Received: 11 January 2023 | Accepted: 25 January 2023

DOI: 10.1002/mawe.202200329

ARTICLE

WILEY VCH

Characterisation of the mechanical properties of polyamide 12 powder when using titanium dioxide as antimicrobial additive

Charakterisierung der mechanischen Eigenschaften von Polyamid 12 Pulver bei Verwendung von Titandioxid als antimikrobieller Zusatzstoff

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Funding information
Federal Ministry for Economic Affairs and Energy (BMWi)

Abstract

Antimicrobial properties of plastic components are an important part of polymer engineering. One commonly used additive with an antibacterial effect is titanium dioxide. The aim of this study is to investigate the influences on the mechanical properties resulting from the addition of titanium dioxide as an antimicrobial additive and the processing of the compounds with selective laser sintering. Compounds with 5 %, 10 % and 15 % titanium dioxide and polyamide 12 as matrix material are fabricated. Tensile test specimen are produced from the compounds, examined and the results compared with virgin polyamide 12. The investigations show a general loss in the ultimate tensile strength compared to the virgin polyamide 12. Comparing the different titanium dioxide contents with each other, an increasing tensile strength with increasing titanium dioxide content of the compound can be examined. A decreasing elongation at break and thus a decreasing ductility can also be observed. Furthermore, the results of the tensile test show a stiffening effect, i. e. an increase in the elastic modulus due to the addition of titanium dioxide.

KEYWORDS
antimicrobial, mechanical properties, polyamide 12, selective laser sintering, titanium dioxide

Abstract

Antimikrobielle Eigenschaften von Kunststoffkomponenten sind ein wichtiger Bestandteil der Kunststofftechnik. Ein häufig verwendetes Additiv mit antibakterieller Wirkung ist Titandioxid. Ziel dieser Studie ist es, die Einflüsse auf die mechanischen Eigenschaften zu untersuchen, die durch die Zugabe von Titandioxid als antimikrobieller Zusatzstoff und die Verarbeitung der

Compounds im selektiven Lasersintern entstehen. Es werden Compounds mit 5 %, 10 % und 15 % Titandioxid und Polyamid 12 als Matrixmaterial hergestellt. Aus den Compounds werden Zugproben hergestellt, untersucht und die Ergebnisse mit reinem Polyamid 12 verglichen. Die Untersuchungen zeigen einen generellen Festigkeitsverlust im Vergleich zu unbehandeltem Polyamid 12. Beim Vergleich der verschiedenen Titandioxidgehalte kann eine steigende Zugfestigkeit mit zunehmendem Titandioxidgehalt des Compounds festgestellt werden. Eine abnehmende Bruchdehnung und damit eine abnehmende Plastizität ist ebenfalls zu beobachten. Darüber hinaus zeigen die Ergebnisse des Zugversuchs einen Versteifungseffekt, also eine Erhöhung des Zugmoduls durch die Zugabe von Titandioxid.

SCHLÜSSELWÖRTER
antibakteriell, mechanische Eigenschaften, Polyamid 12, selektives Lasersintern, Titandioxid

1 | INTRODUCTION

Not only since the pandemic, but even before, antibacterial properties of plastic components play a major role in everyday life. Whether in the kitchen, public transport, the food industry or medical technology, antibacterial properties are already an important part of engineering.

In general, there are four different methods to achieve an antimicrobial modification of polymers [1]. The first method is by a physically modification of the surface, without any antimicrobial agent, for example with the aid of an antimicrobial topography of the surface. Another way to reach antimicrobial properties in polymers is by a direct application of an antimicrobial solvent to the polymer surface, which, however, only has a short duration of effect. The third technique is by a chemical deposition of an antimicrobial agent, i. e., a surface treatment or coating. As last possibility to achieve an antimicrobial polymer, there is the bulk modification of the polymer with the antimicrobial agent, i. e., the production of a compound. Due to its good technical feasibility this method is often used and is also the technique of choice in this study. [1, 2]

One possible filler material to obtain an antimicrobial polymer is titanium dioxide [2–4]. Besides its antibacterial effect, titanium dioxide also has good photocatalytic properties and is often used as ultraviolet stabiliser or as a colour filler [2, 4–6]. The antimicrobial effect is based on the creation of hydroxyl radicals who inhibit cell respiration or damage the outer membrane of the cell [2]. The chemical reaction leading to the creation of the hydroxyl radicals has to be pre-activated by an irradiation with ultraviolet light [2, 6].

