

## Influence of Titanium Dioxide Pigments on the Optical Properties of Polycarbonate and Polypropylene for Diode Laser Wavelengths

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**ABSTRACT:** In laser transmission welding of polymers, additives and colorants could influence the welding result. In this work, polypropylene and polycarbonate probes colored with titanium dioxide (TiO<sub>2</sub>) pigments of various concentrations are investigated. The probes are produced using an extrusion process to obtain a homogeneous distribution of colorants. The TiO<sub>2</sub> pigments change the optical properties of the polymers considerably. The measured reflectance increases with increasing pigment load while the transmittance decreases. From the measured data of transmittance, reflectance, and collimated transmittance, the scattering, the absorption coefficient, and the anisotropy factors are calculated. It is shown that the scattering coefficient at 1530 nm (laser) wavelength is smaller than for 968 nm, while the absorption coefficient is negligible for both wavelengths. Scattering coefficient and anisotropy factor are used to simulate the propagation of the laser radiation in the polymers. The influence of the scattering process on the beam propagation is represented by the change of the power density distribution. It is shown that the maximum intensity of the distribution is reduced more than the transmittance with increasing pigment concentration. The effect is higher for 968 than for 1530 nm wavelength making the larger wavelength more favorable for transmission welding. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2014, 131, 40073.

**KEYWORDS:** spectroscopy; optical properties; dyes/pigments; theory and modeling

Received 26 June 2013; accepted 19 October 2013

DOI: 10.1002/app.40073

### INTRODUCTION

To assemble polymer parts, laser transmission welding has been introduced in industrial applications, but is still also a topic of investigations.<sup>1–3</sup> The fields of industrial application are e.g. household appliance, automotive, and medical products, where a variety of polymers are used. In laser transmission welding, one part of the components is transparent for the laser radiation, the other is absorbing. Both parts are brought in thermal contact and the heat released in the absorbing part will diffuse into the transparent part. Welding takes place if local melting in both parts occurs.<sup>1</sup>

Due to the specific tasks the polymers are loaded with additives and/or colorants. These will change the optical properties of the “natural” or unloaded polymer depending on the type and load of the additives.<sup>4,5</sup> Since the optical properties also influence the quality of the weld seam,<sup>1,3,6</sup> the influence of the additives/colorants on the optical properties are of importance for laser transmission welding.

One of the most used white colorant is titanium dioxide (TiO<sub>2</sub>). It is an inorganic pigment with a high opacity, usually used for white, opaque, and light colors. The typical concentrations are in the range of 0.1 up to 3.0 wt % depending on color

and polymer type. In nature, TiO<sub>2</sub> exists in three crystalline structures: anatase (tetragonal), rutile (tetragonal), and brookite (rhombohedral). Rutile is the thermodynamically more stable version in comparison to anatase. Due to denser lattice elements, the density of rutile (4.0–4.2 g/cm<sup>3</sup>) and anatase (3.9 g/cm<sup>3</sup>) are different. The median mass based particle size  $d_{50m}$  is around 0.3 μm,<sup>7</sup> (see also Ref. 8). In comparison to other white pigments, the rutile structured TiO<sub>2</sub> has the best coloring properties and is therefore, the most used white pigment. The pigments can be homogeneously dispersed in the polymer matrix using a twin-screw extruder, where the polymers are melted and mixed with the pigments.

In this work, the optical properties of polypropylene (PP) and polycarbonate (PC) loaded with TiO<sub>2</sub> pigments are investigated. Joining of such component parts are of interest in manufacturing and not investigated for laser transmission welding until now. Instead of the real component parts flat probes are used to simplify the experimental work.

In general, the optical properties are refractive index, scattering, absorption coefficient, and scattering function describing the

angular dependence of the scattering process. Depending on the pigment load the scattering process will change the power distribution of the laser radiation in the welding zone (i.e., between transparent and absorbing part).<sup>9</sup> The power distribution determines the heat released in the welding zone and, therefore, the quality of the weld seam.

