

CURING CHARACTERISTICS AND ADHESION PERFORMANCE OF PHENOL–FORMALDEHYDE RESINS WITH COMPOSITE ADDITIVES

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MO XF, FAN DB, QIN TF & CHU FX. 2015. Curing characteristics and adhesion performance of phenol–formaldehyde resins with composite additives. The curing characteristics of cure-accelerated phenol–formaldehyde resins with composite additives were investigated by differential scanning calorimetry analysis and gelation test. The pot lives and adhesion performances of phenol–formaldehyde resins were evaluated by viscosity variations and wet shear strength test of plywood respectively. Results indicated that the incorporation of triacetin and urea effectively accelerated the curing rate and improved the adhesion performances of phenol–formaldehyde resins with their pot lives for more than or equal to 8 hours. The individual triacetin-accelerated phenol–formaldehyde resin could fast cure at relatively low temperature with higher wet shear strength, but its pot life was less than 1 hour which was useless for the plywood industry. Urea as additive did not accelerate the curing rate of phenol–formaldehyde resin, but it was better at improving wet shear strength compared with control resin. At least 4 min were necessary for the wet shear strength of all specimens to reach 0.7 MPa required by the Chinese National Standard. Composite additive at 0.7% urea + 0.3% triacetin showed the best acceleration effects on curing process and wet shear strength of the phenol–formaldehyde resins and had suitable pot life for plywood production.

Keywords: Differential scanning calorimetry, gel time, pot life, wet shear strength

INTRODUCTION

Phenol–formaldehyde resin, the first synthetic polymer, has been widely used for manufacturing high strength and extreme heat resistant wood composites materials, especially for plywood manufacture (Pizzi 1983). However, one of the main drawbacks of the phenol–formaldehyde resin is its relatively low curing rate when compared with other thermosetting adhesives such as urea–formaldehyde. The low curing rate significantly influences cost and productivity of the plywood industry. For decades, scientists have strived to find ways of accelerating the curing rate, including using various catalysts and additives such as esters and urea.

Esters are often used as catalysts or additives for phenol–formaldehyde resin. Triacetin as catalyst could significantly increase the rate of phenol–formaldehyde condensation reactions (Anthony et al. 2002). The mechanism of esters

as additives in accelerating the process of phenol–formaldehyde curing is elaborated by Pizzi and Stephanou (1993).

Pot life, measured as the variation of viscosity after additives are mixed with phenol–formaldehyde, is important for the plywood industry. Short pot life means increase of viscosity within a few hours. This leads to a low flowability of the resin when wheat flour is added as filler, making it difficult to apply on the veneer. In our previous experiment, we found that triacetin, used individually as additive, led to rapid increase of viscosity from 679 mPa s to over 1000 mPa s in the first 2 hours. In other words, pot lives of triacetin-accelerated phenol–formaldehyde resins were too short for the plywood industry.

Fast curing phenol–formaldehyde resins could also be catalysed by urea. Small amounts

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of urea have been added during the reaction process of phenol–formaldehyde resin to shorten the gel time of the resin (Pizzi et al. 1993). Effects of adding urea to strand board core-layer phenol–formaldehyde resins were investigated and results indicated that urea added in the later part of the synthesis of phenol–formaldehyde resin resulted in better overall performance (Sang & Moon 2007). Urea is often used as substitute for phenol during the preparation of phenol–formaldehyde resins but little research has been focused on urea as additive.

Although there are many articles about curing characteristic and adhesion performances of phenol–formaldehyde resins with triacetin or urea as catalyst, few papers have focused on pot lives of phenol–formaldehyde resins with triacetin–urea composite additives applied in the plywood industry. The aim of this study was to (1) evaluate the curing characteristics, pot lives and adhesion performances of phenol–formaldehyde resins with triacetin–urea composite additives and (2) investigate if triacetin–urea composite additives could accelerate curing rate and improve adhesion performances of phenol–formaldehyde resins with suitable pot lives. In this study, the curing characteristics were investigated by gelation test and differential scanning calorimetry analysis. Adhesion performances of phenol–formaldehyde resins were evaluated by wet shear strength.

