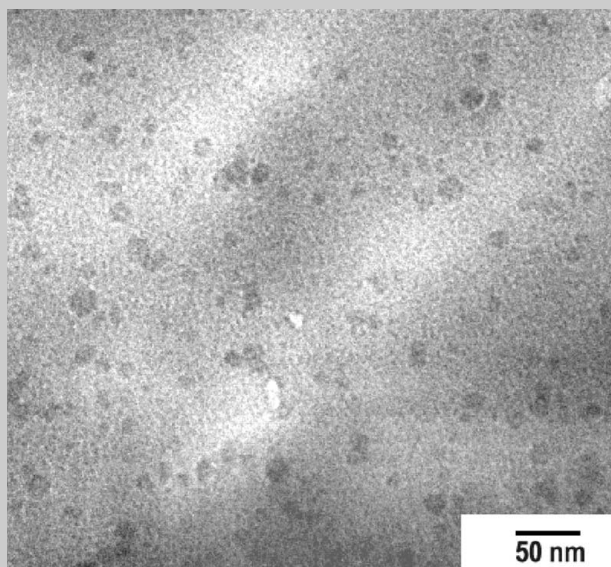


Communication: A hybrid inorganic-polymer composite was formed through nanosize silica filler particles (<30 nm) that were incorporated inside a nylon-6 matrix. The composite was microtomed and examined with TEM which revealed that the silica particles were well dispersed and non-aggregated. Optimization of the synthesis conditions relied on appropriate choice of organic solvent and pH control. Crystallinity of the composite was examined with XRD and showed the silica phase remains amorphous while the polyamide phase was semi-crystalline. Compared to pure nylon-6, mechanical tests on the hybrid composite showed an increase in impact toughness, an increase in E-modulus as a function of filler percentage, and a strain-at-break of >0.5.



TEM image of a nylon-6/silica (3 wt.-%) nanocomposite.

Hybrid Polyamide/Silica Nanocomposites: Synthesis and Mechanical Testing

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Introduction

Polymer nanocomposites constitute a class of hybrid materials composed of a polymer matrix and an inorganic filler component which has at least one dimension in the nanometer (<100 nm) size domain.^[1,2] Compared to other particle morphologies and despite its higher cost, fibers have historically received the most attention as reinforcement in plastic composites.^[3] The properties of a polymer-reinforced composite are mostly influenced by the size, shape, composition, state of agglomeration, and degree of matrix-filler adhesion.^[4] Optimum surface curvature at the polymer-filler interface can be realized when large surface

areas are created, which is possible when the filler particles are sufficiently small.^[5] Decreasing the particle size to the nano-size dimension influences the macroscopic properties of the polymer because a breakdown of the common rule-of-mixture theory occurs.^[6] This breakdown is caused by the amount of interfacial zone that gains importance with respect to the phase relative to bulk behavior. Demonstrated application of such composites can be found, among others, in the fields of optics, mechanics, iono-electronics, biosensors, flame retardants, and membranes.^[7] A major challenge remains, however, to effectively incorporate monodisperse nanoparticles inside a polyamide

matrix since a drawback of such small particles is their tendency to aggregate, particularly when higher particle concentrations, intimate mixing and prolonged heating are part of the reaction conditions. Presently, polymer nanocomposites are primarily prepared by:

- sol-gel methods, whereby metal alkoxides are reacted to undergo catalyzed hydrolysis under mild conditions to form, following polycondensation reactions, inorganic metal oxides,^[8,9]
- *in-situ* intercalative polymerization, which is a common method to prepare polymer/phyllsilicate (e.g. clay) nanocomposites,^[10–13]
- *in-situ* polymerization, where inorganic particles are dispersed in an appropriate monomer, followed by heat treatment of the reaction mixture to induce polymerization,^[14–16]
- catalyzed polymerization, where a silicate is intercalated by a catalyst or initiator and upon addition of a monomer an intercalated polymer nanocomposite is formed,^[17,18]
- melt intercalation through direct intercalation of a molten polymer that is heated above its glass-transition temperature.^[19]

The advantages of *nano-* over *micro*structured particles in polymer matrices was reported by Sumita et al. almost two decades ago,^[20] but practical application have only been realized since the early 1990s, especially through the pioneering efforts of the Toyota Motor Co., forming nylon-6/clay hybrids which became the first practical example of polymeric nanocomposites used in the automotive industry.^[21]

