Cellulose Nanofiber-reinforced Unsaturated Polyester as a Potential Substitute for Glass Fiber-reinforced Plastics.

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ABSTRACT

Nanocomposites of unsaturated polyester (UP) reinforced with nanofibers obtained by applying shear stress to pulp fibers through extrusion were produced. Paper-like sheets of nanofibers were impregnated with UP, stacked in layers and hot pressed at 1.5 MPa, a compressing pressure typical of plywood manufacturing. When nanofibers extracted from needle-leaf unbleached pulp (NUKP) fibers were used, composites with 14 wt% UP content exhibited flexural modulus of 13.6 GPa and strength of 260 MPa, with an Izod impact strength of 38 kJ/m^2.

INTRODUCTION

Cellulose nanofibers are composed of amorphous and crystalline portions, the latter possessing tensile modulus of 138 GPa [1]. Despite the presence of amorphous portions along their length, the practical tensile strength of these nanofibers is supposed to be well above 2 GPa, based on the strength of pulp single fibers [2]. However the extraction of nanofibers from plant fibers has been the bottleneck in terms of cost since nanofibrillation is highly time and energy demanding, significantly raising the cost of originally low cost raw materials. Here we present a new approach to nanofibrillate pulp that significantly reduces the energy input and increases yield, by the application of shear forces in a twin-screw extruder.

MATERIALS AND METHODS

The raw materials from which the cellulose nanofibers were obtained consisted of needle-leaf unbleached pulp (NUKP). The resin was unsaturated polyester dissolved in styrene and benzoyl peroxide was used as the free radical initiator. Pulp fibers were fibrillated by an intermeshing co-rotating twin-screw extruder equipped with a screw pattern optimized to apply shear force to the fibers. The pulp fibers had the moisture content adjusted to approximately 30 wt% before feeding and the extruder's barrel was cooled to prevent the temperature to exceed the boiling point of water. The screw rotation speed was set to 400 rpm. Hand sheets were obtained by a papermaking process according to TAPPI T 205 sp-02. The sheets were cut into 40 mm by 30 mm rectangles and dried in a convection oven at 105°C for 1 hour. Unsaturated polyester (UP) was mixed with 1 wt% benzoyl peroxide and the sheets were dipped in the UP solution and maintained at reduced pressure for 30 minutes. The impregnated sheets consisting of about 20 layers were stacked inside a metal mold and compressed at 1.5 MPa and 90°C for 30 minutes.

RESULTS AND DISCUSSION

The fabrication of cellulose nanofiber-reinforced UP composites required relatively low compressing pressures. Differently from nanocomposites fabricated with another thermoset resin, phenol formaldehyde, which demanded pressures in the order of 50 MPa [3], UP-based nanocomposites required pressures less than 10 times lower. Higher pressures tend to squeeze out the impregnated UP resin from the sheets and the composites fail by delamination. As shown in Table I the flexural modulus and strength of the composites were significantly improved over the neat resin UP, however the impact strength was not striking (up to 38 kJ/m^2). Interface modification is still needed to enhance this property. The refining pre-treatment prior to extrusion fibrillation seems not to affect the performance of the composites, nevertheless nanofibrillation by extrusion significantly enhances the mechanical properties of the composites relative to the solely refined pulp fiber-based composites.

Table I. Flexural properties of neat UP and NUKP nanofiber-reinforced UP composites.

Reinforcing fiber	Compres. pres. (MPa)	Resin cont. (wt%)	E (GPa)	σ_b (MPa)
Neat UP, no reinforcement	-	100	3.07±0.09	126±6
NUKP 4 passes refiner	1.5	20.7	9.5±0.3	136±3
NUKP 0 pass refiner, extruded	1.5	15.5	12.2±0.2	254±2
NUKP 4 passes refiner, extruded	1.5	13.9	13.6±0.2	260±4

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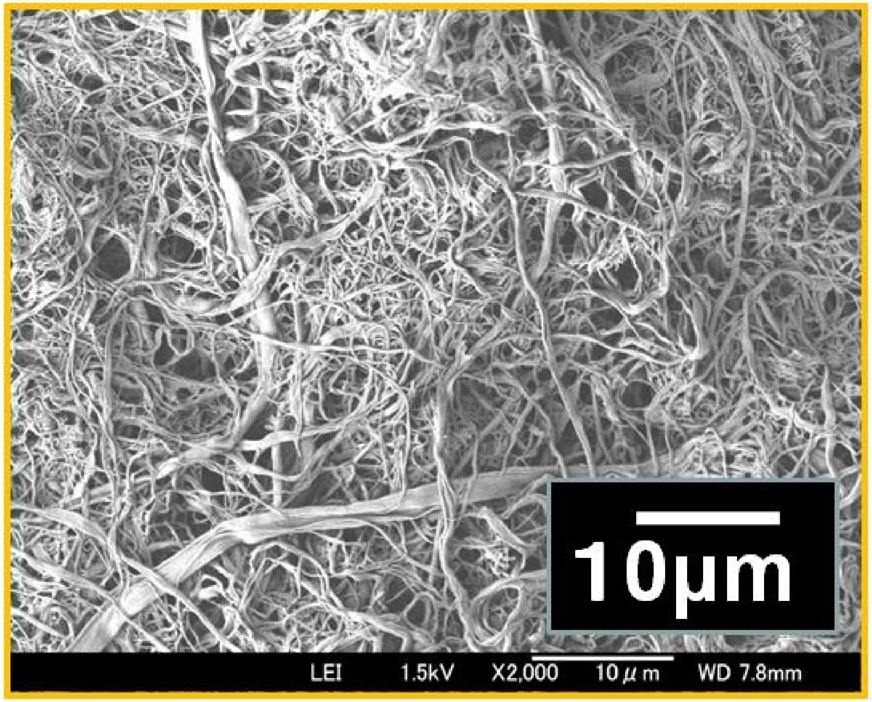
Problem and proposed solution

