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# Strain rate and temperature effects on elastic properties of polycaprolactone/starch composite

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**Abstract:** Composite of polycaprolactone (PCL) and starch is a potential biomaterial for tissue engineering scaffolds. During implantation, its mechanical properties might be compromised considering the various strain rates it is subjected to and that human body temperature is close to polycaprolactone's melting temperature. This study aims at revealing the effect of strain rate and temperature to the elastic properties of polycaprolactone-starch composite. Tensile test at strain rates of 5, 0.1, and 0.01 mm/min at ambient and body temperatures were performed. It was revealed that strain rate as well as temperature readily have significant effects on the composite's elastic properties. Such effects have similar trends with that of PCL homopolymer which is used as the composite's matrix. Further analysis on the consequence of the finding was performed by applying the behavior to a finite element model of a porous scaffold and it was found that the discrepancy in elastic properties throughout the construct is even greater.

**Keywords:** composite; mechanical properties; strain rate; temperature.

## 1 Introduction

Among the pool of polymeric biomaterials, polycaprolactone (PCL) is an option to be a biomaterial for tissue engineering scaffolds, in particular for cardiovascular, dental, and musculoskeletal applications (1–4). The scaffolds must give temporary support and be able to withstand external loading before extracellular matrix of the cells matures. PCL, possessing fair mechanical properties and being bioresorbable, can be used for some of these applications (4, 5).

Despite its potential as a biomaterial, PCL's properties and biocompatibility are often deemed inadequate when implemented as scaffolds, e.g. in terms of mechanical properties, bioresorbability, and hydrophilicity. Blending with other biomaterials is a possible approach to address these issues, and starch is one of them (6–8).

During use, scaffolds are exposed to loads at various strain rates. Moreover, the scaffold's highly porous architecture may in itself exhibit non-uniform strain rate distribution within the construct. Another point of note is the fact that scaffolds when implanted are subjected to body temperature. Polymeric scaffold materials' melting temperature is low; it is 55–60°C for PCL (5). The material's properties at temperatures near its melting point are distinct from those at ambient temperature. Our previous report on PCL found that mechanical properties of the homopolymer were indeed significantly altered when it is exposed to body temperature (9). In accordance with this, it is highly likely that it behaves in a similar manner when used as a matrix, and consequently affects the composite's properties. Therefore, the study on the PCL/starch composite's mechanical properties at different strain rates and at body temperature is needed. Specifically, considering scaffolds should withstand loading without yielding, it is of interest to analyze the elastic behavior of the composite below its yield point.

Previous investigations on strain rate or temperature effects on the mechanical properties of polymers were often done on a wide range of strain covering the elastic-to-plastic or viscoelastic properties. Some examples include the study on mechanical behavior of polyolefins (10, 11), polycarbonate (12), polymethylmethacrylate (12), polyethylene terephthalate (13), and hydrogels (14), among others. It is evident that within the wide strain range reported, elastic properties at small strains are readily affected. Therefore, this work intends to report the elastic properties of PCL/starch composite at different strain rates and temperatures.

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## 2 Materials and methods

The polycaprolactone used was of molecular weight (Mn) of 70,000–90,000. Its density is 1.15 g/ml at 25°C, and its melting temperature of 60°C, as noted by the supplier (Sigma-Aldrich Korea, Yongin, Korea). The starch used is locally produced edible corn starch consisting of 95% corn starch and 5% wheat flour (PJ Food, Seoul, Korea). The corn starch was of normal type with 25–30% amlylose content (manufacturer's data).