Since titanium dioxide is a ceramic material, it also has the advantage of not having the allergenic potential like the often-used copper or silver-based additives and can therefore be applied in medical applications [2, 5, 6].

Combining these material properties with an additive manufacturing process can open up new potential and expand the product range. In polymer production, selective laser sintering is the most significant additive manufacturing process and is, due to the high accuracy of the sintered parts, currently at the transition stage from prototype manufacturing to series production [3, 7–11]. The selective laser sintering process is a powder based additive manufacturing technology, where the powder is successively applied in thin layers to the construction area and then melted locally using a carbon dioxide laser. Subsequently, the molten polymer solidifies and creates the layer fragments of the desired component. In the next step, the construction area is lowered by one layer thickness and new powder is applied. By repeated melting and solidifying of the newly applied powder, the desired component is produced, layer by layer [12]. Besides exceptions for special application, the most commonly used materials for selective laser sintering are polyamide 11 and polyamide 12, which are semi-crystalline thermoplastics [7–9, 13, 14]. In fact, it is assumed that 95 % of the polymer powder used in selective laser sintering are based on polyamide 12 [7]. For this reason, polyamide 12 is also used as the matrix material in this work.

This study aims to evaluate possible changes in the mechanical properties of polyamide 12 when using titanium dioxide as an antimicrobial additive. For this purpose, tensile tests are performed on specimens produced by selective laser sintering from compounds with different content of titanium dioxide. Mechanical properties of titanium dioxide compounds have already been investigated in several studies [3–6]. Most of them are carried out with nanoparticles as filler material, whereas the present research is focused on the usage of the micro sized powder.

2 | METHODOLOGY

With the aid of a laboratory mixer M3 (Zeppelin Systems GmbH, Germany) three compounds with different content of titanium dioxide are produced. The mixtures made for the purpose of this study contain 5 %, 10 % and 15 % titanium dioxide (weight percent). In order to provide a sufficient amount of powder for the additive manufacturing process, 12 kg of powder material are produced per compound using a mixing temperature of 130 °C and a mixing time of 1 : 45 h. The matrix material used for the compounds is the polyamide 12 powder DuraForm PA (3D-Systems Inc., Germany), which is developed for the application in selective laser sintering. To achieve an antibacterial effect of the compound, titanium dioxide is added. The titanium dioxide chosen for this study is a titanium (IV) oxide powder from IoLiTec Ionic Liquids Technologies GmbH (Germany) with a mean particle size of 200 nm. It is supplied in the crystal modification rutile. With its mean particle size above 100 nm, the powder does not belong to the category of nanomaterials [15, 16]. For safety reasons, only macro powders are used in this study and no nanoparticles are processed [16].