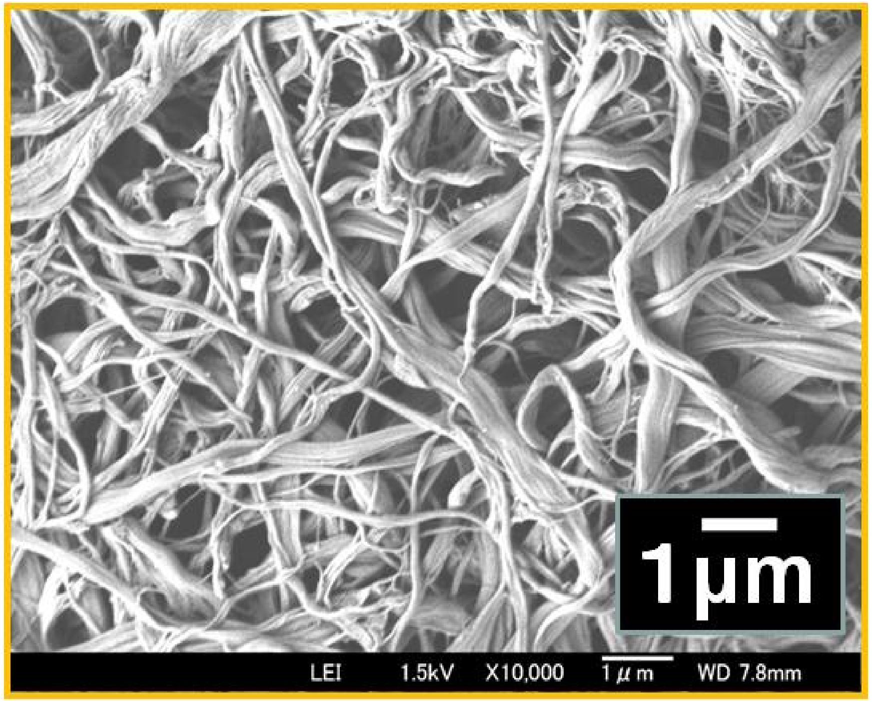
- Disposal of GFRP;
- Make composites with cellulose and UP with mechanical properties comparable to GFRP;
- Bio-based nanofiber as substitute for glass fiber;
- Low cost nanofibrillation by extrusion.

