

Effect of Molecular Weight on the Properties of Liquid Epoxidised Natural Rubber Acrylate (LENRA)/Silica Hybrid Composites

(Kesan Berat Molekul ke Atas Sifat-sifat Komposit Hibrid Getah Asli Terepoksida Berakrilat Cecair (LENRA)/Silika)

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ABSTRACT

This paper reports on the effect of molecular weight on the morphological and mechanical properties of liquid epoxidised natural rubber acrylate (LENRA)/silica hybrid composites prepared by sol-gel technique. The sol-gel reaction was conducted at different concentration of tetraethylorthosilicate (TEOS), used as a precursor of silica. TEOS were introduced in 10, 20, 30, 40 and 50 parts per hundred rubber (phr) in the composites. Two different molecular weights of ENR were used to study the effect of molecular weight on the mechanical and morphological properties of the compounds. These compounds were cured by ultraviolet (UV) irradiation. The mechanical properties were studied through pendulum hardness and scratch tests. Higher molecular weight of ENR showed better mechanical properties than lower molecular weight. Transmission electron microscope was used to determine the silica size and to study the distribution and dispersion of the silica particles. High molecular weight showed greater distribution and dispersion of silica particles with diameter of 13 nm–256 nm. Morphological and mechanical properties of LENRA/silica hybrid composites were improved by using high molecular weight of ENR.

Keywords: Epoxidised natural rubber; molecular weight; organic-inorganic hybrid; sol-gel technique

ABSTRAK

Kajian ini adalah mengenai kesan berat molekul terhadap sifat mekanik dan morfologi komposit hibrid getah asli terepoksida berakrilat cecair (LENRA)/silika, menggunakan teknik sol-gel. Tindak balas sol-gel dilakukan pada kepekatan tetraetilortosilikat (TEOS) yang berbeza, yang digunakan sebagai bahan pemula silika. TEOS dimasukkan sebanyak 10, 20, 30, 40 dan 50 bahagian per seratus getah (phr) dalam komposit. Dua berat molekul ENR yang berbeza digunakan untuk mengkaji kesan berat molekul terhadap sifat mekanik dan morfologi komposit. Komposit ini dimatangkan dengan menggunakan sinaran ultralembayung (UV). Sifat mekanik diuji melalui ujian kekerasan pendulum dan ujian calaran. Berat molekul ENR yang tinggi menunjukkan sifat mekanik yang lebih baik berbanding berat molekul ENR yang rendah. Mikroskop elektron transmisi digunakan untuk mengukur saiz silika dan mengkaji taburan partikel silika. Berat molekul yang tinggi menunjukkan taburan partikel silika yang lebih baik dengan diameter partikel dalam julat 13 nm–256 nm. Sifat mekanik dan morfologi komposit hibrid LENRA/silika dapat dibaiki dengan menggunakan berat molekul ENR yang tinggi.

Kata kunci: Berat molekul; getah asli terepoksida; hibrid organik-inorganik; teknik sol-gel

INTRODUCTION

Silica as white reinforcing filler has been used in the rubber industry for a long time. The conventional silica by the precipitation method is highly aggregated in the rubbery matrix due to filler-to-filler interaction resulting in a dispersion which is not good for reinforcement (Patel et al. 2005). A new alternative method of silica incorporation into rubbers is by the sol-gel process. Silica filled rubber by sol-gel technique has been extensively studied in recent years. Sol-gel chemistry offers a unique advantage in the creation of organic-inorganic hybrid. The sol-gel process begins with a combination of metal alkoxide precursor and water. Hydrolysis and condensation of the metal alkoxide are the fundamental steps to produce inorganic network in

the presence of an acidic catalyst (Kohjiya & Ikeda 2003). Tetraethylorthosilicate (TEOS) is the most commonly used metal alkoxide due to the mild reaction condition. The reaction parameters that influence the sol-gel chemistry are the pH of the solution, the mole ratio of Si to H₂O, catalysts, solvents and reaction temperature.

Generally, it is known that molecular weight of a polymer has influence on its properties. The influence of molecular weight on the properties of the natural rubber has been studied by Bhowmick et al. (1986). The study showed that effect of gel is more dominant than molecular weight. Natural rubber of high molecular weight behaves similarly when compared to low molecular weight samples. Kok (1985) reported that tensile strength increased with

the increase of molecular weight until the tensile strength reached a constant value at a molecular weight of about 500 000.

