

Effects of the Rice Husk Ashes and Titanium Dioxide on Properties of ABS Composites Parts Obtained by 3D Printing



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Abstract The purpose of this study was to evaluate the effects of incorporation of the rice husk ashes and titanium dioxide on properties of acrylonitrile butadiene styrene (ABS). The incorporation of rice husk ashes (RHA) (2.5 wt.%) and titanium dioxide (2.5; 5.0 wt.%) into ABS matrix was carried out by melting extrusion process using a twin-screw extruder. Neat ABS and its composites filaments for FDM 3D printing were produced using the melting extrusion process to obtain specimens for tests. The properties of ABS/RHA/TiO₂ composite samples were investigated by the properties of the ABS/RHA/TiO₂ composite samples were evaluated using tensile tests, SEM, XRD analysis, Charpy impact test, and water contact angle measurements. This study contributes to our understanding of the behavior of ABS composites containing RHA and TiO₂ for various industrial applications.

Keywords RHA · TiO₂ · ABS · Mechanical tests · SEM · DRX

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Introduction

In recent years, the field of materials science and engineering has seen a surge in innovative research aimed at addressing pressing environmental and industrial challenges. ABS (acrylonitrile butadiene styrene) is a widely used thermoplastic in industries due to its excellent mechanical properties and processability [1, 2].

The use of fillers in polymeric composites has been gaining popularity in recent years due to the advantages they offer, such as improved mechanical, thermal, and electrical properties [3]. One type of filler that has attracted much attention is rice husk ash (RHA), which is a byproduct of the rice milling industry. RHA is a renewable and sustainable material that is abundant and low-cost. It is also a good reinforcing filler due to its high content of silica. Chaudhary et al. reviewed the performance of RHA in polymeric composites [4]. The authors emphasized the need for better characterization of RHA to obtain a better understanding of its behavior. The authors also proposed a new approach to RHA modification to improve its performance as a filler.

Among the different fillers used, such as clays, silicas, nanotubes, inorganics, etc., titanium dioxide (TiO_2) plays a special role in polymeric matrices, to synthesize high-performance and malleable polymer networks (e.g., improving viscosity, obtaining filaments for 3D printing) [5]. TiO_2 is found in many applications due to its good photocatalytic properties, hence it is used in antiseptic and antibacterial compositions, degrading organic contaminants and germs, as a UV-resistant material; this is due to its chemical inertness properties, non-toxicity, low cost, high refractive index, and other advantageous surface properties [6, 7].

Among these challenges, the treatment of oily water has gained significant attention, driven by the increasing offshore oil transportation activities and the unfortunate incidents of oil leakages. This study explores the pioneering work of Lei Han and his team, who have introduced a groundbreaking approach to tackle this issue. Their research revolves around the development of a functional TiO_2 -ABS composite membrane, created through a cutting-edge three-dimensional (3D) printing strategy.

To enhance ABS for specific applications, additives such as rice husk ashes (RHA) and titanium dioxide have been investigated. The incorporation of RHA (2.5 wt.%) and titanium dioxide (2.5; 5.0 wt.%) was achieved using a twin-screw extruder in a melting extrusion process. Through this process, neat ABS and its composite filaments for Fused Deposition Modeling (FDM) 3D printing were produced, allowing the generation of test specimens. The properties of the ABS/RHA/ TiO_2 composite samples were evaluated using tensile tests, SEM, DSC, XRD analysis, Charpy impact test, water absorbency test, and water contact angle measurements.

Materials and Methods

Materials

The materials used in this work to prepare the polymeric matrix was ABS (acrylonitrile butadiene styrene) from BASF, and as fillers, rice husk ashes (RHA) waste disposed by Brazilian Rice Industry and titanium dioxide (TiO₂) was purchased from Sigma Aldrich.

Methods

Rice Husk Ashes (RHA) and Titanium Dioxide (TiO₂) Preparation

Rice husk ashes (RHA) and titanium dioxide (TiO₂) powders were previously dried in an oven with air circulation at 60 °C for 24 h.

Composite Preparation

ABS was firstly dried in an oven with an air circulation system, at 80 °C for 24 h, to reduce moisture content to less than 2%. Polymeric composites were prepared in different compositions by weight: ABS with addition of rice husk ashes (RHA) (2.5 wt.%) and titanium dioxide (2.5 and 5.0 wt.%), according to composition presented in Table 1.