Scattering coefficient, absorption coefficient, and anisotropy factor could be calculated from measured data of transmittance, reflectance, and collimated transmittance of the flat probes applying UV–Vis–NIR spectroscopy.<sup>4</sup> The calculation is based on the Four-Flux approximation of the radiation propagation equations.<sup>10,11</sup> Instead of the scattering function in this approximation the anisotropy factor is obtained with values ranging from  $-1$  to  $1$ . Its deviation from zero displays the deviation of the scattering from the isotropic case. If its value is positive the scattering is forward directed, if it is negative it is backward directed. The index of refraction of the polymers is given in the literature (e.g. Refs. 12,13). As an add-on to the work presented in Refs. 4, 9, the calculated scattering properties are used to simulate the propagation of the radiation through polymer probes with different pigment loads. The simulations are made using ray tracing software based on the Monte Carlo method.<sup>14,15</sup>

This article reports on the results of UV–Vis–NIR spectroscopy measurement to calculate the scattering properties and the simulation of radiation propagation for PC and PP probes loaded with TiO<sub>2</sub> pigments.

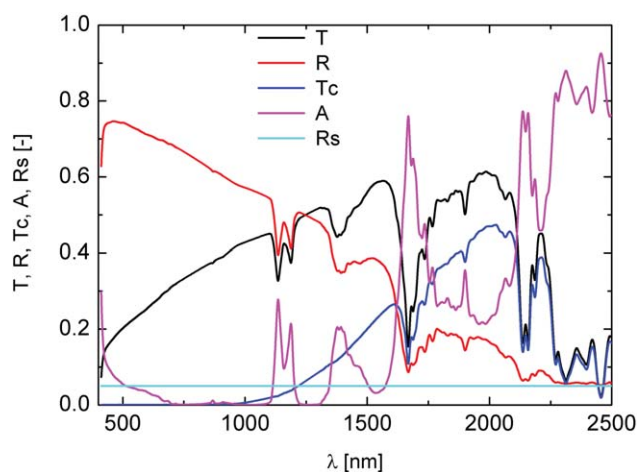
#### UV-VIS-NIR SPECTROSCOPY AND OPTICAL PROPERTIES

Transmittance  $T$ , reflectance  $R$ , and collimated transmittance  $T_c$  are measured using an UV–Vis–NIR spectrometer. The measurements were made for wavelengths from 400 to 2500 nm. The details of the experimental set-up are described elsewhere.<sup>4</sup> The PC and PP probes have dimensions of  $50 \times 50 \times 1 \text{ mm}^3$  and are loaded with TiO<sub>2</sub> pigments of various concentrations. PC (nature) is generally addressed as a non-scattering polymer, while for PP (nature) scattering is also attributed to the crystalline structure<sup>3</sup> (e.g., spherulites<sup>16</sup>) of this polymer.

As an example the measured spectroscopy data of a PC-probe loaded with 0.4 wt% TiO<sub>2</sub> are shown in Figure 1.

The transmittance  $T$  varies strongly with the wavelength and is smaller than 0.7 (70%) for all wavelengths. The dips are attributed to absorption of radiation at carbon-hydrogen bonds.<sup>17</sup> The reflectance  $R$  has higher values than the transmittance  $T$  for wavelengths smaller than 1200 nm meaning that most of the radiation is back-scattered due to multiple scattering events. At wavelengths around 2450 nm the absorption extinguishes nearly all part of the radiation with a transmittance below 0.05. The reflectance  $R$  at this wavelength is given by the surface reflectance  $R_s$  with a value of  $\sim 0.05$ . For simplification this value is taken for  $R_s$  over the entire wavelength range in Figure 1. The error made by this simplification is negligible due to the small variation of the refractive index with the wavelength, at least above 500 nm.<sup>12</sup>

