

TENSILE PROPERTIES OF SURFACE MODIFIED BAMBOO SLICES COATED WITH EPOXY RESIN CONSIDERING THE CORROSION OF ACID AND ALKALI ENVIRONMENT

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ABSTRACT

This paper presents an anticorrosive method to protect bamboo from the corrosion induced by coating a layer of epoxy resin on the surface of bamboo slices. Four surface modifications including heat treatment, alkali treatment, coupling treatment and acetylation treatment are applied to bamboo slices. The results indicate that the ultimate tension of bamboo slices decreases when corroded in solutions with different pH for different time, while epoxy resin protects the bamboo slices from corrosion to maintain the tensile properties by coated on its surface. The surface morphology indicates that four modifications have different degrees of influence on the surface and material of bamboo slices, which can reduce the ultimate tension of bamboo slices, but improve the interfacial combination between the surface of bamboo slices and epoxy resin. Acetylation treatment was the most effective modification analysed by Fourier-transform infrared spectroscopy (FT-IR) among them.

KEYWORDS: Bamboo slices, epoxy resin, corrosion, tensile properties, surface modifications, interfacial combination.

INTRODUCTION

With the continuous deepening of the concept of green economy and sustainable development, the application of ecological building materials, especially those used as reinforcement in construction technology for reinforced soil, has been increasingly attended. Some natural plant materials with high strength and favorable toughness, such as bamboo root, palm fiber and wheat straw, when be used as reinforcement, can effectively improve the mechanical properties of the reinforced soil (Hegde and Sitharam 2015, Li et al. 2012). Moreover, the tensile properties

of the reinforcement are the most basic technical indicators for reinforced soil structural design, which can directly affect the mechanical properties and service life of the reinforced soil (Shinoda and Bathurst 2004, Wesseloo et al. 2004, Subaida et al. 2008). For example, slope soil maintains its slope stability when reinforced with plant roots, and the tension of plant roots plays a leading role in the stability of soil, which has been proved by the tensile test and the direct shear test on roots-reinforced soil (McIvor et al. 2008, Ghestem et al. 2011, Ma et al. 2018). Compared with some synthetic materials, natural plant materials provide better reinforcement in construction technology for reinforced soil. More importantly, they are degradable and environmentally friendly, which have better economic and ecological benefits as traditional geopolymer replacement for reinforcement engineering.

The recent progress of green building materials presents a great opportunity for the application of bamboo in the reinforced soil. As a kind of natural reinforcement, bamboo is recognized as a viable, sustainable and engineering alternative to other materials in many areas worldwide (Ahmad and Kamke 2005, Yan et al. 2017). It possesses various applications in the engineering field for its strong adaptability, regeneration and reproduction ability, and can play a better role than other natural plant material in the reinforcement process (Khalil et al. 2012, Luo et al. 2014, Trujillo et al. 2014). At present, there are many researches on the mechanical properties of bamboo and its application in practical engineering. Tensile strength of single bamboo fiber isolated chemically is 47.6% higher than that of isolated mechanically, and the tensile strength and modulus of bamboo strips made from the outer portion of the bamboo are higher than that of inner portion (Chen et al. 2015). The shear strength of soil can be improved by reinforcing with bamboo slices, and the peak shear strength of bamboo root reinforced soil increases with increasing soil-root volume ratio (Ma'arif 2012).

However, the degradability of natural plants makes them prone to corrosion in acid and alkali environment, which may affect their mechanical properties and makes them difficult to chronically exert their reinforcing effect (Hsu et al. 2010). Notably, due to the influence of civil engineering environment, the natural bamboo material will be corroded when be applied as reinforcement in the soil (Qin et al. 2015), which will decrease the mechanical properties of the reinforced soil. Therefore, to extend the service life of bamboo and maintain the mechanical properties of reinforced soil, it is particularly important to conduct corrosion prevention on bamboo (Shafizadeh and Kavanagh 2005). The anticorrosion of bamboo mainly include physical and chemical methods. However, The validity of physical methods is short, and such as heat treatment will decrease the mechanical properties of bamboo (Yun et al. 2016, Zhao et al. 2019). Chemical method is to use preservatives to kill fungi and pests in bamboo, which will easily pollute the environment and has been pointed out that preservatives are not evenly distributed in bamboo (Qin et al. 2015). An effective and economic anti-corrosion method is to coat the material with epoxy resin, a kind of polymer with good physical properties, corrosion resistance, abrasion resistance, stability and low cost (Yang et al. 2014). However, the poor adsorbability towards polymers, induced by the hydrophilicity of nature plant, makes adhesion between the nature plant and polymer inadequate (Luft 1961, Antov et al. 2020). On the basis of maintaining the form and strength of natural plant, the surface modification of natural plant by physical or chemical methods can improve the interfacial compatibility between the surface of natural plant and epoxy resin (Bledzki et al. 1996). Although there are many research articles concerning the tensile properties of bamboo, the focus is seldom concentrated upon the bamboo corrosion that occurs during application in the recent literature. And there are few studies on the regularities of mechanical properties of bamboo slices under corrosion, the anticorrosion effect of epoxy resin on bamboo slices, and the influences of surface modification in improving the interfacial combination between epoxy resin and bamboo slices.