Polyamides, and in particular the nylon series of thermoplastics, constitute a family of compounds with exceptional mechanical properties.^[22,23] Further improvement through addition of nanoscale filler particles would have to rely on a synergetic effect between the rigid-particle filler and the polymer matrix. Decreasing the diameter of the filler-particles leads to an increase in volume fraction and a consequent improvement in materials' properties.^[24]

Results and Discussion

State-of-the-art nylon-6/silica composites are presently formed through an *in-situ* polymerization process.^[14] Typically, such reactions require a catalyst and the silica particles require a surface pre-treatment. The solid particles are then dispersed in ϵ -caprolactam and the mixture is heated at relatively high temperatures ($>200^\circ\text{C}$) to form nylon-6 through a ring opening polymerization (ROP) mechanism. However, due to the thermal energy originating from the heating process, sol particles collide which lead to aggregation and grain growth of the silica particles.^[14] The phenomenon becomes particularly problematic when the silica particles are below 50 nm in diameter.^[16] Furthermore, such a process is limited to the

family of nylons that rely on a ROP mechanism, where the monomer can act as polymer precursor. The method is therefore not amenable to nylons where a condensation mechanism is involved (e.g. nylon-6,6). In their recent study, Reynaud et al.^[16] used the *in-situ* polymerization method and found that small silica particles (≈ 12 nm) 'do not appear as single entities but tend to form aggregates'. By contrast, larger particles (≥ 50 nm) 'are rather well dispersed'. Our study departs from those results and demonstrates that for particles in the 10–30 nm range, a low degree of aggregation could be obtained. We ascribe this result as a consequence of the new synthesis method we employed (*vide infra*).

The aim of the present investigation was to a) seek a general and facile synthesis strategy by which nanoscale inorganic filler particles (<30 nm) can be well dispersed into a polyamide matrix, b) subject the composites to mechanical tests and compare processing conditions. The motivation to obtain good dispersion stemmed from the observation that if any properties are to be further improved, then the distribution of the inorganic filler particles in the polymer matrix has to be as homogeneous as possible. Our procedure was based on selecting appropriate reaction conditions, particularly with regard to solvent choice and pH control. The silica dispersion remained stable due to sufficient proton adsorption that maintained a (positively) charged surface in solution. The best result was therefore obtained from addition of silica particles (either from aqueous or ethanolic acidified sol medium) to formic acid as bulk solvent; the least successful result (premature gel-formation and inhomogeneity) was obtained from a basic (pH 8–10) silica sol medium added to cresol. Through addition of small amounts of aqueous HCl, a positive charge on the silica surface was maintained at ca. pH 1–2. Such a low pH was necessary since the iso-electric point of silica is in the pH 2–3 range. Solvent use was kept to a minimum to ensure concentrated, highly viscous solutions could be cast on clean glass surfaces followed by a combination of vacuum and heat (60 – 80°C) treatments to remove solvent.

The appropriate choice of organic solvent was essential. For example, although cresols, trifluoroethanol and chloroxylenes all dissolve polyamides over a period of time, such solutions showed immediate and unwanted gel-formation upon addition of the sol. Formic acid not only dissolves nylon-6, but compared to the other solvents is a much stronger Brønsted acid and hence effective in keeping the charge on the silica surface, prohibiting dissipation of charge and consequent gel-formation. Polyamides react strongly with acids such as H_2SO_4 , HCl and HCO_2H and it has been established that dissolution of this class of polymers is associated with the protonation of the amide group.^[25–27] We utilized the *polyamide:formic acid:water* ternary phase diagram^[28] to obtain an estimate of nylon-soluble regions (as mol-% fraction).