MATERIALS AND METHODS

Materials

Phenol (> 99%), formaldehyde (37% aqueous solution), urea (≥ 99%), sodium hydroxide (≥ 96%) and triacetin (99%) were purchased locally. All the chemical reagents used were of analytical grade. Wheat flour was of food grade.

Synthesis of control resin

A mixture of 282 g of phenol, 360 g of formaldehyde, 85 g of 40% sodium hydroxide solution and 48 g distilled water were charged into a three-neck reactor equipped with thermometer, stirrer and reflux condenser. The mixture was stirred and temperature was raised stepwise to 90 °C in 40 min and maintained at this temperature for 30 min. A total of 43 g of 40% sodium hydroxide solution and 78 g of formaldehyde were added to the reactor and the temperature was then maintained at 85 °C until the resin reached dynamic viscosity between 300 and 500 mPa s (measured at 20 °C) after which the resin was cooled to 65 °C. Following that 16 g of 40% sodium hydroxide solution was added to the resin and the reaction product was slowly cooled to room temperature (25 °C) in a cold water bath. The phenol–formaldehyde resin produced had pH of 10 ± 0.1, solids content 53 ± 1% and average molecular weight 800–1000.

Additives

The additives used were triacetin, urea and triacetin–urea (Table 1).

Differential scanning calorimetry analysis

All differential scanning calorimetry measurements were made using differential scanning calorimetry instrument with thermal analysis software. Resin sample (5–7 mg) was sealed in an aluminum crucible which can resist pressure of up to 5 MPa. Dynamic scans were recorded from 25 to 300 °C with heating rate of 10 °C min⁻¹. Two samples were replicated for each resin.

Table 1 Loading level of additives for phenol–formaldehyde resins

| Triacetin | Urea | Triacetin–urea composite additives | | | |
|-----------|------|------------------------------------|-------------------------------|-------------------------------|-------------------------------|
| 1.0% | 1.0% | 0.9% urea + 0.1% triacetin | 0.8% urea + 0.2% triacetin | 0.7% urea + 0.3% triacetin | 0.6% urea + 0.4% triacetin |

Each additive was fully mixed with control resin, loading level was based on liquid resin weight

Gel time

Gelation is defined as the point at which resin changes from viscous liquid to elastic, soft solid. Resin (5 g) was weighed in a 16 mm × 180 mm test tube and then a thin wire spring was placed in the tube. The test tube was placed in a constant temperature oil bath and the thin wire spring was moved gently up and down by hand until gelation. A stopwatch was used to record the gel time and the gelation test was done at 140 °C. Each value of gel time was an average of three test results.

Measurement of pot life

Pot life was measured as variation of viscosity. Viscosity measurements were made using viscometer at room temperature (25 °C). Each sample was measured at hourly intervals for 8 hours.

Preparation and test of plywood panels

Three-layer poplar plywood panels (300 mm × 300 mm × 4.8 mm) were prepared using control and cure-accelerated phenol–formaldehyde resins. Based on the weight of liquid resin, 15% wheat flour was added as filler into all the cure-accelerated phenol–formaldehyde resins. The resin was applied on both sides of each poplar veneer. The veneer was stacked between two uncoated veneers with grain direction of each two adjacent veneers being perpendicular. Three-layer poplar plywood panels were prepared using the following parameters: glue spread 300–320 g m⁻² (double line), hot press pressure 1.0 MPa, hot press temperature 140 °C and hot pressing time 2–5 min.

Test specimens for determining wet shear strength were cut from each plywood panels along the face-grain axis (Figure 1). Specimens were soaked in boiling water for 4 hours and dried at 63 °C for 20 hours. The specimens were boiled again for 4 hours and cooled to room temperature. Wet shear strength was tested according to the Chinese National Standard GB/T 17657 (Chen et al. 1999). The standard stipulates that, following treatment, minimum wet shear strength value for plywood is 0.7 MPa. Wet shear strength was measured using tensile testing machine at loading speed of 10 MPa

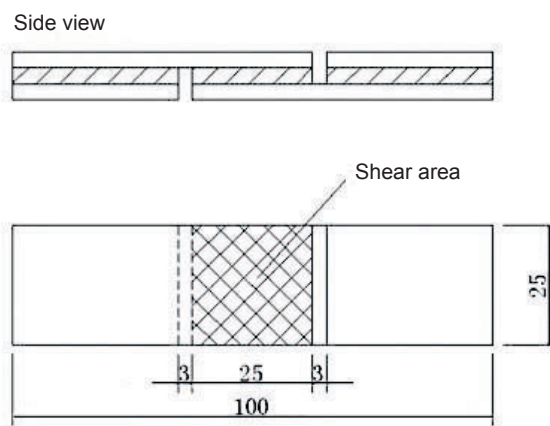


Figure 1 Test specimen of plywood; units are in mm

min⁻¹. Each value of wet shear strength was an average of 20 specimens.

