Wavelength dependent haze of transparent glass-particle filled poly(methyl methacrylate) composites

Wolfgang Wildner, wildner@lkt.uni-erlangen.de
Dietmar Drummer, drummer@lkt.uni-erlangen.de
Institute of Polymer Technology, Friedrich-Alexander-University Erlangen-Nürnberg, Am Weichselgarten 9, 91058 Erlangen, Germany

Abstract: Glass particles as filler were incorporated in a poly(methyl methacrylate) matrix. The refractive indexes of both materials match at a wavelength of about 400 nm. The effect of particle volume fraction on the light transmittance and light scattering (haze) in dependence of the refractive index difference was studied. The curve shape of the haze in dependence of the wavelength is comparable to that of the refractive index difference, but the base line of the haze increases with the filling grade. This indicates that there are other scattering or absorbing mechanisms, like defects in the filler binding.

1 Introduction

Particle-filled Polymers are normally non-transparent. By the use of a transparent polymer as a matrix and an optical glass with a matching refractive index \( n \) as filler particles, a transparency could be achieved for at least one temperature and wavelength of light. These transparent composites are expected to have, compared to the bulk material, increased mechanical properties (higher stiffness, increased strengths by the use of fibers) a lower expansion coefficient an increased thermal conductivity. In the case, when the particle size \( d \) is one order of magnitude greater than the wavelength of light \( \lambda \) in the visible range (\( d \gg \lambda \)) the light scattering theories of Rayleigh and Mie cannot be applied. [1] First experiments on this subject have been done by Breuer and Grzesitza [2]. They analyzed a mixture between two polymers to adapt the refractive index to that of the used glass fibers. Specimens show a wavelength- (because of the different dispersion) and temperature-dependent extinction-curve of the indecent light. Significant work on this subject has been carried out in Japan by the group of Kagawa. They studied the influence on light transmittance, mechanical and thermal properties of many parameters, such as refractive index difference, particle size, particle surface area and filler content. [3-8]. The investigated materials are an epoxy resin as a matrix and different optical glasses as filler particles. The light transmittance clearly shows a dependence of the refractive index difference because of the different dispersions of the materials. Nevertheless, the light transmittance of the compound is always less than that
of the pure matrix. Weaver and Stoffer [9] investigated glass-fiber reinforced PMMA. They used optical glass as fiber material and studied the optical properties in dependence of the temperature among others. Experiments show that the temperature dependence of the polymer changes with the filling grade due to the reduced thermal expansion of the compound.

To archive a transparent composite, a matching refractive index of filler particles and polymer matrix is necessary. The refractive index of a specific material changes with the wavelength of the incident light (dispersion) and with the temperature of the material. These two dependencies are not the same for commercial available polymers and glasses. Therefore plastics and glasses have a matching refractive index at only specific wavelengths and temperatures. Many publications report investigations about the effects of the refractive index difference between filler particles and the surrounding matrix on the transmission of the compound. Despite the transmission is very important to see through the specimen, it is also necessary that the light is not distracted by the compound for a clear view. Otherwise, objects behind will appear blurry. The amount of distracted light and the haze in dependence of the refractive index difference is analyzed in this paper.

2 Experimental Procedure

2.1 Materials

As matrix, the polymer poly(methyl methacrylate) (PMMA, Plexiglas® 7N by Evonik Industries AG) and as filler the glass “N-PK52A” (Schott AG) was chosen. This glass was selected to obtain a matching refractive index with the polymer matrix for at least one wavelength in the visible range at room temperature. Table 1 shows relevant properties of the glass and polymer.

| Property         | Matrix: polymer | Filler: glass |
|------------------|-----------------|---------------|
| density [g/cm³]  | 1.19 (1)        | 3.7 (1)       |
| refractive index n₀ [-] | 1.4919 (2) | 1.4966 (1) |
| abbe number vₑ [-]  | 55.82 (2)      | 81.52 (1)    |

Table 1: properties of the materials used
(1) according to supplier
(2) in-house measurement

2.2 Milling of glass and characterization of particles

The bulk glass was crushed with a mortar and then thieved by a sieving machine with two laboratory sieves and a mesh width between 63 and 180 µm. Afterwards, the glass was washed with acetone to remove small particles. The glass particles were characterized by SEM-images (SEM Ultra Plus type, supplier: Zeiss), the volumetric and numeric particle-
distribution was determined by the measuring instrument “Morphology” of Malvern Instruments. For each measurement, at least 42000 particles were photographed and analyzed.