The compositions (ABS/RHA/TiO₂) were hand premixed and then processed in a Thermo Scientific HAAKE twin-screw co-rotating extruder, model Rheomex 332p, with 16 mm screw diameter and a length-diameter-ratio of 25. The biobased composites were processed in a two-step to better dispersion of RHA and TiO₂ into the ABS matrix. The compositions were processed in the temperature profile of 150/165/175/175/165/150 °C, and screw speed of 30 rpm. The extruded biobased composites were cooled down, pelletized, and dried again in an oven with an air circulation system at 80 °C for 4 h.

Table 1 ABS/RHA/TiO₂ biobased composites composition

Composition	Pure ABS (wt.%)	RHA (wt.%)	TiO ₂ (wt.%)
Neat ABS	100	0	0
ABS/RHA 2.5%/TiO ₂ 2.5%	95.0	2.5	2.5
ABS/RHA 2.5%/TiO ₂ 5.0%	88.0	2.5	5.0

Note The composite contained 5 wt.% silane

Filaments Preparation

The biobased composites, with different amount of TiO_2 , were fed to a Thermo Scientific HAAKE twin-screw co-rotating extruder to produce the filaments for 3D FDM. The temperature profile was 145/160/175/175/165/145 °C, screw speed set to 30 rpm, temperature of cooling water of the filaments was 35 °C, and filament diameter of 1.75 ± 0.01 mm.

Fused Deposition Modeling (FDM) 3D Printing

The specimens for tensile and water absorption tests were manufactured using the FDM technique on a 3D printer, and they were pre-sliced using the Cura3D software, employing the following settings: 100% infill density, printed with a 0.4 mm nozzle, at a speed of 80 mm/s. The printing temperatures for all blends were set at 180 °C for the nozzle and 70 °C for the build platform to ensure adequate adhesion of the printed components. The components were produced using an Artillery Sidewinder X1 3D printer.

Characterization

X-ray Diffraction (XRD)

XRD patterns of ABS and the biobased composites were recorded with a Siemens-d5000 Diffractometer operated at 40 kV and 40 mA, with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5406$ Å), over the 2θ range from 5° to 40°.

Scanning Electron Microscopy (SEM) Analysis

SEM analyses were conducted in a Model LX-30 Philips instrument operated at an electron acceleration voltage of 12 kV. The samples' cryofractured surfaces under liquid nitrogen were sputtered with a gold layer before SEM analyses of the morphology of the samples' surfaces.

Water Contact Angle Measurements

The absorption of water by a material's surface is related to the wetting process of water on the material's surface and, consequently, the hydrophilic/hydrophobic

character of the material's surface. A high degree of wettability between water and material means a greater contact area between them and a greater probability of absorption, making the material more hydrophilic. Wettability is commonly assessed by the contact angle of the liquid with the solid surface. In this phenomenon, the greater the contact angle, the lower the wettability, meaning that the material has a hydrophobic character when the liquid wets less the solid surface in contact. The surface wettability of composite samples was determined through water contact angle (WCA) measurements using a DSA 100 Kruss goniometer equipped with a camera to capture images of water droplets and then determine the contact angles. Deionized water was used to evaluate the wettability properties of these samples. Angle measurements were performed in triplicate, and the average values were taken [8].

Water Absorbency Test

Water absorbency measurements of the bionanocomposite film samples were conducted in triplicate, and the average values were recorded. The water absorption of the bionanocomposite films was assessed in terms of swelling. Each film sample was cut into a $2 \times 2 \text{ cm}^2$ piece, dried at $45 \pm 2^\circ\text{C}$ for 24 h in a circulating air oven, and pre-weighed. The pre-weighed samples were immersed in a Petri dish filled with 20 mL of deionized water and left undisturbed for 24 h at room temperature until equilibrium swelling was achieved. The samples were then removed from the deionized water, quickly dried with filter paper to remove surface droplets, and re-weighed. The samples were weighed at specific time intervals until equilibrium swelling was reached. The swelling ratio was calculated using the following expression, Eq. (3) [8, 9]:

$$\text{Swelling Ratio (\%)} = ((W_s - W_d) / (W_d) \times 100) \quad (3)$$

where W_s = weight of the swollen samples, W_d = weight of the dry samples in all three replicates.

Tensile Tests

Printed specimens from the neat ABS and the biobased composites were submitted to tensile tests using an Instron model 5564, according to ASTM D 638–99, at room temperature and with a cross-head speed of 50 mm/min. For each composition, five specimens were tested, and the average value of five specimens with the standard deviation was recorded.

Charpy Impact Test

The Charpy impact test involved striking a notched specimen with a pendulum hammer and measuring the energy absorbed by the specimen during fracture. The specimen was typically a rectangular bar with a V-shaped notch at its center. The specimen was placed on two supports, and the pendulum was released from a fixed height. The energy absorbed by the specimen was calculated by subtracting the final height of the pendulum from the initial height. The higher the energy absorbed, the tougher the material.

