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ARTICLE

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Determination of the flexural properties of additively manufactured polyamide 12 components with antimicrobial titanium dioxide additives

Bestimmung der Biegeeigenschaften von additiv gefertigten Polyamid 12 Bauteilen mit antimikrobiellen Titandioxid Zusätzen

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Abstract

Antibacterial properties of components are increasingly becoming an important challenge in material development especially in polymer technology. A well-known additive with which an antibacterial effect can be achieved is the metal oxide titanium dioxide. The aim of this research work was to investigate possible influences on the flexural properties of additively manufactured components resulting from the addition of titanium dioxide as an antimicrobial additive. Compounds with 5 %, 10 % and 15 % titanium dioxide and polyamide 12 as matrix material were produced. Three-point bending test specimens were fabricated out of these compounds, anaylsed and the results were compared with specimens made of virgin polyamide 12. The investigations show a general loss in ductility compared to the virgin polyamide 12. A comparison of the different titanium dioxide contents shows no clear change in the flexural stress at conventional bending. The flexural strain at break seems to decrease for higher titanium dioxide contents.

KEYWORDS
antibacteriel, polyamide 12, selective laser sintering, three-point bending, titanium dioxide

Abstract

Antibakterielle Eigenschaften von Bauteilen werden zunehmend zu einem wichtigen Bestandteil in der Werkstoffentwicklung, insbesondere in der Polymertechnologie. Ein bekannter Zusatzstoff, mit dem eine antibakterielle Wirkung erzielt werden kann, ist das Metalloxid Titandioxid. Ziel der vorliegenden Forschungsarbeit war die Untersuchung möglicher Einflüsse auf die Biegeeigenschaften von additiv gefertigten Bauteilen durch die Zugabe von

Titandioxid als antimikrobielles Additiv. Hierfür wurden Compounds mit 5 %, 10 % und 15 % Titandioxid und Polyamid 12 als Matrixmaterial hergestellt. Aus diesen Compounds wurden Biegeproben gefertigt, untersucht und die Ergebnisse mit Proben aus reinem Polyamid 12 verglichen. Die Untersuchungen zeigen einen Verlust an Duktilität durch Zugabe des Titandioxids gegenüber den Proben aus reinem Polyamid 12. Werden die verschiedenen Titandioxidgehalte miteinander verglichen, so konnte keine deutliche Veränderung der maximalen Biegespannung bei konventioneller Biegung festgestellt werden. Die Bruchdehnung scheint bei höheren Titandioxidgehalten erneut abzunehmen.

SCHLÜSSELWÖRTER
antibakteriell, Biegeversuch, Polyamid 12, selektives Lasersintern, Titandioxid

1 | INTRODUCTION

Whether in the kitchen, on public transportation, in the food industry or in medical technology: even before the pandemic, the antibacterial properties of polymer components play a major role in everyday life.

In general, a distinction can be made between four methods to achieve an antimicrobial activity of polymers [1]. On the one hand, this can be obtained without any antimicrobial agents by a physical modification of the component surface, for example with the help of an antimicrobial surface topography as also found in nature. Another way to reach antimicrobial properties in polymers is to apply an antimicrobial solvent directly to the polymer surface, although this only has a short-term effect. The third option is by chemical deposition of an antimicrobial agent, i. e. a surface treatment or coating. Finally, the last way to obtain antimicrobial activity is by bulk modification of the polymer with an antimicrobial agent, i. e. to produce a compound. Because of its good technical feasibility, this is often the method of choice in the industrial context and is thus also used for the present study [1, 2].

Titanium dioxide is considered a possible additive to achieve antibacterial material properties in polymers [2–4]. Apart from that, titanium dioxide has good photocatalytic properties and is commonly used as an ultraviolet stabiliser or colour filler [2, 4–6]. However, the antimicrobial effect of titanium dioxide relies on the formation of hydroxyl radicals and superoxide radicals, which inhibit cell respiration or damage the outer cell membrane [2]. To initiate the chemical reaction responsible for the formation of hydroxyl and superoxide radicals, the titanium dioxide requires pre-activation by irradiation with ultraviolet light [2, 6].

