

The Dependence of Properties of Cellulose Acetate Propionate on Molecular Weight and the Level of Plasticizer

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Synopsis

Thermal and mechanical properties were measured for solvent-cast films of cellulose acetate propionate plasticized with triphenyl phosphate. Probabilistic models for the glass transition temperature, tensile heat deflection temperature, tensile modulus, break stress, and initial tear strength as functions of weight-average molecular weight and level of plasticizer were developed. The glass transition temperature and the tensile heat deflection temperature were modeled well by functions of the level of plasticizer as the only variable, whereas models for the tensile modulus, break stress, and initial tear strength included molecular weight. Only the break stress showed a statistically significant term of interaction between molecular weight and level of plasticizer. This term was such that, for unplasticized films, increasing the molecular weight increased the break stress, whereas, for films formulated with 20 pph plasticizer, increasing the molecular weight decreased the break stress. Physical explanations for this interaction term are discussed.

INTRODUCTION

At present, only plasticized formulations of cellulose esters have commercial utility as extruded films or sheets. For this reason, the formulation of cellulose esters with plasticizers is critical to their performance and has been the subject of considerable research. The effect of a plasticizer on the viscoelastic properties of a cellulose ester plastic has been shown to be dependent on the chemical structure of the plasticizer.¹ The relationship between the level of plasticizer in cellulose esters and the thermal transitions in these plastics has been examined by differential scanning calorimetry, dynamic mechanical analysis, and dielectric relaxation.²⁻⁴ Generally, increasing plasticization of cellulose ester plastics is reported to decrease the mechanical properties of the plastics such as tensile modulus and break stress.⁵ One area which has not been thoroughly investigated is the effect of interactions between the level of plasticizer and the molecular weight of the cellulose ester on the mechanical properties of the plastic.

In related articles, the effect of molecular weight and molecular weight distribution on various mechanical properties of poly(vinyl chloride) has been reported but these materials were formulated to a constant level of dioctyl phthalate.⁶ Others have studied the combined effects of plasticization, either internal or additive, and molecular weight on fatigue crack propagation.^{7,8} These researches did not specifically identify interactions between the two variables.

The work presented here examined the dependence of the thermal and mechanical properties of a cellulose ester on its molecular weight and the level of

TABLE I
Molecular Weights of Batches of CAP-482-20

Batch no.	Weight-average ^a molecular weight	Polydispersity
1	247,000 (5000)	3.07 (0.22)
2	247,000 (6000)	3.16 (0.35)
3	240,000 (4000)	3.12 (0.31)
4	234,000 (8000)	3.16 (0.23)
5	225,000 (5000)	3.19 (0.27)
6	223,000 (5000)	3.31 (0.32)

^a The molecular weights and polydispersities are the average of five determinations with the standard deviation given in parentheses.

plasticization. The cellulose ester used in this research was a cellulose acetate propionate, CAP-482-20, which is used commercially in both extruded and injection-molded applications. Triphenyl phosphate was used to plasticize the CAP-482-20. Triphenyl phosphate acts as both a plasticizer and as a flame retardant.⁹

EXPERIMENTAL

Materials

Cellulose acetate propionate, CAP-482-20, was supplied from individual batches of production by Tennessee Eastman Co. The molecular weights and degrees of acyl substitution are given in Tables I and II, respectively. Triphenyl phosphate was purchased from Kodak Laboratory Chemicals. The solvents were all reagent or spectro grade as required.

Methods

The number-average and weight-average molecular weights were determined by gel permeation chromatography with two columns, mixed and 100 Å, arranged in series and calibrated with polystyrene standards. The standards and the

TABLE II
Degrees of Acyl Substitution of Batches of CAP-482-20

Batch no.	DS propionyl	DS acetyl	DS hydroxyl ^a
1	2.69	0.04	0.27
2	2.68	0.03	0.29
3	2.67	0.03	0.30
4	2.68	0.03	0.29
5	2.69	0.04	0.27
6	2.69	0.04	0.27

^a The DS hydroxyl is calculated from the equation: DS hydroxyl = 3 - (DS propionyl + DS acetyl).

