POLYMERS FOR ADVANCED TECHNOLOGIES
Polym. Adv. Technol. 2007; **18**: 712–719

The structure of submicron polyethylene/silica composite particles[†]

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Received 1 March 2007; Accepted 19 March 2007

A novel method for a one-step preparation of silica/low-density polyethylene (LDPE) composite particles has been developed recently, based on performing sol–gel polycondensation within an emulsion of LDPE dissolved in xylene and tetraethyl othosilicate which is stabilized by poly (ethylene-block-ethylene glycol) block copolymer surfactant (PBP), all dispersed in a basic ethanolic medium. The particle dimensions are in the sub-micron range with diameters of 200–500 nm. Small-angle X-ray scattering (SAXS) measurements with contrast variation, in conjunction with other characterization methods, provide information on the inner structure of the nanoparticle's composition and inhomogeneity, which has a characteristic dimension of about 7 nm. Increase in the PBP amount and the presence of LDPE result in decrease in volume fraction of voids. The surface of the particles is heavily coated with the organic material. The crystallinity and melting behavior of LDPE is unaffected by its confinement to the particles. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: polyethylene; silica; sol-gel processing; nanoheterogeneity; SAXS

INTRODUCTION

Composite particles made of organic polymers and oxides such as silica, and having sub-micron dimensions find application in several areas such as catalysis, chromatography, controlled drug delivery, optics, etc.[1] The synthesis routes developed in the past for composite silica/organic polymers include layer-by-layer deposition,[2] incorporation of colloidal silica particles within latex particles by spray drying[3] or covalent bonding methods,[4] polymerization of organic monomers with silane-modified surfaces of latex particles followed by Si-alkoxide polycondensation[5] and polymerization of an organic monomer in the presence of silica particles.[6]

A novel method was presented by Avnir and Shertchook for a one-step preparation of polystyrene/silica composite particles, based on sol–gel chemistry.[7] In addition to being a simple procedure at ambient temperature, this process results in narrow dispersion of particle size and guest molecules can be readily entrapped within the particles. Recently, composite particles with low-density polyethylene (LDPE) or other polyolefins were also prepared.[8] Facile entrapment in sol–gel composite particles can have several applications depending on the nature of the guest molecule.[1]

Structural evaluation of these unique composite particles is lacking as yet. This work investigates different aspects of the composite particle morphology by different physical methods namely small-angle X-ray scattering (SAXS), thermal gravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and X-ray diffractions (XRD). SAXS is a useful tool for the investigation of complex structures. When there are several structural elements in the particles' inner structure, the contrast variation method is predominantly a suitable analysis.[9–11] As a first step, a straightforward indication of particle heterogeneity can be obtained by recording of several scattering curves, each having a different scattering density of the dispersing medium. The scattering curves of homogeneous systems are essentially independent of contrast, simply scaling as the contrast is changed. The inner structure, which exists in the colloidal particles, contrarily, causes changes in the angular dependence of the scattered intensity, as the contrast is changed. Further information on the surface composition and structure may be obtained by XPS and SEM analyses.

The physical properties of polymers in confined geometries, such as glass transition temperature, degree of crystallinty and crystal size are not necessarily the same as of corresponding bulk polymers.[12,13] The cause for such effects

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Contract/grant sponsors: NFM Consortium supported by the MAGNET program of the Israel Ministry of Industry, Trade and Employment; Center for Absorption in Science of the Ministry of Immigrant Absorption under the framework of the KAMEA program.

[†]This paper is presented as part of a special issue in memory of Professor Yair Avny.

is usually the strong influence of the presence of an interface on the thermodynamics of polymers.[14–16] In this work we also attempt to evaluate the effect of polymer confinement in these particles on its crystallinity, using XRD and differential scanning calorimetry (DSC).

EXPERIMENTAL

Materials

TEOS—Tetraethyl orthosilicate 98%; Block copolymer surfactant, PBP-poly(ethylene)-block-poly(ethylenglycol) $M_n \sim 1400$, 50% (w/w) block content; and LDPE–low-density polyethylene pellets (melt index 55) were obtained from Aldrich Chemicals.

Composite particle synthesis

0.2 g of PBP and 0.2 g of LDPE were melted in a glass vial and 4.0 ml of xylene and 2.0 ml of TEOS were added to the molten polymers.