Results and Discussion

XRD Analysis Results

The XRD patterns of neat ABS and the biobased composites are shown in Fig. 1. For the neat ABS it can be seen the prevalence of the ABS characteristics, mainly amorphous, with peaks at around 15°, 22° and 42°. This behavior will be used for the comparison of all samples. For the composite with 2.5 wt.%TiO₂, these three peaks decreased intensities, showing the presence of crystalline material, as expected for the TiO₂, with peaks at 27°, 36°, 42°, 54°, and 56°, corresponding to the crystalline planes of TiO₂. Similar behavior can be seen for the sample prepared with 5.0 wt.%TiO₂, mainly showing only the peaks concerned to the crystalline phases. Increased amount of addition lead to the prevalence of characteristic diffraction peaks associated with TiO₂ in the X-ray diffraction (XRD) pattern. ABS, conversely, exhibits prominent peaks at 15°, 22° and 42°. It is noteworthy that the relative intensity of these peaks diminishes while their width increases for the samples containing increased amount of TiO₂.

SEM Analysis Results

The SEM images of cryogenic fracture surfaces of neat ABS and its biobased composites are shown in Fig. 3. It can be observed from Fig. 2a that neat ABS exhibits morphology characteristic of immiscible systems, with globular volumes. Upon the addition of TiO₂, the micrographs exhibit irregular particles embedded in the ABS matrix, indicating a low compatibility between ABS and TiO₂. Figures 2b, c show increasing amount of white spots, corresponding to the increased amount of TiO₂ (2.5 and 5.0 wt.%).

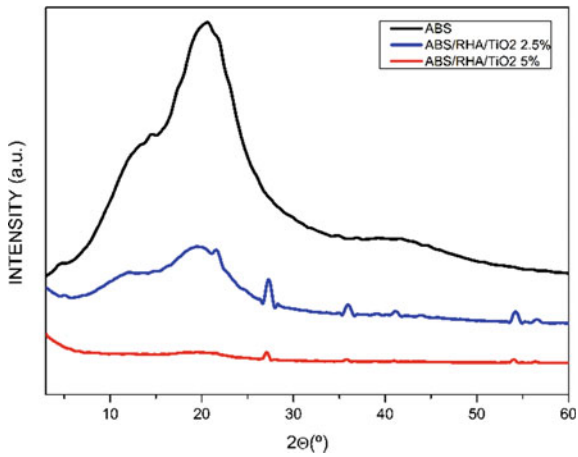


Fig. 1 XRD patterns of ABS matrix and its composites containing TiO₂

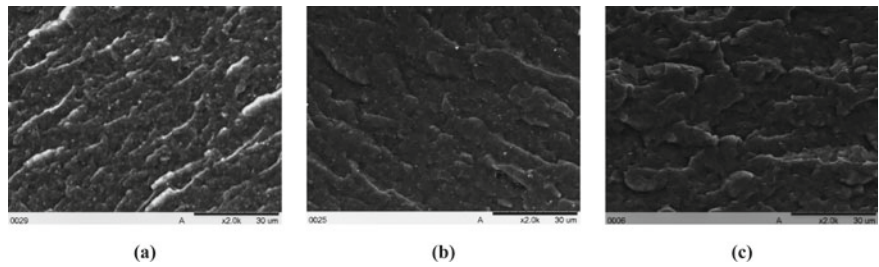


Fig. 2 SEM images of cryogenic fracture surfaces at 2000 X of magnification: **a** ABS; **b** ABS with 2.5 wt.%TiO₂; **c** ABS with 5.0 wt.%TiO₂

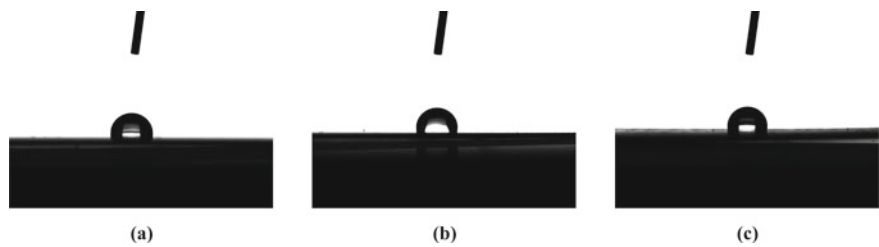


Fig. 3 Water contact angle (WCA) of samples: **a** ABS; **b** ABS with 2.5 wt.%TiO₂; **c** ABS with 5.0 wt.%TiO₂

