

Synthesis and application of silica/alumina mixed oxide nanoparticles for transparent polyurethane nanocomposites

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Introduction

Reinforcing polymers with the help of inorganic nanoscale particles has opened a wide field of properties that was inaccessible by conventional fillers. Polymer properties such as tensile strength, wear and scratch resistance can be improved without deterioration of optical properties and embrittlement [1-3]. Nanoscale fillers are particularly interesting in transparent applications such as clear coating systems. In order not to interact with incident light and thus cause a reduction of transparency either the particle size of the filler has to be in the lower nanometre range and/or the refractive index of the particles has to match that of the polymer matrix.

A promising solution to improve the coating transparency is to match the refractive indices of filler particles to that of the polymer matrix. Thus no scattering of light occurs on filler surface and the coating remains transparent.

Commercially available two pack polyurethane clear coating systems typically have refractive indices of about 1.50. Particles in that range can be produced by mixing silica with alumina, titania or zirconia in an adequate proportion. Only by mixing silica with alumina having refractive indices of 1.46 and 1.69, respectively, was it possible to produce continuously amorphous nanoparticles in the RI range in question. To obtain optimum transparency in the lacquer the refractive index throughout the particles has to be constant. In consequence the synthesised material has to be a homogeneously mixed oxide and not a nanocomposite of the two oxides used. Furthermore a spherical morphology is preferable due to low specific surface area which results in low viscosity of the uncured coating composition.

Nanometre sized oxide particles are commonly synthesised by sol gel route, more specific the Stöber process [4]. The advantage of this synthesis route is that high monodispersity can be achieved and resulting nanoparticles are non-agglomerated. In the case of mixed oxide particles this method has the

major drawback that the precursors have to show similar reaction rates to form mixed oxide particles of a given composition [5]. Flame spray synthesis is an alternative allowing the production of a variety of powders only limited by the miscibility of precursors [6]. To produce mixed oxide nanopowders precursors of component A and B are mixed in the required molar ratio and subsequently processed. As the precursor feed is operated with a syringe pump high flexibility concerning changing compositions is provided. Also long term experiments with regular sampling and determination of refractive indices showed high process stability.

Experimental

The flame spray device consists of gas and liquid feed controllers, a spray burner and a powder collection unit. The flow rate of the precursor solution was controlled volumetrically via a continuous double syringe pump to the capillary tube and atomized at the exit by the oxygen supplied through the centre gas outlet. The powder produced was collected on a glass fibre filter by means of a vacuum pump. To produce silica/alumina mixed oxide nanoparticles of a certain composition precursors A and B, in this study hexamethylenedisiloxane (SiO_2) and aluminium sec.-butoxide (Al_2O_3) respectively, are mixed in the required molar ratio and subsequently processed.

X-ray diffraction (XRD) was used to determine the phase composition of the powders. The analysis was performed with a Siemens D500 instrument. Diffraction patterns were recorded from 20° to 80° 2θ angles using Ni-filtered $\text{CuK}\alpha$ radiation. Analysis of the particle morphology was performed by means of a transmission electron microscope (TEM). Refractive index (RI) of the powders was determined using the Becke Line Method [8]. The accuracy of measurement is given by the step size and accuracy of immersion oils used and was 0.002.

10 and 20 wt.% mixed oxide nanopowder of refractive index 1.512 and for comparison the same amount of silica nanopowder (Aerosil OX50) having

a refractive index of 1.460 was incorporated in a Desmophen/Desmodur polymer matrix. Coatings were cured for 1 h at 80°C and transmission measurements carried out to determine light scattering caused by refractive index matched particles and silica particles having different refractive index.

Results and Discussion

The theoretical refractive index of SiO₂/Al₂O₃ mixed oxides calculated by the equation of Huggins and Sun [7] is shown in Fig 1 along with measured refractive indices of SiO₂/Al₂O₃ mixed oxide powders produced in this work. Up to 60 wt% alumina calculated values correspond very well with those measured.

