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Optimization and the Influence of Additive on the Interfacial Bonding between Cocoa Fruit Shell Powder and Polypropylene-Based Composite

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Abstract

Agricultural residues are excellent alternative materials to lignocellulosic materials because they are inexpensive, easily processed, plentiful, and renewable. Optimization and the influence of additive on the interfacial bonding between Cocoa fruit shell powder and Polypropylene-based composite was carried out. The methods use include, water absorption, tensile strength, impact strength, hardness, and SEM. From the studies it was shown that the water absorption property of the composites decreases with increase in $CaCO_3$ content in the matrix for all the composites investigated. The tensile strength of the modified composite increases with additive. The impact strength results are 4.17 kJ/m^3 to 5.58 kJ/m^3 for unused/treated composites, 3.47 kJ/m^3 to 5.27 kJ/m^3 for waste/treated composites. It was observed that the hardness for the modified composite ranges from 39 MPa to 63 MPa for unused polypropylene/treated and, 33.43 MPa to 52.77 MPa for waste polypropylene/treated composites. Based on SEM images, it can be said that the use of Alkaline treated Cocoa fruit shell powder and microcrystalline cellulose resulted in better-dispersed structures in the polymer matrix. This project mitigates environmental impact without compromising structural integrity by exploring Theobroma cacao and Polyethylene modified composite materials.

Keywords: Cocoa, Composite, Polypropylene, Shell

INTRODUCTION

In the realm of sustainable construction solutions, composite materials have emerged as a beacon of hope, offering a promising alternative to conventional materials like plywood (Ashori, 2021). Unlike their monolithic counterparts, composites are engineered marvels, meticulously crafted by uniting two or more disparate constituents to forge a material imbued with superior properties (Al-Oqla & Omari, 2017). This synergistic fusion of materials, often a harmonious blend of matrix and reinforcement, can be meticulously tailored to fulfill specific performance requirements, making composites a versatile tool in the construction industry's arsenal (Hassan *et al.,* 2019).

Composites are heterogeneous systems with two distinct phases having different properties (Shalkuhtala *et al.,* 2024). Composites typically consist of a matrix material, which serves as a continuous phase, and a reinforcement, such as fibers or particles, embedded within the matrix. The resulting composite material exhibits a synergistic combination of properties from its individual components, often achieving a superior strength-to-weight ratio, increased durability, and specific performance advantages (Eze *et al.,* 2022). Common examples include fiber-reinforced polymers, metal matrix composites, and ceramic matrix composites, each tailored for diverse applications across industries such as aerospace, automotive, and construction due to their versatile and advantageous qualities (Shanchez *et al.,* 2023).

Agro-industrial waste is an option for developing new low-cost materials derived from renewable sources (Ortega *et al.,* 2021). The use of natural additives obtained from agro-industrial waste in polymer matrices has gained interest in recent years because they take advantage of materials that do not have an industrial application and reduce environmental pollution while improving specific mechanical and thermal properties (Wahab *et al.,* 2019).

One of the main applications of agro-industrial waste materials is as absorbents of polluting metals such as chromium; their absorption capacity of waste materials has been improved by treating them with acidic aqueous solutions (Komnitsas *et al.,* 2019). Furthermore, the absorption properties of walnut shells have also been studied (Altun *et al.,* 2018), finding an improved sorption capacity due to the presence of functional groups in the shells after the modification process. Another application of this kind of material is as a source of cellulose nanocrystals which are highly appreciated (Zheng *et al.,* 2019). Despite the vast researches carried out on plastic waste and agricultural materials, the market is still in need of more industrial materials (Mikyitsabu & Aasegh, 2024).

However, researches on utilization of solid agro-wastes are gradually receiving attention from the scientific community with little or no attention from the industries in developing nations. The use of these wastes as fillers in polymer composites (Uzochukwu *et al.,* 2020), nano fillers in reinforcing plastics and rubber (Umunakwe *et al.,* 2019). lignin-containing cellulose nanomaterials biodegradable polymer films (Ewulonu *et al.,* 2020) and many other functional materials have been reported. The excellent mechanical properties and biodegradability of most crop residue/waste have positioned them as choice reinforcing materials in polymer composites.