The collimated transmittance  $T_c$  deviates from the transmittance  $T$  for wavelengths smaller than 2200 nm, indicating the strength

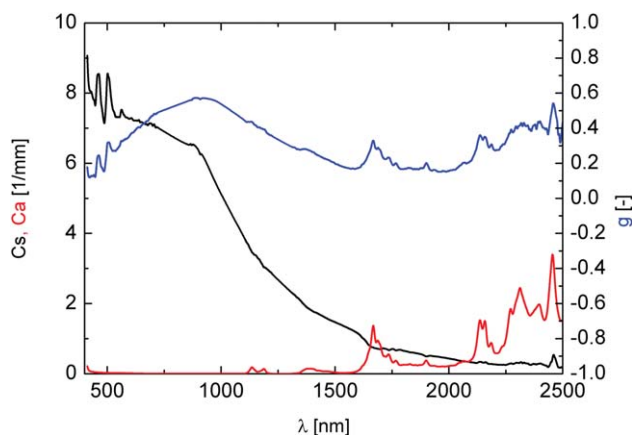


**Figure 1.** Transmittance  $T$ , reflectance  $R$ , collimated transmittance  $T_c$ , and absorbance  $A (= 1 - T - R)$  versus wavelength for 1 mm PC, 0.4 wt % TiO<sub>2</sub> load, surface reflectance  $R_s$  is set to 0.05 for all wavelengths.

of the scattering effect. For wavelengths above 2200 nm the two transmittances are (nearly) equal, since absorption dominates over scattering. For 0.4 wt % TiO<sub>2</sub> load and wavelengths below 600 nm, the measured values of  $T_c$  become smaller than the fluctuation of the measured data ( $< 0.001$  (0.1%)). Increasing the load also increases the wavelength where  $T_c$  becomes too small for evaluation. The absorbance  $A$  ( $:= 1 - T - R$ ) gives the amount of radiation which is absorbed. From the absorbance one can choose the wavelength where a probe is (nearly) transparent.

As shown in our previous article,<sup>4</sup> once  $T$ ,  $R$ ,  $T_c$ , and  $R_s$  are given for a certain thickness of a probe, one can calculate the scattering coefficient  $C_s$ , the absorption coefficient  $C_a$ , and the anisotropy factor  $g$  as a function of the wavelength. The results are obtained by solving the radiation propagation in a homogenous medium with the four-flux approximation (four-flux model).<sup>4,10,11</sup>

The scattering coefficient  $C_s$  decreases with increasing wavelength (Figure 2). The absorption coefficient  $C_a$  stays smaller than the scattering coefficient for wavelengths smaller than 2100 nm, with the exception around 1650 nm. For larger wavelengths the absorption coefficient becomes larger than the scattering coefficient. Comparing the absorption coefficients and the absorbance  $A$  indicates that the absorbance does not depend linearly on the absorption coefficient. For example, the absorption coefficient at wavelength 1200 nm is an order of magnitude smaller than the one at 1650 nm, while the values of the absorbance differ only by a factor two. This could be explained with the optical path of the radiation. Scattering increases the path length and also the probability of absorption. The scattering coefficient at 1200 nm is approximately three times larger than the one at 1650 nm. So for radiation at 1200 nm the optical path is longer than for 1650 nm enhancing the probability of absorption. Therefore, the absorbance at 1200 nm is comparably high (Figure 1).



**Figure 2.** Scattering  $C_s$ , absorption coefficient  $C_a$  (left labels), and anisotropy factor  $g$  (right labels) versus wavelength, calculated from data of Figure 1, ripples at small wavelengths due to erroneous data of the collimated transmittance  $T_c$ .

The anisotropy factor  $g$  is positive for all wavelengths ( $0 < g < 0.5$ ). Meaning that on the average the single scattering event is forward directed, while the accumulation over a sufficient number of events might result in a back-scattering with  $R > T$  (Figure 1).