Intermeshing co-rotating twin-screw extruder

Screw pattern: continuous version of a kneader

SEM of nanofibers obtained by twin-screw extruder

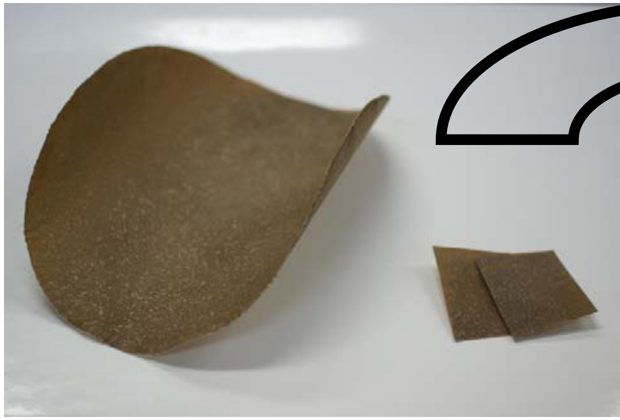




Experimental

- Sheets obtained according to TAPPI T 205 sp-02

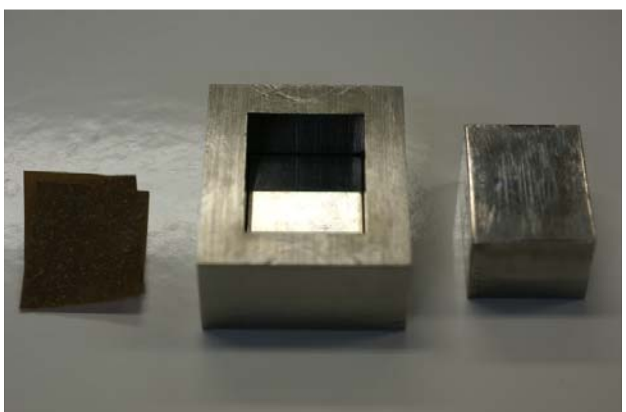
Experimental



Nanofiber sheets

UP + benzoyl peroxide

30 min., vacuum

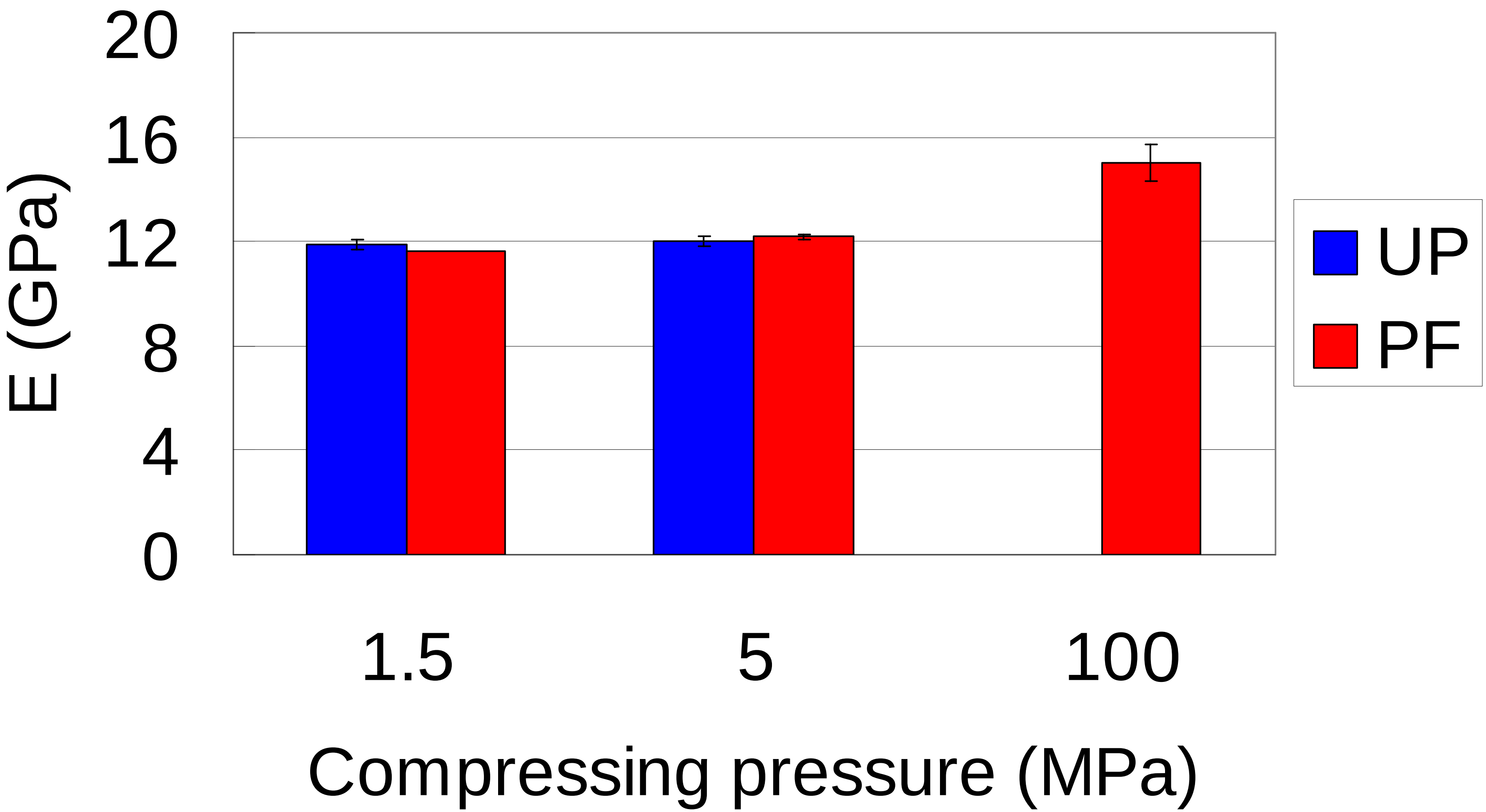


Metal mold

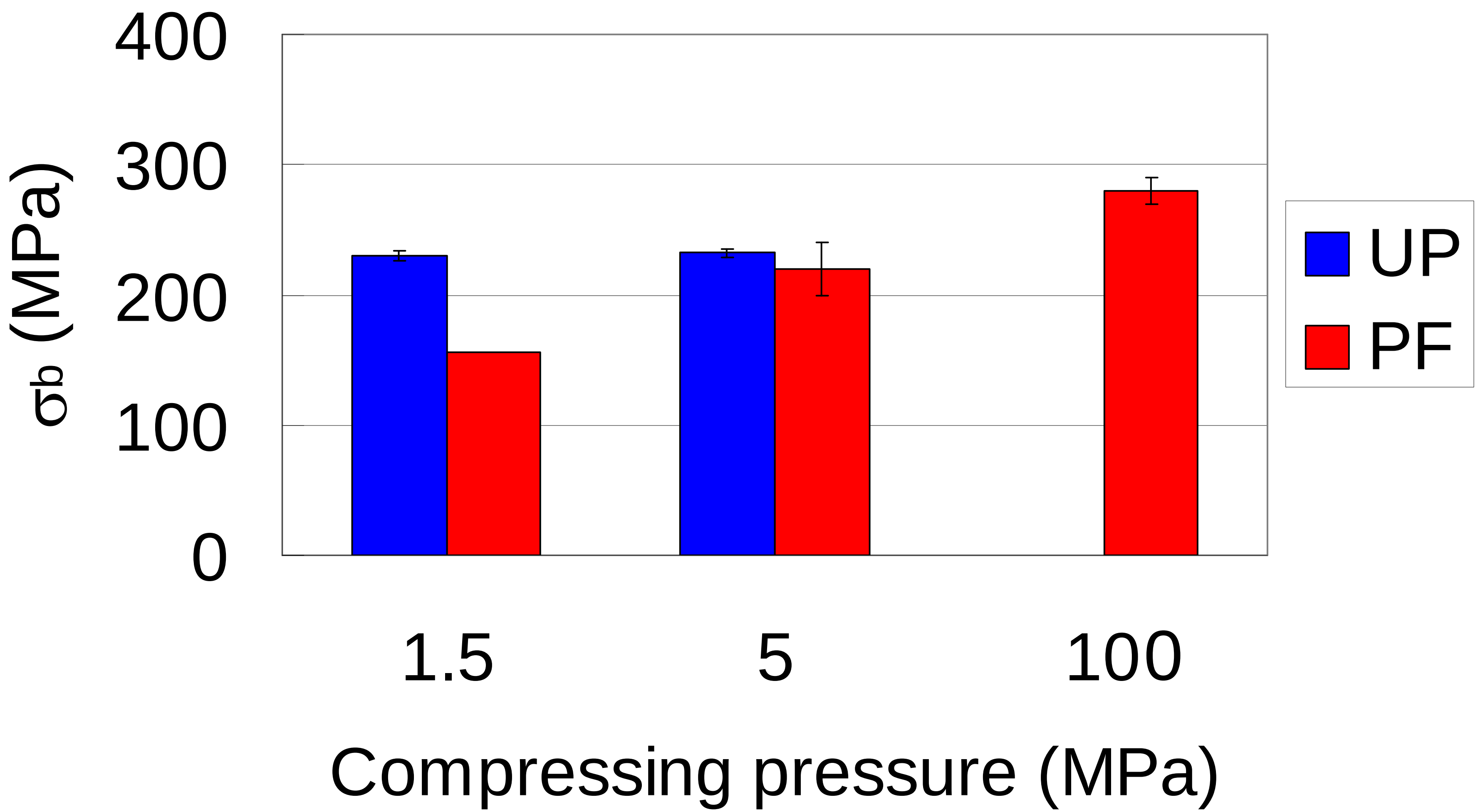
90°C, 30 min., ≤ 5 MPa

Composite RC 10~20%

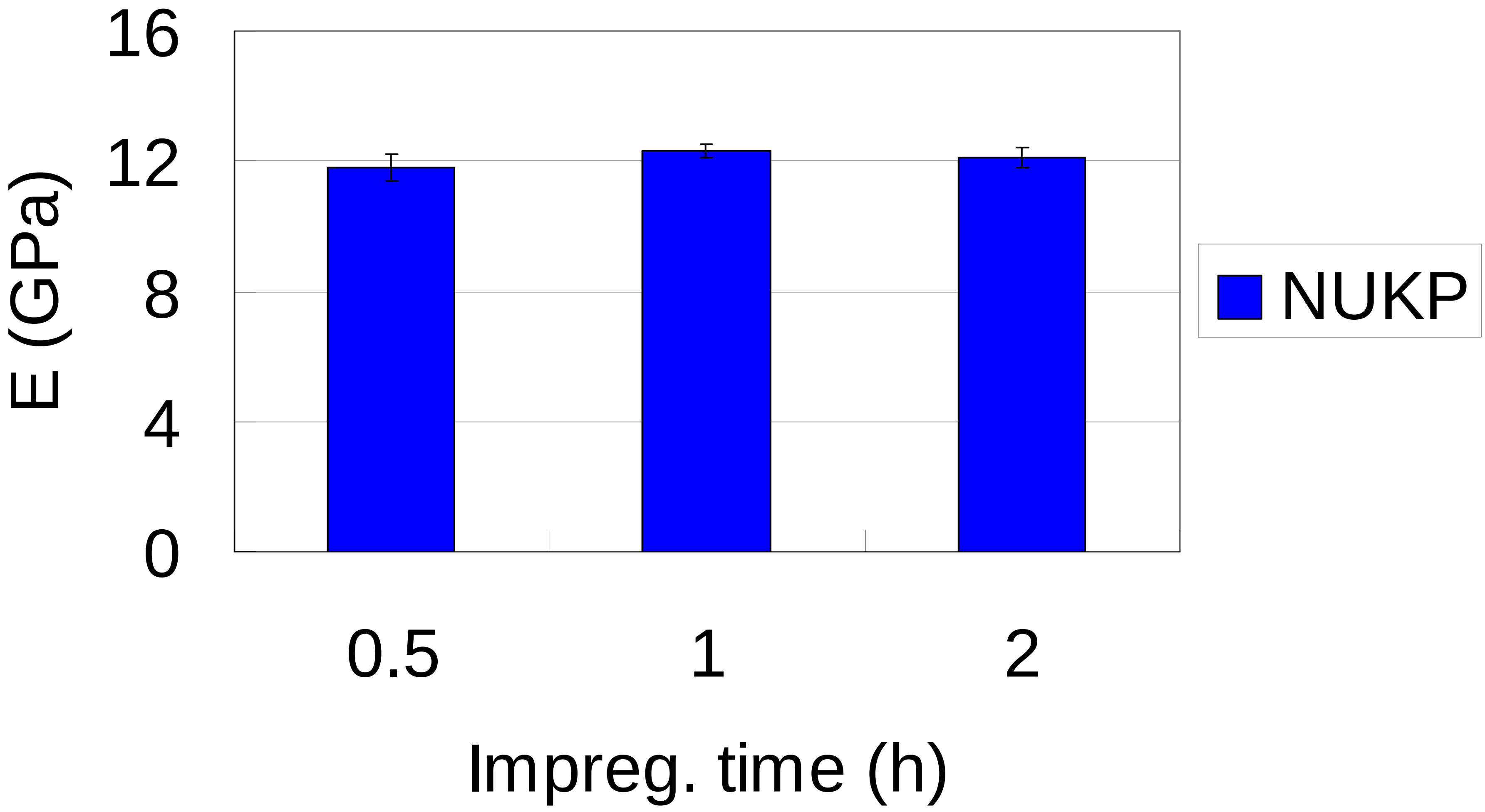
Effect of compressing pressure (E)



