A Statistical Analysis of Epoxy Polymer Reinforced with Micro Ceramic Particles

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Abstract: A significant amount of research has been focused on the use of ceramic nano/micro particles to enhance the strength and stiffness of polymeric matrices. This work evaluates the effect of Portland cement or crystalline silica (quartz) particle inclusions into epoxy polymer. Two experiments were conducted based on a full factorial design analysis. Experiment I investigated the effect of Portland cement amount (ASTM III), two types of hardeners (HY 951 and 956) and two curing times (7 and 28 days) on the compressive behaviour and density of particulate composites. Experiment II evaluated the incorporation of quartz or cement particles by mixing different mass fraction levels, considering 28 days of curing time and HY 951 hardener. The samples were prepared in a randomized manufacturing process and tested in compression. The mechanical properties were significantly affected by the type of hardener used. Both particles can enhance the compressive strength and stiffness of the composites.

Keywords: Ceramic particles, epoxy polymer, particulate composites, mechanical properties.

1. INTRODUCTION

Aviation and aerospace industries have demanded new lightweight and durable materials for non-structural parts. The increase in stiffness and toughness have been the focus of hybrid composite materials. The incorporation of micro and nano particles into laminated composites has led to enhanced mechanical properties and modified fracture modes, due to reduced crack propagation and the interlocking effect between layers [1]. Lerchenthal and Brenman [2] have investigated inorganic particles in polymers to obtain an economically attractive material with high mechanical strength and low specific weight. The inclusion of inorganic particles promotes barriers against the propagation of cracks, thereby avoiding premature failure of the material. Particles of silicon carbide (SiC) and graphite (Gr) have been added to the epoxy polymer providing a significant improvement in the abrasion resistance [3].

Detomi *et al*. [4] have investigated the effect of Portland cement (ASTM III) in glass fibre reinforced composites, identifying an increase in flexural strength and specific strength up to 110 % and 112 %, respectively. The use of ceramic particles at the compressive beam side under bending loads enhances the stiffness of the matrix phase, consequently compensating the low compressive strength of the fibres. Low cost cement particles have been considered a promising inclusion in structural hybrid composites for the aerospace, automotive and other fields of engineering industries. Chemical bonds between the epoxy matrix and Portland cement may occur albeit with low probability. Panzera *et al*. [5] have evaluated a blend consisting of epoxy polymer and structural white Portland cement with no water incorporation. The cement/polymer ratio of 50/50 has achieved superior mechanical properties. This behaviour has been attributed to a possible cement hydration by the epoxy polymer. Peaks of portlandite have been identified by spectroscopy tests in the infrared area (FTIR).

Silva *et al*. [6] have investigated hybrid natural composites consisting of sisal fibres (30 vol% and 50 vol%), quartz microparticles (0 wt%, 20 wt% and 33 wt%) and maleic anhydride (0 wt% and 2 wt%). Quartz incorporation into the matrix phase has led to reduced ultimate strain and increased compressive modulus. This behaviour has been attributed to the increased surface area which affects the system rheology and the fibre wettability. Torres *et al*. [7] has investigated the effect of quartz or cement particles (3 wt%, 5 wt% and 10 wt%) into unidirectional fibre glass composites. A higher mechanical performance has been achieved when 5wt% of particles were incorporated. Cement particles have led to superior flexural strength and stiffness when compared to quartz particles.

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This work investigates particulate composites consisting of epoxy polymer and ceramic particles, such as quartz and Portland cement. Particle inclusions in the epoxy matrix may improve strength and stiffness of hybrid fibre reinforced composites. A design of experiment (DoE) was conducted to investigate the effect of particle mass fraction (2.5; 5.0; 7.5; 10.0 wt%), type of hardener (HY 951 and HY 956), type of particles (quartz and cement) and curing time (7 and 28 days) on density and compressive strength and modulus of the composites.