Statistical analysis

SPSS 17.0 software was used to perform statistical analyses for wet shear strength. Duncan's multiple range tests were employed to determine statistical differences between variables investigated at a 95% significance level.

RESULTS AND DISCUSSION

Curing characteristics

The differential scanning calorimetry curves of control, 1.0% urea-accelerated, and 1.0% triacetin-accelerated phenol–formaldehyde resins are shown in Figure 2. Each curve presents an exothermic peak with maximum between 130 and 136 °C. This peak was attributed to the condensation of phenol and methylol groups to form methylene bridges (Christiansen & Gollob 1985). Exothermic peak temperature of the phenol–formaldehyde resin decreased (though not significant) when 1.0% triacetin was used as additive. However, peak temperature increased when 1.0% urea was used additive. The onset temperature of 1.0% triacetin-accelerated phenol–formaldehyde resin was only 100.5 °C, which was 1.6 and 3.0 °C lower than control and 1.0% urea-accelerated phenol–formaldehyde resins respectively. Ester, or residue of its decomposition, attacked the negatively-charged phenolic nuclei in polycondensation, which led to increased curing

reactivity of phenol–formaldehyde resin and, subsequently, decreased onset temperature (Pizzi & Stephanou 1994a, b). Using 1.0% urea as additive did not help accelerate the curing rate of the phenol–formaldehyde resin. The 1.0% urea-accelerated phenol–formaldehyde resin had unreacted urea and short-chain monosubstituted urea. However, reaction with phenolic methylol groups needs higher temperature, thus, leading to the increase in exothermic peak temperature (Fan et al. 2009).

Pot life

Figure 3 shows the gel time of cure-accelerated phenol–formaldehyde resins compared with that of control resin at 140 °C. Urea added as catalyst during the phenol–formaldehyde resin reaction would form phenol–urea–formaldehyde resin and shorten gel time (Tomita & Hse 1998). On the other hand, when used as additive, urea would prolong the gel time of phenol–formaldehyde resin for about 40 s compared with that of control resin. Urea may not completely react with phenol–formaldehyde resin when used as additive and the formation of methylolurea between urea and the residual free formaldehyde may absorb heat and lead to longer gel times. The 1.0% triacetin effectively accelerated curing of phenol–formaldehyde

resin nearly 90 s faster than control resin. Four composite additives, namely, 0.9% urea + 0.1% triacetin, 0.8% urea + 0.2% triacetin, 0.7% urea + 0.3% triacetin and 0.6% urea + 0.4% triacetin could shorten gel time compared with that of control resin, and the gel time dropped steadily as the amount of triacetin increased.

Viscosity variations were monitored as function of time (Figure 4). The viscosity of the phenol–formaldehyde resin with 1.0% triacetin increased very rapidly from 679 to 1745 mPa s in the first 2 hours but reached an apparent plateau after that. Triacetin is easily hydrolysed in alkaline condition so that a number of hydrogen ions are released, then condensation occurs between phenol and hydroxymethyl. The heat release leads to gelation of phenol–formaldehyde resin and the viscosity increases at room temperature (Pizzi 1983). The pot life of 1.0% triacetin-accelerated phenol–formaldehyde resin was less than 1 hour, which is useless for the plywood industry. Once viscosity reached 1000 mPa s, it would lead to low flowability of phenol–formaldehyde resin when 15% of wheat flour was added as filler, making it difficult to be applied on the veneer (results not shown). When triacetin was added as catalyst during phenol–formaldehyde resin preparation, it greatly accelerated the reaction process at higher temperature but the pot life of triacetin-