In contrast to the commonly used copper- or silver-based additives, titanium dioxide as a ceramic material has no allergenic potential and is therefore suitable for medical applications [2, 5, 6].

By combining the antibacterial material properties of titanium dioxide with an additive manufacturing process, it is possible to open up new potential and extend the product portfolio. The currently most important additive manufacturing process in the field of polymer technology is the selective laser sintering, which is already in the transition phase from prototype production to series production due to the high manufacturing accuracy of the sintered parts [3, 7–11]. Selective laser sintering is a powder-based additive manufacturing process in which thin layers of polymer powder are applied successively to the construction space before being melted locally by a carbon dioxide laser. Following this, the molten polymer solidifies and forms the layer fragments of the desired component. Now the construction area is lowered by the height of one layer thickness before new powder is applied again. The desired component is thus created layer by layer through repeated melting and solidification of the newly applied powder [12]. Apart from a few special applications, the most commonly used materials for selective laser sintering are the semi-crystalline thermoplastics polyamide 11 and polyamide 12 [7–9, 13, 14]. With a market share of approximately 95 %, plastic powder based on polyamide 12 is the most commonly used material in selective laser sintering [7]. Hence, polyamide 12 is also the matrix material of choice in this work.

In previous studies, the antibacterial effect and the tensile properties of the compounds have already been determined [15, 16]. The aim of the present study is to investigate possible changes in the flexural properties of different polyamide 12 compounds when using titanium dioxide as an antimicrobial additive. For this purpose, three-point bending tests are carried out on samples produced by selective laser sintering from compounds with different titanium dioxide contents. In several studies, the mechanical properties of titanium dioxide compounds have already been investigated [3–6]. However, in most of them, nanoparticles were used as filler material, and the investigations were predominantly based on classical tensile tests. In contrast, the present work focuses on the use of micro-sized powders and the investigation of bending properties.

2 | METHODOLOGY

Three polyamide 12 compounds with different content of titanium dioxide were fabricated with the aid of a laboratory mixer M3 (Zeppelin Systems GmbH, Germany). The mixtures investigated in this study contain 5 %, 10 % and 15 % titanium dioxide, which are percentages by weight. In total, 12 kg of powder material was produced for each compound in order to provide a sufficient amount of powder for the laser sintering process. For the production of the compounds, matrix material and additive were processed in the mixer for 1 : 45 hours at a temperature of 130 °C. These mixing parameters have already proven to be suitable in previous studies [11, 15, 16]. The polyamide 12 powder DuraForm PA (3D-Systems Inc., Germany) was selected as the matrix material since this material has been developed for usage in the selective laser sintering process. Titanium dioxide powder was added to the polyamide 12 to obtain antibacterial properties. The powder used for this study is a titanium(IV)oxide powder from IoLiTec Ionic Liquids Technologies GmbH (Germany), supplied in the crystal modification rutile and with a mean particle size of 200 nm. As the mean particle size lies above 100 nm, the powder does not belong to the category of nanomaterials [17, 18]. For safety reasons, no nanoparticles are processed in this study [18].

With the aid of a laser sinter system Vanguard HS from the manufacturer 3D-Systems Inc., three-point bending specimens were fabricated to examine possible changes in the flexural properties of the different compounds due to the titanium dioxide, Figure 1. In order to have complete data for the comparison between the compounds and the virgin material, one set of specimens was produced out of pure polyamide 12. The laser sintering system used in this research operates with a 100 W carbon dioxide laser and a maximum build envelope capacity of 380 mm×330 mm×275 mm. All samples to be analysed are printed in x-direction, i. e. parallel to the scanning direction of the printer. From this follows that