2. MATERIALS AND METHODS

The matrix phase consists of epoxy resin (Renlam M) with hardener (HY 951 and HY 956) being manufactured by Huntsman Brazil (see Table **1**). HY 951 hardener is a low viscosity, primary amine (Triethylenetetramine - TETA), while HY 956 is an aliphatic amine with low shrinkage and high dimensional stability. Crystalline silica-quartz (SiO2) particles were sourced by Moinhos Gerais Company (Brazil) and Portland cement (ASTM III) was supplied by Holcim Brazil. The cement and quartz particles were classified by sieving in particle size ranges of 325-400 mesh (37-44 µm) and up to 400 mesh (<44µm), respectively. The surface area of cement and quartz particles were measured via Micromeritics BET Surface Area and Porosity Analyser, finding 1.447 m^2/g and 1.236 m^2/g, respectively.

The apparent densities for cement and quartz particles were measured by a gas pycnometer, obtaining 3.17 g/cm³ and 2.20 g/cm³, respectively. According to Huntsman [8] the polymer viscosity during the beginning of the curing process is largely modified. This effect can affect the dispersion of the particles. Thermally catalysed polymerization reduces the (less viscous) gel phase time, preventing particle clustering. Table **1** shows the physical characteristics of the epoxy polymer and hardeners investigated in this work [8].

Cylindrical models (Ø20mm x 40mm) were machined in aluminium according to ASTM D 695 [9] (see Figure **1a**). Silicone moulds were used to fabricate cylindrical specimens for compression tests (Figure **1b**). This type of silicone is able to resist temperatures up to 200 °C. The epoxy polymer and the particles were firstly hand-mixed for 5 minutes; the hardener was subsequently added and mixed for 5 minutes. The moulds were slowly filled up in order to avoid the presence of internal bubbles. The samples were cured in an oven at 50 °C for 12 hours, and subsequently wrapped in a plastic bag at room temperature to complete the curing process for 7 days.

Four mass fractions of particles (2.5; 5.0; 7.5, 10.0 wt%) were investigated using two types of hardeners (HY951 and HY956), two types of particles (quartz and cement) and two curing times (7 and 28 days). This work was divided in two full factorial designs of

Table 1: Materials Properties (Huntsman [8])

Resin and hardener	Viscosity at 25°C [mPa·s]	Specific weight at 25°C [g/cm³]	Proportion of moisture [resin:hardener]	Gel time 100 g at 23ºC [minutes]	Cure time
RenLam® M	1250 - 1600	1.1 – 1.15			
Aradur® HY 951	30	0.97	10:1	160	24 - 48h at RT or 4h at RT + 4h at 60°C
Aradur® HY 956	290 - 500	1.02	5:1	31	7 days at room temperature or 14h at 40ºC

Figure 1: a) Cylindrical sample model; **b**) silicone mould; **c**) compression test.

experiments. Experiment I evaluated the effect of curing time, hardener type and fraction of particles on the compressive strength and modulus and bulk density of polymer reinforced with cement particles. A full factorial design of $2^2 5^1$ was performed totalizing 20 experimental conditions. Experiment II investigated the effects of fraction of particles and particle type (quartz and cement), considering a DoE of $2^1 4^1$, running a total of 8 treatments. Three samples were manufactured for each experimental condition, with two replicates. The compression tests were carried out in a Shimadzu AGX plus (100 kN) testing machine with a speed of 2 mm/min (Figure **1c**). The compressive strength and modulus were calculated according to ASTM D695 [9]. The compressive strength was determined by dividing the maximum compressive load by the original minimum cross sectional area of the specimen. The modulus of elasticity was calculated through the slope of the initial linear portion of the stress-strain curve. The bulk density was obtained via Archimedes principle following the recommendations of ASTM D792 [10]. The bulk density was calculated by the dry mass/external volume ratio, including pores. The external volume is determined subtracting the apparent wet mass from the wet mass, under vacuum.