The welding experiments have been done with diode lasers working at 1530 and 968 nm, respectively. The optical properties for PC-probes with different  $\text{TiO}_2$  loads at these wavelengths are presented in Table I.

**Table I.** Optical Properties, PC (1 mm), Wavelengths (WL): 968 and 1530 nm

WL (nm)	$\text{TiO}_2$ (%)	$T$	$R$	$A$	$T_c$	$C_s$ (1/mm)	$C_a$ (1/mm)	$g$
1530	0.0	0.9	0.1	0.0	0.89	0.0	0.0	0.0
1530	0.4	0.58	0.38	0.04	0.2100	1.4	0.080	0.14
1530	1.0	0.42	0.53	0.05	0.0300	3.5	0.020	0.36
1530	2.0	0.32	0.63	0.05	0.0015	6.5	0.020	0.47
968	0.0	0.9	0.1	0.0	0.89	0.0	0.0	0.0
968	0.4	0.42	0.57	0.01	0.0035	5.5	0.004	0.57
968	1.0	0.26	0.73	0.01	0.0001	9.0 <sup>a</sup>	0.004 <sup>a</sup>	0.47 <sup>a</sup>

<sup>a</sup> Values are erroneous since  $T_c < 0.001$ .

**Table II.** Optical Properties, PP (1.2 mm), wavelengths (WL): 968 and 1530 nm

WL (nm)	$\text{TiO}_2$ (%)	$T$	$R$	$A$	$T_c$	$C_s$ (1/mm)	$C_a$ (1/mm)	$g$
1530	0.0	0.9	0.09	0.01	0.700	0.25	0.0	0.73
1530	0.4	0.63	0.33	0.01	0.0400	2.60	0.010	0.67
1530	1.0	0.5	0.45	0.05	0.0130	3.50	0.022	0.61
1530	2.0	0.34	0.6	0.06	0.0034	4.60	0.020	0.46
968	0.0	0.91	0.09	0.0	0.5200	0.54	0.0	0.75
968	0.4	0.45	0.54	0.01	0.0026	4.90	0.004	0.63
968	1.0	0.32	0.67	0.01	0.0006	6.00 <sup>a</sup>	0.004 <sup>a</sup>	0.51 <sup>a</sup>

<sup>a</sup> Values are erroneous since  $T_c < 0.001$ .

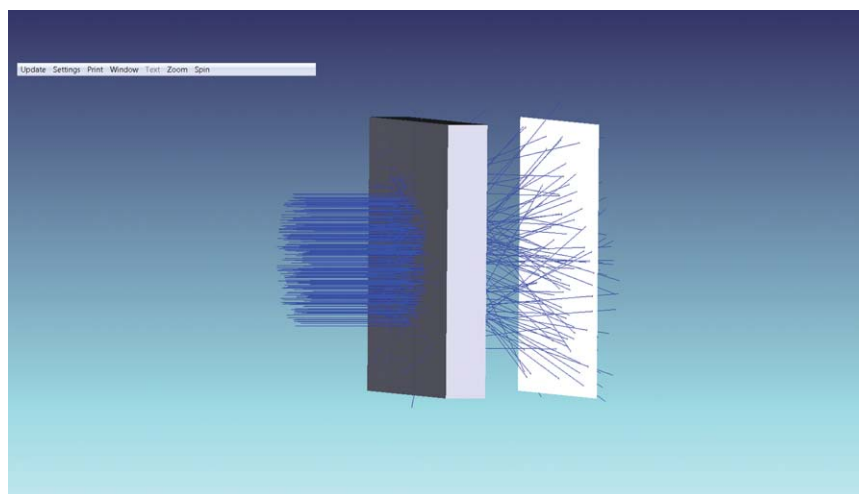
The transmittance  $T$  decreases and the reflectance  $R$  increases with increasing  $\text{TiO}_2$  load. The collimated transmittance for 968 nm is smaller than for 1530 nm at the same  $\text{TiO}_2$  concentration indicating stronger scattering behavior at this wavelength. The value of the scattering coefficients increases (approximately) linearly with the  $\text{TiO}_2$  concentration. The absorbance and the absorption coefficient are negligible for both wavelengths. The anisotropy factor increases with increasing  $\text{TiO}_2$  concentration.