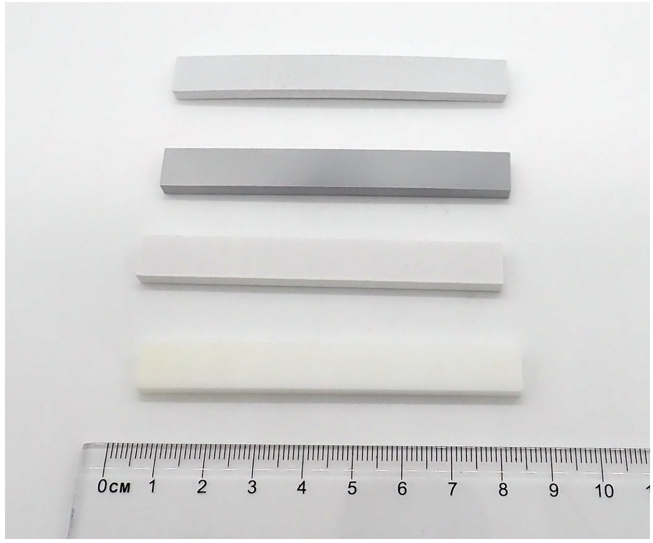

FIGURE 1 Three-point bending test specimen made out of different polyamide 12 compounds with 0 %, 5 %, 10 %, 15 % titanium (the button to the top).

BILD 1 Biegeproben aus verschiedenen Polyamid 12 Mischungen mit 0 %, 5 %, 10 %, 15 % Titandioxid (von unten nach oben).

the testing direction of the three-point bending test is orthogonal to the scanning direction. In fact, the scanning direction has an influence on the mechanical properties, which has already been worked out in previous studies on the basis of tensile tests [11, 19, 20]. However, as this is not the focus of this work, only one orientation of the specimen in the printer is considered for the investigation. The specimens were produced with the dimensions of 80 mm×10 mm×4 mm according to the standard DIN EN ISO 178, using a layer thickness of 100 μm. The three-point bending tests were performed on a Zwick 1445–02, 10 kN universal testing machine using a constant testing speed of 1.7 mm/min, which corresponds to a strain rate of 1 %/min as required by the standard, Figure 2. In order to avoid possible time-related influences due to the viscoelastic behaviour of polymers the testing speed is kept constant during the complete test procedure [21, 22]. In accordance with the standard, the length of span between the supports is set to be 64 mm and a radius of 5 mm is chosen for the supports, as the thickness of the specimen is > 3 mm. A central loading edge with a radius 5 mm is used to initiate the force. However, five specimens were examined for each compound ensuring a statistically validated assessment of the flexural behavior. Since polyamide belongs to the category of hygroscopic materials, the samples are stored in a climate chamber for 88 h at standard climate conditions as required according to DIN EN ISO 291 before testing [21, 22]. In this case, the climatic conditions

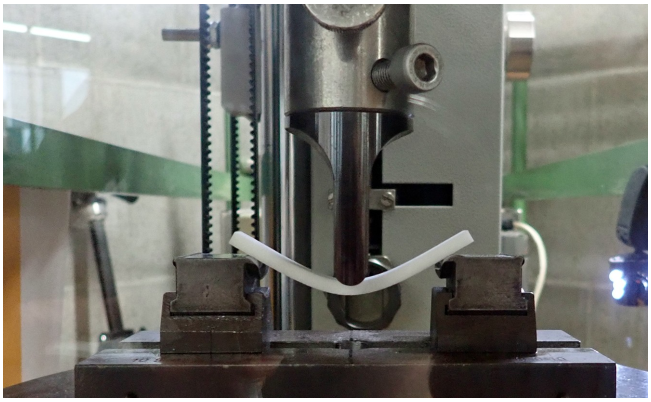

FIGURE 2 Test setup for the determination of the flexural properties.

BILD 2 Versuchsaufbau zur Bestimmung der Biegeeigenschaften.

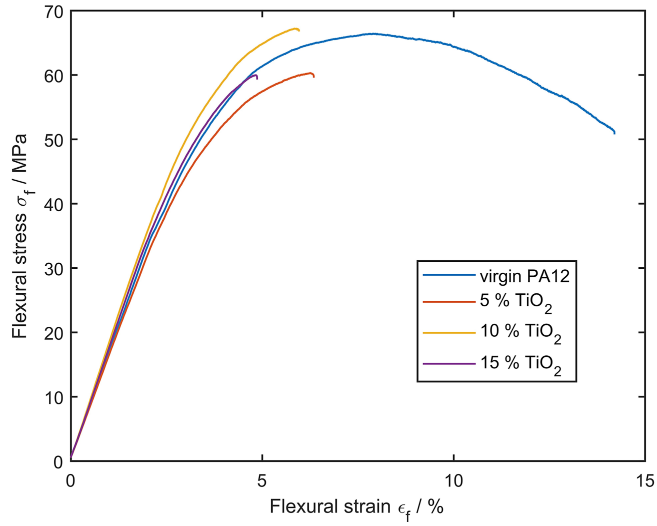

FIGURE 3 Examined curves of flexural stress versus flexural strain of three-point bending specimen fabricated out of polyamide 12 with different contents of titanium dioxide.