To solve the above problems, in this paper, the mechanical properties of Moso bamboo slices under different pH and corrosion time were studied, and the anti-corrosion effect of epoxy resin on bamboo slices was investigated. And four surface modification treatments (heat treatment, alkali treatment, coupling treatment and acetylation treatment) were conducted on the bamboo slices. The regularities of mechanical properties of bamboo slices were illustrated by tensile tests and surface morphology analysis of modified bamboo slices, and the surface modification effects of different modification methods were characterized by Fourier-transform infrared spectroscopy (FT-IR). The research can provide scientific guidance for the utilization of bamboo in civil engineering and the epoxy resin in the anti-corrosion of natural plant

MATERIAL AND METHODS

According to the test methods for physical and mechanical properties of bamboo used in building (Chen et al. 2015), five-year-old Moso bamboos obtained from Enshi, Hubei Province in China were selected as objective materials. All pristine samples were selected from the outer portion of the bamboo and the location between 4 - 5 m measured from the bottom of the bamboo trunk, and were processed into slices with a uniform dimension of 200 mm (L) × 5 mm (W) × 1 mm (T). The physical and mechanical parameters of Moso bamboo are listed in Tab. 1 according to relevant studies (Lakkad and Patel 1981, Jin et al. 2014).

Tab.1: Physical and mechanical parameters of Moso bamboo.

Parameter	Value range
Density ($\text{g}\cdot\text{cm}^{-3}$)	0.6 ~ 1.1
Tensile strength (MPa)	140 ~ 800
Elastic modulus (GPa)	11 ~ 32
Ultimate elongation (%)	2.5 ~ 3.7
Acid and alkali resistance	weak

Corrosion test

In order to study the influence of pH and corrosion time on the tensile properties of bamboo slices, as well as the anticorrosion property of epoxy resin on bamboo slices, solutions with different pH were prepared with a concentration of 35% HCl reagent and a concentration of 5% NaOH reagent, and the coated samples were prepared by applying a layer of epoxy resin adhesive (E7730) evenly on the surface of the pristine sample followed by curing at room temperature for 24 h. Correspondingly, one set of pristine samples and coated samples were marinated in the solutions with different pH in range 2 - 13 for 15 days, and the other set of pristine samples and coated samples were impregnated in the solution of pH 4.0 and pH 10.0 for different time (1, 3, 5, 7, 15, 28 days), respectively. The mass lose induced by corrosion were measured after soaked samples were washed with distilled water and followed by being stored under laboratory temperature ($20 \pm 2^\circ\text{C}$) and relative humidity ($65 \pm 15\%$) for 2 days. Afterwards, their tensile properties were measured.

Surface modification treatment of bamboo slices

The surface modification of bamboo slices consisted of following two physical methods: heat treatment and alkali treatment, and two chemical methods: silane coupling and acetylation coating: (1) *Heat treated bamboo slices (HTBS)*. Bamboo slices were heated

in a high-temperature test chamber (H/GDWJ-500L) at 120°C for 4 h. When the slices were cooled to room temperature, the mass loss rate was measured. (2) *Alkali treated bamboo slices (ATBS)*. Bamboo slices were immersed in a solution of 5% NaOH for 2 h at room temperature. After being taken out, they were washed repeatedly with dilute acid solution until the washing solution became neutral measured by pH meter, then they were dried in a high-temperature test chamber at 80°C for 4 h. (3) *Coupling agent treated bamboo slices (CTBS)*. Bamboo slices were immersed in mixture solutions (six part 95% ethanol solution and four part 0.6% A-174 silane coupling agent) with pH 4.0 adjusted by 50% acetic acid for 2 h, then removed and dried in a high-temperature test chamber at 80°C for 4 h. (4) *Acetylated bamboo slices (ALBS)*. Neutralize the alkali-treated bamboo slices with dilute acid, then immersed them in 50% acetic acid for 2 h. After being taken out, they were washed with distilled water and dried in a high-temperature test chamber at 80°C for 4 h.