2.3 Fabrication of composite

To incorporate glass particles into the polymer matrix the micro-compounder “HAAKE MiniLab” by Thermo Fisher Scientific Inc., with two conical screws was used. The temperature was set to 210°C. To distribute the particles equally in the melt a circle mode was held up for at least 3 minutes. Subsequently specimens were pressed with a thickness about 250 µm and a diameter of 20 mm. The particle volume fraction was controlled by thermal gravimetric analysis (TGA) measurements.

2.4 Characterization of optical properties

2.4.1 Refractive index

The refractive Index of the polymer was determined with the refractometer (Abbemat WR MW by Anton Paar) which works by the total reflection method. To archive an optical contact between the polymer and the measuring prism, the contact liquid Diiodmethan with a refractive index \( n_d \) of 1.74 was used. To determine whether the refractive index of the particles is higher or lower than that of the surrounding PMMA-matrix the oblique illumination and the Becke line test were utilized at different wavelength under a microscope.

2.4.2 Haze

The Haze of the specimens was analyzed with an UV/VIS spectrometer (Lambda 18 by Perkin Elmer Inc.). Therefore, the transmission and the light scattering of the specimens were investigated at different wavelengths. Figure 1 shows the fundamental set up for these measurements. For transmission measurements, all the incoming light is collected by the sphere and so measured by the detector (a). If the beam trap is installed at the opposite position to the opening of the sphere, only the scattered light is measured by the detector. The undistracted light beam is completely absorbed by the beam trap (b).
The Haze was calculated using the following equation according to [10].

\[
\text{Haze in } \% = \left( \frac{T_4}{T_2} - \frac{T_3}{T_1} \right) \cdot 100
\]  

(1)

Whereas \( T_1 = \text{total incoming light} \), \( T_2 = \text{transmission of the sample} \), \( T_3 = \text{scattered light of the instrument} \), and \( T_4 = \text{scattered light of the sample and the instrument} \).

To determine the haze only caused by the particles and not by the surface of the specimen, the haze of a non-filled specimen was subtracted by the haze of the filled specimen.

3 Results and discussion

3.1 Particles

The numeric particle distribution is shown in Figure 2. The smallest particles observed have a diameter of 2 \( \mu \text{m} \). The volumetric particle distribution of washed particles is characterized as following: \( d_{10,3} = 116.3 \), \( d_{50,3} = 178.7 \), \( d_{90,3} = 246.7 \). In Figure 2 can be seen that there is, despite of sieving and washing, a considerable amount of small particles (d < 63 \( \mu \text{m} \)). Nevertheless, the volumetric amount of these particles is quite small so that they should have a relatively small influence on the light scattering in the compound.
Figure 3 shows the appearance of the glass particles, observed by scanning electron microscopy. According to the production process, they have an irregular shape and vary in size.

![SEM-image of washed glass particles](image)

**Figure 3: SEM-image of washed glass particles**

### 3.2 Compound

Figure 4 shows a computed tomographic image (CT-image) of the particles for two different filling grades. As it can be seen, the particles are distributed homogeneous in the analyzed area. According to the TGA measurements the filler content of the specimen tested is 3.9 vol.-%, 9.4 vol.-% and 17.3 vol.-%.

![CT-Images of two specimens with a different filling grade](image)

**Figure 4: CT-Images of two specimens with a different filling grade**

### 3.3 Optical properties

Figure 5 shows the measured refractive index for PMMA and the refractive index of the glass N-PK52A according to the data sheet in dependence of the wavelength. The modulus of the refractive index difference is represented by the dotted line. The refractive index of both materials is the same at a wavelength of about 400 nm. The curve progression of the polymer was calculated with the Cauchy Equation (2). The constants of the polymer were calculated from the measured values.
The curve progression of the glass was calculated with the Sellmeier Equation (3) with constants according to the data sheet.

\[ n(\lambda) = A \frac{B}{\lambda} + C \frac{1}{\lambda^2} + D \frac{1}{\lambda^6} \quad (2) \]

\[ n^2(\lambda) = 1 + \frac{B_1 \lambda^2}{\lambda^2 - C_1} + \frac{B_2 \lambda^2}{\lambda^2 - C_2} + \frac{B_3 \lambda^2}{\lambda^2 - C_3} \quad (3) \]

Figure 5: refractive index of PMMA Plexiglas 7N and glass N-PK52A at 23°C

Observations of the refractive index difference by the oblique illumination method at different wavelengths nearly confirm these measurements, Figure 6. At a wavelength of 400 nm the particle is nearly invisible. At longer wavelengths a shadow at the side of the particle facing the less illuminated side of the picture can be clearly seen. This indicates that the refractive index of the particle is higher than that one of the matrix.