BILD 3 Ermittelte Kurvenverläufe der Biegespannung über die Biegedehnung von Proben aus Polyamid 12 mit unterschiedlichen Massenanteilen von Titandioxid.

for non-tropical countries apply, i. e. the conditioning of the samples has to be carried out at a temperature of 23 °C and a relative humidity of 50 %. Afterwards, the three-point bending tests are conducted at room temperature.

3 | RESULTS AND DISCUSSION

Determining the stress-strain curves (flexural stress and flexural strain) of the tested samples shows that all specimens neither gave a maximum nor broke before reaching the conventional deflection, which is defined as 1.5 times the thickness of the specimen, Figure 3. Exemplary measurement results of the first tests of each compound are illustrated by these stress-strain curves.

For the present study, a conventional deflection of 6 mm is obtained (1.5×4 mm = 6 mm), which corresponds to a flexural strain of 3.5 %. As mentioned before, the three-point bending tests are thus evaluated regarding the flexural stress at conventional deflection as recommended by the standard for the material behaviour occurring in this study.

Investigating the specimen made out of pure polyamide 12 showed no failure of the specimen at all. The difference can be clearly seen when comparing the stress-strain curves with each other, as the flexural strain of the virgin polyamide 12 is significantly higher than the one resulting from the titanium dioxide compounds, Figure 3. In the case of the virgin PA12, the tests had to be terminated at roughly 14.5 % flexural strain because the maximum traverse path of the machine had been reached. Furthermore, a general loss in ductility can be observed through the addition of titanium dioxide, as all specimens made from a titanium dioxide compound fail during the test.

For a better comparison, the results of the complete tests are evaluated and visualised below as boxplot diagrams, in which the examined compounds are displayed on the axis of abscissae and the corresponding measured flexural properties are shown on the axis of ordinate. The advantage of this representation is the complete illustration of all important statistical characteristics like the extreme values of each series of measurements which are shown as so-called whiskers, and in addition, the median which is illustrated by the red central mark. Moreover, the 25 % and 75 % percentiles can be taken from the upper and lower edges of the blue box.

The values for the flexural stress at conventional deflection slightly decrease in the case of the compound with 5 % titanium dioxide compared to the virgin material, whereas the measured stress values for the 10 % compound increase, Figure 4. However, when further increasing the titanium dioxide content to 15 % the resulting stress values from the three-point bending test are similar to the results of the virgin material. This trend can be also seen when comparing the mean values of the flexural stresses, Table 1. Nevertheless, the decrease in flexural stress for the 5 % titanium dioxide compound amounts to only an average value of 8.5 % compared to the resulting mean values for the virgin material, Table 1. In addition, the increase in flexural

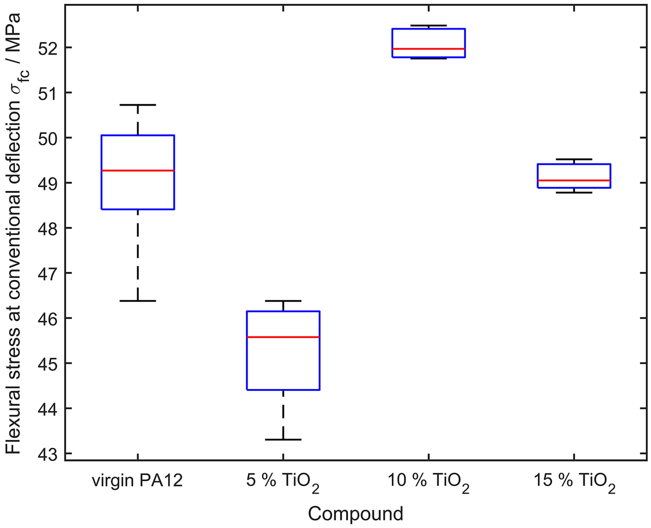

FIGURE 4 Flexural stress at conventional deflection of specimen fabricated out of polyamide 12 with different contents of titanium dioxide.