After the modification, the surface morphology of all samples were observed by high-power microscope. Meanwhile, to characterize the influence of modification on chemical functional groups of the samples surface, Fourier transform infrared (FT-IR) spectra were measured by infrared spectroscopy (Thermo Nicolet 6700). Afterwards, applying a layer of epoxy resin (E7730) evenly on the surface of the modified samples. When the epoxy resin adhesive was completed cured by stored at room temperature for 24 h, the ultimate tension of coated and uncoated samples was measured

Tensile tests

The preparation and test method of the tensile properties of bamboo slices was in accordance with the procedure described in testing methods for physical and mechanical properties of bamboo used in building (Chen et al. 2015). The laboratory Max Test universal testing machine (WDW-10E) was adopted for the tensile tests. A slice of polyethylene plastic with 10 mm length are glued by epoxy resin adhesive on each end of the testing sample to be fixed into the fixtures without splitting. When loading, the tensile direction of the testing machine should follow the longitudinal length direction of the bamboo slice. Only when the fracture location is at least 10 mm away from the fixture, can experimental results be judged as valid data. The test was terminated upon the sample was broken. The loading speed is uniformly 0.1 mm.min⁻¹, and five effective replicates were conducted for each sample type

RESULTS AND DISCUSSION

Tensile tests

Effect of pH on ultimate tension of samples during laboratory

Fig. 1a shows that in the acidic environment, when UTBS were corroded in the solution with pH 6.0 and pH 2.0 for 15 days, respectively, the mass loss rate increased from 2.5% to 5.2%, and the corresponding ultimate tension decreased from 0.525 kN to 0.453 kN, which decreased by 24.1% and 34.5% respectively compared with that of uncorroded UTBS (0.692 kN). Notably, because the pH of bamboo was between 5.1 and 6.6 (Lo et al. 2012), the bamboo slices corroded and the ultimate tension decreased by 0.163 kN (23.6%) even under the neutral environment of pH 7.0 for 15 days. In alkaline environment of pH 8.0 and pH 13.0, the mass loss rate increased from 1.34% to 5.3%, and the corresponding ultimate tension decreased by 16.4% (0.114 kN) and 55.6% (0.385 kN) compared with that of uncorroded UTBS, respectively. However, as shown in Fig. 1b, when corroded for 15 days in both acidic and alkaline environments, the mass loss rate of the ERBS was negative and changed only slightly (the maximum was -0.24% in pH 13),

which was attributed to the water absorption of epoxy resin adhesive (Popineau et al. 2005). Meanwhile, the ultimate tension of corroded ERBS only decreased slightly compared with that of ERBS without corrosion (0.677 kN), and the maximum decrease was by 0.04% (0.027 kN) when corroded at pH 12.0 for 15 days. It can be inferred that under the condition of constant corrosion time, the tensile properties of bamboo slices decrease with the increase of corrosion solution concentration, whereas epoxy resin can protect the tensile properties of bamboo slices from the influence of pH

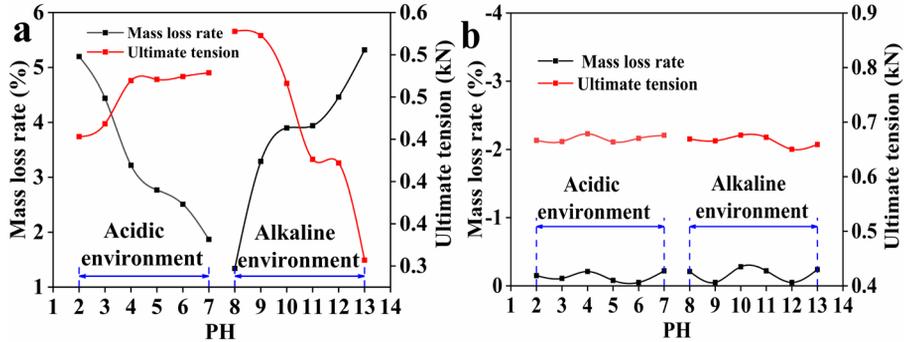


Fig. 1: Regularities of mass loss rate and ultimate tension of (a) pristine samples (UTBS) and (b) samples coated by epoxy resin adhesive (ERBS) under different pH.