3. RESULTS

In Experiment I, the compressive strength and modulus data varied from 64.43 MPa to 76.02 MPa and from 1.96 GPa to 2.48 GPa, respectively. The bulk density values ranged between 1.14 g/cm^3 and 1.25 g/cm^3. In Experiment II, the strength and modulus data varied from 64.43 MPa to 70.25 MPa, and 1.77 GPa to 2.34 GPa, respectively. The bulk density data ranged between 1.18 g/cm^3 and 1.25 g/cm^3.

The Analysis of Variance (ANOVA) was used to investigate the effect of each factor and their interaction on the compressive strength, modulus and bulk density of the composites. The normality analysis was performed via Anderson-Darling test (P-values≥0.05). P-values found for the compressive strength (0.942), elastic modulus (0.594) and bulk density (0.074) responses were higher than 0.05, which validates the ANOVA. R^2 values higher than 95% indicate the models are well fitted to the experimental data. Table **2** shows the ANOVA for Experiment I. Main factors can be analysed jointly if there is evidence of significant interaction effect [11]. In this case, only those factors of superior order (see underlined P-values in Table **2**) will be evaluated via interaction effect plots (see Figure **2**). F-values reveal which significant factor mostly affects the responses. The elastic modulus is more affected by the hardener type (129.86), followed by the particle fraction (46.25) and curing time (13.33) factors. The compressive strength is largely affected by the hardener type (198.53), followed by the curing time (42.24) and particle fraction (42.24) factors. In contrast, the bulk density response is more affected by the particle fraction (126.74) and hardener type (39.49) factors.

HY 956 hardener provided superior strength compared to HY 951 for all particle fractions (see Figure **2a**). HY 956 hardener achieved a high strength level at 7 days, while HY 951 reached similar values at 28 days curing time (Figure **2b**). Figure **2c** shows that HY 956 hardener achieves higher compressive modulus than HY 951 for all cement amount levels. Increased elastic modulus was achieved when 5% of particles were incorporated in HY 956 polymer, with a subsequent reduction at higher particle fractions. The curing time factor did not affect the elastic modulus when HY 956 was considered, however, HY 951

Table 2: ANOVA - Experiment I (P-Values ≤ 0.05)

		Compressive modulus		Compressive strength		Bulk density	
		F-value	P-value	F-value	P-value	F-value	P-value
Main	Hardener type (HT)	**129.86**	0.000	**198.53**	0.000	39.49	0.000
	Curing time (CT)	13.33	0.000	42.24	0.000	0.08	0.782
	Particle fraction (PF)	46.25	0.000	20.28	0.000	**126.74**	0.000
Interaction	HT * CT	30.40	<u>0.000</u>	235.77	<u>0.000</u>	0.76	0.394
	HT * PF	11.71	<u>0.000</u>	35.05	<u>0.000</u>	3.28	<u>0.032</u>
	CT * PF	1.60	0.214	1.20	0.341	1.35	0.288
	HT * CT * PF	0.64	0.638	1.46	0.253	0.60	0.669
	R^2	95.89 %		97.25 %		96.60 %	

