Chemical treatment of coconut fiber and its composite

Tratamento químico da fibra de coco e seus compósitos

DOI:10.34117/bjdv8n5-179

Recebimento dos originais: 21/03/2022
Aceitação para publicação: 29/04/2022

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ABSTRACT

Composites with natural fibers usually present poor adhesion of filler to the matrix, as consequence of the hydrophilic nature of the fiber and hydrophobic nature of the polymer. These composites also display processing limitations due to the low thermal stability of the fiber. In order to reduce these issues, chemical treatments are usually employed. Thus, the present work aims to combine the processes of mercerization and bleaching to evaluate changes in thermal stability, tensile and impact strengths, flow behaviour and morphology of composites based on HDPE/coconut fiber, with treated and untreated fibers. The results showed that the treated fiber showed better thermal stability comparing to untreated one. The composites produced with both fibers showed an increase in elastic modulus and a reduction in the flow behaviour. However, only those obtained with the treated fiber showed an increase in impact strength in relation to neat HDPE, indicating a better interaction between the treated fiber and the HDPE matrix. These results corroborate the images obtained in SEM micrographs.

Keywords: coconut fiber, polymer composite, chemical treatment, high density polyethylene.

RESUMO

Compósitos com fibras naturais geralmente apresentam baixa adesão da carga à matriz, como consequência da natureza hidrofílica da fibra e hidrofóbica do polímero. Esses compósitos também apresentam limitações de processamento devido à baixa estabilidade térmica da fibra. Para reduzir esses problemas, geralmente são empregados tratamentos químicos. Assim, o presente trabalho visa combinar os processos de mercerização e branqueamento para avaliar alterações na estabilidade térmica, resistência à tração e ao impacto, comportamento de escoamento e morfologia de compósitos à base de PEAD/fibra de coco, com fibras tratadas e não tratadas. Os resultados mostraram que a fibra tratada apresentou melhor estabilidade térmica em relação à não tratada. Os compósitos produzidos com ambas as fibras apresentaram um aumento no módulo de elasticidade e uma redução no comportamento de escoamento. No entanto, apenas os obtidos com a fibra tratada apresentaram aumento na resistência ao impacto em relação ao PEAD puro, indicando uma melhor interação entre a fibra tratada e a matriz PEAD. Esses resultados corroboram as imagens obtidas em micrografias MEV.

Palavras-chave: fibra de coco, compósitos poliméricos, tratamento químico, polietileno de alta densidade.

1 INTRODUCTION

Natural fiber composites are a viable alternative to composites reinforced with synthetic fibers, used as structural components or not, especially in applications whose lightness is desirable (SANJAY et al., 2018).

The replacement of synthetic fibers by natural fibers currently brings environmental, economic and social benefits. In this sense, natural fibers have aroused interest of researchers and engineers, since composites of natural fibers are becoming a viable alternative to non-renewable sources (ZAH et al., 2007).

Natural fibers, comparing to synthetic fibers, have low cost and lower density, are ecologically viable and present low health risks. It is believed that its use in the development of composites has value not only in the economic aspect, but also in the perspective of sustainability. In addition, they are renewable raw materials for obtaining new green products. The chemical, biological, environmental and economic properties of natural fibers can significantly improve the final properties of polymer matrix-based composites (VIGNESHWARAN et al., 2020).

Polymer/natural fiber composites have some advantages, including: low density, excellent electrical resistance, biodegradability, high rigidity and high acoustic insulation (M.R. et al., 2019). However, they have the disadvantage of high moisture absorption capacity, low thermal stability and low tensile and impact strength generated by poor fiber/matrix adhesion

The weak fiber/matrix interaction is related to the composition of the natural fiber, in particular the non-cellulosic components such as: lignin, waxes and pectin. The removal of these components will contribute to increase the mechanical strength of the composite, as their presence makes it difficult the fiber/matrix interaction (FARUK et al., 2012).

To improve the polymer/fiber interaction, chemical treatments can be used, through the removal of non-cellulosic components: (i) alkaline treatment (mercerization), with sodium hydroxide (NaOH), capable of increasing the fiber roughness, removing the amorphous material and, consequently, leading to increase interaction with the matrix (FIORE; DI BELLA; VALENZA, 2015; MAHJOUB et al., 2014) and (ii) bleaching process, that leads to increased thermal stability (RAYUNG et al., 2014)

Based on this knowledge, this work aims to study the effect of the combination of two chemical treatments (alkaline and bleach) performed on coconut fiber, in the mechanical, thermal, rheological and morphological properties of high-density polyethylene (HDPE) matrix, a green HDPE commercial grade.

