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Research Article

Wavelength Dependent Haze of Transparent Glass-Particle Filled Poly(Methyl Methacrylate) Composites

Wolfgang Wildner and Dietmar Drummer

Institute of Polymer Technology, Friedrich-Alexander-University Erlangen-Nürnberg, Am Weichselgarten 9, 91058 Erlangen, Germany

Correspondence should be addressed to Wolfgang Wildner; wildner@lkt.uni-erlangen.de

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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 nontransparent. By the use of a transparent polymer as a matrix and an optical glass with a matching refractive index n as filler particles, transparency can 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 and an increased thermal conductivity. In the event the particle size d is one order of magnitude greaterthan the wavelength λ 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 materials that have been investigated are an epoxy resin as a matrix and different optical glasses as filler particles. The light transmittance clearly shows the 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. Waver et al. [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 achieve 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, selected plastics and glasses have a matching refractive index only at 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 fact that 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,

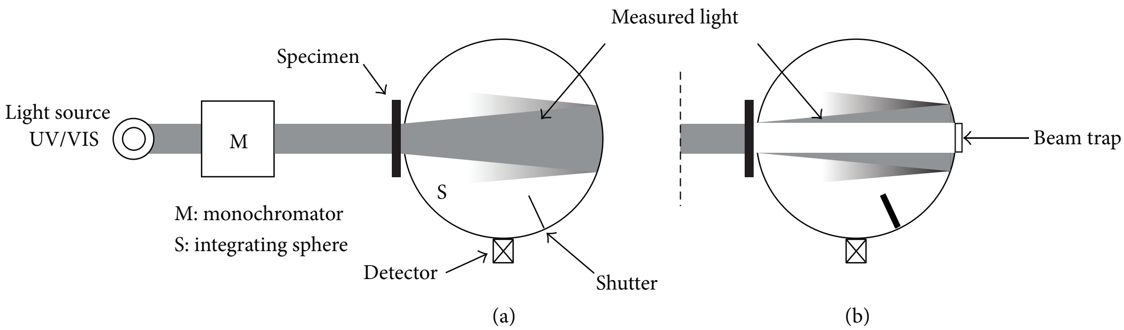

Figure 1: UV/VIS spectrometer with the setup for transmission measurements (a) and measurements of the scattered light (b).

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 a matrix, the polymer poly(methyl methacrylate) (PMMA, Plexiglas 7N by Evonik Industries AG), and as a 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.

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 (mesh width between 63 and 180 μm). Afterwards, the glass was cleaned with acetone to remove the small particles ($d < 63\,\mu$m). The glass particles were characterized by SEM images (SEM Ultra Plus type, supplier: Zeiss), and the volumetric and numeric particle-distribution was determined by the measuring instrument "Morphology" of Malvern Instruments. For each measurement of the particle distribution, at least 42000 particles were photographed and analyzed.

2.3. Fabrication of Composite. To incorporate the glass particles into the polymer matrix, the micro-compounder "HAAKE MiniLab" by Thermo Fisher Scientific Inc. was used. The processing temperature was set to 210°C. To distribute the particles evenlyin the melt, a circle mode was held up for at least 3 minutes. Subsequently, specimens (melt films) 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 a refractometer (Abbemat WR MW by Anton Paar) which works by the total reflection method. To achieve an optical contact between the polymer and the measuring prism, the contact liquid diiodomethane with a refractive index $n_d = 1.74$ was used. To determine whether the refractive index of the particles lies above or below the refractive index of the surrounding PMMA-matrix, the oblique illumination and the Becke line test were utilized at different wavelength under a microscope.

Table 1: Properties of the materials used.

	Matrix: polymer	Filler: glass
Density (g/cm^3)	1.19[1]	3.7[1]
Refractive index n_d (—)	1.4919[2]	1.4966[1]
Abbe number ν_e (—)	55.82[2]	81.52[1]

[1] according to supplier; [2] in-house measurement.

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 measured in the visible range. Figure 1 shows the fundamental setup for these measurements. For transmission measurements, all the incoming light is collected by the sphere and measured by the detector (a). If a 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]:

$$\text{Haze in } \% = \left(\frac{T_4}{T_2} - \frac{T_3}{T_1}\right) \cdot 100, \quad (1)$$

where T_1 is the total incoming light, T_2 is the transmission of the sample, T_3 is the scattered light of the instrument, and T_4 is the scattered light of the sample and the instrument.