Shah *et al.,* 2019 prepared epoxy composites containing 0.5, 1.0, 1.5, and 2.0 wt% Acacia Catechu powder. Adding a very small amount of filler (1.0 wt%) resulted in a 14% increase in the FS and 94% improved IS due to the modification in morphology and crosslink density. Kommula *et al.,* 2021 studied the effect of incorporation of untreated and alkali-treated Napier grass in the epoxy matrix. Randomly oriented short and long unidirectional fibers were used for the fabrication of the composites. The fiber loading used was 10%, 20%, and 30%, and the NaOH concentration used was 5%, 10%, and 15%. The TS, TM, FS, FM, and IS of the composites were improved with fiber addition and NaOH treatment.

This project aims to study optimization and the influence of additive on the interfacial bonding between Cocoa fruit shell powder and Polypropylene-based composite in order to mitigates environmental impact without compromising structural integrity by exploring Theobroma cacao and Polyethylene modified composite materials.

MATERIALS AND METHODS

Shell/polypropylene composite preparation

The polypropylene composite of the fruit shell of *Cocoa* powder was prepared by thoroughly mixing 10 g of polypropylene with appropriate filler quantities (10, 15, 20, 25 and 30 g). The polypropylene melted and homogenized with the filler in a beaker. The composites were molded using the aluminum sheets. This was also repeated for 10 g each of *Cocoa* powder with appropriate matrix quantities (10, 15, 20, 25 and 30 g).

Modification

The modification of the composites was carried out using $CaCO_3$ as modifiers. 0.1 g of $CaCO_3$ was added to 10 g of the filler content and mix together. 10 g of the matrix was melted in a beaker after which the filler containing $CaCO_3$ was added and mixed properly before casting. This was used for the preparation of the composite. The process was repeated at 0.3, 0.5, 0.7 and 1.0 g of $CaCO_3$.

Water absorption (ASTM D 570-98)

Water absorption test was performed following the ASTM D 570-98 method. Water absorption of the composites was determined after 2 h and 24 h by immersion in distilled water at room temperature, 24°C. Five specimens of each formulation was dried in an oven for 24 h. The dried specimens are weighed with a precision of 0.001 g. All specimens were immersed in distilled water. At the end of the immersion periods, the specimens were removed from the distilled water, the surface water was wiped off using tissue, and wet weight values is determined. Water absorption percent was calculated using equation 1. (Dass *et al.,* 2016).

$$M\ (\%) = \frac{(mt - m^\circ)}{m^\circ} \times 100 \qquad\qquad Equation\ 1$$

Where m_o and m_t denote the oven-dry weight and weight after time t, respectively. Water absorption and thickness swelling

Tensile Strength test

The dimensions of tensile strength test specimens were in accordance with ASTM D 638-14. In the tensile tests, five specimens of composites were analyzed, with dimensions in agreement with the ASTM D 638 standard for each of the composites.

Impact Strength properties

The impact tests on the formulated composite samples were carried out using Cat. NV. 412. Standard impact test samples measuring 80 x 10 x 10 mm with notch depth of 2 mm was prepared according to (ASTM, D2000), and at angle of 450 as shown in figure below.

Three spacemen for each of the composition was used and the average value was recorded in Joules (J). The impact strength of the composite was calculated using equation (3).

$$Impact\ strength = \frac{Impact\ energy\ (J)}{Thickness} \qquad -----\ Equation\ 3$$

Hardness Test (ASTM D-2240)

Hardness is referred to the resistance of a material to indentation, the higher this resistance the harder the material and vice-versa. The hardness test was carried out using Modified Meyer hardness tester. The hardness for the samples was determined using the expression stated in equation 2. (Mikyitsabu *et al.*, 2023).

$$BHN = \frac{F}{\pi\left(D - \sqrt{D2} - Di\right)2} \qquad Equation\ 2$$

Where; F = The imposed load, D = Diameter of the indenter, D_i = Diameter of the indentation

Scanning Electron Microscopy (SEM) (ASTM E9862-97)

A morphology study was carried out using scanning electron microscopy (SEM) to evaluate the fractured surface of samples. The changes in morphology are important to predict fiber interaction with the matrix in composites.