Preparation of tensile specimens were done by blending 20 g of mixture at 120±20°C in a heated cup fitted with a spiked motor and injection molding (Mini Max Molder, model CS-183MMX, Custom Scientific Instruments, Inc., Easton, PA, USA) to dies of ASTM D638 type V. The shear speed was set at 80 rpm with the blending was done for 8 min. For the tensile test, H5KT (Tinius Olsen, Horsham, PA, USA) utilizing a 5 kN load cell was used. Extension rates of 5 mm/min, 0.1 mm/min, and 0.01 mm/min were assigned. In determining the upper limit, recommendation of the standard which suggests 1–5 mm/min speed of testing was considered. It was assumed that this is the range of speeds to perform mechanical testing on solid polymers and it is also used for testing porous scaffold constructs. For the lower limit, the tensile test machine's sensitivity limit (0.01 mm/min) was chosen. The 0.1 mm/min rate is an order in between the upper and lower limits. The tensile testing was done at room temperature of 23±2°C as well as at elevated temperature (of the human body). A radiant heater was used to increase the temperature of the specimen to 37±2°C, while ensuring that the insulation did not give a direct impact to the tensile test machine's load cell. Conditioning of the specimens by preheating at the relevant temperature for at least 4 h was employed prior to the tensile tests. The stress-strain curves up to inflection point were analyzed.

Thermal analysis was conducted using a Perkin-Elmer (Waltham, MA, USA) DSC 7 differential scanning calorimetry (DSC) set for scanning from 20 to 80°C at 10°C/min under nitrogen atmosphere. Fourier transform infrared spectroscopy (FTIR) was conducted on the samples using a Nicolet iS10 FTIR (Thermo Scientific, Madison, WI, USA) utilizing a KBr/Ge beam splitter. For each sample, an average of over 32 scans was taken from FTIR spectra with 2 $cm^{-1}$ resolution, recorded from 4000 to 600 $cm^{-1}$. Morphology analysis was conducted using a JEOL (Tokyo, Japan) JSM 5800 scanning electron microscope (SEM).

For determining how much effect on elastic properties was caused by the strain rate and temperature, a statistical method was used by a factorial design of two categorical variables, which are strain rate (at 3 levels) and temperature (at 2 levels). Analysis of variance (ANOVA) of each experimental result was utilized to measure the significance of each input variable along with possible interaction between variables. Probabilistic value, *Prob>F*, of 0.05 was the criterion for a variable to be determined as significant. A commercially available statistics software package (Design Expert, Stat-Ease, Inc., Minneapolis, MN, USA) was used for the design of experiments and calculating the results.

Finite element models are developed in this study for complementing data points obtained from experiments and for offering an example on the implication of the finding. Commercial finite element analysis software (ABAQUS, Simulia, Providence, USA) was used. Specifically, a scaffold construct with the size of 0.8 mm×0.8 mm×0.8 mm with 50% porosity was modeled. The material is assumed to be isotropic, with two independent components in the generalized Hooke's law, i.e. Poisson's ratio and Young's modulus. The input for the material's elastic properties included the values related to strain rates and temperatures. Afterwards, loading was applied on the model and the strain's magnitude and distribution were observed.

## 3 Results and discussion

Initial work was conducted to determine the most appropriate PCL/starch composite composition, from the perspective of the mechanical properties. Tensile test results of PCL, composite of 90 wt% PCL and 10 wt% starch (PCL/S10), and composite of 80 wt% PCL and 20 wt% starch (PCL/S20) at a strain rate of 5 mm/min are compared (Figure 1). Increasing starch content causes increased modulus of elasticity but

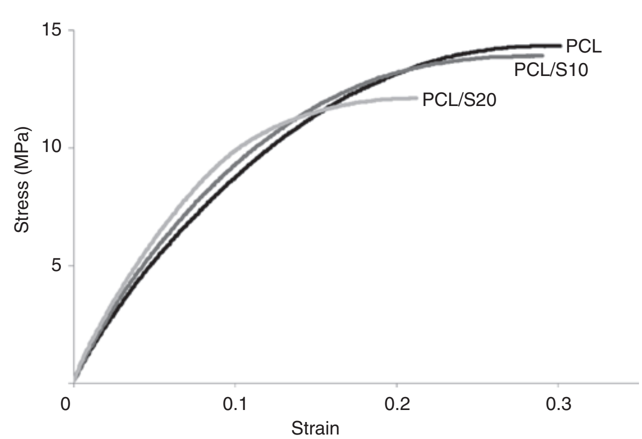


**Figure 1:** Typical stress-strain curves for PCL and its starch composites.

decreased strength and elongation at yield. This phenomenon of increased stiffness and decreased strength when starch is added to PCL is consistent with previous work on the particular composites, as a consequence of the immiscibility of the polymers with a wide polarity gap (6, 15). A cross section image of the composite (Figure 2) revealed gaps between its constituents, an indication of immiscibility. Considering that PCL/S10 showed higher stiffness and was only slightly weaker than PCL, the PCL/S10 was the composite selected for further analysis.