In a 100 ml Erlenmeyer flask, 50 ml of ethanol and 30 ml of ammonium hydroxide (25% of NH_3) were mixed and heated. The xylene/TEOS/LDPE solution was then poured into the basic ethanol solution and stirred vigorously for 24 hr. The heating was stopped 20–30 min after all the reagents were mixed. The product particles were isolated by centrifuging for 15 min at the speed of 1000 r.p.m. For further use or storage, the obtained white precipitate may be either dried under vacuum or dispersed in water.

For reference, the same experimental procedure was used, without the addition of LDPE. Two particles compositions, at different PBP:LDPE ratios, and their reference particles, were studied, as listed in Table 1.

Particle analysis

SEM imaging of the powder samples was performed using a JEOL 5400 microscope, at 15 kV acceleration voltage, after sputtering of a thin gold layer. XPS measurements were performed at UHV (10^{-9} torr base pressure) using a Thermo VG Scientific Σ probe XPS. The samples were irradiated by Al K_α monochromatic source (1486.6 eV) and a concentric hemispherical analyzer (CHA) was used to analyze the emitted electrons. Analysis was performed at an angle about 45° and 10° between the X-ray beam and sample surface. High-resolution measurements were performed at pass energy of 20 eV with 0.05 eV/step interval. The surface of the samples was positively charged during measurements, using a charge neutralizer for charge compensation. DSC analysis was performed using a Mettler DSC 821^e system in air with a heating rate of $5^\circ C\,min^{-1}$.

SAXS measurements were performed using a slit-collimated compact Kratky camera with Cu K_α radiation, slit height 20 μm and length 15 mm. The scattering intensity was recorded using 30–40 kV and 15–25 mA in interval $0.1 < h < 6.4\,nm^{-1}$, where h is the scattering vector defined as $h = (4\,\pi/\lambda)\sin(2\theta/2)$, 2θ being the scattering angle and λ the wavelength (0.1542 nm). Sample temperature was retained at 22°C. Particle dispersions were sealed in thin-walled glass capillaries (Glass) of about 2 mm diameter and 0.01 mm wall thickness. For contrast variation experiments, the electron density of the dispersing medium ρ_m (el/nm^3) was varied by means of adding sucrose to the sample dispersions, which were diluted to about 1 vol.%. ρ_m was calculated using the equation given by Digenouts and Ballauff[17]:

$$\rho_m(C) = 332.79 + 1.2827C \tag{1}$$

where C is the weight percentage of sucrose in the solution.

TGA measurements were performed using TGA 2050 Termo gravimetric Analyzer (TA Instruments, Inc.). The heating rate for all tests was $20^\circ C\ min^{-1}$.

X-ray diffraction patterns were obtained at ambient temperature using a flat-film camera (Blake) with Ni filtered Cu K_α radiation (Philips PW1730 generator), pinhole collimation (0.3 mm diameter), and a $8 \times 10\,cm^2$ X-ray sensitive film that is positioned perpendicular to the beam 5.4 cm behind the examined sample. The powder samples were placed between polyimide films. XRD patterns were also obtained using a Philips powder diffractometer (Cu K_α radiation from a sealed tube generator at 40 kV, monochromator before the detector, Philips PW3020 goniometer system). The Bragg–Brentano scheme was used for beam focusing.

SAXS DATA EVALUATION

The scattered SAXS intensity $I_s\,(h)$ was normalized to time, solid angle, first beam intensity, capillary diameter, transmission, and the Thompson factor. The scattering from the solvent and empty capillary was subtracted. In contrast variation measurements, the addition of sucrose resulted in some change in particle concentration, which was also taken into account. The SAXS intensity $I_s\,(h)$, measured using a slit-collimated incident beam, is thus termed ‘smeared’ intensity. Most theoretical expressions relating the SAXS pattern to structural characteristics refer to a point-collimated incident beam $I_d\,(h)$, (‘desmeared’ intensity). Some equations can be applied to both types of data. In such cases the scattering intensity was marked as $I(h)$.

If the chemical composition is identical for all particles, the scattering intensity can be split into three contrast-independent ‘basic functions’.[9–11] The homogeneous part $i_h\,(h)$ determined by the particle shape, the heterogeneous part $i_i\,(h)$ determined by the particle inner structure, and the

Table 1. Compositions for particle preparations

Sample	Amount of TEOS (ml)	Amount of polyethylene (g)	Amount of polyethylene-block-polyethylene glycol (g)
LDPE 1:1	2.0	0.2	0.2
LDPE 4:1	2.0	0.2	0.05
Reference 1/1	2.0	0	0.2
Reference 1/4	2.0	0	0.05

DOI: 10.1002/pat