RESULTS AND DISCUSSION

Water Absorption for Cocoa Fruit Shell Particles (CFS) and Polypropylene Composites

As shown on plate 1: (A) is the treated Cocoa fruit shell and unused polypropylene composites, (CFS) (B) is only polypropylene waste. Figure 1 shows the effect of $CaCO_3$ content on water absorption of treated Cocoa fruit shells (CFS) of unused and waste polypropylene-based composites after 2 h water immersion. As shown in the Figure, the water absorption property of the composites decreases with exposure time and increase in $CaCO_3$ content in the matrix for all the composites investigated. This shows a decrease in water absorption especially at 0.5 g to 1 g must water uptake was observed. When the content of the $CaCO_3$ increases in the composite, the presence of free -OH groups in the cellulose and hemicellulose structure are blocked and then these hydrophilic shell particles are less available to absorb water through hydrogen bonding between water molecules and the OH-groups on the surface of wood particles (Das, *et al.,* 2018).

(A) (B)

Plate 1: (A) Treated Cocoa fruit shell and unused polypropylene composites, (CFS) (B) Only polypropylene waste

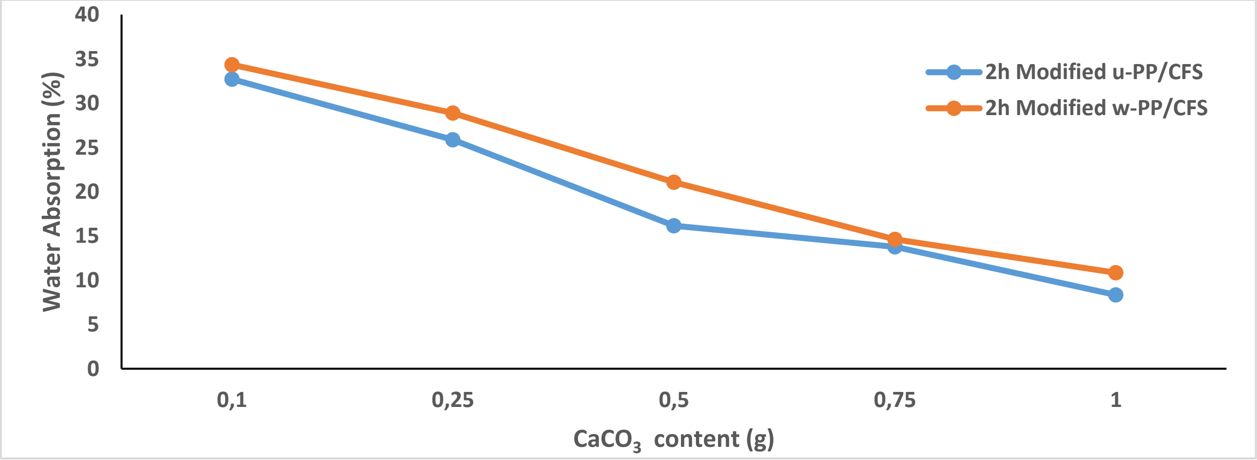


Figure 1: Effect of $CaCO_3$ content on water absorption of treated Cocoa fruit shell (CFS) with unused and waste polypropylene-based composites after 2 h water immersion

The effect of $CaCO_3$ content on water absorption of treated Cocoa fruit shell (CFS) with unused and waste polypropylene-based composites after 24 h water immersion is shown in Figure 2. As seen, 58.4 % to 13.65 % for treated/unused composite, 61.9 % to 14.6 % for treated/waste composite. Several researchers have reported that the water absorption of natural filler polymer composite increases with increase in filler loading; and decreases with matrix loading. Kocaman, & Ahmetli, (2020) reported linear relationship between filler loading and water absorption.

In general, the water absorption decreased with increasing $CaCO_3$ content – a trend that is true for both the 2 hours and 24 h water immersion tests. The water absorption property of polymer-filled composites is influenced by factors, such as processing techniques, type of matrix, type of filler, filler/matrix composition of the composites, and contact time in water (Ramkumar *et al.,* 2020).