columns were both supplied by Polymer Laboratories, Ltd. The cellulose acetate propionate was eluted with tetrahydrofuran and was detected with a Perkin-Elmer LC95 UV-VIS detector. The concentration of the cellulose acetate propionate was assumed to be linearly proportional with the absorption at 230 nm. The degree of substitution of the cellulose ester was determined by nuclear magnetic resonance on a Jeol GX-270 MHz spectrometer. The sample was dissolved to a concentration of 1.5 wt % in dimethyl sulfoxide which was 1 wt % trifluoroacetic acid. The spectrum was integrated and analyzed after 64 transients were collected. The area of the region from 2.5 to 5.3 ppm chemical shift was normalized to 7 protons for the anhydroglucose ring. With the assignment of the region from 0.6 to 1.5 ppm to the methyl group of the propionyl esters, the degree of propionyl substitution can be calculated from the following ratio:

$$\text{DS propionyl} = \frac{7 \times \text{area (0.6-1.5 ppm)}}{3 \times \text{area (2.5-5.3 ppm)}}$$

With the assignment of the region from 1.7 to 2.45 ppm to protons from both the methylene group of the propionyl esters and the methyl group of the acetyl esters, the degree of acetyl substitution can be calculated from

$$\text{DS acetyl} = \frac{7 \times \text{area (1.7-2.45 ppm)}}{3 \times \text{area (2.5-5.3 ppm)}} - (0.667 \times \text{DS propionyl})$$

Films of plasticized CAP-482-20 were cast in the following manner. First the cellulose ester was dissolved in 2-butanone to a final concentration of 15 wt %. Then triphenyl phosphate was added to these solutions and was allowed to dissolve at room temperature with gentle agitation. These dopes were cast on clean glass plates to a wet film thickness of 0.127 cm. The plates were then placed in trays at room temperature and the solvent was allowed to evaporate slowly for 24 h. Then the plates were placed in a forced-air oven at 55°C for 72 h. To remove the films from the glass, the plates were immersed in deionized water for 30 min. Finally the free films were placed in a vacuum oven at 80°C under 100 torr pressure with a nitrogen purge for 24 h. For mechanical testing in quintuplicate, five films were cast from each dope and all of the films were cast in a random order.

Strips of the films of CAP-482-20 were cut for mechanical testing with JDC precision samples cutters. The film tensile modulus was tested according to ASTM-D882 on an Instron testing machine, Model TT-1125. The gage length was 5.08 cm and the crosshead speed was 5.08 cm/min. The break stress and elongation at break were measured according to ASTM-D882 on an Instron testing machine, Model TT-C. The initial tear force for film tear propagation was tested according to ASTM-D1938 on an Instron testing machine, Model TT-1125. The gage length was 5.08 cm and the crosshead speed was 25.4 cm/min. The mechanical testing was performed at 23°C and 50% relative humidity. The tensile heat deflection temperatures for the films were determined according to ASTM-D1637 at a shear stress of 345 KPa.

Differential scanning calorimetry was performed on a DuPont 912 differential scanning calorimeter with the samples sealed under nitrogen. For the first cycle, the samples were heated from 40 to 280°C at 20°C/min. Then the samples were quenched to room temperature and the second cycle was run from 40 to 280°C at 20°C/min. The glass transition temperature T_g was taken from this second cycle.

The statistical analysis of the data was performed with RS/1 supplied by BBN Software Products Corp. The computations are based on a stepwise regression procedure.¹⁰

RESULTS AND DISCUSSION

The range of the weight-average molecular weights was relatively narrow. This range was due to natural variability and was not the result of alteration of the synthetic protocol. Three advantages of avoiding such alterations are that large changes in the molecular weight distributions are avoided, as shown in Table I, uniformity of the substitution of the product is maintained, as shown in Table II, and hidden process variables are not introduced. The disadvantage of a narrow range is that extrapolation of the models to molecular weights of interest beyond the experimental range is speculative.