The stress-strain curves obtained from tensile test of PCL/S10 composite at different strain rates and temperatures reveal that strain rate and temperature indeed affect the composite's elastic properties (Figure 3, Table 1). Elastic properties of the polycaprolactone/starch composite at elevated temperature were less than the composite's properties at room temperature. Its strength and Young's modulus at room temperature become lower with decreasing strain rate. In a consistent trend at elevated temperature, elastic properties also become lower, although only slightly when strain rate is lowered from 0.1 to 0.01 mm/min. This marginal difference occurs at any

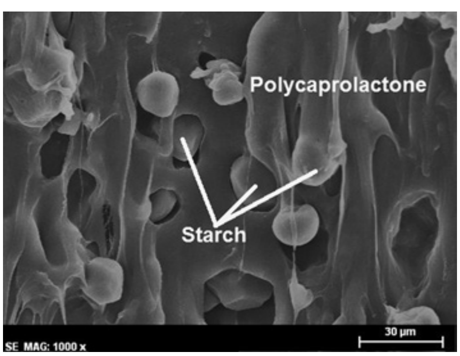


**Figure 2:** Morphology of PCL/S10 composite cross section.

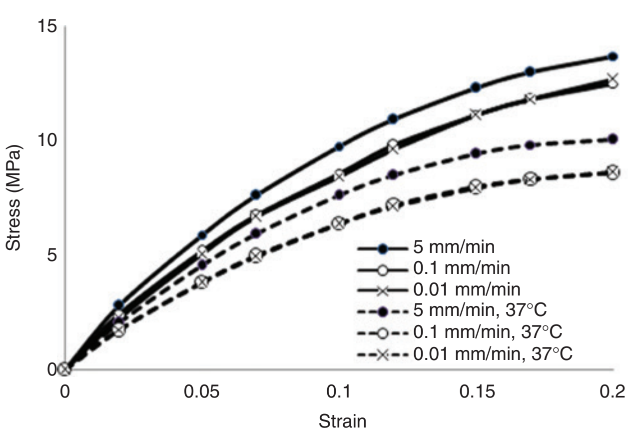


**Figure 3:** Stress-strain curves of PCL/starch composite at various strain rates measured at 23°C and 37°C.

**Table 1:** Mechanical properties of PCL/S10 composite at various strain rates and temperatures.

| Strain rate (mm/min) | Temp (°C) | Yield strength (MPa) | E (MPa) | Elongation (%) |
|---|---|---|---|---|
| 5 | 23 | 14 (1) | 116 (5) | 28 (2) |
| 0.1 | 23 | 13 (1) | 102 (4) | 28 (3) |
| 0.01 | 23 | 13 (1) | 100 (6) | 26 (2) |
| 5 | 37 | 10 (1) | 91 (4) | 21 (1) |
| 0.1 | 37 | 9 (1) | 76 (3) | 23 (2) |
| 0.01 | 37 | 9 (1) | 75 (1) | 25 (1) |

Value inside bracket is standard deviation.

given temperature. Yield strength and modulus of elasticity of PCL/starch composite are directly proportionate with strain rate yet inversely proportionate with temperature. Quantitatively, reducing the strain rate from 5 to 0.01 mm/min lowers the strength and elasticity modulus of the composite to 12% and 17%, respectively. Also, when temperature increases from room to human body temperature, the composite's yield strength and elasticity modulus decreases up to 35% and 25%, respectively. The values are in a similar range for the PCL homopolymer (9), which means addition of up to 10 wt% of starch did not really alter the mechanical properties of the matrix (in terms of strength, stiffness, and elongation) or change of the matrix's elastic behavior at different strain rates and temperatures.