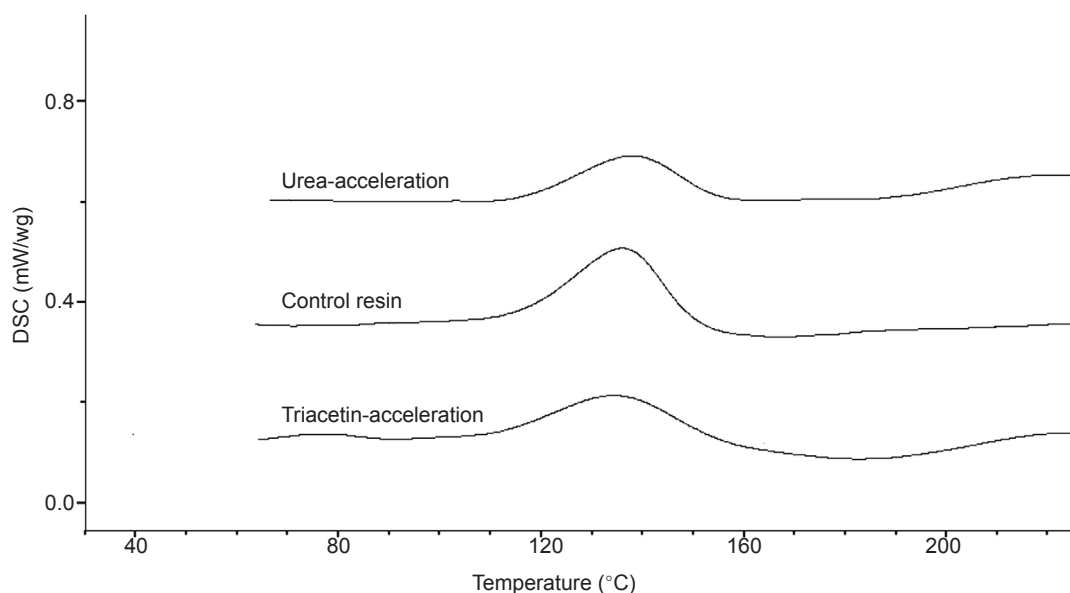


Figure 2 Differential scanning calorimetry (DSC) curves of cure-accelerated phenol–formaldehyde resins

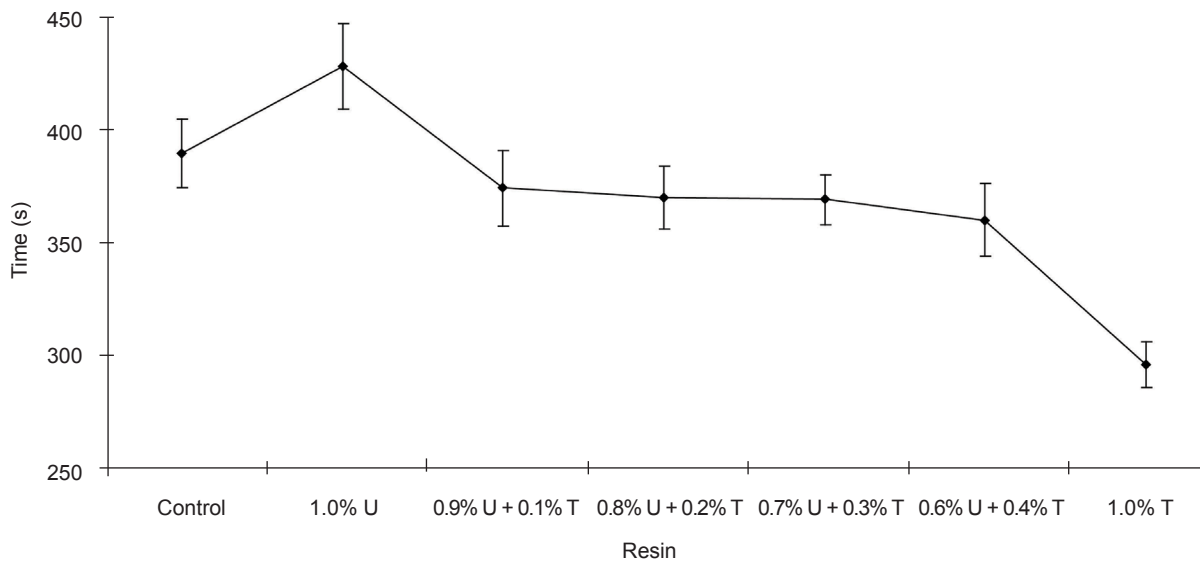


Figure 3 Gel time of cure-accelerated phenol-formaldehyde resins at 140 °C; U = urea, T = triacetin