In order to investigate possible changes in the mechanical properties of the titanium dioxide compounds, tensile test specimens are fabricated with the aid of a laser sinter system Vanguard HS from the manufacturer 3D-Systems Inc., Figure 1. Furthermore, one set of specimens is produced out of pure polyamide 12 powder to compare the measurement results between the compounds and the virgin material. The printer operates with a 100 W carbon dioxide laser and has a possible build volume of 380 mm × 330 mm × 275 mm. As already investigated in previous studies, the orientation of the samples in the building chamber has a significant influence on the mechanical properties, i.e., the tensile strength, but since this is not the subject of this work, the specimens are only manufactured in one orientation [11, 17, 18]. They are placed parallel to the scanning direction of the printer, i.e., the testing direction corresponds to the scanning direction. The tensile test specimens are produced using a layer thickness of 100 µm with the dimensions chosen according to the standard DIN EN ISO 527-2, Type 1 A. Using a Zwick 1445-02, 10 kN universal testing machine, the specimens are analysed regarding their ultimate tensile strength, their elastic modulus and their elongation at break. To ensure a high accuracy for the measurement of the strain values, modular sensor arm extensometers are used during the hole test run and thus until the ultimate tensile strength is reached and the specimen fails. In accordance with the standard, five specimens are examined for each compound ensuring an explicit and statistically validated assessment of the mechanical behavior. The testing velocity used in this study is set to be constantly at 1 mm/min during the complete testing procedure. Although this is not required by the standard DIN EN ISO 527-1, it is applied here in order to avoid possible time-related influences since this may well be the case due to the viscoelastic behavior of polymers [19, 20]. Due to the hygroscopic material properties of polyamide, the samples are stored in a climate chamber for 88 h at standard climate conditions as required according to DIN EN ISO 291 [19, 20]. For this study, the climatic conditions for non-tropical countries apply, i.e., the conditioning of the samples is carried out at a temperature of 23 °C and a relative humidity of 50 %. Afterwards, the tensile tests are conducted at room temperature.

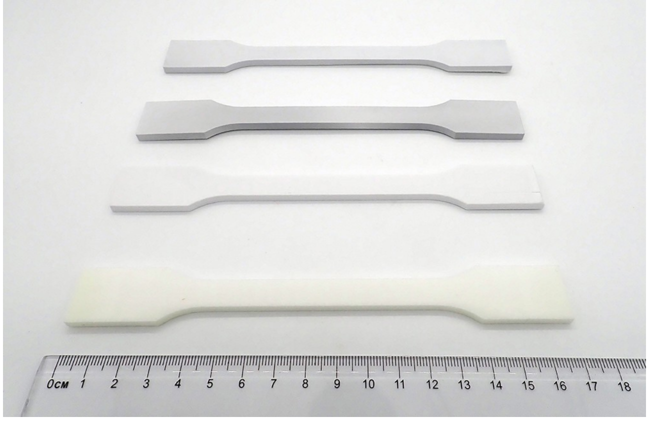

FIGURE 1 Tensile test specimen made out of different polyamide 12 compounds with 0 %, 5 %, 10 %, 15 % titanium (from the button to the top).

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

3 | RESULTS AND DISCUSSION

The results from the tensile 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 mechanical 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.

Determining the stress strain curves of the tested samples indicates a general loss in plasticity for the tensile test specimen produced out of the titanium dioxide compounds compared to the once fabricated out of virgin polyamide 12, Figure 2. Exemplary measurement results of the first tensile tests are illustrated by these stress strain curves. Comparing the results of the ultimate tensile strength show that the strength of the components increases with increasing content of titanium dioxide, Figure 3. However, the increase in strength only amounts small values, Table 1. In fact, the tensile strength only increases from an average value of 40.72 MPa for the virgin polyamide 12 to an average value of 42.29 MPa for the compound with 15 % titanium dioxide, which corresponds to a difference of only 1.6 % and can therefore be considered negligible. Nevertheless, it is noticeable that the strengths drop significantly for the compound with 5 % titanium dioxide, Figure 2. In total, the ultimate tensile strength declines about 20 % from an average value of 40.72 MPa to an average value of 32.61 MPa, Table 1. Generally, the addition of titanium dioxide seems to have a rather negative effect on the strength values, which can be also found in the literature [6]. A possible reason for this could be that the titanium dioxide particles prevent the individual polyamide particles from fusing together. However, what speaks against this is that the strength values increase again for an increasing proportion of titanium dioxide.