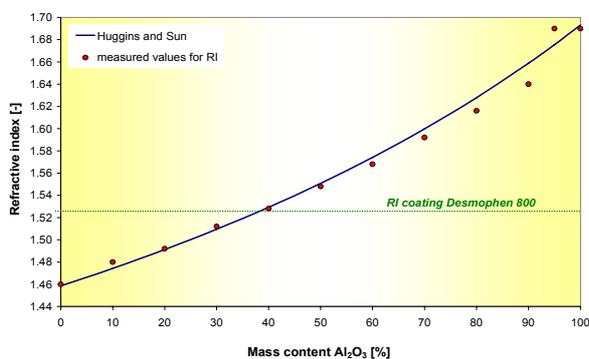


Figure 1. Measured RI (points) and theoretical RI (line) calculated by the equation by Huggins and Sun

XRD measurements show a persistent amorphous phase up to 60 wt% of Al₂O₃. At higher alumina contents several peaks that are typical for crystalline γ -alumina phases appear. This and the deviation of measured refractive index from theoretical starting at 60 wt% alumina indicates the formation of crystalline domains for high alumina content whereas for lower alumina content silica prevents formation of crystalline phases and provide for amorphous behaviour. As shown in Fig. 2 mixed oxide nanoparticles show spherical morphology.

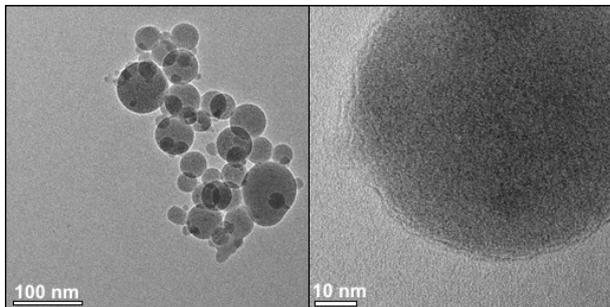


Figure 2. TEM images of mixed oxide nanoparticles containing 70 wt% SiO₂ and 30 wt% Al₂O₃

The results of transmission measurements for compounds filled with 10 and 20 wt% particles are shown in Fig.3. All results are given relative to

unfilled coating. Films reinforced with refractive index matched particles P29 (green line) show higher relative transmission than those filled with silica particles (red line). Transmission can even be improved by the use of a dispersing agent (blue line).

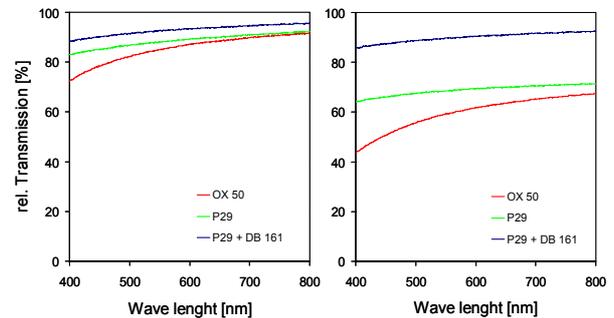


Figure 3 Relative transmission of coatings reinforced with 10 and 20 wt% filler particles, respectively

Conclusion

In this work the production of non aggregated spherical nanoparticles of silica/alumina mixed oxide via Flame Spray Synthesis was achieved. Furthermore the refractive index of the nanoparticles was adjusted to match the refractive index of a commercially available coating system.

Refractive index matched silica/alumina mixed oxides can be produced in the RI range between 1.42 and 1.55. In the amorphous range, up to 60 wt% alumina, measured values for RI are in good agreement with values calculated with the equation by Huggins and Sun. For higher alumina contents deviation between calculated and measured values can be noticed and also the existence of crystalline peaks in XRD.

Coatings reinforced with RI-matched nanoparticles showed significantly higher transmittance than coatings filled with the same amount of silica nanoparticles of comparable size. Thus a minimum of light scattering on the polymer/particle interface can be observed and can be attributed to minimum differences in refractive index.

References

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