The T_g vs. the level of plasticizer is plotted in Figure 1 for all six batches of CAP-482-20. The line shows the model of the data calculated by the following equation:

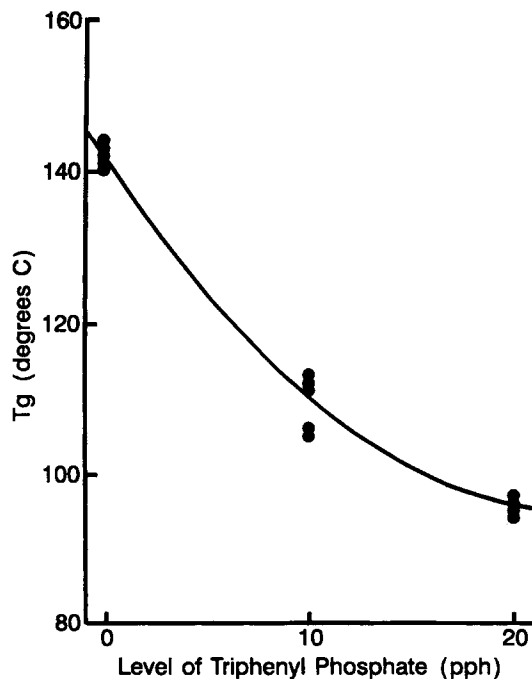


Fig. 1. T_g of CAP-482-20. The curve is calculated from eq. (1).

$$T_g = 142 - (4.06 \times P) + (0.0875 \times P^2) \quad (1)$$

where T_g is the glass transition temperature ($^{\circ}\text{C}$) and P is the level of plasticizer in parts per hundred parts of cellulose acetate propionate (pph). The correlation coefficient R^2 for this model is 0.99. This high value for R^2 and additional analysis of the effect of molecular weight suggest that T_g is largely independent of molecular weight. The correlation coefficient of the molecular weight or the square of the molecular weight with the T_g is less than 0.02. The inclusion of terms for the molecular weight, the square of the molecular weight, or the product of the molecular weight with the level of plasticizer does not increase R^2 more than 0.002 and the significance level for including any of these terms in the model is greater than 0.05. The curvature which arises from the inclusion of the second-order term appears to be real and has been observed in single batches of cellulose acetate plasticized with diethyl phthalate above 15%.¹ The data for the formulations of CAP-482-20 with 10 and 20 pph triphenyl phosphate were also analyzed by the following model¹¹:

$$\ln T_g = \ln T_{g2} + [(\ln(T_{g1}/T_{g2})) / (1 + kw_2/w_1)] \quad (2)$$

where w_1 and w_2 are the weight fractions of the triphenyl phosphate and the CAP-482-20, respectively. The temperature used for the glass transition of triphenyl phosphate, T_{g1} , in eq. (2), was 322 K and the temperature used for the glass transition of CAP-482-20, T_{g2} , in eq. (2), was 415 K. The best fitting curvature parameter k for the data was a value of 0.22. When the model was transformed into the form

$$[\ln(T_{g1}/T_{g2})] / [\ln(T_g/T_{g2})] = a + kw_2/w_1 \quad (3)$$

a linear regression of the data gave $a = 1.09$ and $k = 0.21$ with $R^2 = 0.85$. The curvature parameter k was calculated for each batch of CAP-482-20 and no statistical correlation between k and weight-average molecular weight was observed. A plot of k vs. the molecular weight of each batch of CAP-482-20 is shown in Figure 2.

The tensile heat deflection temperature (HDT) for 2% deflection vs. the level of triphenyl phosphate is shown in Figure 3. The line shows HDT in degrees centigrade as a linear function of the level of triphenyl phosphate calculated from the equation

$$\text{HDT} = 164 - 3.22 \times P \quad (4)$$

with an $R^2 = 0.94$, where HDT is in degrees centigrade. There appeared to be a significant decrease in the variability of the HDT as the level of triphenyl phosphate was increased. One explanation for this decrease in variability is that the effect of higher levels of triphenyl phosphate dominates any plasticization arising from the presence of oligosaccharide esters. In contrast to T_g , a P^2 term in this model did not significantly improve the fit of the model to the data. Also HDT appeared to be largely independent of molecular weight.