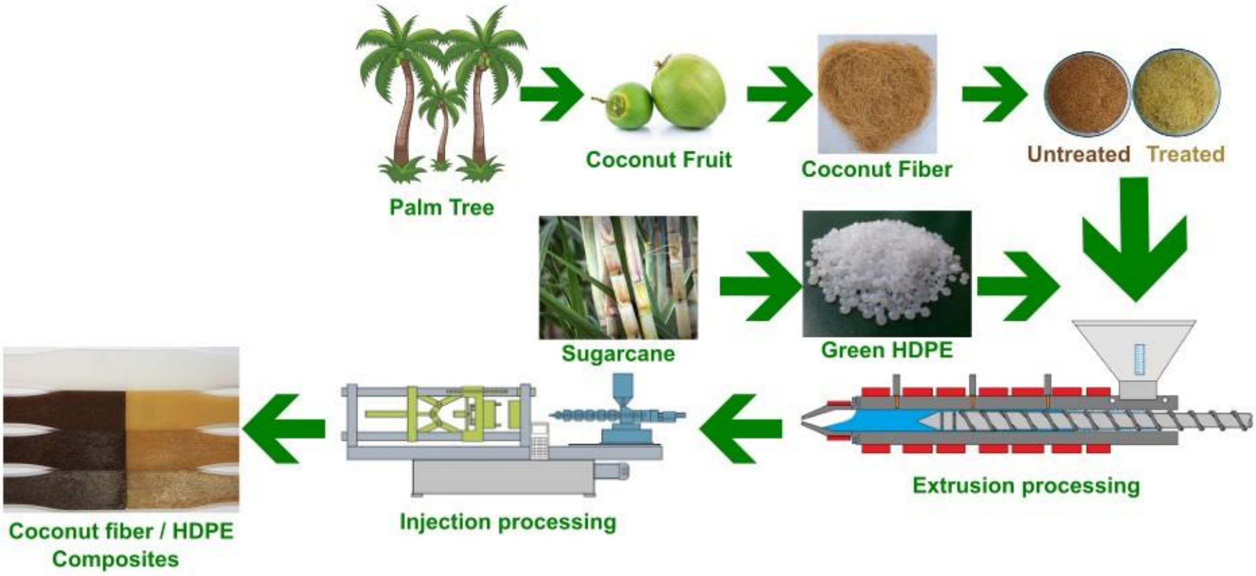
2 EXPERIMENTAL

2.1 MATERIAL

Green polyethylene, grade SHC 7260 (melt flow index 7,2g/10min, at 190 °C, 2.16 kg, ASTM D1238, Density 0.959 g/cm3, ASTM D792) was supplied by BRASKEM company. The coconut fibers were donated by Coco Verde Company.

Figure 1 illustrates the production chain from the coconut fiber up to its processing with the Green-HDPE to produce a more sustainable composite.

Figure 1 - Production chain of the fiber-based composed – Green-HDPE/coconut fiber composite



2.2 COCONUT FIBER TREATMENT

The previously ground coconut fiber went through a chemical treatment divided into three parts, which were: washing, done in distilled water, in a 1:10 proportion of water/fiber, for 2h at 70°C; followed by mercerization in a 5% NaOH (w/v), in a proportion of 1:20 (w/v), for 2h, being stirred; and, finally, a bleaching process in a 6% H_2O_2/5% NaOH (w/v) solution, in a 1:1 ratio, added in a ratio of 1:20 in relation to the fiber mass added, and being left for a period of 2h at 45°C. At the end of the steps, the material was filtered and washed with distilled water until neutral pH and placed to dry in an air circulation oven at 60 °C for 24h.

2.3 EXTRUSION AND INJECTION PROCESSING

Fiber-reinforced composites were produced by compounding Green-HDPE with coconut filler. Composites were prepared with the following filler contents – 5, 10 and 15 wt.%. Specimens were also produced from neat Green-HDPE (unreinforced) for comparison.