When comparing the elastic modulus, it is noticeable that they are increasing slightly with an increasing content of titanium dioxide, Figure 4. The increase amounts to a value of 10.9 % when comparing the mean values of the elastic modulus from the virgin polyamide 12 and

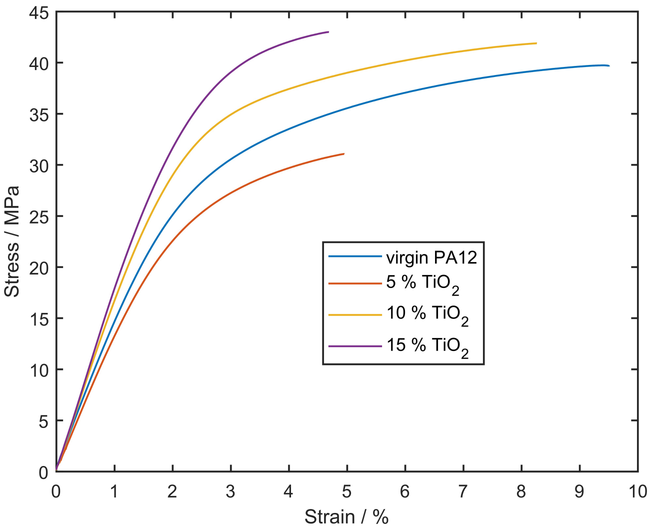

FIGURE 2 Stress-strain curves of tensile test specimen fabricated out of polyamide 12 with different contents of titanium dioxide.

BILD 2 Spannungs-Dehnungs-Diagramm von Zugproben aus Polyamid 12 mit unterschiedlichen Massenanteilen von Titandioxid.

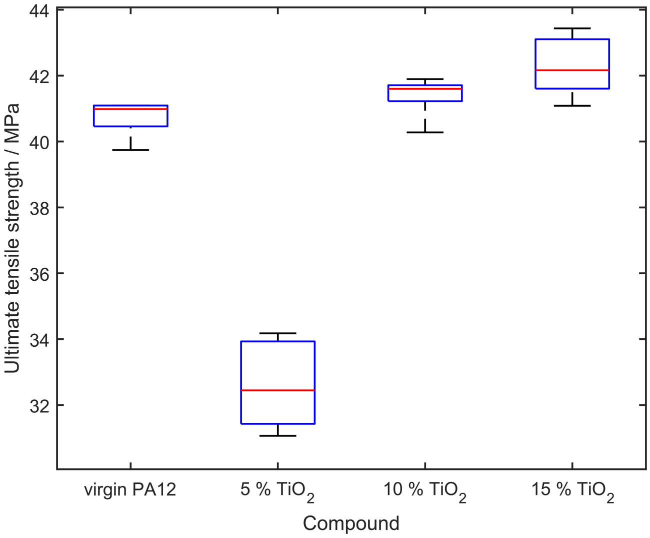

FIGURE 3 Ultimate tensile strength of tensile test specimen fabricated out of polyamide 12 with different contents of titanium dioxide.

BILD 3 Zugfestigkeit von Zugproben aus Polyamid 12 mit unterschiedlichen Massenanteilen von Titandioxid.

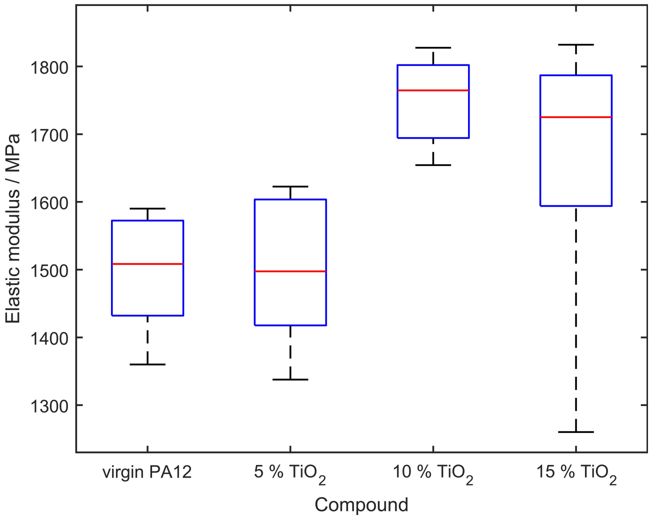

FIGURE 4 Elastic modulus of tensile test specimen fabricated out of polyamide 12 with different contents of titanium dioxide.

BILD 4 Elastizitätsmodul von Zugproben aus Polyamid 12 mit unterschiedlichen Massenanteilen von Titandioxid.

