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Immobilisation of different surface-modified silica nanoparticles on polymer surfaces via melt processing

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ABSTRACT

The immobilisation of silica nanoparticles on the surface of a flowing polymer melt is studied during injection moulding. We use silica nanoparticles of identical size of about 200 nm, but with different surface functionalities: plain unmodified particles with silanole groups as well as amino- and hydrocarbon modified particles. The particles were brought in contact with a polycarbonate melt at a temperature of 300 °C. In our investigation, we show that particles with polar surfaces are more embedded than those with non-polar surfaces. Immobilised polar particles exhibited also a higher adhesion, tested with an adhesive tape, whereas the non-polar particles can be easily removed by peeling off the adhesive tape. This paper reveals that surface properties have a larger influence on embedding of nanoparticles than thermal conditions due to cooling of the melt.

1. Introduction

Nanoparticles and nanostructured materials are the very promising materials for future demands. They are already today applied in many fields of applications. Many applications, e.g. as sensor [1], catalyst [2], require the immobilisation of nanoparticles on solid surfaces. This can be realised very efficiently by adsorption using the layer-by-layer technique [3–6] or by dispersion drying [7]. However, since the nanoparticles are only bound by weak chemical or physical interactions, the mechanical stability of those layers is limited. A higher stability could be approached by embedding in a polymer melt.

Such an embedding of gold nanoparticles was realised in the group of Composto by moulding in a hot press [8]. Here, the particles were embedded, partly completely, in the polymer melt. The authors explained this by the high surface energy of the particles and capillary forces that resulted in extensive wetting by the melt. The time of contact with the melt at high temperature was arbitrary in these experiments, so that conditions for the adjustment of a thermodynamic equilibrium prevailed.

However, fabrication of polymer parts by hot pressing is not very efficient. Our previous work dealt with embedding of small gold nanoparticles using injection moulding [9,10]. Embedding occurred also here. However, some parts of the surface area remained uncovered by the melt and were still accessible for small molecules from solution.

This was used for catalytic reactions. Wetting of the particle surface by melt occurred despite the high cooling rate once the hot melt hit the cool surface. However, this could be a result of the small particle diameter of about 20 nm.

In this paper, we used nanoparticles with equal size and different surface functionalisation. Pure silica particles are polar and exhibit silanole groups on their surface. Amino-modified particles are also polar and have, in addition, groups that can reactively bind onto polycarbonate [11,12]. Hydrocarbon-modified particles are typically non-polar and exhibit a low surface energy. The particle diameters were about 200 nm and, thus, larger than those of the discussed gold nanoparticles. Since the nanoparticles affect the temperature diffusion from melt to mould, we used particles with uniform size to realise equal cooling conditions. The aim of this paper is, to find out, whether there is an influence of the surface modification on wetting and embedding of particles in the polymer melt under the special conditions of injection moulding, or if the rapid cooling dominates the structure formation. The question is to be answered, whether the embedding of nanoparticles into the surface of a thermoplastic part can be controlled by surface functionalisation.

2. Material and methods

Uniform silica nanoparticles with a diameter of about 200 nm were

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obtained from Geltech (Orlando, USA). Octadecyltrimethoxysilane (OTMS), N-(3-Trimethoxysilylpropyl)-diethylenetriamine (DETA), sodium poly(ethylene sulphonate) (PES) and Poly(diallyldimethylammoniumchlorid) (PDADMAC) were ordered at Sigma-Aldrich, Germany. Polyethyleneimine (hyperbranched, M_w 750 kg mol⁻¹, Sigma-Aldrich, Germany, PEI) was ordered as 50 wt.% aqueous solution. Polycarbonate (Makrolon LED 2245, Bayer Materials Science GmbH, now Covestro AG, Germany, PC) was used for moulding experiments.

The plain silica nanoparticles were used as received. They exhibited a low porosity with a surface area of 4.5 m² g⁻¹, as measured by BET using nitrogen gas. This value equalled that given from the manufacturer. Surface modification with amino groups was carried out according to a protocol taken from literature in a 500 ml flask under nitrogen purging [13]. 0.15 g acetic acid, 250 ml water and 2.5 ml DETA were mixed. 0.6 g silica nanoparticles were added and stirred for 6 h at room temperature. After that time, they were centrifuged, and the supernatant solution was changed against water. This procedure was repeated three times. The yield was about 84%. Surface modification with OTMS was carried out in a 100 ml flask with nitrogen purging. 500 mg silica nanoparticles were dispersed in 10 ml toluene in an ultrasonic bath. Then a solution of 3 mmol OTMS in 10 ml toluene was added dropwise via a septum. The solution was stirred first 1 h at 80 °C and then 2 h under reflux. Finally, the mixture was centrifuged three times with exchange of the supernatant solution against toluene. The product was dried in vacuum. The yield of the hydrocarbon-modified nanoparticles was about 62%.

A Zetasizer Nano ZS (Malvern Instruments GmbH, UK) was used for measurements of zeta potential using electrophoresis. Polyelectrolyte titration was carried out at pH 5.8 using a 702 SM Titrino (Metrohm GmbH & Co. KG, Germany) and with PDADMAC and PES as titrant, respectively.