The materials were prepared by melt compounding in a co-rotating twin screw extruder (TeckTril, DCT-20, L/D=36, D=20mm) at 200rpm, feed rate at 4.2 Kg/h and with a temperature profile as showed in Table 1. The screw profile consisted in five KB45 kneading elements at compression zone, assuring the complete fusion of the polymer and leading to a good filler dispersion in the polymer matrix.

After extrusion, all materials were subjected to injection process (Arburg, Allrounder 270S model), at temperature profile set as showed in Table 2 from rear to injection nozzle, mold temperature at 30°C and injection pressure at 1200 bar to produce the specimens (Type I) for tensile test, according to ASTM D638 and izod impact test (ASTM D256).

Table 1 - Extrusion temperature parameters

Zone	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Temperature (°C)	90	140	140	140	160	160	160	160	160	180

Table 2 - Injection temperature parameters

Zone	**1**	**2**	**3**	**4**	**5**
Temperature (°C)	160	165	170	180	190

2.4 CHARACTERIZATION

The thermal stability of coconut fiber, at each step of the treatment, was carried out in Q 500 series analyzer (TA Instruments), using samples in amount of around 15 mg, scanning temperature from 30 to 800°C, heating rate of 10°C/min under nitrogen atmosphere.

The tensile and Izod impact strength tests were performed in a universal testing machine (EMIC DL-3000), according to ASTM D638 and ASTM D256 standards, respectively.

The tensile modulus was obtained from stress-strain curves based on the secant method (between stress values of 2 and 4 MPa). Data related to all mechanical properties were based on five tested specimens with 3 mm of thickness.

The Melt Flow Index (MFI) was determined through a DYNISCO polymer test, model LMI 4000), following ASTM D1238-13 standard.

The morphology of the neat Green-HDPE and Green-HDPE/ Coconut fiber composites was investigated by studying cryogenic fractured surfaces using a scanning electron microscope (SEM, FEI Quanta 400, accelerating voltage of 500X. The fractured samples were coated with gold particles before the experiment.

3 RESULTS AND DISCUSSION

3.1 COCONUT FIBER

Figure 2 shows that the chemical treatment on the coconut fiber altered the color from darker to lighter tones. The greatest change is noticeable in the bleaching step. In this stage, due to the presence of hydrogen peroxide, oxidation reactions occur, changing the color of the coconut fiber, making it yellowish.

Figure 2 - Coconut fiber at each stage of the treatment

The TGA results (Table 3 and Figure 3) were analyzed based on the decomposition of hemicellulose (220-315°C) and cellulose (315-400°C) (ESCÓCIO et al., 2014). It is observed an increase in the T_{onset} (13.96%) was observed at the end of the treatment. It is also noted, from DTG curves, the disappearance of the band referring to the degradation of hemicellulose, which indicates the increase of the α-cellulose content at the end of the treatment.

MONTE et al. (2018) observed that performing the mercerization and bleaching treatments together led to an increase in the T_{onset} temperature and the disappearance of the first degradation stage, referring to the decrease in the hemicellulose content in the rice husk. Figure 3 and Table 3 show similar results for coconut fiber.

Figure 3 - TGA (A) and DTG (B) curves of coconut fibers before and after each step of the treatment.