The modulus could be modeled by the following equation:

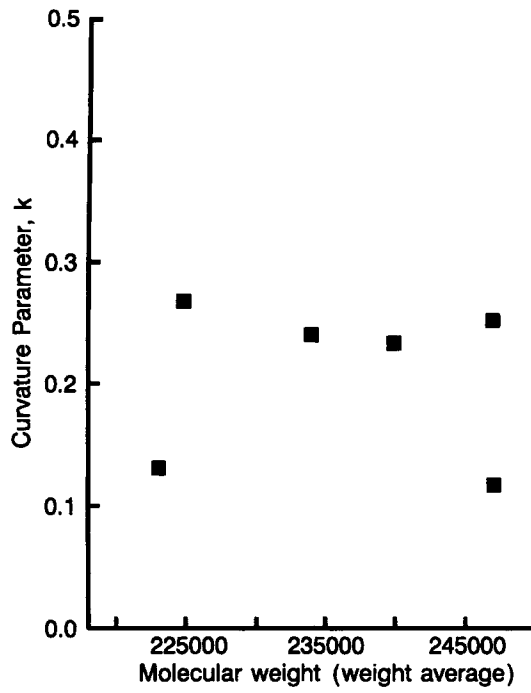


Fig. 2. Curvature parameter k vs. molecular weight.

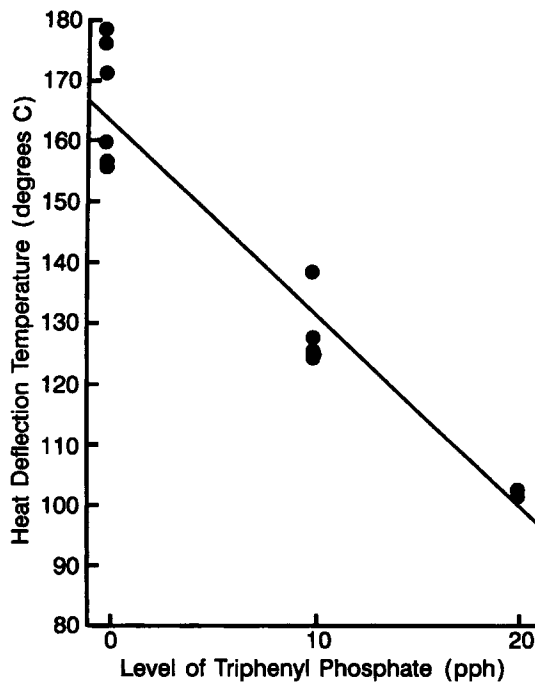


Fig. 3. Tensile heat deflection temperature of films of CAP-482-20. The line was calculated from eq. (4).

$$\text{modulus (MPa)} = 1100 + (417 \times \text{MW}) - (13.3 \times P) - (0.655 \times P^2) \quad (5)$$

where MW is the weight-average molecular weight expressed in units of 100,000. The correlation coefficient for this model of the data is 0.96. The model is plotted in Figure 4. Values for the moduli calculated from eq. (5) are plotted vs. the observed moduli in Figure 5. Over this range of molecular weights and levels of plasticizer, the modulus appears to be largely dependent on the level of plasticizer; however, this effect is due to the narrow range of molecular weights which were examined. When the model is simplified to a linear combination of MW and P , $R^2 = 0.9$.

The break stress of the films could be modeled by the following equation:

break stress (MPa)

$$= (32.5 \times \text{MW}) - (3.254 \times \text{MW} \times P) + (6.92 \times P) - 15.4 \quad (6)$$

The correlation coefficient for this model of the data is 0.78. The model is plotted in Figure 6. Values for the break stresses calculated from eq. (6) are plotted vs. the observed break stresses in Figure 7. The product term appears to make a significant contribution to the model accounting for approximately 20% of the variation in the data with a T value of -2.8 and a significance level of 0.01. The inclusion of this term produces a model in which the effect of the