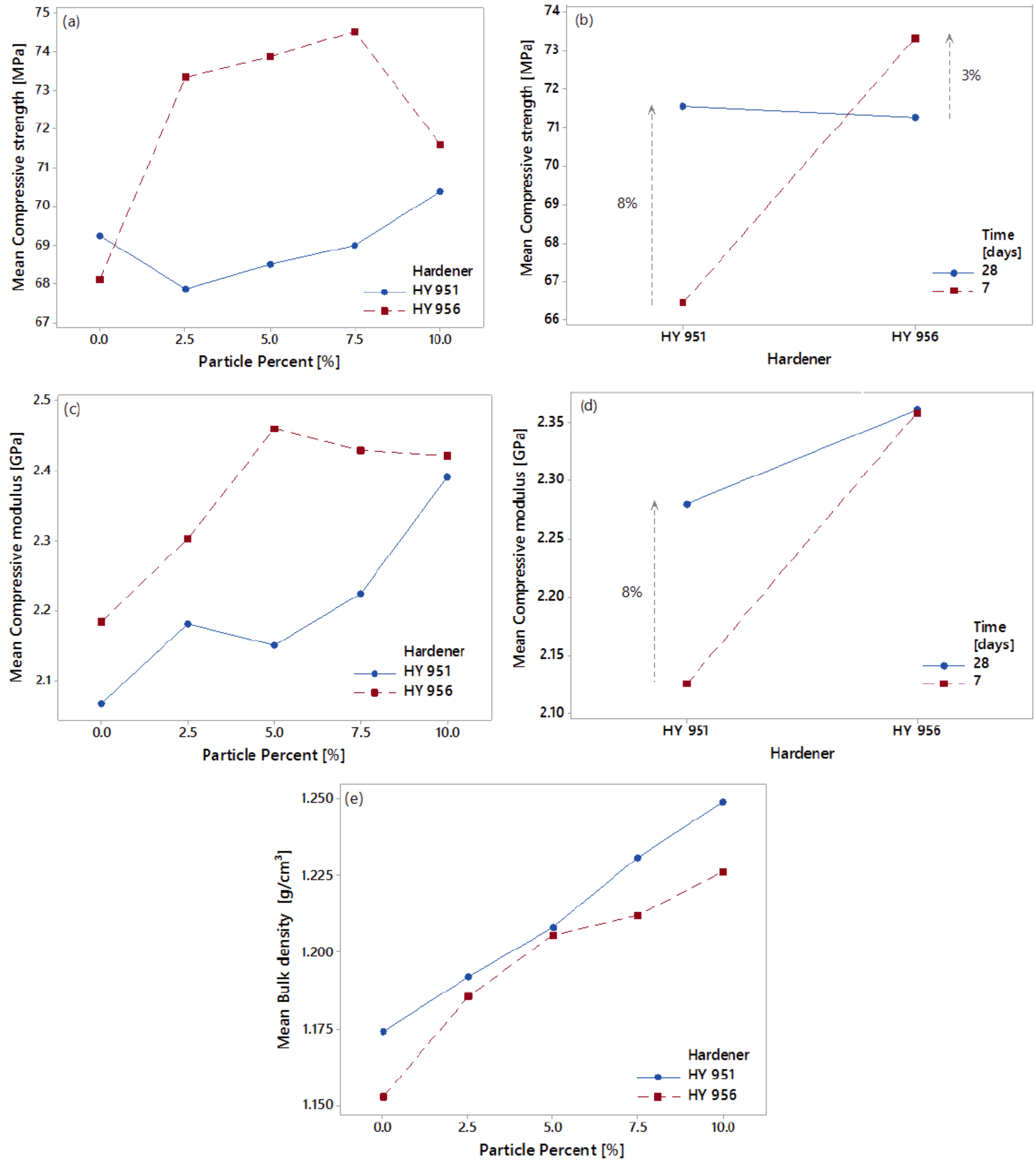

Figure 2: Experiment I. second order interaction effect plots for mean compressive strength (**a-b**), compressive modulus (**c-d**) and bulk density (**e**).

hardener led to increased stiffness at 28 days (see Figure **2d**). Finally, HY 956 hardener promotes a faster curing process than HY 951. The bulk density rises when a large quantity of particles is incorporated in the system.

Table **3** shows the ANOVA for Experiment II. Second order interaction effects were identified for the mean compressive modulus (see underlined P-values), while only main factors were significant for the mean compressive strength and bulk density responses. F-values indicate the particle fraction factor mostly affected the elastic modulus (15.11) and bulk density (139.76) responses, while the compressive strength (72.71) is more affected by the particle type factor.