FTIR analysis on PCL, starch, and the PCL/S10 composite (Figure 4) suggested that the spectra of PCL/S10 composite is similar to that of PCL. The internal C-O-C bond (around 1650 $cm^{-1}$) of the starch had no effect on the internal ester group of the PCL (peak of around 1700 $cm^{-1}$) within the composite (16). This means there was no molecular bond that occurred between PCL and starch within the composite.

Differential scanning calorimetry (DSC) analysis (Table 2) found that melting temperature of the composite is 63°C, which is higher than neat PCL's 62°C. The PCL/S10 composite's crystallinity is 44%, which is lower than PCL's 45%. The composite's matrix was actually in a rubber-like state [$T_g$ is around -62°C for neat PCL (17)]. Presumably, its behavior shows similarity to semi-crystalline thermoplastics (10–14). On the effects of strain rate and temperature, variation in friction within the crystalline and amorphous phases (11) is likely influential. Friction decreases with less strain rate following the reduced local deformation speed that makes increased polymer chains' mobility and the friction lowers with temperature as high heat facilitates texture rearrangement (10, 12). It is suggested that

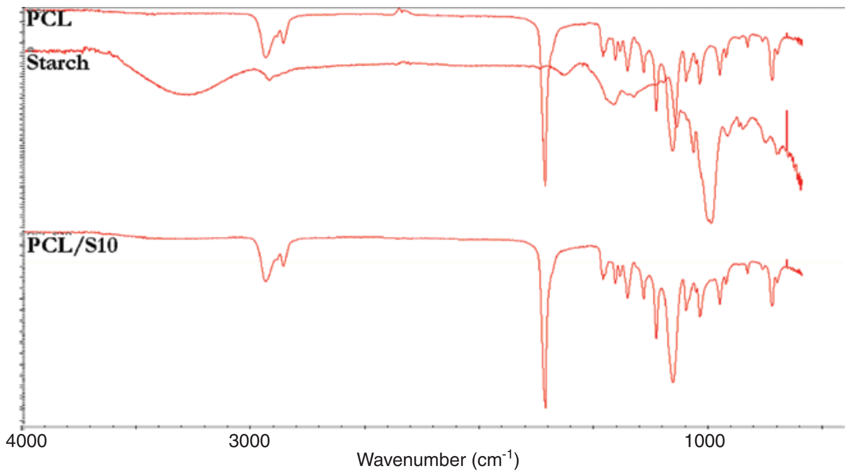


**Figure 4:** FTIR spectra of polycaprolactone, starch, and PCL/S10 composite.

**Table 2:** Differential scanning calorimetry (DSC) results on PCL and PCL/S10 composite.

| Type | $T_m$ (°C) | Crystallinity (%) |
|---|---|---|
| PCL | 62 | 45 |
| PCL/S10 | 63 | 44 |

the presence of starch causes higher melting temperature of the composite and lower crystallinity of the matrix. Higher melting temperature and higher crystallinity often mean higher mechanical properties for semi-crystalline polymers. The net effect of higher melting temperature and PCL's lower crystallinity in the composite seems to cause the overall elastic behavior of the composite and is similar to that of the matrix. The trend of slight elastic behavior difference between 0.1 and 0.01 mm/min strain rates at both temperatures indicates there is a saturation level of strain rate below which reduction in elastic properties is negligible.

It was a concern that the data points may not be sufficient, especially for the temperature effect to come to the above conclusion. The reason is due to the narrow range of temperature (viz. from ambient to body temperatures) being studied, associated with the composite's low melting point and its condition during service. However, similar trends reported previously on other types of thermoplastics (9–14) justifies the reasoning. Nonetheless, finite element analysis is used in this study to complement the data points and to simultaneously verify the finding.

For numerical analysis of tensile specimens, the finite element models are based on the results obtained from the tensile test experiments. The model's geometry is based on the size of standard tensile specimen and its gage length. For verification, the model is tensile loaded until 5% strain is reached at strain rates and temperatures according to the input. Stress-strain curves are generated from the loaded tensile specimens and matched to the input. A perfect match was obtained for all input parameters and, thus, the models are verified. The models are employed to generate elastic properties of the materials at 30°C at various strain rates. An example of the built models is displayed in Figure 5, with its boundary conditions, loading, meshing, and the calculated result of the loaded condition are shown. The calculated stiffness of the particular composite at 30°C tensile loaded at 5, 0.1, and 0.01 mm/min is 103, 89, and 88 MPa, respectively. These values are reasonably within the measured stiffness range.