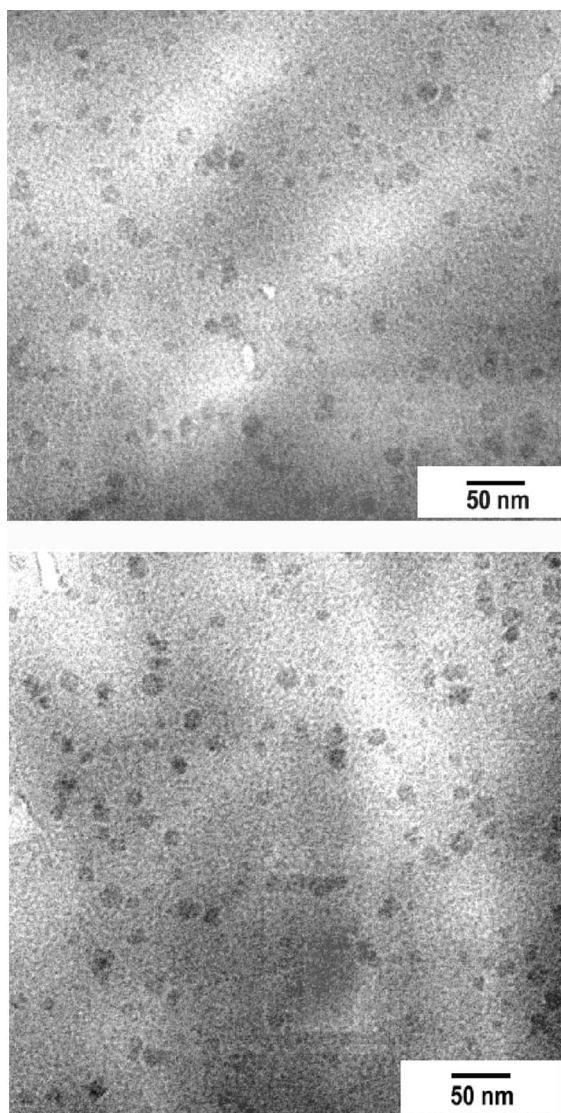


Figure 1. TEM images of a nylon-6/silica (3 wt.-%) nanocomposite. The micrographs were obtained from ultramicrotoming different regions of the composite.

The ‘dissolution-method’ used for this composite system has a number of advantages when compared to other preparative methods currently available, namely a) the formation and isolation of the desired composite could be performed at ambient temperature, b) no particle surface modification, initiator, or catalyst was required c) a variety of inorganic filler types could be considered, also metallic and non-oxidic phases, and d) the method was suitable for all nylon classes susceptible to formic acid dissolution, including nylon-6,6. Because the synthesis procedure can be conducted under mild conditions, the filler size in the final composite was unchanged compared to the filler size in the initial sol (and can thus be tuned to the appropriate size); the filler sizes are not affected by the reaction conditions employed. Clear, transparent solutions were obtained which resulted in bet-

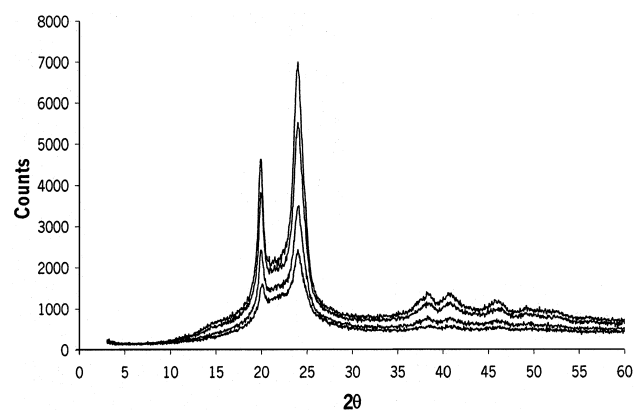


Figure 2. XRD spectrum of nylon-6 with variable quantities of silica filler added. The nylon-6 is semi-crystalline and the silica phase is amorphous. The spectrum with highest intensity (top) is pure nylon-6, and in decreasing order of intensity, spectrums are shown with, respectively, 3, 15 and 30 wt.-% silica additions.

ter control of homogeneity at the macromolecular level. This is an important requirement for all ensuing properties/processes to be investigated, for example in the areas of chemical modifications (e.g. addition of soluble organic dyes^[29] and fire retardants^[30]), mechanical reinforcements (e.g. formation of transparent electrospun fibers^[31]) and processing (e.g. spin coating, casting).