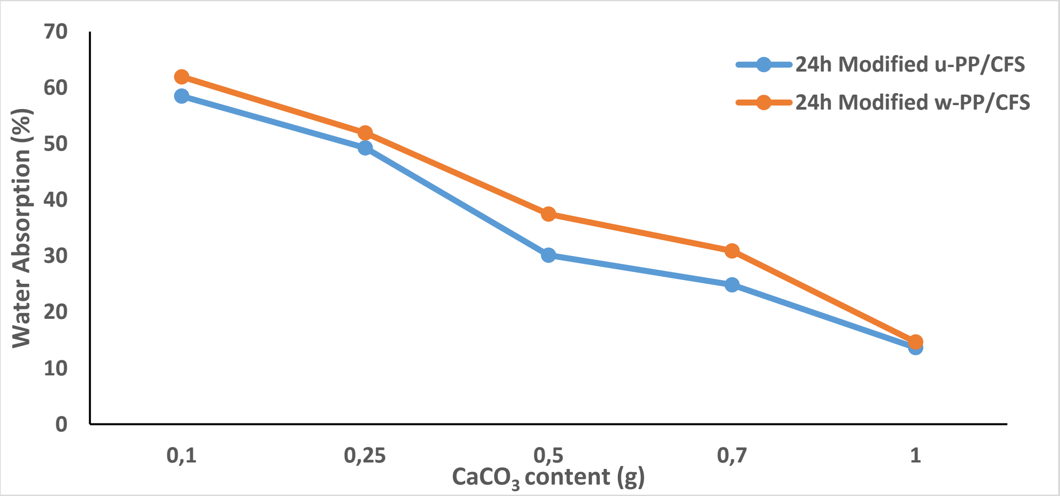


Figure 2: Effect of $CaCO_3$ content on water absorption of treated Cocoa fruit shell (CFS) with unused and waste polypropylene-based composites after 24 h water immersion

Figure 3: Effect of $CaCO_3$/filler on tensile strength of treated Cocoa fruit shell (CFS) with unused and waste polypropylene-based composites. The effect of chemical modification and concentration of the reinforcing agent on the properties of composites has been investigated. Also, the tensile strengths of all chemically modified Cocoa fruit shell (CFS) composites are higher than that obtained with pure polypropylene and unmodified Cocoa fruit shell (CFS) composites. It was observed that the modification increased the tensile strength when compared to the unmodified. The tensile strength ranges from 66.34 MPa to 52.55 MPa for unused/treated, 61.62 MPa to 49.34 MPa for waste/treated composites.

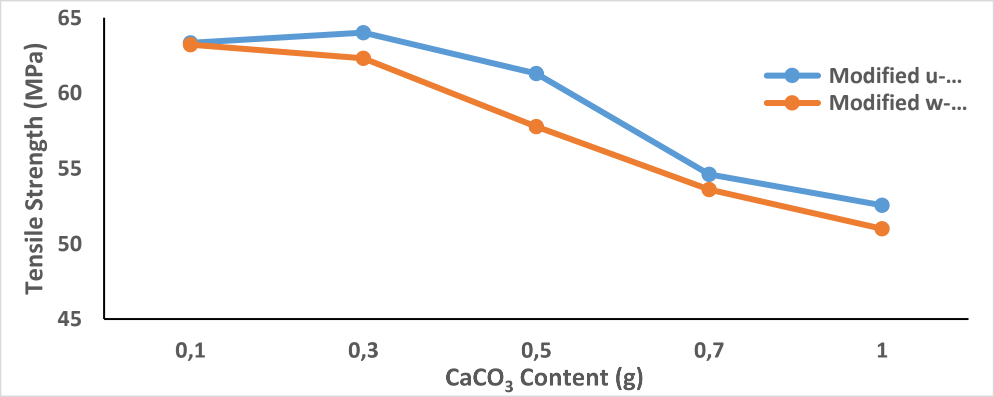


Figure 3: Effect of $CaCO_3$/filler on tensile strength of treated Cocoa fruit shell (CFS) with unused and waste polypropylene-based composites

The effect of $CaCO_3$ content on impact strength of treated Cocoa fruit shell (CFS) with unused and waste polypropylene-based composites is shown on Figure 4. When a composite is subjected to impact, rapid crack propagation is initiated through the material. When this type of crack propagation encounters filler particles in the filled composites, the filler particles can absorb the energy and stop the propagation, if filler matrix interaction is strong (Levytskyi *et al.,* 2020). The impact test result is graphically illustrated in Figure 4. The various results were recorded, 4.17 kJ/m^3 to 5.58 kJ/m^3 for unused/treated composites, 3.47 kJ/m^3 to 5.27 kJ/m^3 for waste/treated composites. The addition of $CaCO_3$ particles increased the impact strength of the composites investigated. The highest impact strength of 5.58 kJ/m^2 at 1.0 g $CaCO_3$ loading.