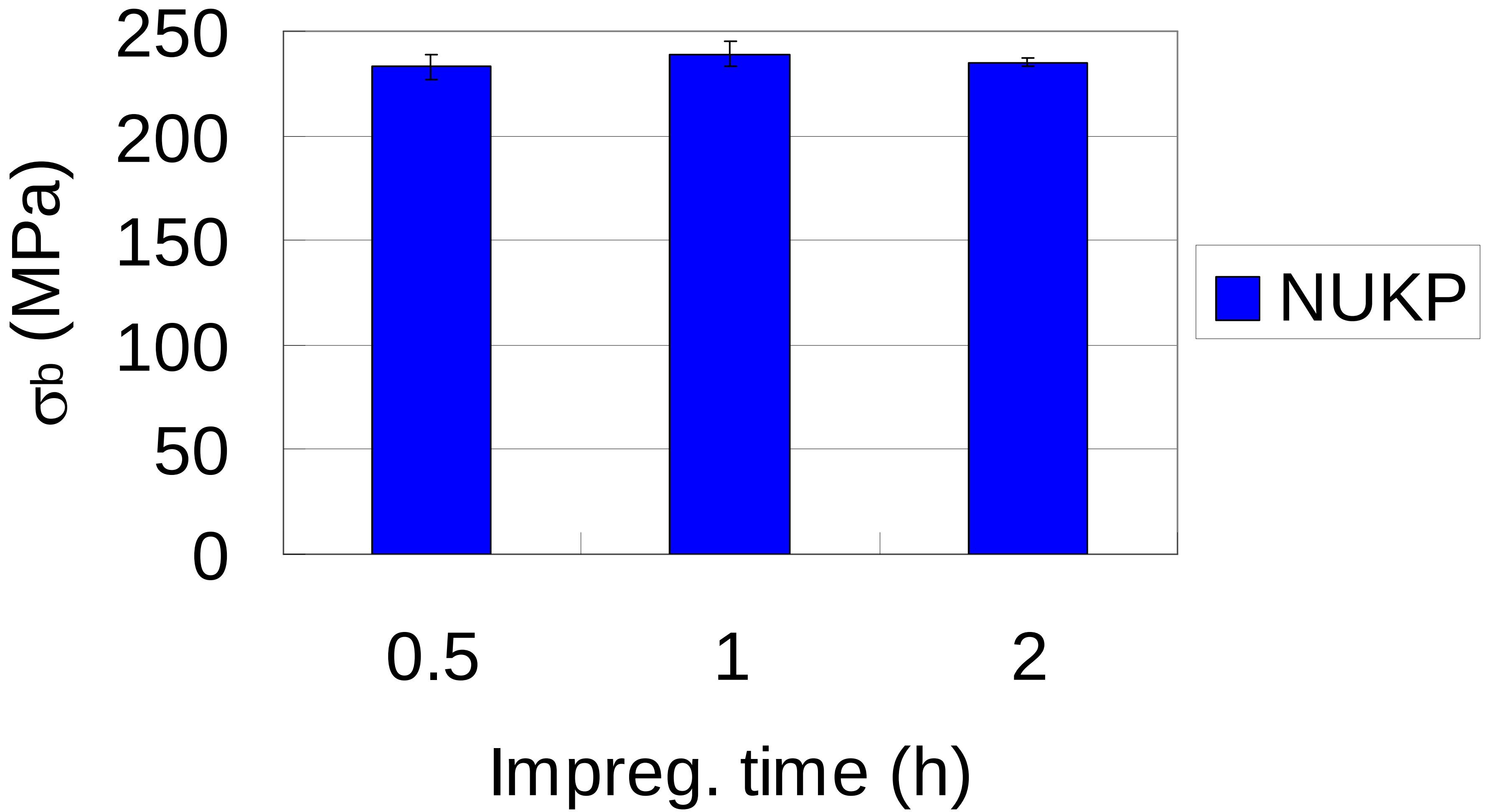
Effect of compressing pressure (σ_b)