The optical properties of PP-probes are summarized in Table II.

In first approximation, the radiation propagation for PP is determined by the  $\text{TiO}_2$  load. The crystallinity plays a minor role concerning the scattering coefficient but it influences the anisotropy factor, which is larger for PP than for PC. For  $\text{TiO}_2$  loads of 0.4 and 1 wt %, the anisotropy factor displays more forward directed scattering for PP than for PC. This is also displayed in the ratios between transmittance and reflectance for both materials. Similar as for PC the transmittance decreases with increasing  $\text{TiO}_2$  concentration, while the reflectance increases, but the transmittance of PP is bigger than of PC. The absorbance and the absorption coefficient are negligible as for the PC-probes. The scattering coefficient increases with increasing load but not linearly. One reason for this might be the inhomogeneous distribution of the pigments, which is not described by the model. Also surface effects such as (irregular) roughness influence the measurement, especially the values of the collimated transmittance.

#### Simulation of Radiation Propagation

Once scattering  $C_s$ , absorption coefficient  $C_a$ , and anisotropy factor  $g$  are known, the propagation of radiation in the polymer



**Figure 3.** ZEMAX scheme, blue lines: radiation, gray body: probe, white area: (simulation) detector.

probes can be simulated. For this purpose, we use the ray tracing software ZEMAX<sup>®18</sup> where from a large number of rays ( $>10^6$ ) the propagation of every single ray is monitored. The mean free path of a ray is given by the inverse of the scattering coefficient. The scattering function  $p$  is a “Henyeey–Greenstein phase function”<sup>10,19</sup>:

$$p(\mu) = \frac{1}{2} \frac{1-g^2}{(1+g^2-2g\mu)^{3/2}}$$

$$\mu = \cos(\Theta), \quad -\pi < \Theta < \pi$$

$\Theta$ : the scattering angle is a random variable and, therefore, also  $\mu$  is a random variable. It could be shown that the mean value of  $\mu$  ( $\langle \mu \rangle$ ) built by the phase function is equal to the anisotropy factor  $g$ .<sup>14</sup>

The simulations are carried out for flat probes with a thickness of 1 mm and a rotational symmetric beam (top-hat) with a diameter of 800  $\mu\text{m}$ , which is a typical value for laser transmission welding.

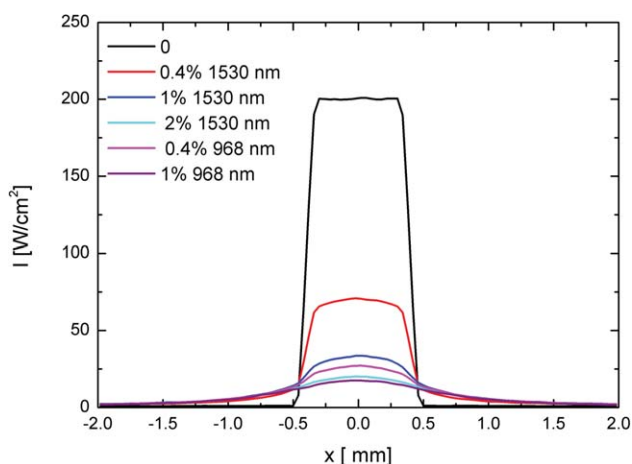
Rays are detected on an area at the exit side (right side of the probe in Figure 3), called detector. The detector gives the power

density distribution (PDD) at this plain normalized to 1 W of total beam power. Due to the rotational symmetry the values of the PDD are shown along the  $x$ -axis.

