

# Material Properties of Polymer Nanoparticle Composites for Micro Optical Applications

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## ABSTRACT

Nanosized ceramics, highly dispersed into polymer matrix materials, are widely being discussed for the modification of polymer properties. The addition of ceramics with primary particle sizes of several nanometres allows specific tailoring of relevant optical properties, e. g. refractive index and optical damping. Also the influence of ceramic nanoparticles on the mechanical properties e. g. tensile strength, of the polymers, was analysed. A process chain for polymer nanoparticle composite formation using improved dispersing methods to destroy ceramic agglomerates was developed to obtain polymer nanoparticle composites. In microsystem technologies the durability of a polymer device is of great importance. Therefore, the influence of elevated temperatures on material properties like refractive index, optical damping and tensile strength was investigated.

**Keywords:** polymer, nanocomposite, refractive index, tensile strength, ageing

## 1 INTRODUCTION

Polymers have been blended with different inorganic fillers to alter material properties like mechanical strength [1] and optical properties like refractive index [2]. Polymer nanocomposites are to be assumed to have a great potential for applications in fields of high technology, e.g. aerospace [3] and automotive [4]. Dispersing ceramic particles into a polymer leads to imperfections and disturbances in the resulting composite matrix. Disturbances of the matrix become less with decreasing filler particle size but the interaction of the fillers with the polymer matrix increases due to an increased specific surface of the particles. Best interaction is assumed by using fillers with a surface polarity adapted to the polarity of the surrounding polymer matrix. Current work deals with the influence of ceramic nanoparticles either with a hydrophilic or hydrophobic surface polarity on the optical properties like transmission and refractive index and on tensile strength of the composites. For assuring long time stability of the composite materials the influence of ageing at elevated temperatures was investigated.

## 2 EXPERIMENTAL

### 2.1 Materials

As polymer host system, Plexit 55, a mixture of 65% PMMA and 35% MMA from Roehm Degussa was used. Hydrophilic alumina Al<sub>2</sub>O<sub>3</sub>-C with a primary particle size of 13 nm and hydrophobic Aerosil R8200 with a primary particle size of 12 nm were also purchased from Degussa. Irgacure 1700 from Ciba Speciality Chemicals as polymerisation initiator and INT-54 from Würtz as mould release agent as well as Dilauroyl peroxide from Fluka as thermal curing agent were further mixed into the reactive resin.

### 2.2 Nanocomposite formation

Plexit 55 was diluted with 20 wt% MMA to decrease viscosity. 0.5 wt% INT-54 and 1 wt% Irgacure 1700 were added using a high speed stirrer UltraTurrax from IKA. To disperse nanoceramic particles into the polymer matrix system for tensile testing also a high speed stirrer was used. For formation of nanocomposites for optical tests either an UltraTurrax or a high pressure homogeniser (HPH) EmulsiFlex C5 from Avestin with a maximum working pressure of 10<sup>8</sup> Pa was applied. The dispersions were degassed in an ultrasonic bath at 40°C for 15 minutes. The polymerisation was performed using a UV-photo moulding setup for 30 minutes. In a subsequent thermal curing step at 70°C for 24 hours remaining monomer units were polymerised using Dilauroyl peroxide as initiator. Resulting PMMA-nanocomposite solids were granulated with a granulator.

### 2.3 Fabrication of Test Specimens

A specimen design following DIN EN ISO 527-2 [5] was chosen for tensile testing. Test specimens were fabricated on a Ferromatic Milacron E 50 S injection moulding machine. Polymer melt temperature was 205°C. Mould temperature was 100°C and injection pressure 850 bars.

## 2.4 Ageing

Ageing of the specimens was performed according to DIN ISO EN 2578 [6]. Temperature was set to 70°C well below the glass transition temperature of the polymer ceramic composites [7].

## 2.5 Analysis

Slices for TEM investigations were cut with a Leica EM UC6 Microtome. The thickness of the slices was 30 nm – 50 nm. TEM images were taken using a Zeiss EM 109 transmission electron microscope working with energies of 50 and 80 keV, respectively, equipped with a 1.8 Megapixel CCD camera. The refractive indices of the polymer nanocomposites were measured using an Abbé refractometer with a broad band light source and an IR camera. Transmission behaviour was analysed with a getSpec NIR1.7-128-TS spectrometer. Tensile testing of the PMMA nanocomposites was performed using an Instron 4505 tensile testing machine with a 50 kN load cell. Thermal ageing took place in an oven at 70°C.