Figure **3a** shows that composites made with 2.5 wt% of quartz particles achieved lower stiffness compared to the reference condition (2 GPa). In contrast, at the same level, the cement particles were

Table 3: ANOVA Experiment II (P-Values ≤ 0.05)

	Compressive modulus		Compressive strength		Bulk density	
Factors	**F-value**	**P-value**	**F-value**	**P-value**	**F-value**	**P-value**
Particle type	2.25	0.172	**72.71**	0.000	6.44	0.035
Particle fraction	**15.11**	0.001	6.26	0.017	**139.76**	0.000
Particle type * Particle fraction	5.25	0.027	2.18	0.168	2.10	0.178
R^2	88.78 %		92.46 %		98.18 %	

sensitively superior. Higher stiffness was achieved for both particle types at 10wt% of incorporation, being 14 % superior to the reference condition (without particles). The highest strength was achieved when 10 wt% of quartz particles were added (Figure **3b**). The use of cement particles and 2.5 wt% of particle fraction (Figure **3b**) provided lower strength compared to reference condition (66.8 MPa). Moreover, the bulk density of the composites is increased when the amount of particles rises, as shown in Figure **3c**.

Figure **4** shows the mechanical behaviour of the composites made with HY 956 (Figure **4a**) and HY 951 hardeners (Figure **4b**). A representative curve for each experimental condition was plotted in these graphs. In general, an increase in stiffness is noted when a long period of curing and particle inclusions are considered (Figure **4a**, **b**). Quartz reinforced polymers revealed lower initial stiffness.

4. CONCLUSIONS

The incorporation of ceramic particles into epoxy polymer at appropriate levels can promote increased compressive strength and modulus of elasticity. HY 951 hardener exhibits quite higher polymerization time. The curing time factor significantly affected the mechanical properties of the composites with different hardeners. Polymers reinforced with both particles achieved higher strength, especially when incorporated