Effect of corrosion time on ultimate tension of samples

As can be seen in Fig. 2a, with the increase of corrosion time, the mass loss rate of UTBS increases and the ultimate tension decreases under the condition of constant pH. When UTBS were corroded in the solution with pH 4.0 for 1 day and 28 days, respectively, the mass loss rate increased from 1.9% to 3.4%, and the corresponding ultimate tension decreased from 0.678 kN to 0.490 kN, which decreased by 2.0% and 29.2% respectively compared with that of uncorroded UTBS (0.692 kN). The alkaline environment of pH 10.0 had a greater impact on the ultimate tension of UTBS, which decreased by 9.0% (0.064kN) and 38.6% (0.243 kN) when be corroded for 1 day and 28 days, respectively. As shown in Fig. 2b, the ultimate tension of corroded ERBS only decreased slightly compared with that of uncorroded ERBS (0.677 kN), and the maximum decrease was by 0.08% (0.046 kN) when corroded at pH 4.0 for 5 days, which means that corrosion time had slightly effect on the ultimate tension of ERBS.

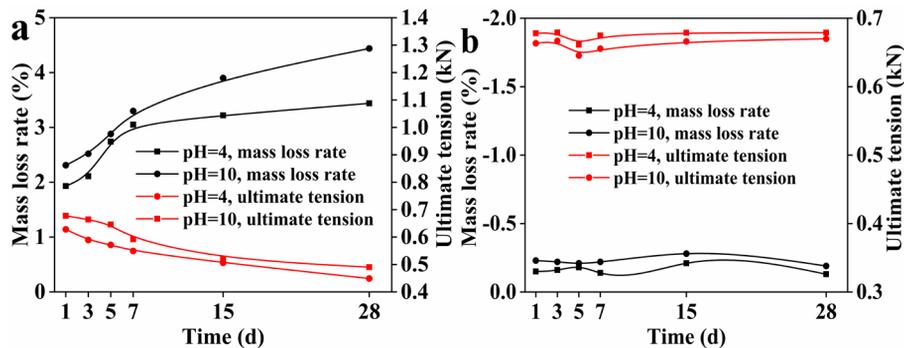


Fig. 2: Regularities of mass loss rate and ultimate tension of (a) UTBS and (b) ERBS under different corrosion time.

The chemical composition of bamboo slices is mainly composed of cellulose, hemicellulose and lignin (Chen et al. 2011). Cellulose mainly determines the longitudinal tensile properties of plant cell walls, and the higher the cellulose content, the better the longitudinal tensile properties of cells (Li and Shen 2011). Hemicellulose is closely related to cellulose and lignin in the cell wall and mainly acts as an adhesive (Vanholme et al. 2010). Lignin has the ability to increase the mechanical strength of cell walls, and to resist microbial erosion (Boerjan et al. 2003). The HCl and the NaOH are capable of degrade the cellulose, hemicellulose and lignin in the bamboo slices (Silverstein et al. 2007), which will further affect the tensile properties of bamboo slices. Consequently, with the increase of concentration of HCl and NaOH solution and corrosion time, the UTBS were prone to be affected by corrosion and tensile properties significantly decreased. However, the epoxy resin adhesive with good anti-corrosion performance, can work as a protective layer to protect the bamboo slices from corrosion induced by contacting with HCl and NaOH solution, so as to maintain rather than improve the excellent tensile mechanical properties of the bamboo slices. Therefore, the changes of pH and corrosion time have little effect in the tensile properties of ERBS.

Tensile properties of surface modified bamboo slices

Surface modification can cause different degrees of damage to the bamboo slices. Only when the improvement of the interface adhesion between the bamboo slices and the epoxy resin exceeds the reduction in the strength of the bamboo slices, the surface modification is meaningful (Liu et al. 2010).