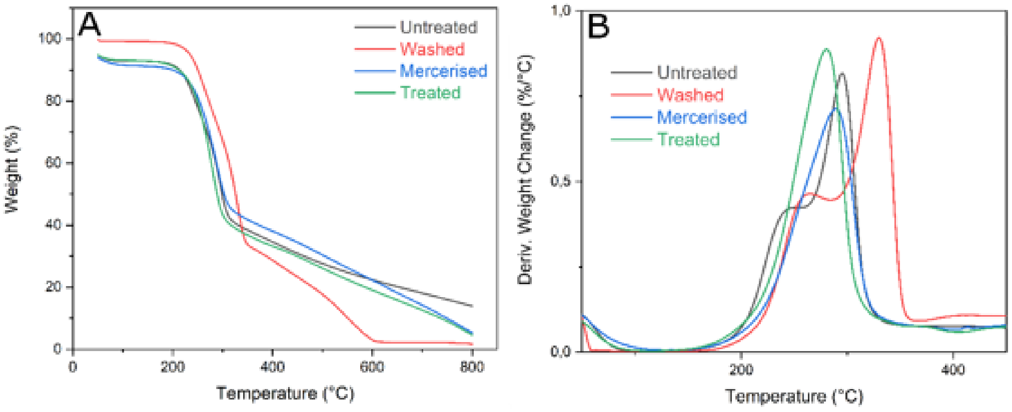


Table 3 - TGA results of the fiber

		T_{Max} °C	
Fiber	**T_{onset} °C**	**Peak 1**	**Peak 2**
Untreated	215	254	293
Washed	232	264	330
Mercerised	246	-	288
Bleached	245	-	282

The results of holocellulose, α-cellulose and hemicellulose contents, for treated and untreated fibers (Table 4) show a slight increase (3.2%) for holocellulose content from treated fiber in relation to the untreated fiber. In addition, occurred an increase in the α-cellulose content (28.75%) and a reduction of hemicellulose content (23.54%). This reduction is also observed through the DTG curves (Figure 3).

Table 4 - Composition of treated and untreated coconut fiber

	Coconut fiber	
Content (%)	**Untreated**	**Treated**
Holocellulose	83.2 ± 0.2	88.4 ± 1.9
α-cellulose	44.9 ± 1.6	73.6 ± 1,8
Hemicellulose	38.2 ± 1.8	14.7 ± 3.7

3.2 HDPE / COCONUT FIBER COMPOSITES

It is possible to notice that the composites produced (Figure 4) present a different color than neat HDPE. Composites produced with untreated fiber present a darker color comparing to those made from treated fiber, since the treated fiber has a much more yellowish color, as can be seen in Figure 2. In both types of fiber, the color becomes more intense as the fiber content increases.

Figure 4 - Zoom of tensile strength specimen (left untreated fiber / right treated fiber)

Table 5 shows that as coconut fiber is added to the HDPE matrix, there is a decrease in the deformation behaviour of the final composite, with the greatest decrease of 65% for the HDPE/coconut fiber composite (untreated fiber) and 63.5% for the HDPE/coconut fiber composite (treated fiber), both with 15 wt.% of fiber. This result is expected, since the presence of fibers produces points of stress concentration, resulting in premature fracture of the polymer matrix.

It is also possible to observe that the composites produced from the treated fiber presented a slightly higher elastic modulus, comparing to the untreated fiber with the same content, Probably, it is due to the increase in roughness and in the surface area of the fiber caused by the treatment process. These results are in accordance to TGA data. As observed in Figure 3 and Table 3, the treated coconut fiber showed the disappearance of hemicellulose phase and the increase of the cellulose phase content. This fact led to the more pronounced anchoring of the fibers in the HDPE matrix, leading to the increase of the rigidity of the final composites. F. SOUSA et al. (2013) noticed that when sponge-gourd fiber was added to the HDPE, the composite presented a higher elastic modulus and lower yield stress and strain, as the fiber content increases. These results are like those observed in Table 5.

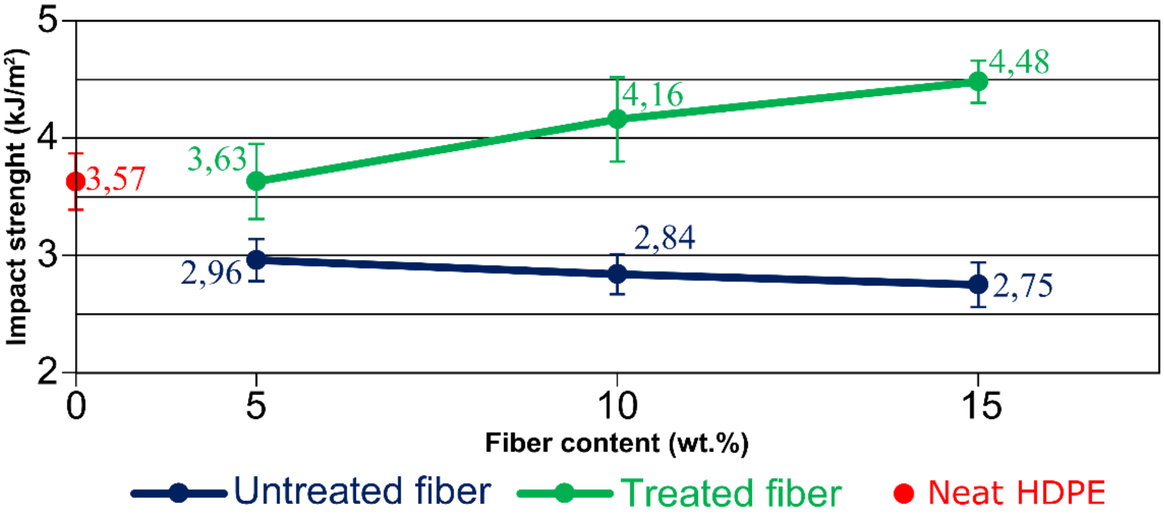
Table 5 - Tensile strength properties of HDPE/ treated and untreated fiber composites