The effect of molecular weight on the properties of LENRA/silica hybrid composites have not been reported elsewhere. In this article the effect of molecular weight on the properties of LENRA/silica hybrid composites prepared by sol-gel method and using LENRA with two different molecular weights are reported.

EXPERIMENTAL DETAILS

MATERIALS

ENR with 50 mol.% epoxidation (ENR-50) was used for preparing liquid epoxidised natural rubber and was supplied by Guthrie Corp (M) Bhd. Two different molecular weights were used. The molecular weights of liquid epoxidised natural rubber (LENR), as determined by the gel permeation chromatography (GPC) were M_w , 14.1×10^4 Da and 7.65×10^4 Da. Liquid epoxidised natural rubber acrylate (LENRA) was prepared by reacting liquid epoxidised natural rubber with acrylic acid (Dahlan & Ghani 1993b). Irgacure 184 and 1,6-hexanediol diacrylate (HDDA) were supplied by CIBA and Cytec, respectively. Other chemicals were used as received.

HYBRID LENRA/SILICA

Silica was synthesized via the sol-gel technique. Tetraethylorthosilicate (TEOS) was used as a precursor and the concentration of TEOS was varied as 10, 20, 30, 40 and 50 phr. Ethanol, distilled water and hydrochloric acid were added to TEOS based on the ratio of 1:1.13:3.2:0.05 (TEOS: ethanol: distilled water: hydrochloric acid). The process was conducted at room temperature and was stirred for 15 min (Ishak 2001). Homogenizer (model Silent Crusher) was used to stir LENRA at 6000 rpm. At the same time, silica was added slowly into LENRA solution while stirring intensively. The process was conducted for 1 h at 50°C.

UV IRRADIATION

Hybrid LENRA/silica was added with Irgacure184 and 1,6-hexanediol diacrylate (HDDA) as a photosensitizer and reactive diluent and was stirred for 20 minutes. The prepared formulations were coated on glass plates using a drawdown bar coater (model Sheen 1107A/80 S214609) to achieve 150 μm thickness and then irradiated with a 20 cm width IST Minicure 200 machine fitted with UV lamp of 80 W per linear cm and operating current at 7.0 A. The conveyor speed was at 3 m/min. Curing conditions were observed by tackiness and finger marring.

CHARACTERIZATION OF LENRA/SILICA HYBRID

Pendulum Hardness The hardness of 150 μm thick coatings was measured by monitoring the damping time of the oscillations of a pendulum placed on the UV-cured

sample coated onto a horizontal glass plate, with the pendulum swinging in a vertical plane from an initial angle of 12° to a final angle of 4° (Persoz hardness). Persoz values ranged from 30 s for soft elastomeric up to 350 s for hard and glassy polymers (Decker et al. 2005). The pendulum hardness test of the samples were carried out according to ASTM D4366.

Scratch Test The scratch resistance of UV-cured samples was measured by means of a scratch tester from Taber Industries on 150 μm thick film coated onto a glass plate. A single scratch was generated by a conical diamond indenter with an angle of 90° under a constant load, at a speed of 3 cm s^{-1} . The scratch resistance value corresponds to the minimum load applied to the samples. The load was increased from 0.1N until fish bone appeared. The scratch was determined via optical microscope (Decker et al. 2005). The test was carried out according to ASTM C1624-05.

Morphological Study The morphology of the composites and the size of silica particles was observed by using a transmission electron microscope (TEM) (model no JEM 2100 JEOL Co., Japan). The samples were sectioned with a diamond knife on a cryo-ultramicrotome (model Leica Ultracut UCT) at -70°C to yield specimens of approximately 80 nm in thickness that were then placed on copper grids. Photograph of the samples were obtained using a Gatan Dualview digital camera.

RESULTS AND DISCUSSION

The effect of particle loading on mechanical test has actually been done for some material systems, in which the mechanical properties increased with increasing particle loading (Fu et al. 2008). The pendulum hardness for low and high molecular weight are shown in Figure 1. The mechanical properties of the composites can be improved with the addition of TEOS content. Pendulum hardness of the composite increased with the increase of silica content until an optimum content was reached and decreased on further addition of silica (Frings et al. 1998). High molecular weight gave a good result on the pendulum hardness percentages. The pendulum hardness reached the optimum at 30 phr with the value of 60.3% for the high molecular weight. Pendulum hardness for the low molecular weight also reached the maximum at 30 phr with the value of 29.4%.