BILD 4 Biegespannung bei konventioneller Durchbiegung von Proben aus Polyamid 12 mit unterschiedlichen Massenanteilen von Titandioxid.

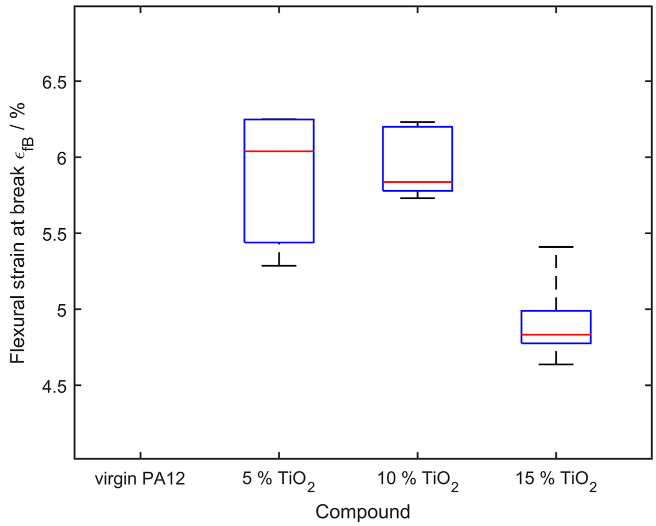

FIGURE 5 Flexural strain at break of specimen fabricated out of polyamide 12 with different contents of titanium dioxide.

BILD 5 Biegedehnung beim Bruch von Proben aus Polyamid 12 mit unterschiedlichen Massenanteilen von Titandioxid.

TABLE 1 Mean values of the results from the three-point bending tests.

TABELLE 1 Mittelwerte der Ergebnisse aus den Biegeversuchen.

Parameter	virgin PA12	5% TiO_2	10% TiO_2	15% TiO_2
Flexural stress at conventional deflection σ_{fc} [MPa]	49.06	45.22	52.08	49.13
Flexural strain at break ε_{fb} [%]	–	5.86	5.96	4.91

stress in the case of the compound with 10% titanium dioxide can only be determined with an average value of 5.8%. From this follows that the addition of titanium dioxide has a rather small influence on the flexural stress at conventional deflection.

Comparing the flexural strain at break indicates a loss in ductility for increasing content of titanium dioxide as the strain values decrease for the specimen made out of the 15% titanium dioxide compound, Figure 5. This can be also seen when evaluating the mean values, Table 1. Keeping in mind that the specimens fabricated out of pure polyamide 12 were not breaking at all further confirms this behaviour. In the case of the virgin powder, no measurement results could be provided for the flexural strain, as the samples did not fail, which is why no boxplot diagram can be seen.

4 | CONCLUSIONS

Based on the present study on the flexural properties of additively manufactured samples made of polyamide 12 with different proportions of titanium dioxide, no clear change in the flexural stress at conventional deflection can be determined when increasing the titanium dioxide content. A general loss in ductility can be observed for the specimens with added titanium dioxide compared to the specimen out of virgin polyamide 12, as the components made of virgin material do not fail at all. However, the specimens made out of the titanium dioxide compounds do fail and the flexural strain at break could be determined. Furthermore, it was found that the flexural strain of the present samples seems to decrease with increasing titanium dioxide content of the compounds. This behaviour has to be further validated.

In summary, it can be stated that this study only vaguely shows the influence of the additive titanium dioxide on the flexural properties and only allows an initial estimate to be made. However, in order to confirm the results, the test series must be extended and, for example, a larger number of different compounds with varying titanium dioxide contents must be analysed.

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CONFLICT OF INTEREST STATEMENT

The authors declare no financial or commercial conflict of interest.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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