To determine the haze which is only caused by the refractive index difference between matrix and particles and not by the surface of the specimen, the haze of a nonfilled specimen was subtracted from 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 which can be detected by

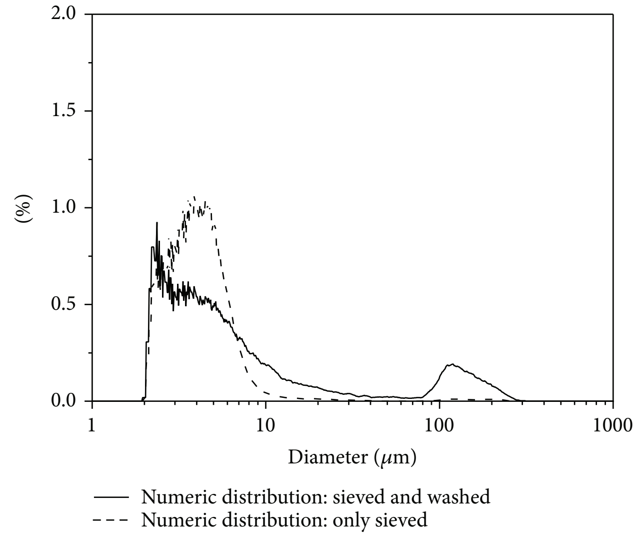

Figure 2: Numeric distribution of the unwashed and washed particles.

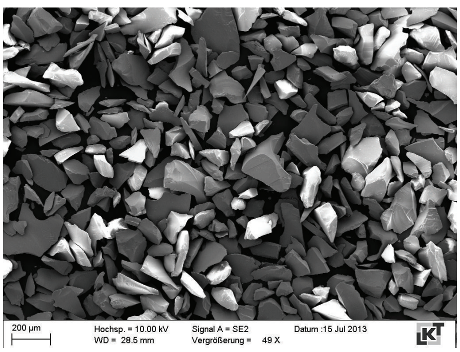

Figure 3: SEM image of washed glass particles.

the measuring instrument have a diameter of 2 μm. The volumetric particle distribution of the washed particles is characterized as follows: $d_{10,3}$ = 116.3, $d_{50,3}$ = 178.7, and $d_{90,3}$ = 246.7. Figure 2 shows, despite sieving and washing the particles, a considerable amount of small particles (d < 63 μm). Nevertheless, the volumetric amount of these particles is quite small so that they should have a minor impact on the light scattering in the specimens.

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.

3.2. Specimens. Figure 4 shows a computed tomographic image (CT image) of two melt films with different filling grades. As it can be seen, the particles are uniformly dispersed in the analyzed area. According to the TGA measurements, the filler content of the specimens tested is 3.9 vol.-%, 9.4 vol.-%, and 17.3 vol.-%.

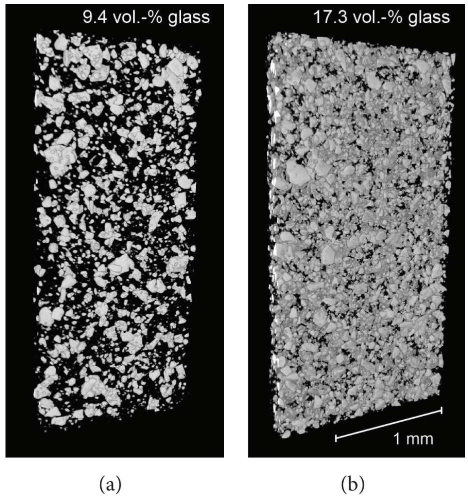

Figure 4: CT images of two specimens with a different filling grade.

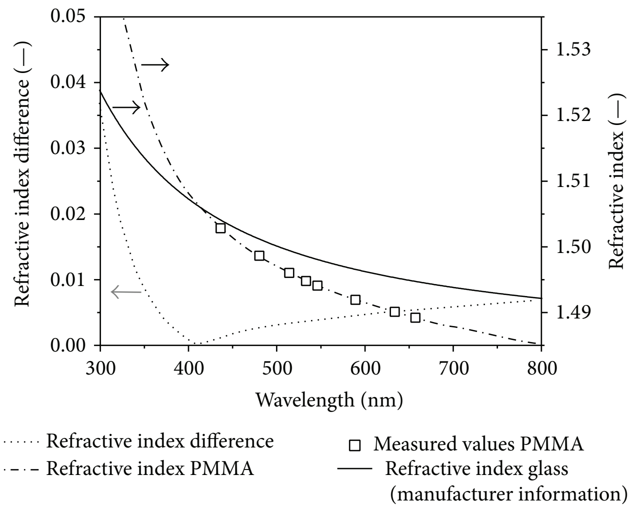

Figure 5: Refractive index of PMMA Plexiglas 7N and glass N-PK52A at 23°C.