It is generally accepted that the molecular weight of a polymer has a significant influence on its mechanical properties (Kok 1985). The mechanical properties of the composites can be improved with the increasing of the molecular weight (Kok 1985). The mechanical properties of composites are highly related to the filler-matrix interfacial interaction and the size of filler particles (Xiangmin et al. 2008). The use of sol-gel precursors is appealing in order to obtain a good distribution of silica within the polymer matrix with a strong interaction

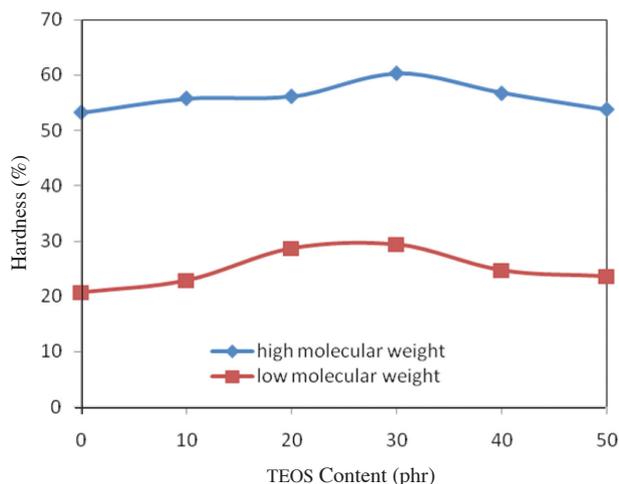


FIGURE 1. Effect of TEOS to pendulum hardness for low and high molecular weight

between the organic and inorganic domains (Amerio et al. 2008). This interaction is needed to limit the mechanical damage (Amerio et al. 2008). The presence of fillers leads to high stress concentration around the particles themselves making the matrix more fragile. On the other hand defects can be created at the interface because of a weak compatibility between the filler and the matrix (Amerio et al. 2008). These phenomena could lead to debonding and void formation close to silica particles and worsening of the mechanical properties (Amerio et al. 2008). If the TEOS content is increased until a certain limit, the excess silica that form might be excluded from the bonding networking interaction with the polymer. Particle at higher silica contents has a tendency to agglomerate which decreases the mechanical properties of the composites (Amerio et al. 2008). These explain why the pendulum hardness decreased for the sample of 40 phr and 50 phr TEOS. Interaction between silica-silica particles are much higher than interaction between silica particles-polymer matrix and it caused silica no longer acts as a reinforcement filler (Akron & Wang 1998). Agglomeration in the composite will interrupt the polymer chain movement and when pressure is applied on the composite, it will lead to the deformation of the polymer chain (Akron & Wang 1998; Noraiham et al. 2008).

According to Amerio et al. (2005), increasing the surface hardness of the coatings caused the scratch resistance to increase. The influence of mechanical response of coatings was investigated by carrying out progressive load scratch test. Increasing TEOS content will increase load on the composite. All the composite showed substantial improvements in their mechanical properties with increasing TEOS content within the matrix (Bandyopadhyay et al. 2004). The scratch resistance can be improved with the addition of inorganic filler (Fu et al. 2008). The use of inorganic fillers is to improve the properties of the polymers by controlling the degree of interaction between