catalysed phenol-formaldehyde resin was only a few hours (Zhao et al. 2000). In our experiment, as additive, triacetin shortened the pot life of phenol-formaldehyde resin to less than 2 hours at room temperature. In the presence of urea, the viscosity of the phenol-formaldehyde resin decreased from 680 to 550 mPa s in the first 6 hours and then leveled off. This may be due to the residual-free formaldehyde captured by urea in alkaline conditions (Turunen et al. 2003). Viscosity variations of four composite additives accelerated phenol-formaldehyde resins were not as drastic as 1.0% triacetin-accelerated phenol-formaldehyde resin and their pot lives were more than or equal to 8 hours. The range of viscosity increase was in direct proportion to the amount of triacetin added, thereby, confirming the influence of composite additives on viscosity variations.

Adhesion performance

The cure-accelerated phenol-formaldehyde resins with additives had significantly higher wet shear strength at different hot press times than that of control resin (Figure 5). Short hot press time was not enough for complete curing of phenol-formaldehyde resin between poplar veneers. The bonding interfaces of plywood specimens were separated after boiling

when the hot press time was 2 min although the hot press temperature had surpassed the curing temperature (approximately 135 °C) of phenol-formaldehyde resins. When hot press time was 3 min, wet shear strength of control, 1.0% urea-accelerated, 0.9% urea + 0.1% triacetin-accelerated and 0.8% urea + 0.2% triacetin-accelerated phenol-formaldehyde resins did not surpass the 0.7 MPa required by GB/T 17657 standard. The gel time was 5–7 min for phenol-formaldehyde resins with different additives at 140 °C (Figure 3), At least 4 min were necessary for the wet shear strength of all specimens to reach 0.7 MPa. The wet shear strength of 1.0% triacetin-accelerated phenol-formaldehyde resin was significantly higher than that of the rest of the resins when the hot press time was 5 min. Faster curing process could lead to weaker and looser network (Zhao et al. 1999), but it was obvious that cure-accelerated phenol-formaldehyde resins with shorter curing time had better wet shear strength than that of control resin. Maximum wet shear strength was observed in 1.0% triacetin-accelerated phenol-formaldehyde resin at different hot press times. However, when considering suitable pot life, gel time and production efficiency comprehensively, acceleration effect of 0.7% urea + 0.3% triacetin was best in this research.