## 3 RESULTS AND DISCUSSION

Transmission losses due to Rayleigh scattering are dominating in polymer nanocomposites [8]. Therefore, deagglomeration of the ceramic powders is essential for good transmission properties of the nanocomposites.

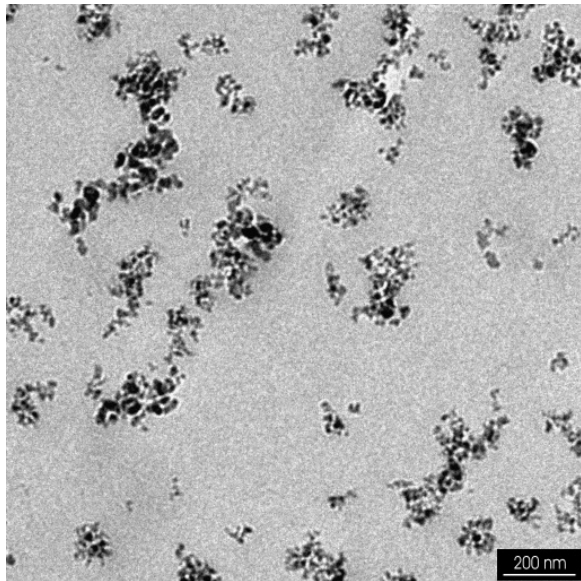


Figure 1: 10 wt% of Aerosil R8200 in a PMMA matrix dispersed with an UltraTurrax.

In general, high shear forces during homogenisation lead to a homogenous distribution of ceramic particles with sizes in the range of the primary particles. In case of the

hydrophobic particle surface of the Aerosil R8200 powder, highest shear forces of the HPH result in a smaller particle size of ceramics in the polymer matrix, as can be seen in figure 1 and figure 2, respectively. Figure 1 shows a TEM image of a polymer host system containing 10 wt% of Aerosil R8200 dispersed by using an UltraTurrax high speed stirrer. As can be seen, agglomerates in the range of several hundred nanometres could not be destroyed and therefore remain in the composite. The TEM photograph in figure 2 shows a sample with the equal amount of hydrophobic Aerosil in the polymer being incorporated into the matrix by applying the high pressure homogeniser with  $10^8$  Pa. The resulting particles in the nanocomposite are of smaller size leading to an improved transmission property compared to the sample shown in figure 1.

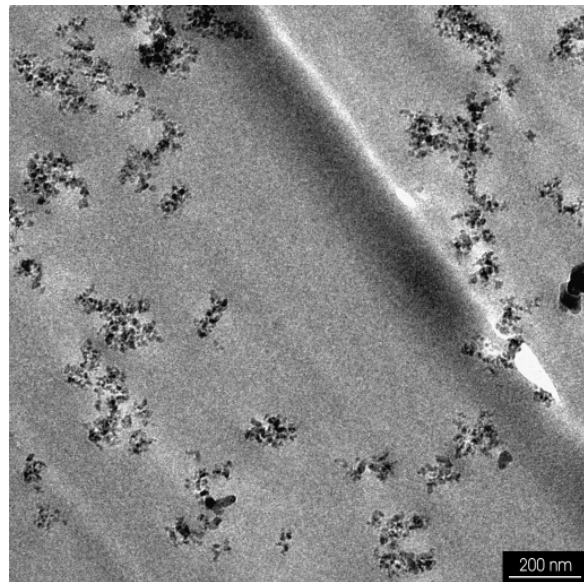


Figure 2: 10 wt% of Aerosil R8200 in a PMMA matrix dispersed with a high pressure homogeniser ( $10^8$  Pa).

The main cause avoiding the reagglomeration of the Aerosil particles after applying highest shear forces using the HPH is the fact that the hydrophobic nanoparticles are adapted more suitable to the surrounding polymer matrix. Therefore, a steric stabilisation of the particles in the polymer matrix is realised leading to less reagglomeration in the polymer nanocomposite compared to hydrophilic alumina powders, as can be seen in figures 3 and 4, respectively.