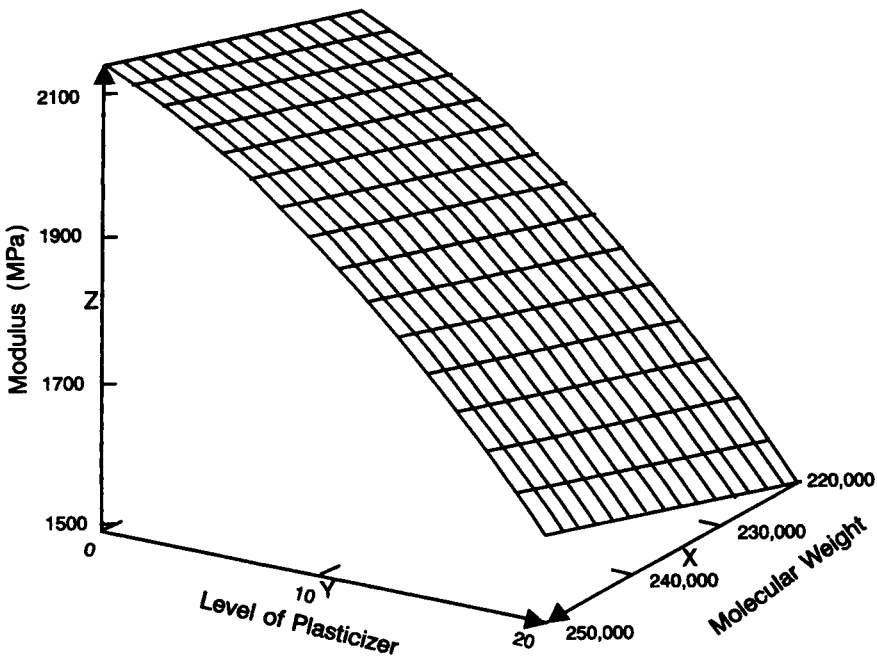


Fig. 4. Modulus of films of CAP-482-20 as a function of molecular weight and the level of triphenyl phosphate. The X-axis is the molecular weight from 220,000 to 250,000. The Y-axis is the level of triphenyl phosphate from 0 to 20 pph. The Z-axis is the tensile modulus calculated from eq. (5).

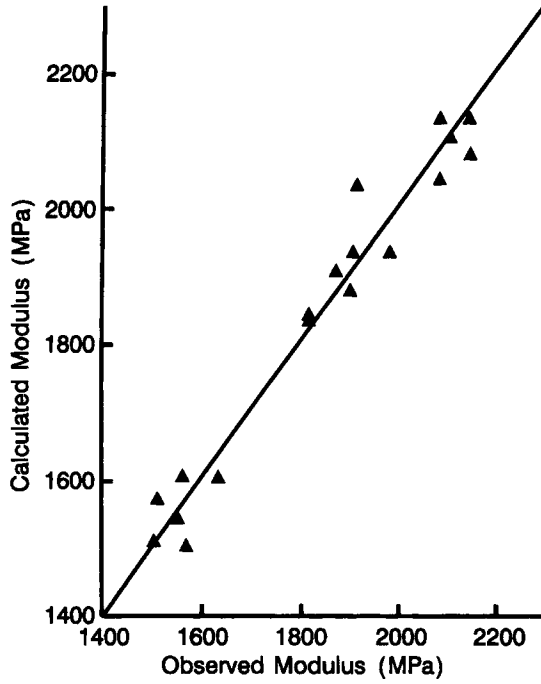


Fig. 5. Modulus calculated from eq. (5) vs. observed modulus.

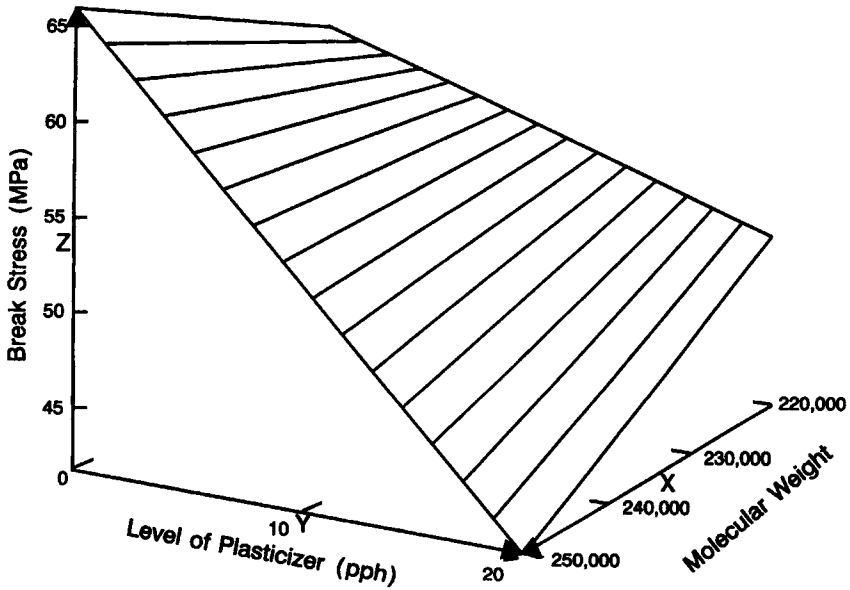


Fig. 6. Break stress of films of CAP-482-20 as a function of molecular weight and level of triphenyl phosphate. The X-axis is the molecular weight from 220,000 to 250,000. The Y-axis is the level of triphenyl phosphate from 0 to 20 pph. The Z-axis is the break stress calculated from eq. (6).