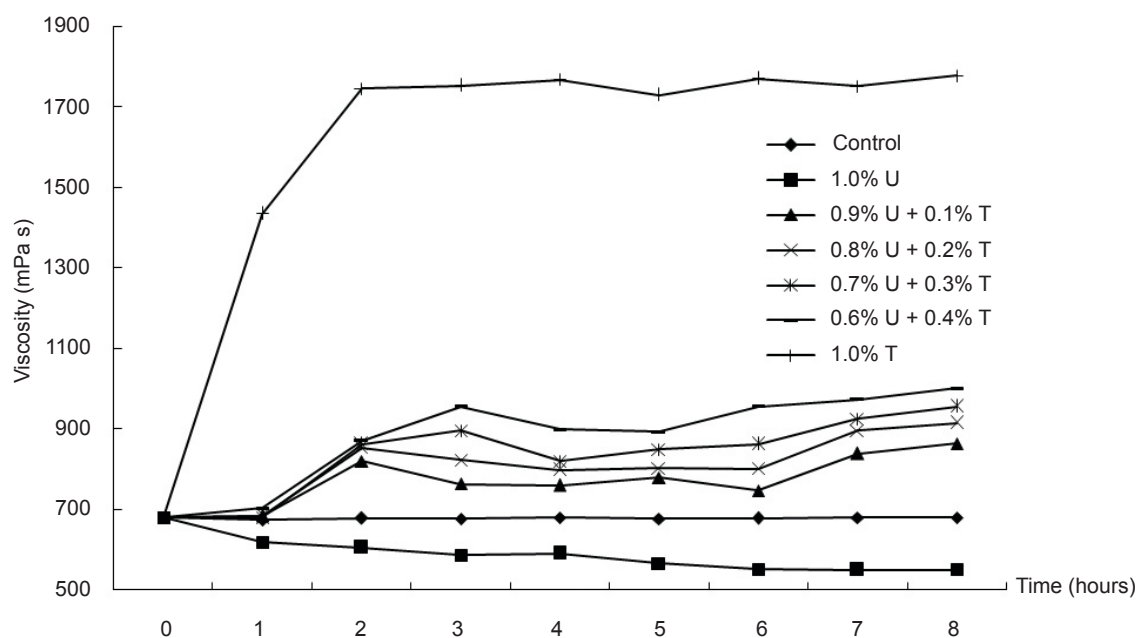


Figure 4 Viscosity variations during 8 hours of cure-accelerated phenol–formaldehyde resins; U = urea, T = triacetin

CONCLUSIONS

Triacetin used individually as additive favoured the phenol–formaldehyde resin curing at relatively low temperature with high wet shear strength, but its short pot life is useless for the plywood industry. Cure-accelerated phenol–formaldehyde resins with composite additives effectively accelerated curing rate and improved adhesion performances with suitable pot lives.

The differential scanning calorimetry and gel time analysis indicated that triacetin effectively accelerated the curing rate of phenol–formaldehyde resin. Pot lives of cure-accelerated phenol–formaldehyde resins with composite additives were more than or equal to 8 hours. Cure-accelerated phenol–formaldehyde resins with additives had significantly higher wet shear strength at different hot press times than that of the control resin. At least 4 min were necessary for the wet shear strength of all specimens to reach 0.7 MPa as required by the Chinese National Standard GB/T 17657.

When considering all curing characteristics involved in this paper, combined with adhesion performance, 0.7% urea + 0.3% triacetin showed the best acceleration effect between

four composite additives besides having suitable pot life for plywood production.

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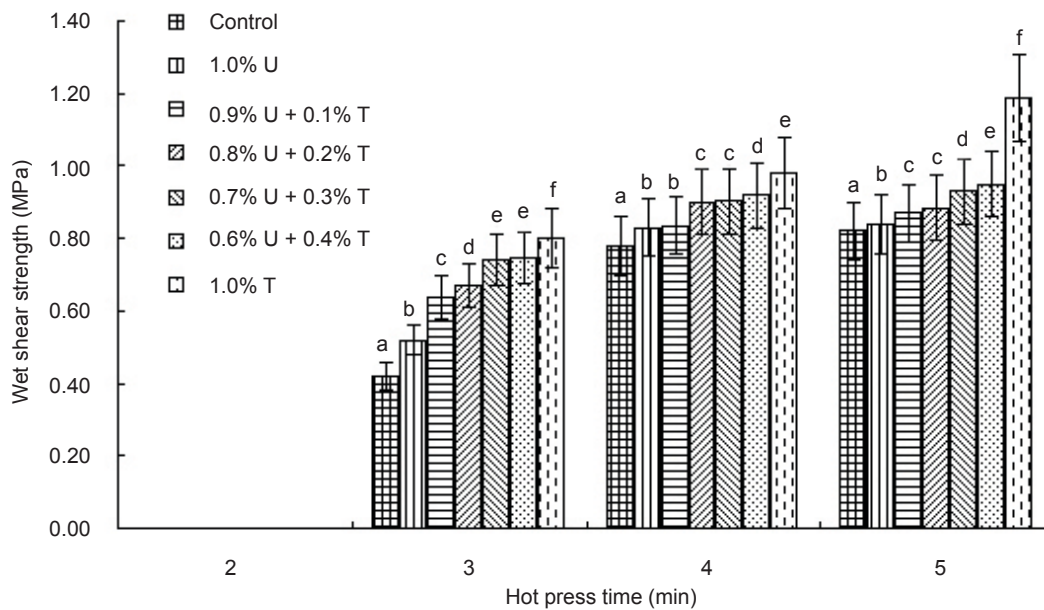


Figure 5 Wet shear strength of cure-accelerated phenol–formaldehyde resins, different letters denote significant difference ($p < 0.05$); U = urea, T = triacetin

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