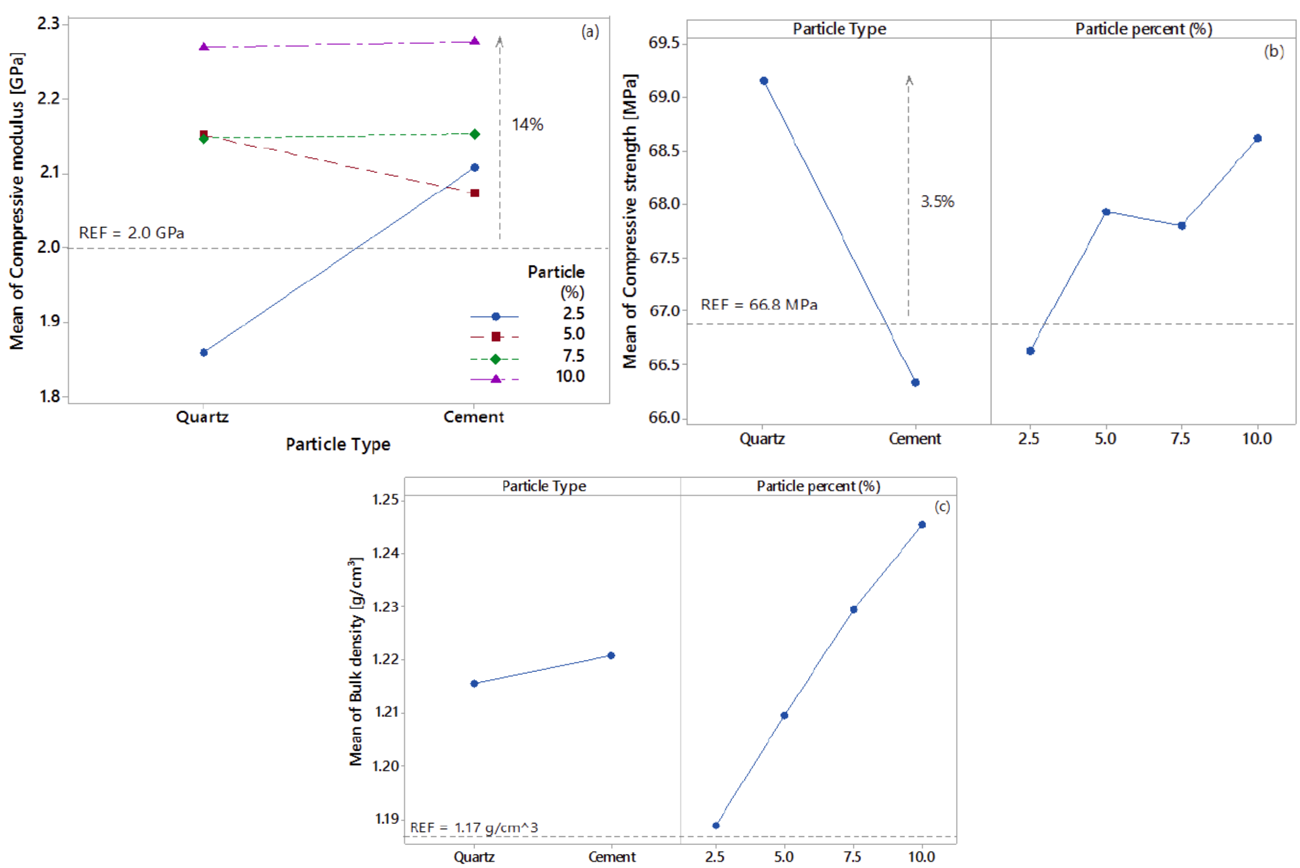

Figure 3: Experiment II. Interaction effect plot for mean compressive modulus (**a**) and main effect plots for mean strength (**b**) and bulk density (**c**).

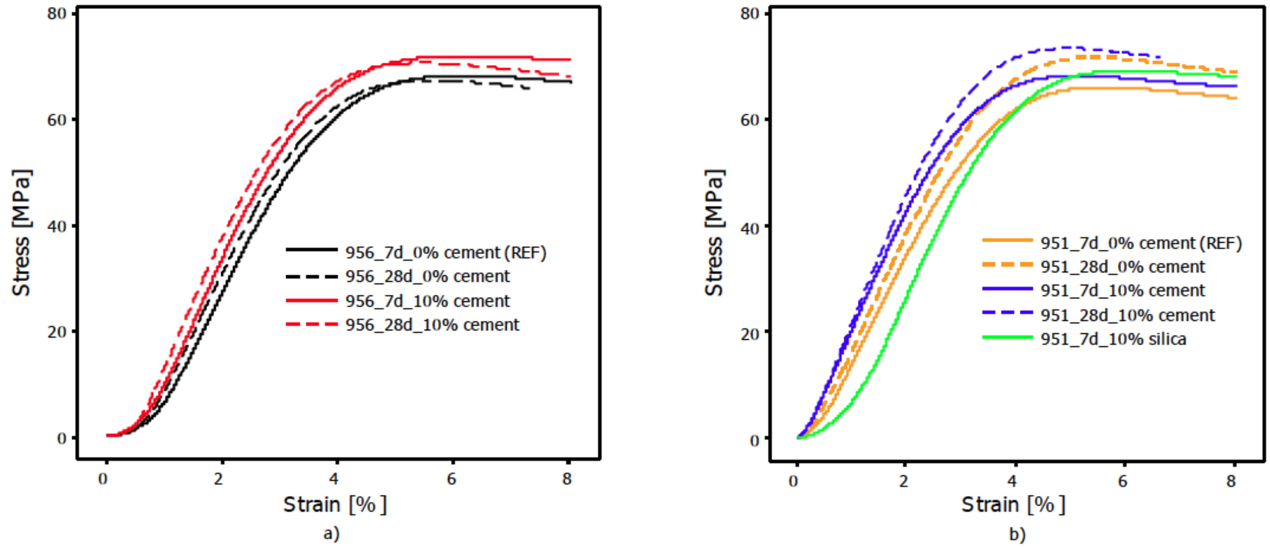

Figure 4: Mechanical behaviour in compression test for polymers using: HY 957 (**a**) and HY 951 (**b**) hardeners.

at 10 wt%. Cement particles can be considered a promising reinforcement in hybrid composites, due to their low cost and ease of dispersion. The inclusion of 10 wt% of Portland cement particles into HY 951 hardener epoxy polymer at 28 days of curing time led to increased compressive elastic modulus (~14 %), being a promising polymeric matrix phase for use in hybrid composites.

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