ANOVA of the yield strength and the elasticity modulus for the composite confirms the significance of the effects of strain rate and temperature (Table 3). It was

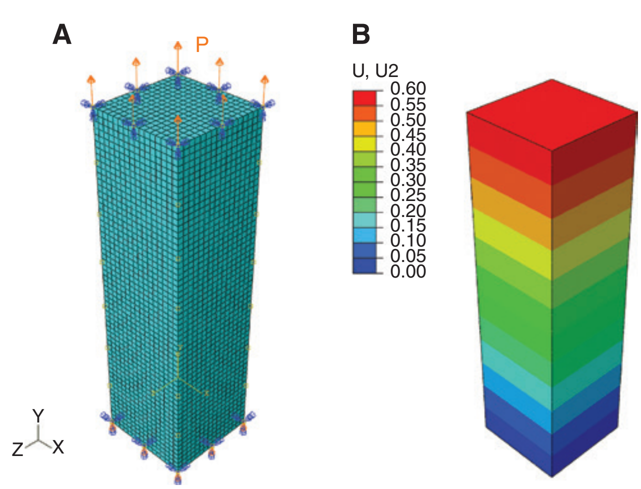


**Figure 5:** (A) Tensile test specimen with boundary conditions and loading P shown and (B) strain (in Y direction U2) distribution within the tensile specimen loaded at 5 mm/min at 30°C.

**Table 3:** ANOVA for strength and stiffness.

| Source | Sum of squares | Degree of freedom | Mean square | F-value | Prob>F |
|---|---|---|---|---|---|
| Yield strength | | | | | |
| Strain rate | 4.85 | 2 | 2.43 | 4.55 | 0.04 Significant |
| Temperature | 70.11 | 1 | 70.11 | 131.34 | <0.01 Significant |
| Strain rate and temperature | 0.07 | 2 | 0.04 | 0.07 | 0.93 Not significant |
| Modulus of elasticity | | | | | |
| Strain rate | 863.27 | 2 | 431.63 | 15.65 | <0.01 Significant |
| Temperature | 2308.49 | 1 | 2308.49 | 83.68 | <0.01 Significant |
| Strain rate and temperature | 0.51 | 2 | 0.25 | 0.01 | 0.99 Not significant |

indicated through the small probabilistic value, *Prob>F*. The non significant effect of interaction between strain rate and temperature suggested the strong influence of the strain rate and the temperature themselves to the composite's strength and stiffness.

Evidence on the implication of the finding in this study was observed by measuring strains on the tensile specimens made of the composite. The space between marked points is 4 mm within the 16 mm gage length (Figure 6). The tensile specimens were tested at 5 mm/min extension rate under room temperature until the specimens were 7% and 14% strained (denoted as Strain1 and Strain2, respectively). The strain distribution was not linear, which indicates the presence of different strain rates. This is similar to the finding of a similar experiment on PCL homopolymer (7).

The finding implicates the design and fabrication of tissue engineering scaffolds. The porous architecture of scaffolds has even more effects because porous plastic's elastic behavior is also sensitive to temperature and strain rate (18). Mechanical properties of scaffold are determinant to give mechanical support before the seeded cells' extracellular matrix establishes and in the proliferation of cells. Substrates with higher stiffness and rigidity spreads endothelial cells, fibroblasts, myoblasts, epithelial cells, chondrocytes, glia, and aortic smooth muscle cells more efficiently (19, 20). With scaffolds made of PCL homopolymer reportedly possessing mechanical properties within lower range of trabecular bone (4) or hard tissue (21), a change in mechanical properties might alter the tissue growth and proliferation.