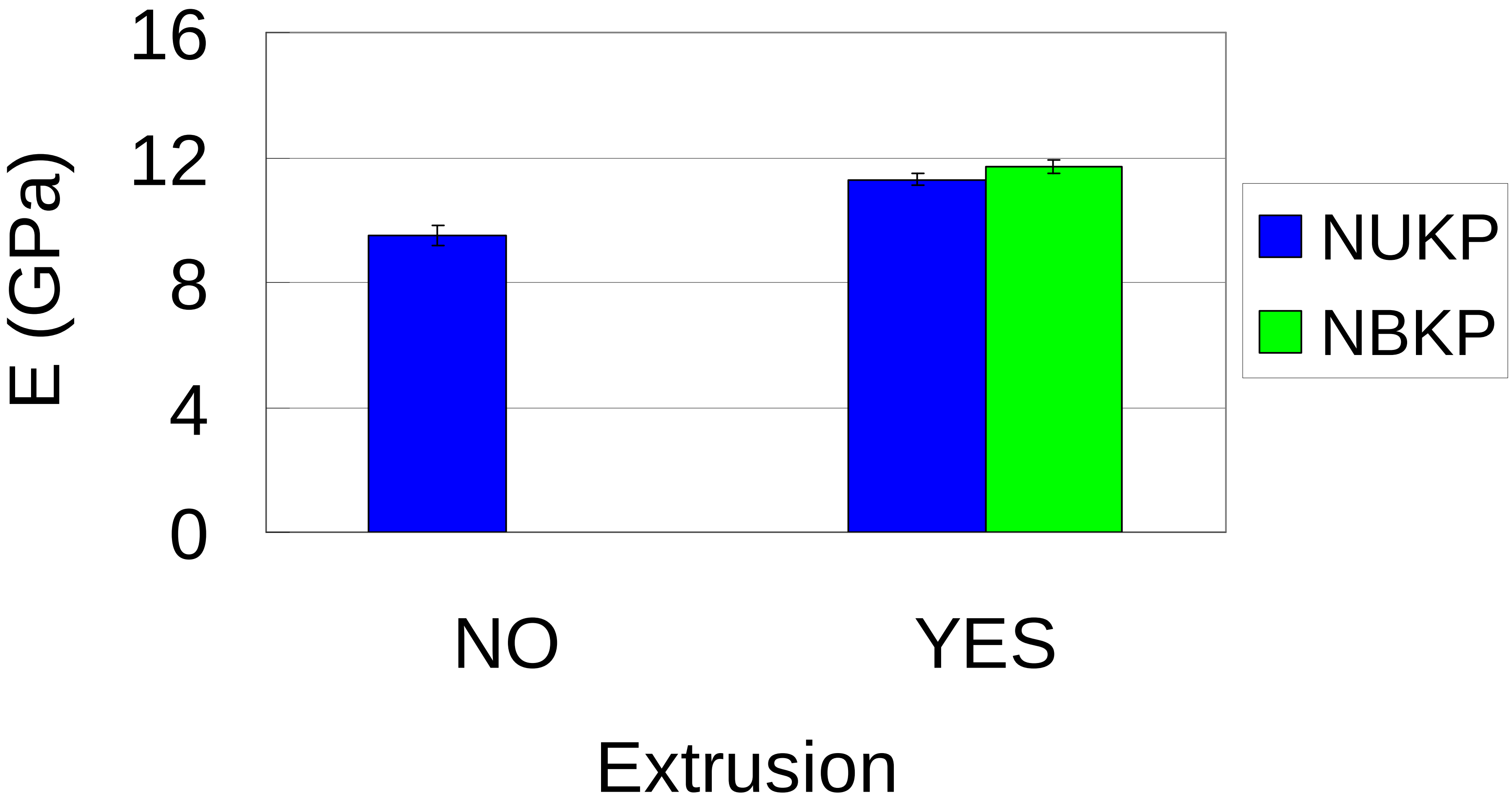
Effect of impregnation time (E)



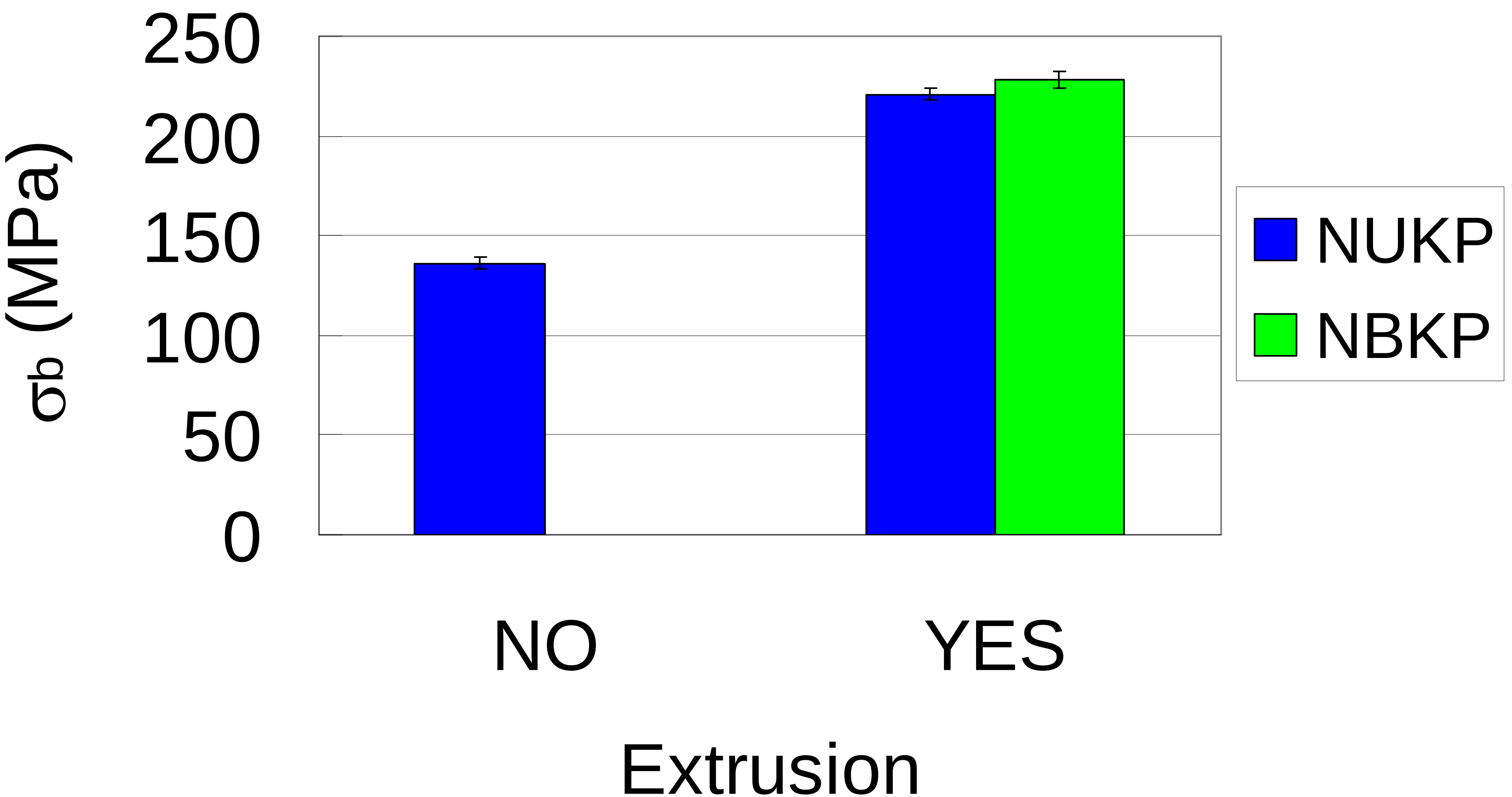
Effect of impregnation time (σ_b)