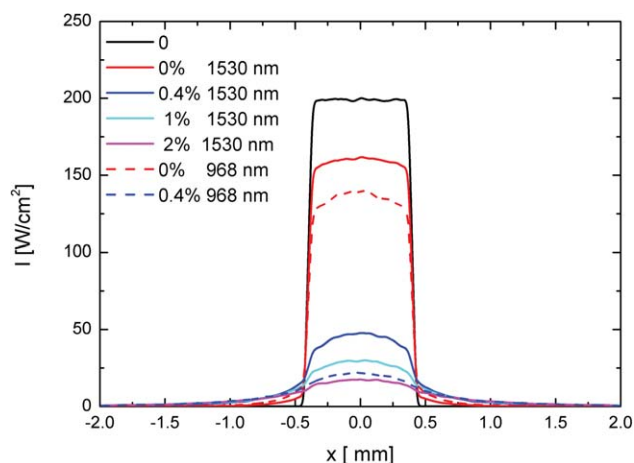
The non-smooth appearance is due to the statistics of the ray tracing software. Although, the transmittance at 1530 nm and 0.4 wt %  $\text{TiO}_2$  is 0.6 (Table I) the maximum value of the PDD is reduced from 200 to 70  $\text{W}/\text{cm}^2$  (s. Figure 4). For 1 wt%  $\text{TiO}_2$  this effect is even more pronounced. So scattering leads first of all to a broadening of the PDD with smaller maximum value. The PDD for 968 nm at 0.4 and 1 wt % seems similar to the one at 1530 nm at 1 and 2 wt %  $\text{TiO}_2$ .

For PP the data look similar with the exception that PP also scatters radiation without any  $\text{TiO}_2$  load.

From Figure 5 it is seen that also without any  $\text{TiO}_2$  load (0 wt %) PP scatters radiation due to the partial crystal structure. At 1530 nm the maximum value of the PDD is reduced from 200 to  $\sim 160 \text{ W}/\text{cm}^2$ , which is also attributed to the surface reflectance ( $R_s = 0.05$ ). A load of 0.4 wt % reduces this value to  $\sim 50 \text{ W}/\text{cm}^2$ , so the reduction of the maximum value is similar to PDDs of PC.



**Figure 4.** ZEMAX<sup>®</sup> results of the PDD (rotational symmetric), original beam (0) and 1 mm PC probes for different wavelengths and  $\text{TiO}_2$  loads, total power: 1 W.



**Figure 5.** ZEMAX results of the PDD, original beam (0) and 1 mm PP probes for different wavelengths and  $\text{TiO}_2$  loads, total power: 1 W.

## CONCLUSIONS

TiO<sub>2</sub> pigments change the transmittance, reflectance, and absorbance of the PC- and PP-probes. At the two wavelengths 1530 and 968 nm, the 1 mm probes are considered as transparent since the absorbance is negligible at these wavelengths. The reflectance increases with pigment concentration, while the transmittance decreases. The calculated scattering coefficients increase with pigment concentration and is larger at 968 nm than at 1530 nm wavelength.

The simulations of the radiation propagation show that the scattering process reduces the total power of the transmitted radiation and also changes its PDD. The distribution becomes broader and its maximum value smaller. The reduction of the maximum value is more pronounced than the reduction of the transmission value. Therefore, if the pigment load is enhanced the laser power has to be enhanced too. Not only to overcome the decrease in transmission but also to match with the decrease of the maximum value of the PDD. This effect is more pronounced for 968 nm than for 1530 nm laser sources making the later more favorable for laser transmission welding of polymers.

Furthermore, the calculated PDD could be used to calculate the temperature distribution of the transparent and absorbing part. So incorporating the influence of the scattering process on the radiation propagation would make the simulation of laser transmission welding more realistic.<sup>9</sup>

## ACKNOWLEDGMENTS

The work is part of POLYBRIGHT research project, funded by the European Community's 7th Framework Program under grant agreement no. NMP2-LA-2009-228-725.

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