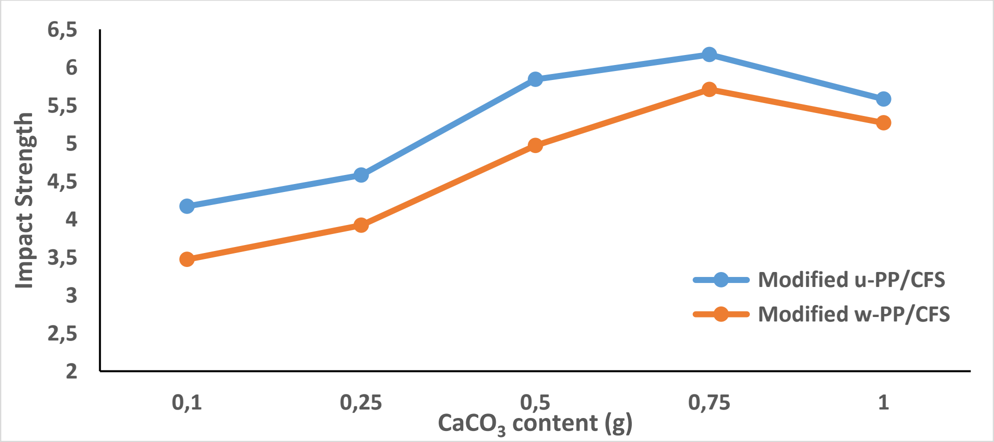


Figure 4: Effect of $CaCO_3$ content on impact strength of treated Cocoa fruit shell (CFS) with unused and waste polypropylene-based composites.

Figure 5 shows the effect of $CaCO_3$ content on hardness of treated Cocoa fruit shell (CFS) with unused and waste polypropylene-based composites. Alkaline treatment improves filler/matrix adhesion due to the removal of impurities (Chatterjee & Singh, 2019). Thus, mechanical properties of natural fillers depend on its surface. As seen from the graph, the hardness increases with increase in $CaCO_3$ content. The harder the surface of a material is, the more abrasion-resistant it is. Generally, the hardness of the composites increases with $CaCO_3$ loading. It was observed that the hardness for the Modified composite ranges from 39 MPa to 63 MPa for unused polypropylene/treated fiber, 33.43 MPa to 52.77 MPa for waste polypropylene/treated composites. This is in consistent with the report of Moorthy, *et al.,* (2017).