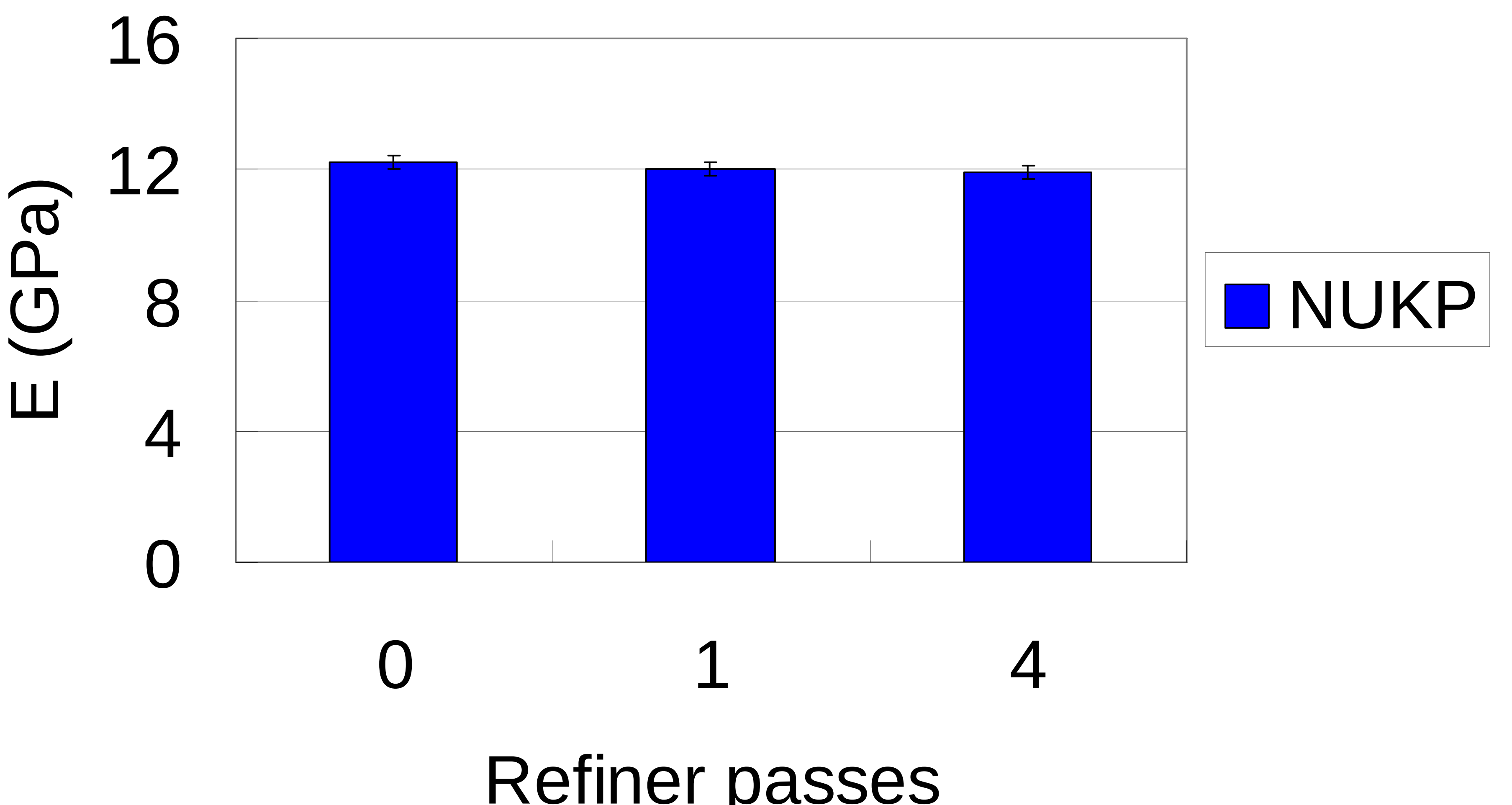
Effect of nanofibrillation by extrusion (E)



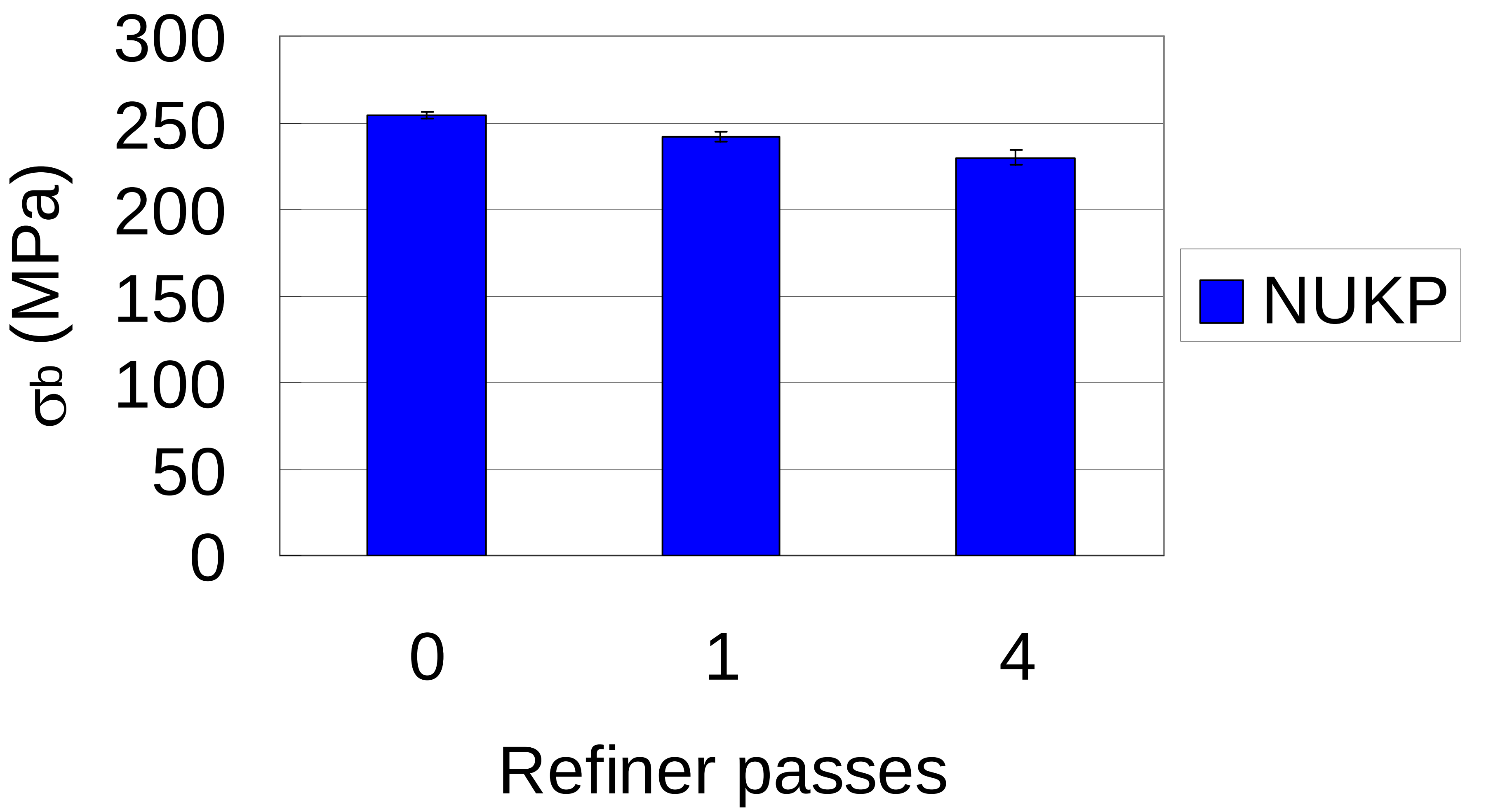
Effect of nanofibrillation by extrusion (σ_b)



