.6	0.79	1.1
T_b (°C)	68	98	100	77	82	197
k (W/m K) [32]	0.120	0.123	0.606	0.103	0.141	0.254
Viscosity (g/m s)[33]	0.2942	0.3967	0.8909	0.9004	2.0436	13.8
Isothermal Compressibility (at 20 °C) (10^{-4}/MPa^{-1})[32]	16.69	14.38	4.59	10.50	13.32	3.64
Polarity [34]	0.009	0.012	1	0.052	0.546	0.79
PBAC solubility	Non-soluble	Non-soluble	Non-soluble	Swelling	Non-soluble	Non-soluble
PBAC particle size (nm)	26 ± 3	27 ± 3	18 ± 2	40 ± 5	29 ± 3	25 ± 3

by PLAL has not been described in detail. In the present work we present results on PLAL of poly (bisphenol A carbonate) (PBAC) in several liquid media paying special attention to their different properties in terms of density, viscosity, thermal conductivity, boiling temperature, isothermal compressibility and polarity.

2. Experimental

As received poly (bisphenol A carbonate) (PBAC) (Lexan ML3021A, SABIC I-P (Innovative Plastics)) was dried in a vacuum oven for 16 h at 100 °C. After drying PBAC pellets were heated in a thermoplastic press at 220 °C for 2 min and a pressure of 20 bar was applied for 3 min. Then, the film was cooled down, inside the press using cold cartridges. The resulting PBAC films had a thickness of 0.9 ± 0.1 mm and were cut into disks with a diameter of 0.9 cm.

Ablation of PBAC targets was performed with the fourth harmonic (266 nm) of a Q-switched Nd:YAG laser (Quantel Brilliant B, 4 ns pulse duration FWHM) operating at a repetition rate of 10 Hz. The experimental setup is similar to the one reported in [23,31]. In brief, the PBAC target was placed at the bottom of a glass vessel filled with a ca. 10 mm column (1.0 mL) of different solvents. The laser beam was focused by a 12.5 cm focal length lens situated approximately at 10 cm from the target to achieve a spot diameter of 1 mm on its surface. The diameter of the laser spot was measured from the trace left by the laser pulse on an uncoated PVC plate. The vessel was rotated at about 10 rpm during ablation to avoid target cratering. Several laser fluences in the range 0.1–1 J/cm^2 were employed and total irradiation time was 1 h (36,000 pulses).

As liquid media we used six different liquids: (1) deionized water (H_2O), purified using a Milli-Q 18.2 MΩ reagent-grade water system from Millipore, (2) 2-propanol (2P) (99.98%, Aldrich), (3) n-hexane (HEX) (HPLC grade, Scharlau), (4) heptane (HEP) (99%, Aldrich), (5) carbon tetrachloride (CCl_4) (99%, Panreac) and (6) ethylene glycol (99%, EG) (Panreac). Some pertinent physical magnitudes of every liquid are listed in Table 1. The solubility was tested in a macroscopic solubility experiment by immersing 24 mg of PBAC in 2 mL of the different liquids. In all the cases PBAC was not soluble except for carbon tetrachloride. In this case, and for time intervals comparable to the experimental time used in the PLAL protocol, the PBAC target did not show any changes by eye inspection. However, after a few days, swelling and whitening of PBAC was observed.

UV–vis absorption spectra of all the liquids employed were recorded with a UV–vis-NIR spectrophotometer (UV-3600 Shimadzu) using 1 cm optical path quartz cuvettes. Fig. 1 shows the absorption spectra collected in the 200–300 nm range. It is evident that at the irradiation wavelength of 266 nm, absorption of the liquids employed is negligible, except for carbon tetrachloride which absorbs slightly more.

Size analysis of the obtained nanoparticles was performed by Atomic Force Microscopy, AFM (Multimode 8 equipped with a

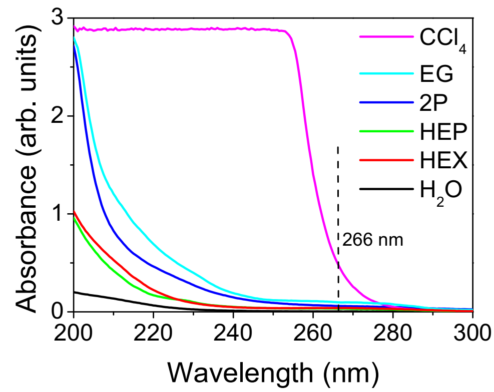

Fig. 1. Optical absorption spectra of the different liquids used in PLAL experiments. The dashed line indicates the laser irradiation wavelength of 266 nm.

Nanoscope V controller, Bruker) in tapping mode, using NCHV probes (Bruker). In all the cases, 20 μL of the resulting suspensions were drop-casted on pieces of silicon wafer (100). Samples were left drying for ca. 20 h at ambient conditions, except for the case of ethylene glycol, which was dried under vacuum at a temperature of 30 °C. Images were analysed with the software Nanoscope Analysis 1.50 (Bruker). For the nanoparticles size study five independent images were analysed. X-ray photoelectron spectroscopy (XPS) data were recorded under a vacuum better than 8×10^{-10} torr using a Phoibos-150 electron analyser (Specs) and Mg K_a radiation ($h\nu$ = 1253.6 eV). All reported spectra were recorded at an electron take-off angle of 90° with a constant analyser pass energy of 20 eV. All binding energies were referred to the main signal in the C 1 s spectrum of PBAC (aromatic carbon), which was set at 284.5 eV. The spectra were fitted using pseudo Voigt line profiles (20% Lorentzian, 80% Gaussian) and a Shirley background.

3. Results

3.1. Dependence on laser fluence

Fig. 2 shows AFM topography images of nanoparticles obtained in water upon irradiation at 266 nm and 3600 pulses at different fluences. For irradiation at fluences of 1 and 0.4 J/cm^2 the deposited material is mainly constituted by round nanoparticles. Additionally, some larger aggregates are observed which can be related to possible agglomeration of material [35]. For lower fluences of 0.2 and 0.1 J/cm^2 the resulting morphology follows a similar behavior, and spherical nanoparticles with smaller diameters are observed together with different morphologies, specifically strand-like structures which will be described below.

The size distribution and average diameter of nanoparticles obtained from the AFM images are shown in Fig. 3. For irradiation