The polyamide matrix contains the smallest spherical silica nanoparticles with negligible aggregation in the range 10–30 nm reported to date (see Figure 1). For the TEM investigation the sample was ultramicrotomed to a thickness where the silica particles showed good visual contrast with the polymer matrix. TEM pictures taken from different sample localities revealed an even distribution of the silica particles throughout the matrix. The TEM micrographs indicated several unique properties of the composite resulting from the new synthesis method, namely a) silica particles were all in the 10–30 nm size range, b) silica particles were non-aggregated and c) silica particles were rather well dispersed (good homogeneity) inside the polyamide matrix. Figure 1 shows the TEM pictures of a sample containing 3 wt.-% silica. We chose filler additions in the range 1–5 wt.-% because it is evident from current literature that a maximum of 5 wt.-% filler loadings already leads to an optimum in mechanical properties.^[14]

The crystallinity of the formed composites was followed with X-Ray diffraction (XRD) as a function of wt.-% filler added. The XRD data of a composite containing variable amounts (0, 3, 15, 30 wt.-%) of silica filler percentage is shown in Figure 2. It was observed that the nylon-6 component was semi-crystalline while the silica phase was, with no discernable peaks, amorphous.

It appeared that even at very low (3 wt.-%) silica additions, a slight decrease in the degree of nylon crystallinity was caused. We note that polyamides with an absence or very low degree of crystallinity are utilized as transparent

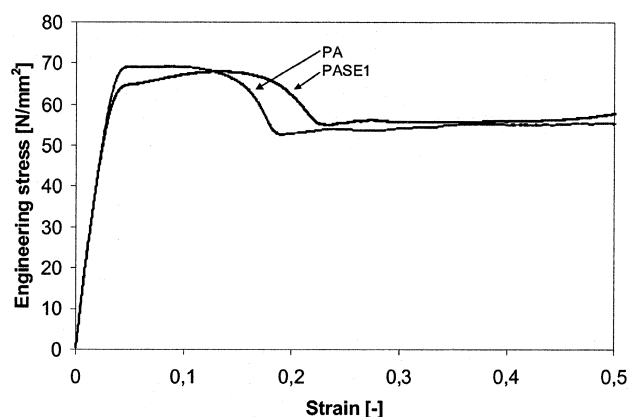


Figure 3. The tensile stress of a composite with 1 wt.-% filler (PASE1) compared to pure polyamide (PA). The composite was compression moulded from silica sol dispersed in ethanol.

nylons, used for food packaging as well as for medical and biological applications.^[22]

All composites were subjected to compression moulding prior to mechanical testing. The media (water vs. ethanol) in which the silica sol was initially prepared influenced the mechanical results. Composites derived from water-suspended silica particles were brittle and broke during determination of the elastic modulus at ca. 2–3% strain; the yield stress was not reached. This result was somewhat akin to that found by Reynaud et al.^[16] where they noted for ‘smaller particles, the draw stress was not reached, the rupture occurring rapidly after the yield point’. We obtained much improved results from composites that were formed from ethanol-suspended silica particles. In such cases the composite did not rupture immediately after the yield point. It started to yield at 4% while at 20% a complete neck was formed and a strain-at-break of >0.5 could be reached. The water vs. EtOH difference was ascribed to the media’s different behavior upon composite melting during moulding, in which case the silica-water system presumably led to more aggregation and probably some degree of degradation, while in the case of silica-ethanol system, these obstacles were either minimized or not encountered. Furthermore, there was a distinct decrease in yield stress from 68 MPa for pure nylon-6 to 65 MPa for a 1 wt.-% silica composite, which is a promising result with respect to impact toughness. Impact toughness is a measure of the amount of energy dissipated when the sample breaks and is typically derived from a high-speed (1 m/s) tensile test on a notched sample. However, analysis of the tensile curves (Figure 3) gives a qualitative measure for the degree of toughness because the dissipated energy is higher if there is delocalization of deformation. The localization effect is observed in tensile tests in the presence of a neck that is formed. When a small neck is formed (large decrease in stress) then the deformation is localized and if no neck is formed (no decrease in stress) then the