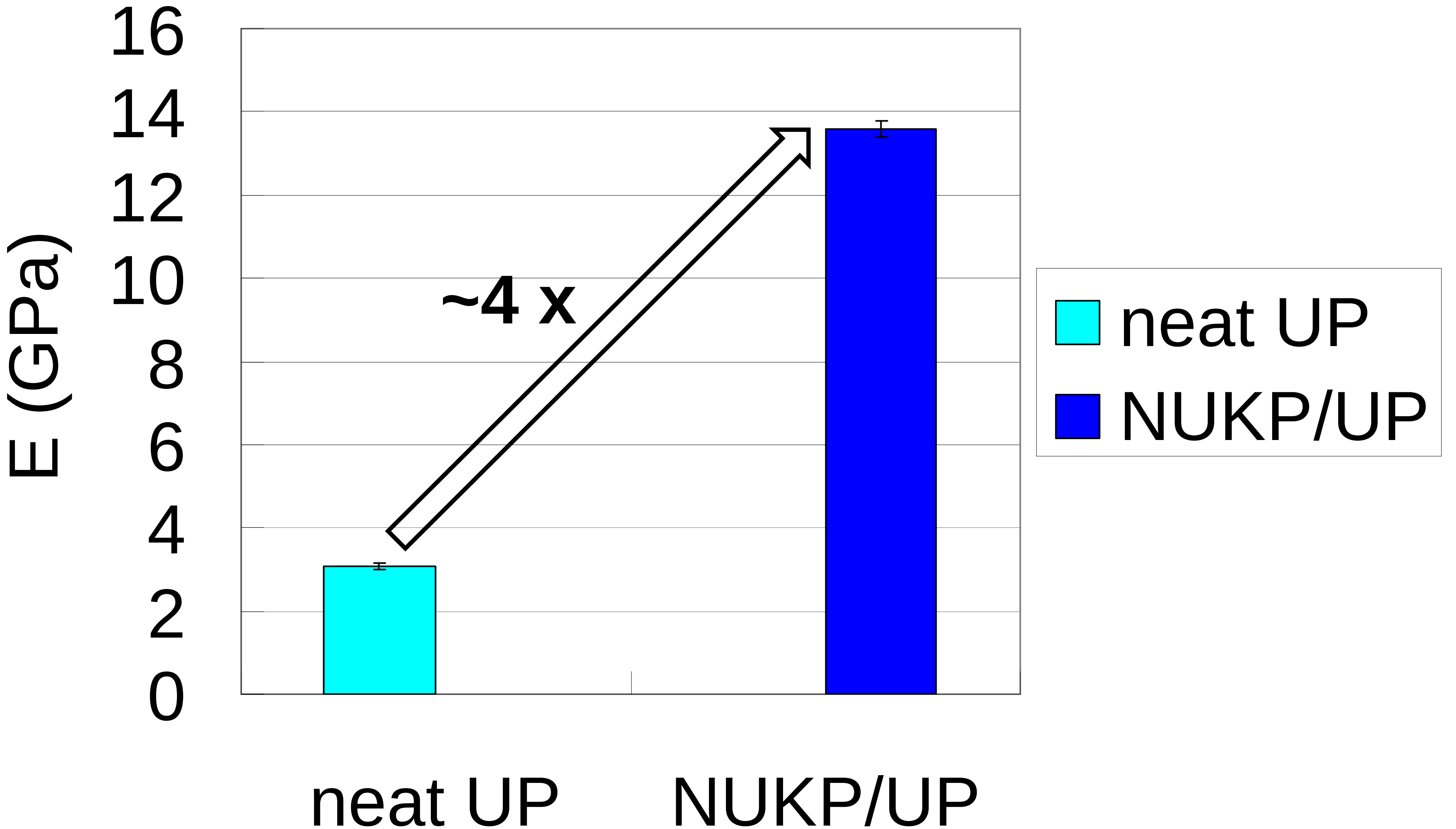
Effect of refining pre-treatment (E)