Tab. 2: Ultimate tension of Moso bamboo slices treated with different surface modification.

Samples of bamboo slices	Ultimate tension (kN)	
	Uncoated	Coated
UTBS	0.692	0.677
HTBS	0.538	0.805
ATBS	0.456	0.789
CTBS	0.369	0.693
ALBS	0.402	0.847

Tab. 2 shows that surface modification reduced the ultimate tension of bamboo slices, among which the maximal reduction is 0.323 kN (46.6%) of CTBS, and the minimum reduction is 0.154 kN (22.3%) of HTBS. Due to the small amount of water contained in the epoxy resin adhesive and the poor interface compatibility between the epoxy resin adhesive and the surface of bamboo slices (Zheng et al. 2018), the epoxy resin cannot improve the tensile properties of the bamboo slice when be coated on the surface of bamboo slice, and the ultimate tension of coated UTBS (0.677 kN) is 0.015 kN (1.4%) less than that of uncoated UTBS (0.692 kN). Moreover, compared with uncoated modified samples, the ultimate tension of coated modified samples has been increased to different degrees. The maximal increase is 0.445 kN (110.7%) of ALBS, the minimum increase is 0.267 kN (38.6%) of HTBS. And compared with coated UTBS, the maximal increase of ultimate tension is by 0.170 kN (25.1%) of ALBS. Owing to the damage of coupling agent treatment to the tensile properties of bamboo slices, the minimum increase of ultimate tension is only by 0.016 kN (2.3%) of CTBS. Which indicates that the four modifications improved the interfacial compatibility between the surface of bamboo slices and the epoxy resin adhesive, the treatment of coupling agent in terms) of improving the tensile properties of bamboo slices is not obvious, and the treatment of acetylation is the most effective method among them.

Surface morphology analysis of bamboo slices

The surface of UTBS (Fig. 3a) is relatively smooth and flat, with a few impurity particles. In comparison, the surface of the physically modified bamboo slices (HTBS and ATBS) has become rough and uneven to varying degrees, which can improve the interfacial combination between the surface of bamboo slices and the epoxy resin adhesive. It can be clearly observed that the surface of HTBS (Fig. 3b) is rougher, with many uneven potholes and the color becomes darker. This is because the heat treatment removed the impurities on the surface of bamboo slices, and made part of cellulose and hemicellulose in the bamboo thermal degradation and carbonization (Kartal et al. 2008). Besides, the surface of ATBS (Fig. 3c) becomes rough which can be attributed to the removal of impurities and the dissolution of some lignin and hemicellulose in bamboo slices by alkali treatment (Zhang et al. 1994). The surfaces of chemically modified CTBS (Fig. 3d) and ALBS (Fig. 3e) do not become evidently rough, but the materials become relatively soft. And the improvement of interfacial compatibility between the surface of bamboo slices and the epoxy resin adhesive, can be reasonably explained by the fact that silane coupling agent can reduce the content of hydroxyl group, and acetyl group can replace the hydroxyl group on the cell wall of the bamboo slices, as shown in Fig. 4. Both chemical modifications reduced the water absorption of bamboo slices and made them malleable.

The interface layer which exists between epoxy resin and the bamboo slice plays a decisive role in the mechanical properties of the epoxy resin-coated bamboo slice (Rong et al. 2001). All the four modification methods can change the surface morphology of the bamboo slices, and improve the interfacial combination between the surface of bamboo slices and the epoxy resin adhesive, which confirms the conclusion that the ultimate tension of coated samples can be enhanced by modification before the epoxy resin is coated

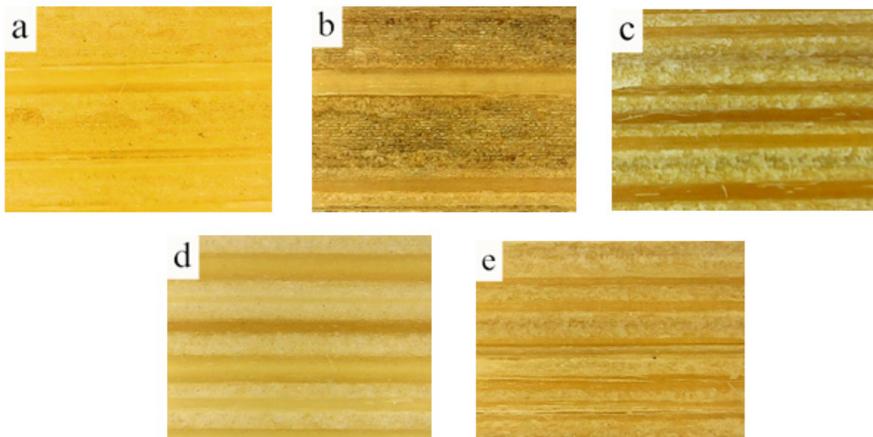


Fig. 3: Surface micrographs of (a) UTBS, (b) HTBS, (c) ATBS, (d) CTBS and (e) ALBS.