Figure 6: oblique illumination in the microscope with a particle at different wavelengths

The analysis of the transmission and the haze of the specimens have been performed at a temperature of 23°C. To exclude the haze of the surface of the specimen and only to investigate the haze caused by the particles, the haze of a pure PMMA sample was subtracted from the haze of the filled samples. Figure 7 shows this calculated haze for the specimen with a filler content of 9.4 vol.-% glass in dependence of the wavelength. The relatively high scattering of the unfilled specimen is mainly caused by the surface.
Figure 7: intensity of transmission, scattering and calculated haze of a specimen filled with 9.4 vol.-% glass and a thickness of 250 µm

Figure 8 shows the particle caused haze for different filling grades. It can be seen in that the haze of the glass-filled specimens changes with the wavelength and the filler content. At the matching refractive index, the hazes of all specimens show a minimum. The curve shape of the haze in dependence of the wavelength is comparable to that of the refractive index difference. The absolute change of haze in dependence of the wavelength increases with higher filling grades. Nevertheless, the particle-caused haze approaches zero only for the low filler content of 3.9 vol.-%, even if the refractive index of the glass and the polymer match totally. The amount of scattered light is nearly the same for all specimens, as the transmission decreases with higher filling grades particularly for shorter wavelengths which leads to higher haze according to equation (1). This decrease in transmission also can be seen as a slight yellow appearance of the specimens with higher filling grade. Measurements of the solution viscosity do not show an indication for aging of the material during the production process. Further investigations will deal with this scattering and the decrease in transmission of the specimens.

Figure 8: particle caused haze of specimens with different filling grades and a thickness of 250 µm
4 Conclusion

The effect of the refractive index difference between a polymer matrix and glass particles as filler on the haze has been studied. The haze shows a minimum at the wavelength with matching refractive indexes and the change of haze increases with higher filling grade. However, the minimum haze is about 10 % and 5 % for the filling grades of 10 vol.-% and 15 vol.-%. Further work will deal with the high haze for higher filling grades and set up a relation between refractive index difference, haze and clear view through the specimens.

5 Acknowledgment

The authors gratefully acknowledge the German Research Foundation (DFG) for the funding of the work, the Institute of Polymer Materials for the use of their micro-compounder, and the industrial partner Evonik Industries AG for providing material.

6 Literature

[1] van de Hulst, H. C.: Light Scattering by Small Particles. New York: Dover Publications, 1981.
[2] Breuer, H., Grzesitz, J.: Trübungerscheinungen in zweiphasigen Polymersystemen (glasfaserverstärkte Polymere), Die Angewandte Makromolekulare Chemie 45 (1975) 681, S. 1-19.
[3] Kagawa, Y., Iba, H., Tanaka, M., Sato, H., Chang, T.: Fabrication and optical/thermal properties of glass particle-epoxy optically transparent composites, Acta Materialia 46 (1998) 1, S. 265-271.
[4] Naganuma, T., Kagawa, Y.: Effect of particle size on light transmittance of glass particle dispersed epoxy matrix optical composites, Acta Materialia 47 (1999) 17, S. 4321-4327.
[5] Naganuma, T., Iba, H., Kagawa, Y.: Optothermal properties of glass particle-dispersed epoxy matrix composite, Journal of Materials Science Letters 18 (1999) 19, S. 1587-1589.
[6] Iba, H., Chang, T., Kagawa, Y.: Optically transparent continuous glass fibre-reinforced epoxy matrix composite: Fabrication, optical and mechanical properties, Composites Science and Technology 62 (2002) 15, S. 2043-2052.
[7] Naganuma, T., Kagawa, Y.: Effect of total particle surface area on the light transmittance of glass particle-dispersed epoxy matrix optical composites, Journal of Materials Research 17 (2002) 12, S. 3237-3241.
[8] Sato, H., Iba, H., Naganuma, T., Kagawa, Y.: Effects of the difference between the refractive indices of constituent materials on the light transmittance of glass-particle-dispersed epoxy-matrix optical composites, Philosophical Magazine B: Physics of Condensed Matter; Statistical Mechanics, Electronic, Optical and Magnetic Properties 82 (2002) 13, S. 1369-1386.
[9] Weaver, K. D., Stoffer, J. O.: Preparation and Properties of Optically Transparent, Pressure-Cured Poly(Methyl Methacrylate) Composites, Polymer Composites 14 (1993) 6, S. 515-523.
[10] N.N.: "DIN EN 2155-9: Prüfverfahren für transparente Werkstoffe zur Verglasung von Luftfahrzeugen; Teil 9: Bestimmung der Trübung," ed: CEN, 1989.