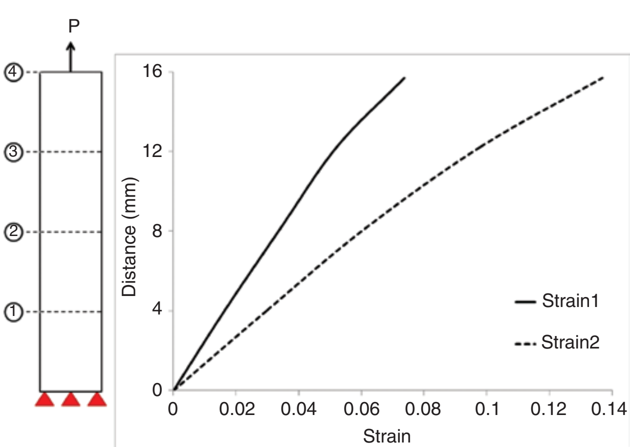


**Figure 6:** Schematic of tensile specimen and the measured strain at various points.

Strain rate's and temperature's effect on polycaprolactone/starch composites may also have an implication in numerical analysis (e.g. finite element method) to simulate scaffold behavior under loading. Refined simulation should involve a range of properties of the material at different temperatures and strain rates. Higher accuracy in simulating the performance of scaffolds is expected through this refining, from the capability to better represent these aspects:

- induced stress and strain on the scaffold at body temperature,
- stress and strain at various loading rates, and
- distribution of strain rates within the highly porous scaffold structure.

As an example of the practical implication mentioned above, a loaded scaffold construct (0.8 mm×0.8 mm×0.8 mm) having 50% porosity was numerically analyzed. The details of the finite element analysis have been reported previously (9). It should be noted that assigned properties of the materials in a finite element model, including models with porous architecture, are obtained from those of their solid form. The model is assigned to have unit cell of a simple cubic, which is manufacturable using solid free-form techniques. The elastic properties of PCL/starch composites at multiple temperatures and strain rates were the set input. The scaffold was then compressive loaded until the strain reached 5%. The calculated stress

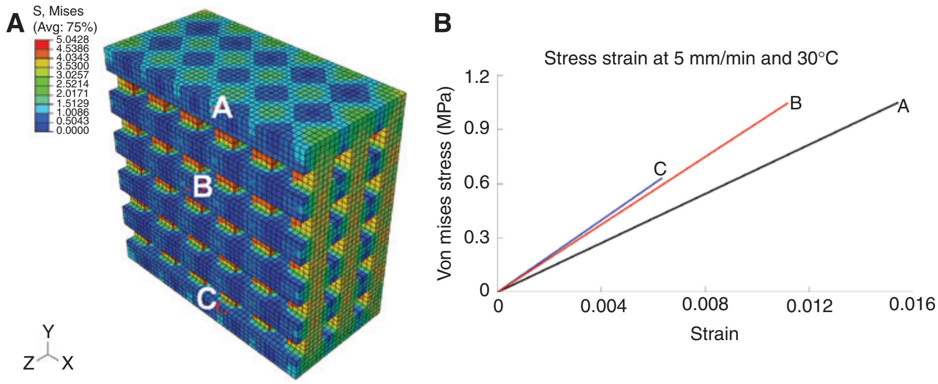


**Figure 7:** (A) Stress distribution within in the loaded PCL/starch composite scaffold model at its cross section and (B) stress-strain curves at three points across the scaffold.

distribution across the scaffold (Figure 7) revealed the wide variety of elastic modulus across the scaffold. The difference of the stress distribution reaches almost 50%. The varying stress and strain which occurred within the scaffold construct during loading can be attributed to the combination between the effect of the scaffold's porous construct and the mechanical properties of the composite at different strain rates (9, 22, 23). Related to this particular finite element analysis, the 25% difference in modulus elasticity measured as the effect of strain rate and temperature translates to 46% stiffness difference in the scaffold construct.

## 4 Conclusions

A composite of polycaprolactone and 10 wt% starch showed improved stiffness with slightly lower strength. Elastic properties of the polycaprolactone/starch composite at body temperature are less than ones at room temperature. The composite's strength and Young's modulus are proportional to the strain rate. Both the temperature and the strain rate significantly affect the composite's mechanical properties, even at narrow range of strains. Supported by the example on a scaffold's numerical analysis, the finding suggests that the effect of temperature and strain rate to the elastic properties of PCL/starch composite should be taken into account during design as well as during fabrication of applications where rigidity is a determinant.

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