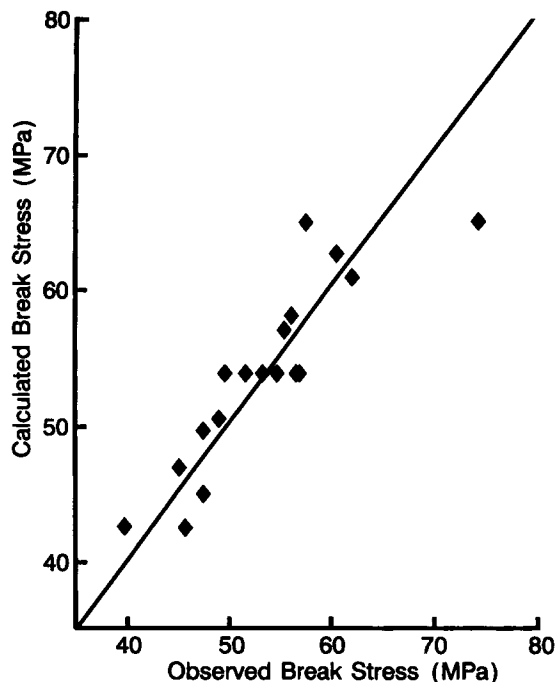


Fig. 7. Break stress calculated from eq. (6) versus observed break stress.

level of plasticizer on the break stress will depend on the molecular weight of the CAP-482-20 being tested. That is to say, the model predicts that, over the ranges examined, increasing molecular weight leads to increasing break stress at low levels of triphenyl phosphate, but, at levels of triphenyl phosphate above 10 pph, increasing molecular weight leads to decreasing break stress. The physical cause of this interaction term is unknown. One possible explanation is that the plasticization is less uniform for higher molecular weight CAP-482-20 at 20 pph triphenyl phosphate due to lessened compatibility. Such an explanation would be supported by the curvature seen in the T_g , although no indication of incompatibility was detected by visual observation or DSC. Alternatively, the morphology of the CAP in the film may be altered by the dependence of the rate of evaporation of the solvent on the level of triphenyl phosphate.¹²

The initial tear strength can be modeled with an $R^2 = 0.74$ by the linear combination of weight-average molecular weight and plasticizer as given in the following equation:

$$\text{initial tear strength (N)} = 1.23 - (0.443 \times \text{MW}) + (0.00454 \times P) \quad (7)$$

Both the weight-average molecular weight and the level of plasticizer are included in such a manner as to correspond to decreasing modulus. The dependence of the initial tear strength on the molecular weight and the level of plasticizer may reflect the assumption that a more elastic material will exert less stress on the introduced defect and thereby give rise to a higher initial tear

strength. However, the MW term dominates more in the model of the initial tear strength than in any other model.

The lower values of R^2 for the models of the break stress and the initial tear strength are largely due to increased test variability. Likewise, the percent elongation at break could not be satisfactorily modeled as a function of MW, MW^2 , $MW \times P$, P , and P^2 because of the test variability. Higher-order terms, MW^3 , P^3 , $MW^2 \times P$, and $P^2 \times MW$, were not included in any of the models. The number of experimental conditions were such that these higher order terms are highly correlated with terms already included in the models and account for little of the unexplained variation in the responses. When included in the stepwise regressions, the significance levels of these terms were greater than 0.05.

In summary, the thermal and mechanical properties of CAP-482-20 plasticized with triphenyl phosphate which were modeled by a function of the weight-average molecular weight and the level of plasticizer were T_g , tensile heat deflection temperature, tensile modulus, break stress, and initial tear strength. Of these properties, only the model of the break stress included an interaction term for the weight-average molecular weight and the level of plasticizer. The T_g and the tensile heat distortion temperature appeared to be independent of the weight-average molecular weight.

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