TABLE 1 Mean values of the results from the tensile tests.

TABELLE 1 Mittelwerte der Ergebnisse aus den Zugversuchen.

Compound [−]	Tensile strength σ_m [MPa]	Elastic modulus E [MPa]	Elongation at break ε_b [%]
virgin PA12	40.72	1496	10.74
5 % TiO_2	32.61	1500	5.24
10 % TiO_2	41.39	1750	7.39
15 % TiO_2	42.29	1659	4.61

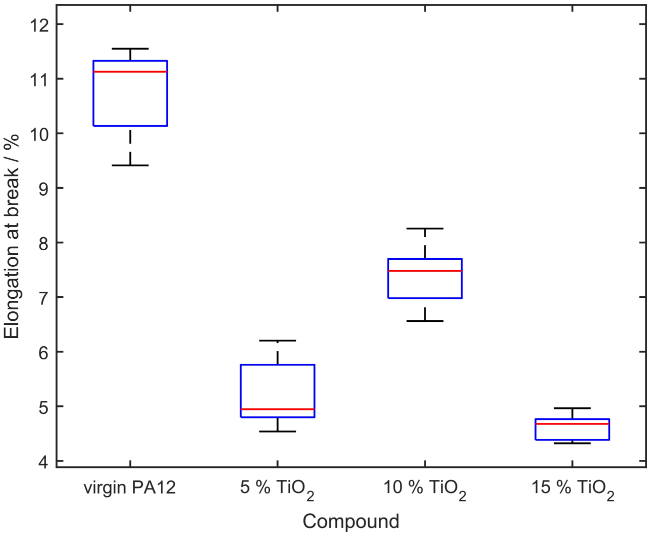

FIGURE 5 Elongation at break of tensile test specimen fabricated out of polyamide 12 with different contents of titanium dioxide.

BILD 5 Bruchdehnungen von Zugproben aus Polyamid 12 mit unterschiedlichen Massenanteilen von Titandioxid.

the 15 % compound, Table 1. Based on these measurements, it can be deduced that the addition of titanium dioxide leads to a stiffening effect. Furthermore, it is striking that the values for the 15 % compound vary greatly. This can be clearly seen from the long whisker, which is evident from the long whisker, i. e., the extreme minimum, Figure 4. This extremum is a single measured value that can be treated as an outlier and might be caused by incorrect clamping. Neglecting this outlier, the increase in stiffness for the specimen produced out of the 15 % titanium dioxide compound amounts a value of 17.6 % compared to the elastic modulus of the specimen made out of virgin polyamide 12.

The evaluation of the measurements for the elongation at break shows a general loss in ductility for the titanium dioxide compounds in comparison with the virgin polyamide 12 material, Figure 5. The results for the 5 % and 10 % compounds indicate an increasing ductility with increasing content of titanium dioxide. However, it is noticeable that the elongation at break for the 15 % is significantly lower and counteracts this trend. In order to provide a clear statement on this, further mixtures need to be investigated.

4 | CONCLUSIONS

A general loss in the ultimate tensile strength can be observed for the specimens with added titanium dioxide compared to the specimen out of virgin polyamide 12. Furthermore, it was found that the ultimate tensile strength of the present samples increases again with increasing titanium dioxide content of the compounds. This behavior has to be further validated with an extended testing range, regarding different titanium dioxide contents and more compounds. This predominantly negative influence on strength is also described in literature [6]. From the results for the elastic modulus, it can be concluded that the addition of titanium dioxide leads to a stiffening effect and thus to an increase in the elastic modulus.

Similar to the measurements of the ultimate tensile strength, the elongation at break also showed a decrease for increase of the titanium dioxide content of the compounds. It follows that the specimens examined undergo a general loss of ductility for the titanium dioxide compounds in comparison with the virgin polyamide. In summary, it can be stated that this study roughly shows the influence of titanium dioxide as an additive on the mechanical properties and allows the first tendencies to be identified. However, to confirm this, the scope of the test must be extended and a variety of different compounds with varying titanium dioxide content must be investigated, for example. In addition, further investigations should be carried out to determine the complete range of mechanical properties and thus the influence of the titanium dioxide, such as impact strength or fatigue behaviour.