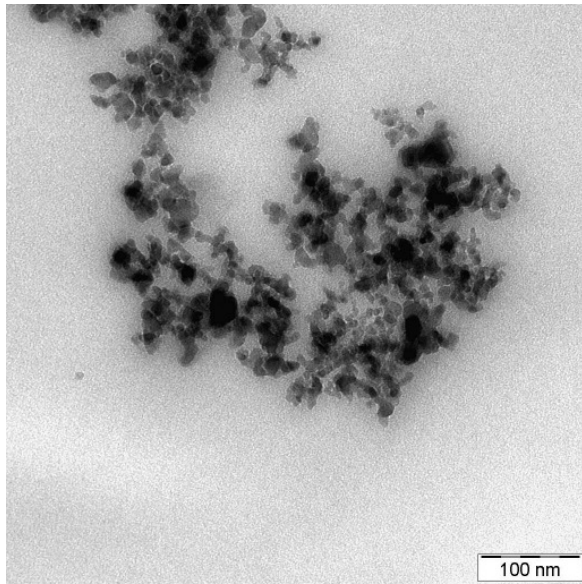


Figure 3: 1 wt% of  $\text{Al}_2\text{O}_3\text{-C}$  in PMMA dispersed using a high pressure homogeniser ( $10^8$  Pa).

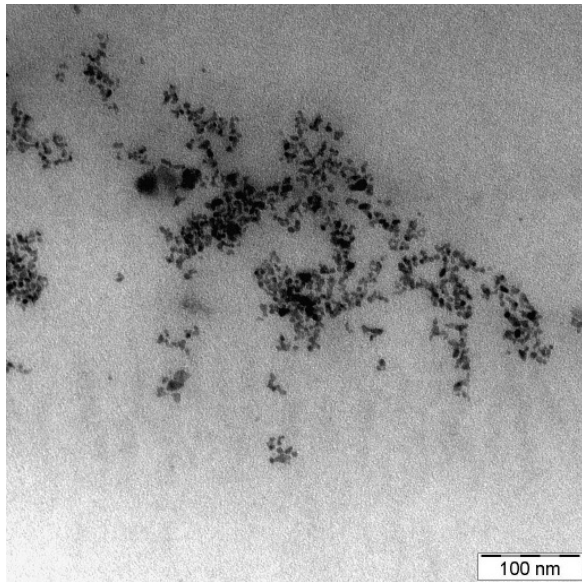


Figure 4: 1 wt% of  $\text{Al}_2\text{O}_3\text{-C}$  in PMMA dispersed using a high speed stirrer.

In case of hydrophilic alumina C as ceramic filler in the nanocomposite, a mirror-inverted result is obtained. Also, the HPH deagglomerates the ceramics better than the UltraTurrax does but due to the high surface energy the deagglomerated ceramic particles tend to reaggregate [1], as can be seen by TEM investigations (figure 3). Therefore, in case of a hydrophilic particle surface, lower shear rates lead to a better particle distribution in the polymer matrix

because of weaker reagglomeration forces. The resulting particle size also affects the transmission of the nanocomposites due to increased contribution to scattering over the entire period of thermal ageing (figure 5).

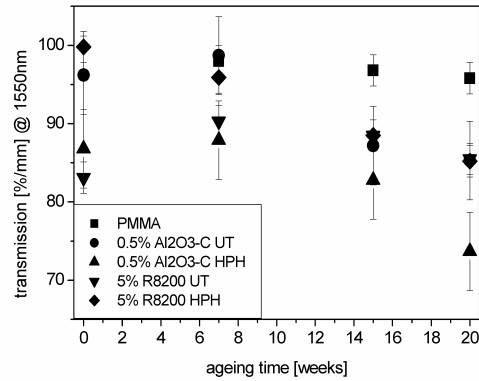


Figure 5: NIR transmission of unfilled PMMA compared to PMMA-Aerosil and PMMA- $\text{Al}_2\text{O}_3\text{-C}$  composites prepared using an UltraTurrax and an HPH, respectively.

Performing ageing tests over 20 weeks at  $70^\circ\text{C}$  reveals that the temperature influences the transmission of the composites in the near infrared. After an initial increase of transmission due to solvent evaporation, in the following the transmissions of polymer nanoparticle composites tend to fall more rapidly than the transmission of pure PMMA.

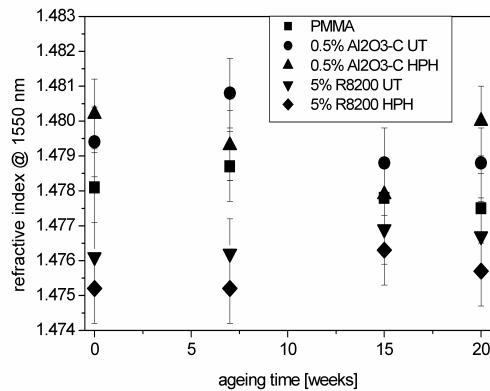


Figure 6: Ageing behaviour of refractive indices at 1550 nm.