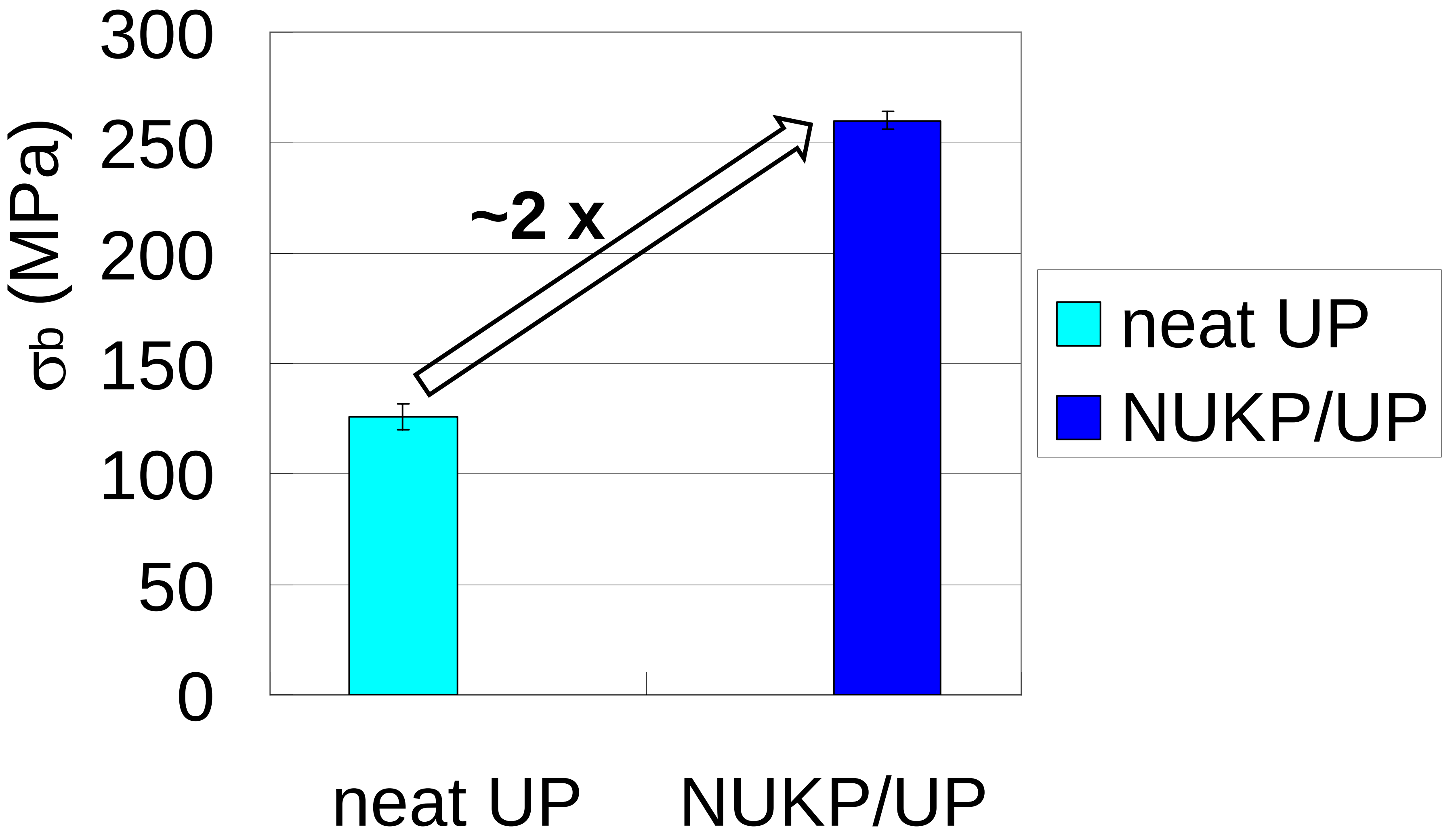
Effect of refining pre-treatment (σ_b)



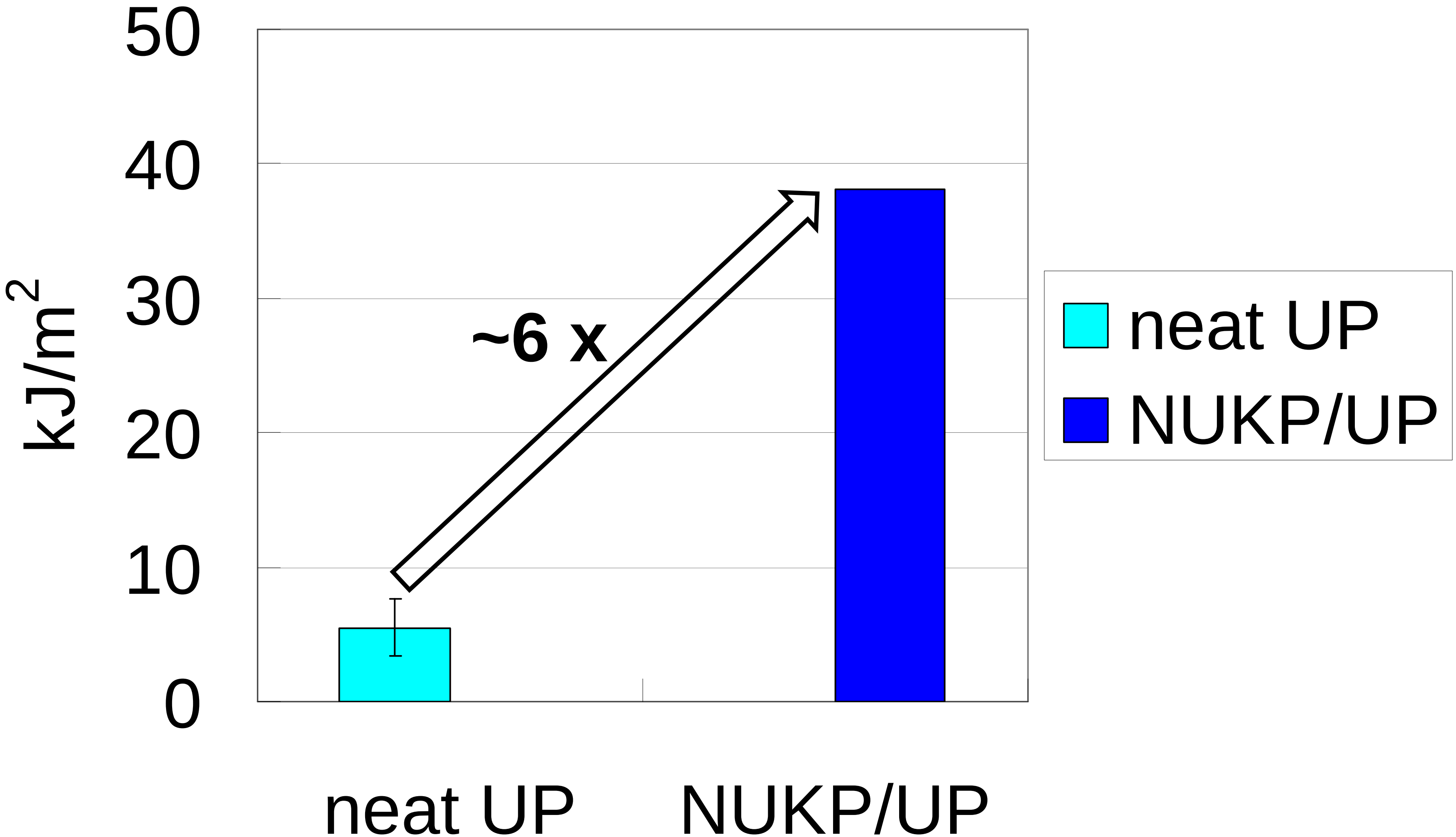
Neat UP vs. NUKP/UP nanocomposites (E)



Neat UP vs. NUKP/UP nanocomposites (σ_b)



Neat UP vs. NUKP/UP nanocomposites (Izod)



Conclusions

- Nanofibrillation by twin-screw extruder;
- Refiner pre-treatment unnecessary;
- Compressing pressure $\leq$ 5 MPa;
- Pulp nanofiber/UP composites:

$$E = 13.6\ \text{GPa}$$

$$\sigma_b = 260\ \text{MPa}$$

Unnotched Izod impact strength = 38kJ/m^2

- **Expected water absorbance.**

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