Water Contact Angle (WCA) Measurements

The water droplet image on the composite film surfaces and the contact angle (WCA) measured for different TiO₂ content of 2.5 wt.% and 5.0 wt.% are shown in Fig. 3 and

Table 2 Water contact angle (WCA) degree of the ABS and the composite films

Composition	Water contact angle (°)	Swelling ratio (%)
Neat ABS	99.3 ± 1.22	0.48 ± 0.04
ABS/RHA 2.5%/TiO ₂ 2.5%	103.2 ± 1.01	0.65 ± 0.04
ABS/RHA 2.5%/TiO ₂ 5.0%	97.2 ± 0.87	0.45 ± 0.01

Table 2, respectively. The WCA of the composite sample surfaces were measured to evaluate the hydrophilic/hydrophobic character of the sample. The water contact angle of the composite samples remained approximately the same with or without TiO₂. The high contact angle values around 100° show that all the surfaces are highly hydrophobic, as expected for ABS. The addition of TiO₂ did not change this behavior, within the measure deviation. The surface hydrophobicity of ABS may explain these results, even with the dispersion of TiO₂ in the ABS matrix. The surface hydrophobicity of ABS reduces diffusion of water molecules on the surface. This behavior may also indicate the good homogeneity of the matrix obtained with the preparation procedure used for this work.

Water Absorbency Test

The results of swelling ratios (%) obtained in this study provide a profound understanding of the water absorbency characteristics of the different materials under investigation (Table 2). Firstly, the results revealed that neat ABS exhibited a swelling ratio of 0.48% ± 0.04. In contrast, the ABS/RHA 2.5%/TiO₂ 2.5% composite displayed a swelling ratio of 0.65% ± 0.04. Finally, the ABS/RHA 2.5%/TiO₂ 5.0% composite recorded a swelling ratio of 0.45% ± 0.01. Surprisingly, despite containing a higher concentration of TiO₂, this mixture showed a slightly lower water absorbency capacity compared to the composition containing only 2.5 wt.% TiO₂.

Tensile Test Results

Table 3 presents the dependence of tensile strength and elongation at break and at yield, and Young's modulus on the content of RHA and TiO₂ in the ABS composites. As shown in Table 3, the tensile strength at break and at yield have the same behavior, decreasing in values with the increase of the TiO₂ content, while the elongation increased for the ABS/RHA 2.5%/TiO₂ 2.5% composites, which was to be expected since the material became more ductile. This declining trend in tensile strength showed in Table 3 could be related to the poor connectivity and low compatibility between the TiO₂ particles and the ABS matrix.

Table 3 Tensile test results of neat ABS and the composites

Composition	Tensile stress at break (MPa)	Tensile stress at yield (MPa)	Elongation at break (%)	Tensile extension at yield (mm)	Youngs' Modulus (MPa)
Neat ABS	46.6 ± 2.2	47.5 ± 1.3	16.9 ± 1.1	5.5 ± 0.4	869.4
ABS/RHA 2.5%/TiO ₂ 2.5%	37.0 ± 1.9	41.2 ± 2.8	23.4 ± 0.7	5.7 ± 0.5	712.4
ABS/RHA 2.5%/TiO ₂ 5.0%	33.4 ± 1.3	35.4 ± 1.3	17.3 ± 1.3	4.2 ± 0.2	852.8

In relation to ABS/RHA 2.5%/TiO₂5.0% composites, the increase in the amount of TiO₂ led to an increase in agglomerates, which act as a defect within the polymeric matrix, causing a non-uniform stress distribution in the ABS/RHA 2.5%/TiO₂5.0% composites capable of reducing the interaction between TiO₂ and the PBAT/PLA matrix and can also act as rupture sites and, consequently, reduce the tensile properties of the material. Regarding the values of Young's modulus for the samples with and without the addition of RHA and TiO₂, it is important to note that the Young's modulus of the composite material depends on the interfacial adhesion and the tension transferred between the matrix and the fillers. In cases where there is a lack of a strong connection or good interfacial adhesion between TiO₂ and ABS, the presence of TiO₂ tends to decrease the Young's modulus value. The decrease of the tensile properties of ABS when the filler amount increases has also been observed in composites of ABS with other fillers [10, 11].

Charpy Impact Test Results

Table 4 presents the results obtained with the Charpy impact tests for the samples with and without TiO₂ addition. The first behavior is the decrease of the necessary energy to fracture the composites with TiO₂, when compared to the neat ABS. This decreasing trend for the Charpy impact energy could again be related to the poor connectivity and low compatibility between the TiO₂ particles and the ABS matrix.