During ageing at  $70^\circ\text{C}$  for several weeks the refractive index values vary. As shown in figure 6, the refractive indices of pure PMMA and PMMA-Aerosil composites change less than the values of PMMA-alumina composites. This specific ageing behaviour can also be attributed to the differences in particle surface properties where

hydrophobic Aerosil powder is adapted better to the polymer matrix system than hydrophilic alumina. Though the values for the refractive indices vary, only a small change within the error of the measurement occurred during ageing, as can be seen in figure 6.

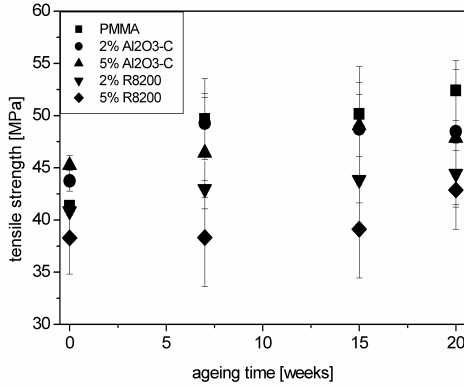


Figure 7: Tensile strength of nanocomposites aged for 20 weeks at 70°C.

Ageing tests of the tensile strength of PMMA-ceramic nanocomposites reveal that initially PMMA-alumina composites are tougher than unfilled PMMA specimens whereas PMMA-Aerosil composites are less stable than pure PMMA (figure 7). In the course of the ageing process the tensile strength values of the tested specimens increase which can be attributed to chain growth. As can be seen in figure 7 the tensile strength of pure PMMA increases more than that of the composite materials. This is caused by increased brittleness of thermally aged polymer nanocomposites due to imperfections in the matrix induced by the ceramic nanoparticles incorporated into the polymer. Modifying the surfaces of alumina powders, e. g. by applying a silane suitable to the polymer matrix, could lead enhanced deagglomeration of the particles and a more stable distribution in the polymer nanocomposite resulting in improved transmission values.

#### 4 CONCLUSION AND OUTLOOK

Polymer nanocomposites based on PMMA and alumina and Aerosil, respectively, possess material properties different from that of unmodified PMMA. The established process chain allows for tailoring the refractive indices of polymer-nanocomposites while simultaneously keeping the transmission high enough for applications in micro optics. Also the tensile strength of PMMA can be increased incorporating alumina-C nanoparticles into the polymer matrix. Unlike the optical properties transmission and refractive index which stay in a relatively constant range over an ageing time of 20 weeks at 70°C the tensile strength of the tested polymer nanocomposites is affected by the

elevated temperature. Filled materials become more brittle than the unfilled PMMA specimens and therefore mechanical stability decreases compared to pure PMMA. For a deeper understanding of PMMA-nanoceramic composites, investigations regarding hardness and crack propagation, Young's modulus have to be done. Future work will also be conducted in the field of assembling and housing as well as in designing new optical structures including active electro optical devices.

#### REFERENCES

- [1] H. Fischer, "Polymer nanocomposites: from fundamental research to specific applications", *Materials Science & Engineering C*, 2003, 23, pp. 763-772.
- [2] E. Ritzhaupt-Kleissl, J. Böhm, J. Haußelt, T. Hanemann, "Process Chain For Tailoring the Refractive Index of Thermoplastic Optical Materials Using Ceramic Nanoparticles.", *Advanced Engineering Materials* 2005, 7, No. 6, pp. 540-545.
- [3] J. Njuguna and K. Pielichowski, "Polymer Nanocomposites for Aerospace Applications: Properties", *Advanced Engineering Materials* 2003, 5, No. 11, pp. 769-778.
- [4] Tomova D. and Reinemann S., "Nanopartikel erweitern Anwendungspotenzial", *Kunststoffe* 2003, 7, pp. 18-20.
- [5] DIN ISO EN 527-2, July 1996.
- [6] DIN ISO EN 2578, October 1998.
- [7] E. Ritzhaupt-Kleissl, J. Haußelt, T. Hanemann, "Thermo-mechanical properties of thermoplastic polymer-nanofiller composites.", *Proc. International Conference on Multi-Material-Micro-Manufacture (4M)*, 29.06.-01.07.2005, Karlsruhe, GER.
- [8] P. Ajayan, L. Schadler, P. Braun, "Nanocomposite Science and Technology", Wiley-VCH 2003, p. 140.