Glass microscope slides with the dimensions 1 inch x 3 inch were used as substrates. They were cleaned in NoChromix solution and rinsed with water prior to use. Layer of amino-modified nanoparticles were prepared using cleaned plain glass slides. The adsorption was carried out using a stirred dispersion with a nanoparticle concentration of 2 g l⁻¹ at pH 6. After an adsorption time of 30 min, the glass slides were rinsed for 15 min with water. For the adsorption of plain silica particles, PEI was adsorbed in advance onto the glass slides. The solution was prepared by dissolving 10 g of the concentrated PEI solution and 29 g NaCl in 400 ml water. Then, the pH was adjusted to 8 by adding HCl, and the volume was adjusted to 500 ml with water. The glass slides were rinsed in this solution for 15 min under stirring and then rinsed in water for 15 min. The adsorption of plain silica nanoparticles was carried out from a colloidal solution with a concentration of 1.2 g l⁻¹ at pH 6. Hydrocarbon-modified nanoparticles were dispersed in toluene at a concentration of 52 mg ml⁻¹. Layers were prepared by dispersion drying of a film of 32 µl of the suspension over the substrate. Substrates with a dense layer of nanoparticles on the surface were translucent.

The substrates covered with nanoparticle layers were mounted in the mould cavity of a plunger injection moulding machine (construction made in-house). PC was dried before use at 110 °C for 5 h in vacuum. PC melt was injected at a melt temperature of 300 °C and with a mould temperature of 80 °C using typical processing parameters of PC (injection rate of 7.3 mm³ s⁻¹, injection pressure of 100 bar, cooling time of 26 s). The specimens produced were round plates with a diameter of 50 mm and a thickness of about 2 mm. The substrates were removed from the formed part. They were clear after the moulding, but the surface of the parts fabricated were translucent, if the substrate were translucent before moulding, pointing to a successful transfer. In some cases, an adhesive tape with an adhesive strength of 5.4 N per 18 mm was mounted on the part surface and removed to characterise the adhesive strength of the particle immobilisation.

Scanning electron images were taken with an Ultra Plus Gemini (Carl Zeiss SMT AG, Germany). The acceleration voltage was varied

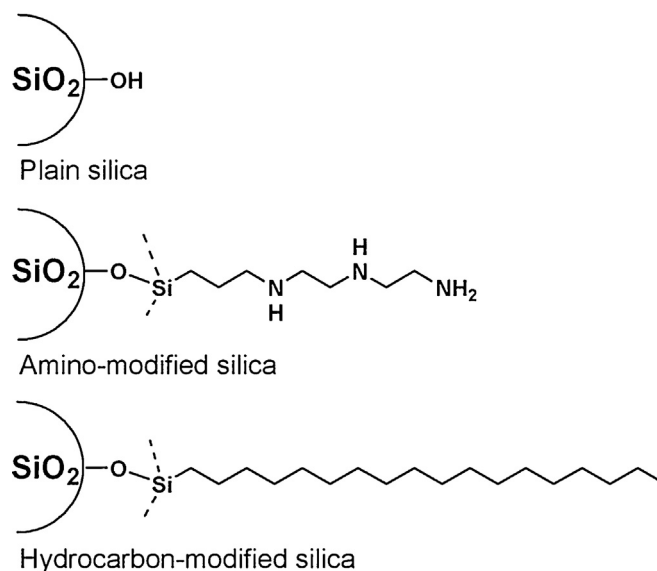


Fig. 1. Zeta potentials of plain and amino modified silica nanoparticles as function of pH. Measured in 10⁻³ M KCl.

between 1 and 20 kV. The working distance was 3 mm 3 nm platinum were sputtered on the sample surfaces in advance using a Leica EM SCD 050 (Leica Mikrosysteme Vertriebs GmbH, Germany). Atomic force microscopy (AFM) images were taken with a Dimension 3100 Nanoscope (Veeco Instruments Inc., USA). The measurements were carried out in tapping mode with silicon SPM sensors (Budget Sensors, Bulgaria) having a spring constant of 4 N m⁻¹ and a resonance frequency of 75 kHz. The radius of the tip was smaller than 10 nm.

The dynamic contact angles were measured using an OCA35 XL (DataPhysics Instruments GmbH, Germany). An average was calculated from at least four measurements per sample.

3. Results and discussion

3.1. Characterisation of the particles

Fig. 1 shows that the isoelectric point (IEP) of the plain silica nanoparticles was around a pH value of 2.5. The zeta potential decreased on increasing pH until a value of -58 mV was approached at pH 10. This is the typical behaviour for silica surface [14]. On the other side, the amino-modified nanoparticles showed an IEP of about 9.7, which is typical for basic functionalities. The plateau value of 50 mV is characteristic for complete protonated functional groups on the particle surface. This result is typical for amino-modified surfaces [15] and pointed to a stable binding of the amino silane onto the silica nanoparticle.

The dispersions were titrated to zero potential with PES or PDADMAC, respectively, and the results are shown in Table 1. The consumption of ions was related to the total surface area, calculated from the particle diameter and the total amount of particles in the dispersion. The surface charge density of plain silica nanoparticles was -5.4·10⁻² C m⁻². The alternation by treatment with the amino silane to 8.1·10⁻² pointed to binding of the amino silane onto the silica surface. The hydrocarbon-treated silica nanoparticles could not be dispersed in

Table 1
Surface charge densities from polyelectrolyte titrations at pH value of 5.8.

Type of nanoparticle	Surface charge density/C m ⁻²
Plain silica	- 5.4·10 ⁻²
Amino-modified	+ 8.1·10 ⁻²
Hydrocarbon-modified	n.a.

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