ACKNOWLEDGEMENTS

The Author acknowledge the staff of the laboratory for polymer technology for the kind support to realize the experiments. Many thanks to the company 4D Concepts for providing the tensile test specimens. This Project is supported by the Federal Ministry for Economic Affairs and Energy (BMWi) on the basis of a decision by the German Bundestag. It is a cooperative research project with the companies 4D Concepts GmbH and M.J. Additive GmbH. Open Access funding enabled and organized by Projekt DEAL.

REFERENCES

1. R. Chamy, F. Rosenkranz, *Biodegradation – Life of Science*, IntechOpen, London, **2013**.
2. T. Huppmann, S. Yatsenko, S. Leonhardt, E. Krampe, I. Radovanovic, M. Bastian, E. Wintermantel, presented at *PPS-29*, Nürnberg, Germany, 15–19 July, **2013**, pp. 440–443.
3. M. Afshari, S. Bakhshi, M. Reza Samadi, H. Afshari, *Polym. Eng. Sci.* **2022**, *1*.
4. C. Cazan, A. Enesca, L. Andronic, *Polymers* **2021**, *13*, 2017.
5. N. Vidakis, M. Petousis, E. Velidaki, J. Kechagias, S. Grammatikos, *Materials* **2021**, *14*, 3076.
6. N. Vidakis, M. Petousis, N. Mountakis, E. Maravelakis, S. Zaoutsos, J. Kechagias, *Int. J. Adv. Manuf. Technol.* **2022**, *121*, 785.
7. M. Schmid, *Additive Fertigung mit Selektivem Lasersintern (SLS)*, Springer Verlag, Wiesbaden, **2015**.
8. J. Breuninger, R. Becker, A. Wolf, S. Rommel, A. Verl, *Generative Fertigung mit Kunststoffen*, Springer Verlag, Berlin, Heidelberg, **2013**.
9. S. C. Ligon, R. Liska, J. Stampfl, M. Gurr, R. Mülhaupt, *Chem. Rev.* **2017**, *117*, 10212.
10. D. L. Bourell, T. J. Watt, D. K. Leigh, B. Fulcher, *Phys. Procedia* **2014**, *56*, 147.
11. P. du Maire, E. Sert, M. Deckert, M. Johlitz, A. Öchsner, *Materialwiss. Werkstofftech.* **2022**, *53*, 503.
12. G. Abts, *Kunststoff-Wissen für Einsteiger*, Hanser, München, **2020**.
13. K. Dotchev, W. Yusoff, *Rapid Prototyp. J.* **2009**, *15*, 192.
14. R. D. Goodridge, C. J. Tuck, R. Hague, *Prog. Mat. Sc.* **2012**, *57*, 229.
15. H. C. Kim, H. Hahn, Y. S. Yang, *J. Compos. Mater.* **2013**, *47*, 50.
16. D. R. Boverhof, C. M. Bramante, J. H. Butala, S. F. Clancy, M. Lafranconi, J. West, S. C. Gordon, R, *Regul. Toxicol. Pharmacol.* **2015**, *73*, 137.
17. M. Rybachuk, C. A. Mauger, T. Fiedler, A. Öchsner, *J. Polym. Eng.* **2017**, *37*, 699.
18. H. Altenbach, M. Johlitz, M. Merkel, A. Öchsner, *Lectures Notes on Advanced Structured Materials*, Springer, Cham **2022**.
19. C. Bonten*, Kunststofftechnik. Einführung und Grundlagen*, Hanser, München, **2020**.
20. G. Abts, *Kunststoff-Wissen für Einsteiger*, Hanser, München, **2020**.

How to cite this article: P. du Maire, M. Deckert, M. Johlitz, A. Öchsner, *Materialwiss. Werkstofftech.* **2023**, *54*, e202200329. https://doi.org/10.1002/mawe.202200329