Material	**Yield stress (MPa)**	**Yield strain (%)**	**Elastic modulus (MPa)**
Neat HDPE	22.22 ± 0.22	10.11 ± 0.17	886 ± 62
HDPE/Untreated fiber (5 wt.%)	21.33 ± 0.14	9.27 ± 0.45	1147 ± 44
HDPE/Untreated fiber (10 wt.%)	19.02 ± 0.57	4.57 ± 0.70	1213 ± 118
HDPE/Untreated fiber (15 wt.%)	18.16 ± 0.24	3.54 ± 0.09	1364 ± 34
HDPE/Treated Fiber (5 wt.%)	21.27 ± 0.24	9.20 ± 0.26	1153 ± 50
HDPE/Treated fiber (10 wt.%)	18.21 ± 0.64	4.04 ± 0.33	1246 ± 34
HDPE/Treated fiber (15 wt.%)	18.30 ± 0.57	3.73 ± 0.30	1410 ± 51

The results of the impact strength test (Figure 5) are different in relation to tensile strength results. The composites produced with the treated fiber showed an increase in the value of impact strength as the treated fiber content increases, with a maximum increase of 25.5% for the composite with 15 wt.% treated fiber content comparing to neat HDPE.

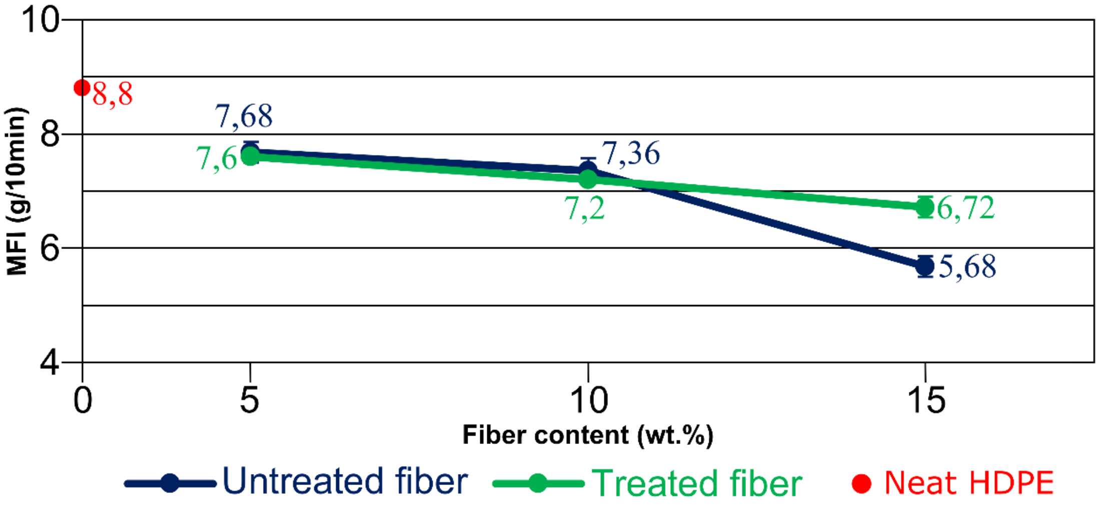
The compositions produced with the untreated fiber showed the opposite behaviour in relation to the treated one. It was observed a decrease in impact strength (maximum reduction of 23%), which is a expected behaviour when natural fibers are added to a polymer matrix, according to the literature (ESCÓCIO et al., 2014). The improvement in impact strength (observed only for the treated fiber), together with an increase in elastic modulus signals the occurrence of better fiber/matrix interaction when the fiber is treated.