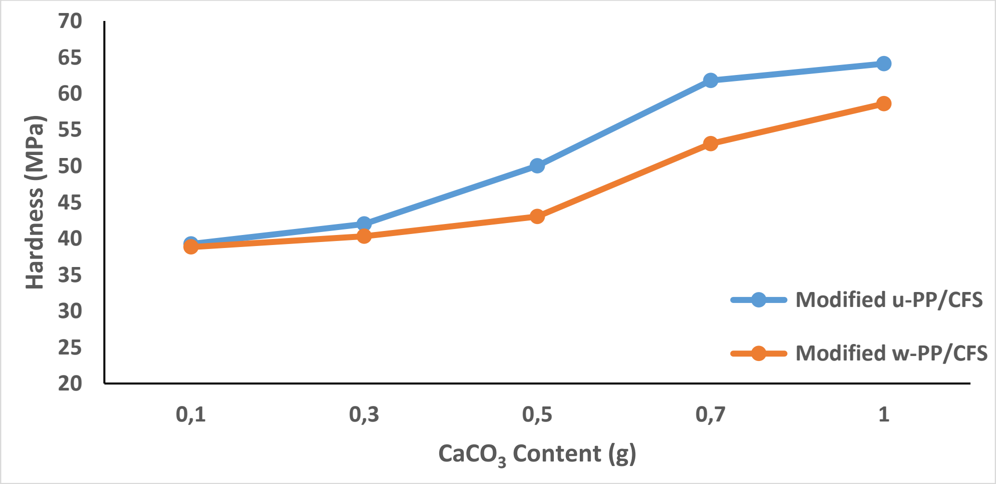
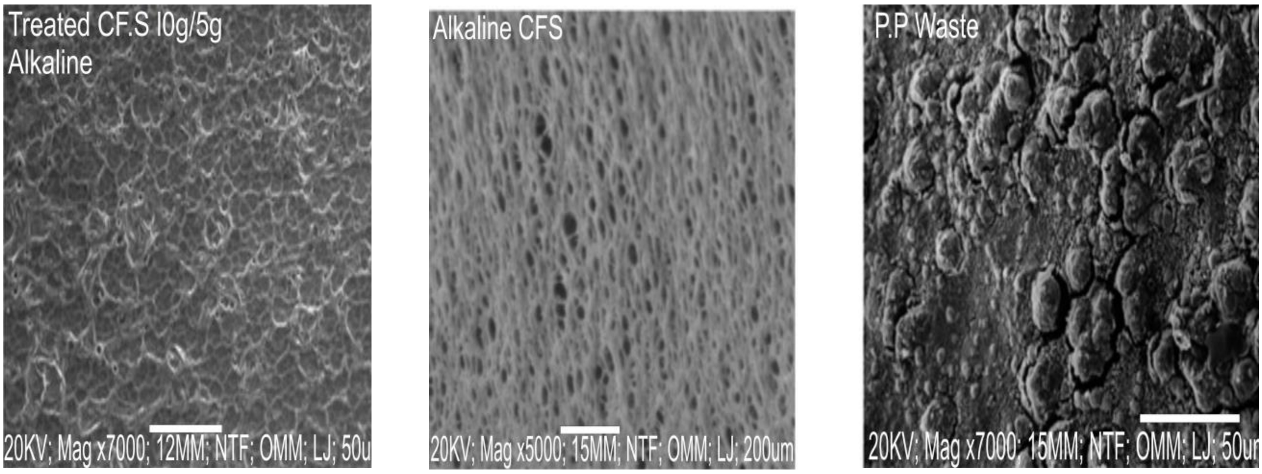


Figure 5: Effect of $CaCO_3$/filler content on hardness of treated Cocoa fruit shell (CFS) with unused and waste polypropylene-based composites.

Figure 6 shows the SEM images; (A) Polypropylene/filler composite, at 20KV; Mag x 6000 (B) Treated Cocoa fruit shell powder, (CFS) at 20KV; Mag x 5000. (C) Polypropylene waste, 20KV; Mag x 7000. (Fig. 6(a)) An increase in void content indicates poor quality composites and changes in mechanical properties. Based on SEM images, it can be said that the use of Alkaline treated Cocoa fruit shell powder, (CFS) and microcrystalline cellulose resulted in better-dispersed structures in the polymer matrix. Thus, the presence of Alkaline treated Cocoa fruit shell powder, (CFS) in PP reinforced with microcrystalline cellulose provided significant improvements in the mechanical properties of the composites. A smoother fractured surface was observed in Figure 6(b). The interfacial adhesion might have been improved by the removal of lignin during pre-treatment 5 % NaOH. The removal of the lignin breaks down the filler bundles, thus exposing more hydroxyl and carbonyl groups on the surface. Alkaline treated Cocoa fruit shell powder, (CFS) at 20KV; Mag x 5000, the treated filler was less agglomerated and rough (Fig. 6(b)).



(A) (B) (C)

Figure 6: SEM images; (A) Modified Cocoa fruit shell powder, (CFS) with $CaCO_3$ 20KV; Mag x 7000 (B) Treated Cocoa fruit shell powder, (CFS) 20KV; Mag x 5000 (C) Polypropylene waste, 20KV; Mag x 7000

CONCLUSION

When the content of the $CaCO_3$ increases in the composite, the presence of free -OH groups in the cellulose and hemicellulose structure are blocked and then these hydrophilic shell particles are less available to absorb water through hydrogen bonding between water molecules and the OH-groups on the surface of wood particles. It was observed that the modification increased the tensile strength when compared to the unmodified. The addition of $CaCO_3$ particles increased the impact strength of the composites investigated. The hardness of the composites increases with $CaCO_3$ loading. The optimization and the influence of additive on the interfacial bonding between Cocoa fruit shell powder and Polypropylene-based composite is an effective means towards development of composites for industrial scale.

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