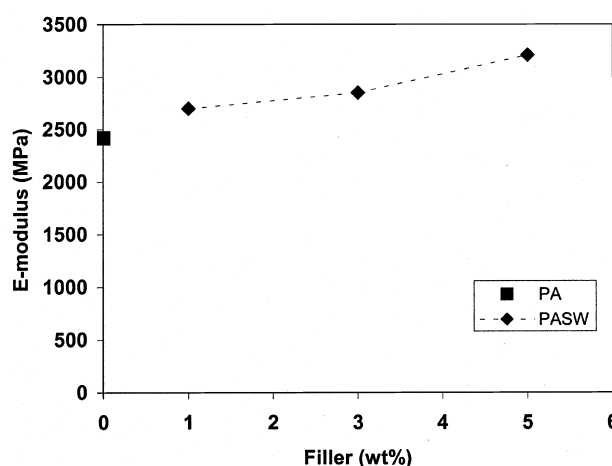


Figure 4. Variation in the elastic modulus for composites with different filler percentages. PA = polyamide (nylon-6), PASW = polyamide with silica (10–30 nm) in water media.

sample is deformed more homogeneously, resulting in a higher impact toughness.

The elastic modulus for composites with different filler percentages as tested with an extensometer is shown in Figure 4. Already with 1 wt.-% silica addition, an increase in E-modulus could be observed; an E-modulus increase for 3 and 5 wt.-% loadings was sustained. Data points represent the average value after four tests for each sample.

Conclusions

The synthesis method described can be generally applied to all classes of polyamide-based composites that are susceptible to solvent dissolution. Inorganic filler material can be readily incorporated into the polymer matrix resulting in a hybrid nanocomposite with unprecedented control in particle size, mono-dispersity and homogeneity. The procedure relied on initiating a positive charge on the silica surface and appropriate solvent choice was important to obtain satisfactory homogeneity. Sample processing conditions (drying, dispersion media) were of particular concern for mechanical testing. An increase in E-modulus as a function of filler percentage added (0–5 wt.-%), a small decrease in yield strength (improvement in impact toughness) and a strain-at-break of >0.5 (from ethanol derived silica sol) were obtained.

Experimental Part

Synthesis

Silica nanoparticles were generously provided by Nissan Chemicals (Japan) under brand name Snowtex™ as an acidified aqueous sol with particle sizes 10–30 nm. Ethanol based silica particles were prepared in-house. Polyamides (as pellets) and reagent grade formic acid were obtained from Aldrich. In a nitrogen atmosphere, nylon-6 (≈ 10 g) was added to formic acid (45 mL) and stirred until a clear solu-

tion emerged (≈ 3 h). The pH of the solution was tested with Universal Indicator and, if necessary, lowered with a drop or two of concentrated aqueous HCl until finally pH ≈ 2 was reached. The silica sol was added to the nylon solution and stirred gently (rapid stirring enhances aggregate formation) at room temperature for 1–3 h. The solution was then cast onto clean glass, and the solvent evaporated under a flow of nitrogen gas. Further vacuum and heat (60–80 °C) treatment formed dry, opaque composites consisting of amorphous silica and semi-crystalline nylon-6.

Instrumentation

Transmission electron microscopy (TEM) micrographs were obtained using a JEOL 2010F equipped with a field-emission gun operating at 200 kV. TEM samples were prepared by ultramicrotoming thin sections of the polyamide/silica nanocomposite with a diamond knife. These thin sections were then captured on Formvar coated Ni grids. The particles observed in the micrographs were unambiguously identified as silica by using both X-Ray energy dispersive spectrometry (EDAX R-TEM sapphire detector equipped with a super-ultra thin window) and energy filtering (Gatan Imaging Filter 2001) attached to the TEM.

Powder XRD data were collected on a Philips X'Pert-1 PW3710 diffractometer using Cu K_{α} ($\lambda = 1.542$ Å) radiation with a secondary curved graphite monochromator. XRD data verified the amorphous state of the silica particles (no peaks observed) while the nylon-6 was semi-crystalline.

Quantitative XRF was used to determine the amount (as wt.-%) silica present in each bulk sample. Analysis was performed on a Philips PW 1480/10 fluorometer (Eindhoven, The Netherlands). The calculation method used the program FPMulti that has been previously described.^[32]

Mechanical Testing

All samples were prepared with compression moulding. The polymer composite was melted and given a certain shape by compression of the melt into the mould. The samples were dried in a vacuum oven at 80 °C for 2 d. Plates of 1 mm thickness were moulded and the test samples were machined out of the plates. The elastic modulus was measured at a tensile speed of 1 mm/min and the displacement was measured with an extensometer with a gauge length of 10 mm. Yield stress, strain-at-yield and strain-at-break were recorded on a Zwick Z010 apparatus.

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