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, depending on 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:

$$n(\lambda) = A\frac{B}{\lambda} + \frac{C}{\lambda^4} + \frac{D}{\lambda^6}. \quad (2)$$

The curve progression of the glass was calculated with the Sellmeier equation (3) with constants according to the data sheet:

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

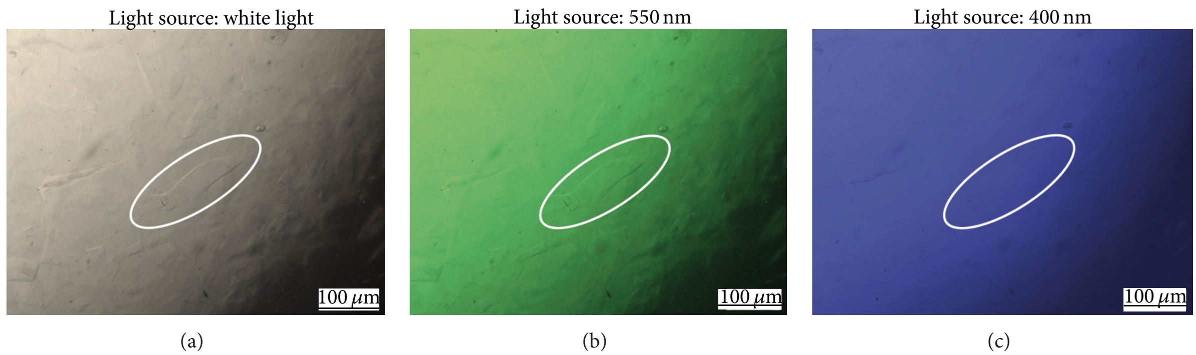

Figure 6: Oblique illumination in the microscope with a particle at different wavelengths.

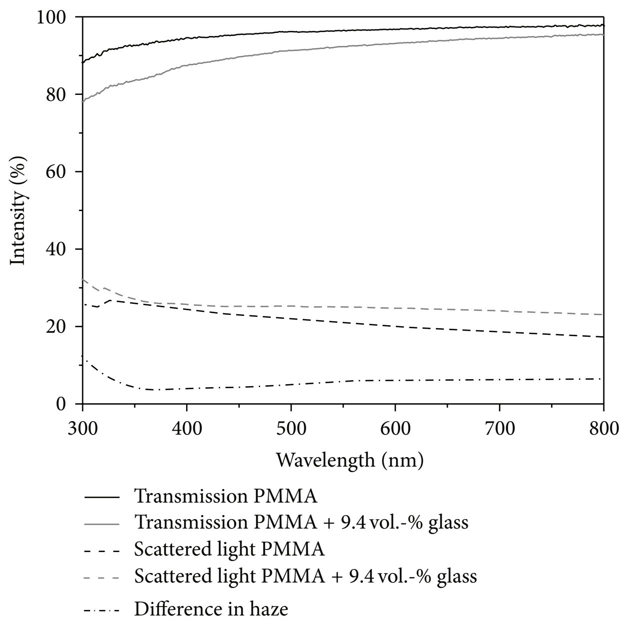

Figure 7: Intensity of transmission, scattering, and calculated haze of a specimen filled with 9.4 vol.-% glass and a thickness of 250 μm.

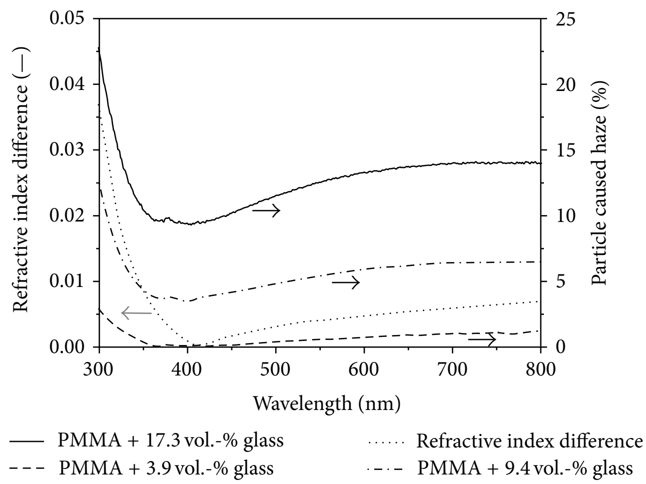

Figure 8: Particle caused haze of specimens with different filling grades and a thickness of 250 μm.

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 seen clearly. This indicates that the refractive index of the particle lies above the refractive index of the surrounding matrix.

The analysis of the transmission and the haze of the specimens were performed at a temperature of 23°C. To exclude the haze caused by the surface of the specimen, the haze of a pure PMMA sample was subtracted from the haze of the filled melt films. Figure 7 shows this calculated haze for the specimen with a filler content of 9.4 vol.-% depending on the wavelength. The relatively high scattering of the unfilled specimen is caused by its surface.

Figure 8 shows the haze caused by particles for different filling grades. It shows that the haze of the glass-filled specimens changes with the wavelength and the filler content. At the wavelength with a matching refractive index, the value of haze is lowest for all specimens. The curve shape of the haze in dependence of the wavelength is comparable to the curve shape 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 indexes of the glass and the polymer match totally. The amount of scattered light at 400 nm is nearly the same for all specimens, whereas the transmission decreases with higher filling grades, in particular at short wavelengths. This leads to higher haze, according to (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. The higher base line of the haze at higher filling grades also indicates that there are more scattering mechanisms, like defects in the filler binding. These may occur because no bonding agent is used by the making of the specimens. Further investigations will deal with this scattering and the decrease in transmission of the specimens.

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.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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