Infrared spectroscopic analysis

FT-IR can be used to qualitatively analyze the change of surface functional groups of bamboo slices caused by modification. As can be seen in Fig. 4, due to the dissolution of hemicellulose in bamboo slices after acetylation treatment, the carbonyl functional group (C=O) at 1720 cm^{-1} of ALBS corresponding to hemicellulose disappeared. Which confirmed the conclusion that the treatment of acetylation is the most effective method for improving the interfacial compatibility between the surface of bamboo slices and the epoxy resin adhesive. Besides, the FT-IR of the other three modified bamboo slices are almost the same with the untreated bamboo slice

(UTBS), which can be attributed to the fact that the physical modification method does not cause chemical changes on the surface of bamboo slices. Although silane coupling agent can reduce the content of hydroxyl groups on the surface of bamboo fibers, the effect is not obvious.

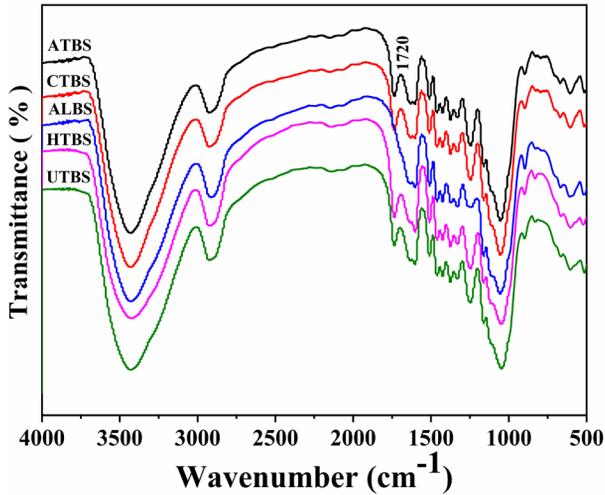


Fig. 4: FT-IR spectra of bamboo slices treated by different modifications.

CONCLUSIONS

(1) As an elastic material, Moso Bamboo has poor corrosion resistance, the acid and alkali environment will cause corrosion to bamboo slices and affect their tensile properties. Moreover, with the increase of acid and alkali solution concentration and marinating time, the ultimate tension of bamboo slices gradually decreases. The maximum reduction is 0.385 kN (55.6%) when be corroded in solution with pH 13.0 for 15 days, and 0.243 kN (38.6%) when be corroded in solution with pH 10.0 for 28 days. Therefore, anticorrosive treatment or other protective measures can be taken to protect the tensile properties and extend the service life of Moso bamboo. (2) Coating the surface of bamboo slices with epoxy resin adhesive can protect them from corrosion by acid and alkali environment. However, due to the poor interfacial compatibility between the surface of bamboo slice and the epoxy resin adhesive, the epoxy resin adhesive can only maintain but not improve the tensile mechanical properties of bamboo. Reasonable surface modification can be taken to improve their interfacial compatibility. (3) Surface modification will reduce the ultimate tension of bamboo slices. Among which the maximal reduction is 0.323 kN (46.6%) of bamboo slices treated by coupling agent, and the minimum reduction is 0.154 kN (22.3%) of bamboo slices treated by heating. The surface morphology indicates that modification can make the surface of bamboo slices become rough or the material become relatively soft, which can improve the interfacial compatibility between the surface of bamboo slice and the epoxy resin adhesive. Compared with the unmodified coated bamboo slice, the treatment of coupling agent in terms of improving the tensile properties of bamboo slices is not obvious, only increases by 0.016 kN (2.3%), and the treatment of acetylation is the most effective modification by reacting with the carbonyl group, which ultimate tension has been increased by 25.1% (0.170 kN).

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