Table 4 Charpy impact test results of the ABS and the composite films

Composition	Charpy impact test (J)
Neat ABS	0.90 ± 0.15
ABS/RHA 2.5%/TiO ₂ 2.5%	0.36 ± 0.04
ABS/RHA 2.5%/TiO ₂ 5.0%	0.50 ± 0.06

Conclusion

This study successfully incorporated rice husk ashes (RHA) and titanium dioxide (TiO_2) into the acrylonitrile butadiene styrene (ABS) matrix using a melting extrusion process. Extensive testing and analysis were conducted to assess the influence of these additives on ABS composites. The addition of TiO_2 resulted in irregularly embedded particles within the ABS matrix, indicating some degree of incompatibility between ABS and TiO_2 , which could impact mechanical properties. Tensile strength at break and yield decreased with the addition of TiO_2 , indicating potential challenges related to the compatibility between TiO_2 particles and the ABS matrix. TiO_2 -containing composites exhibited reduced impact energy compared to neat ABS, possibly due to limited compatibility between TiO_2 and ABS. However, the decrease in tensile strength and impact energy suggests the need for improved dispersion of TiO_2 to avoid compromising mechanical properties. These findings contribute to our understanding of enhancing ABS composites for various industrial applications. Based on this work, new studies must be carried out to develop more effective strategies to improve interfacial adhesion between RHA, TiO_2 and the ABS matrix, and consequently obtain composite materials with superior properties suitable for a wide range of applications.

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References

1. Gong K, Liu H, Huang C, Cao Z, Fuenmayor E, Major I (2022) Hybrid manufacturing of acrylonitrile butadiene styrene (ABS) via the combination of material extrusion additive manufacturing and injection molding. *Polymers (Basel)* 14(23)
2. Almushaikeh AM, Alaswad SO, Alsuhaybani MS, Alotaibi BM, Alarifi IM, Alqahtani NB, Aldosari SM, Alsaleh SS, Haidyrah AS, Alolyan AA, Alshammari BA (2023) Manufacturing of carbon fiber reinforced thermoplastics and its recovery of carbon fiber: a review. *Polym Test [Internet]*. 122:108029. <https://doi.org/10.1016/j.polymertesting.2023.108029>
3. Anwajler B, Zdybel E, Tomaszewska-Ciosk E (2023) Innovative polymer composites with natural fillers produced by additive manufacturing (3D printing)—a literature review. *Polymers* 15(17):3534
4. Chaudhary DS, Jollands MC, Cser F (2004) Recycling rice hull ash: a filler material for polymeric composites? *Adv Polym Technol* 23(2):147–155
5. Vidakis N, Petousis M, Maniadi A, Koudoumas E, Liebscher M, Tzounis L (2020) Mechanical properties of 3D-printed acrylonitrile-butadiene-styrene TiO_2 and ATO nanocomposites. *Polymers (Basel)* 12(7):1–16
6. Anucha CB, Altin I, Bacaksiz E, Stathopoulos VN (2022) Titanium dioxide (TiO_2)-based photocatalyst materials activity enhancement for contaminants of emerging concern (CECs)

- degradation: in the light of modification strategies. *Chem Eng J Adv* [Internet] 10(2):100262. <https://doi.org/10.1016/j.cej.2022.100262>
7. Kamrannejad MM, Hasanzadeh A, Nosoudi N, Mai L, Babaluo AA, Ave H (2014) *Aop*267214.Pdf 17(4):1039–1046
 8. Andrade MS, Ishikawa OH, Costa RS, Seixas MVS, Rodrigues RCLB, Moura EAB (2022) Development of sustainable food packaging material based on biodegradable polymer reinforced with cellulose nanocrystals. *Food Packag Shelf Life* 31
 9. Yadav M, Chiu FC (2019) Cellulose nanocrystals reinforced κ -carrageenan based UV resistant transparent bionanocomposite films for sustainable packaging applications. *Carbohydr Polym* [Internet] 211:181–94. <https://doi.org/10.1016/j.carbpol.2019.01.114>
 10. Al-Mazrouei N, Ismai A, Ahmed W, Al-Marzouqi AH (2022) ABS/silicon dioxide micro particulate composite from 3D printing polymeric waste. *Polymers* 14:509. <https://doi.org/10.3390/polym14030509>
 11. Behera BK, Thirumurugan M (2022) A study on visco-elastic, thermal and mechanical characteristics of injection molded ABS/graphite composite. *Mater Today Proc* 56:2915–2922