Figure 5 – Impact strenght test results of HDPE / Coconut fiber composites



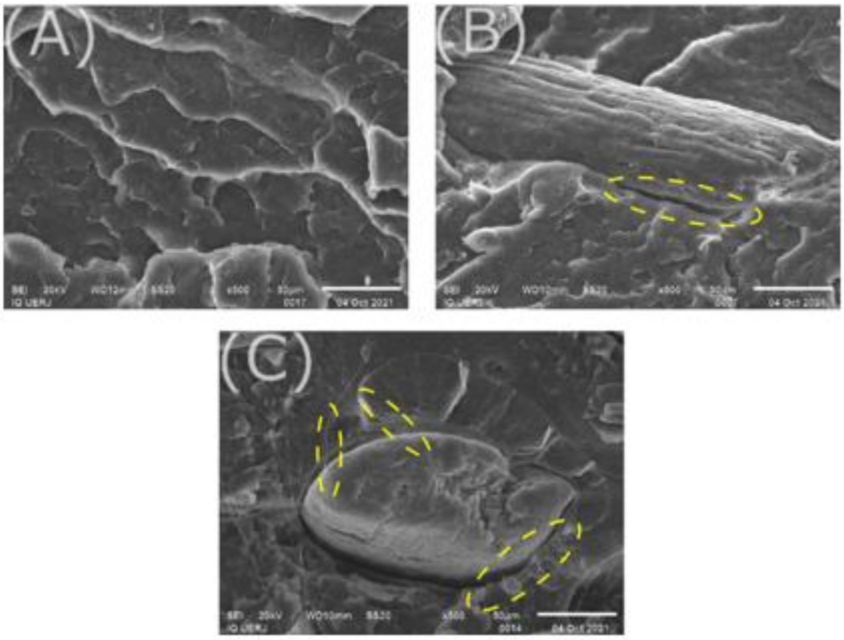
The MFI analysis (Figure 6) showed that when the fiber is added to neat HDPE, the values decrease since the fibers hinder the flow of the polymeric chains. It is also noticeable that the flow behaviour reduction occurred in a more accentuated way in the intervals of 10 to 15 wt.% of untreated fiber content (22.8%). While, during the same interval, the treated fiber reduction was around 6.7%. Probably, it is occurred due to the characteristic of the cellulose in the treated fiber, which tends to align with the flow direction, leading to a more pronounced increasing of the flow of the final composite.

Figure 6 – MFI results of HDPE / Coconut fiber composites



The SEM micrographs of HDPE/coconut fibers (treated and untreated) are showed in Figure 7. In addition, it is also possible to observe the better interaction between treated fiber and HDPE matrix. This can be observed by the presence of fibrils that connect the fibers to the polyethylene matrix. This proves the better fiber/matrix interaction, already observed by the increase in the elastic modulus and impact strength in the composites produced with the treated fiber.

Figure 7 - SEM micrographs neat HDPE (A), HDPE/ untreated fiber 15 wt.% (B) and HDPE/ treated fiber15 wt.% (C)



4 CONCLUSION

After alkaline treatment and bleaching, the TGA analysis showed to an increase in thermal stability of the coconut treated fiber comparing to the untreated fiber.

During the tensile strength test of the composites produced, it was possible to observe an increase of elastic modulus and a reduction in yield stress and yield strain with the increase of content of both types of fiber, treated and untreated. However, it was not observed a significant variation between the two of them.

In the impact strength test, the composites produced with the treated fiber showed an improvement in the property. However, those from the untreated fiber were observed a decrease in this property, being another strong signal that the treated fiber leads to a better fiber/matrix interaction.

The addition of fiber to the polymer increased viscosity, which were observed more intensely in compositions made with untreated fiber. However, it is important to highlight that the treated fiber at higher content, comparing to untreated fiber, showed a higher MFI value, signalling higher flow behaviour in relation to HDPE composite with untreated fiber. This occurred due to the tendency of the align of the cellulose phase, which content is more pronounced in the treated fiber.

SEM micrographs showed the presence of fibrils in the composite with treated fiber, proving the better interaction of the fiber in HDPE matrix, corroborating the impact and tensile strength results.

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