the polymer and the nanofillers via a top-down approach (Fu et al. 2008). A top down approach in the sol-gel process involves a series of hydrolysis and condensation reaction starting from hydrolysable multifunctional metal-alkoxide precursors (Fu et al. 2008). The scratch test of LENRA/silica composites in high and low molecular weights are as shown in Figure 2. High molecular weight showed a higher load than low molecular weight. It has been proven that the molecular weight of a polymer has a significant influence on its mechanical properties (Bhowmick et al. 1986). The mechanical properties of the composites can be increased with the increase of the molecular weight (Bhowmick et al. 1986). The load that can be bear was maximum at 30 phr of TEOS with the value of 0.55 N for the high molecular weight while low molecular weight showed the maximum at 30 phr of TEOS with the value of 0.52 N. Addition of silica amounts to reinforce the matrix are limited (Chen et al. 2008). The load that can be bear decreased after the optimum value because in the high filler's concentration, agglomerations occur. This result was caused by the tendency of aggregate filler to combine with each other to form agglomeration. Agglomeration occurs in a higher filler content because the filler structures are in a chain or cluster form, generally called filler network which was explained as a weak distribution (Akron & Wang 1998). High polarity filler such as silica is not compatible with hydrocarbon rubber where filler network will form between aggregate to get the rigid structure (Akron & Wang 1998). Agglomeration leads to high stress concentration around the particle themselves making the matrix more fragile and defects can be created at the interface because of a weak compatibility between the filler and the matrix (Bandyopadhyay et al. 2004). These phenomena lead to debonding and void formation close to the particles and they are responsible for worsening of scratch resistance (Amerio et al. 2008; Bandyopadhyay et al. 2004). This explains why the scratch resistance decreases for the sample of 40 phr and 50 phr TEOS.

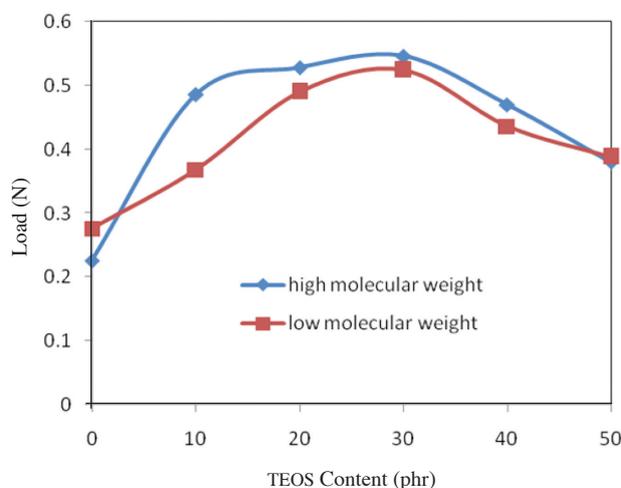


FIGURE 2. Effect of TEOS to scratch test for low and high molecular weight

TEM micrographs for LENRA/silica hybrid composite are shown in Figures 3 and 4. Silica particles were determined as dark spots that were distributed in the polymer matrix (Bandyopadhyay et al. 2005; Bandyopadhyay et al. 2006). Figure 3 shows the TEM micrograph for LENRA/silica hybrid composite by using high molecular weight of LENR. According to the micrograph, silica was well dispersed and distributed in the polymer matrix at the low concentration of TEOS. Silica size for 10 phr samples is in the nanometer range. Silica size started to increase until 116 nm for sample 30 phr. The silica particles were well distributed in the polymer matrix. The silica size increased with the increase of TEOS content (Bandyopadhyay et al. 2005; Bandyopadhyay et al. 2006; Heping et al. 2008). The silica started to agglomerate at higher concentration of TEOS, 50 phr. At this concentration, silica size was between 32 nm and 298 nm. Agglomeration of silica was due to the extent of hydrolysis and condensation reaction. When a lot of silica particles were formed, they tend to attract each other and start to agglomerate (Bandyopadhyay et al. 2005; Bandyopadhyay et al. 2006; Heping et al. 2008; Patel et al. 2005). The TEM micrographs were supported with the pendulum hardness test and scratch test. Mechanical

test depends on the dispersion and distribution of silica. Pendulum hardness test and scratch test results showed the increments until 30 phr TEOS because silica are well dispersed and distributed in the polymer matrix but start to decrease at the higher concentration of TEOS where silica are agglomerated. Composite with the lower filler loading show higher mechanical properties when comparing to composites with higher filler loading since there were less agglomeration in the composites (Noraiham et al. 2008).

Figure 4 shows the TEM micrograph for LENRA/silica hybrid composite by using low molecular weight of LENR. According to the micrograph, silica sizes in this composite are much bigger than LENRA/silica hybrid composite by using high molecular weight of LENR. Silica sizes that were formed for 10 phr sample were between 14 nm and 95 nm. Silica sizes for 20 phr samples were over 100 nm. With the increase of loading of TEOS, the average size of the silica particles increased (Abhijit et al. 2004; Bandyopadhyay et al. 2005; Bandyopadhyay et al. 2006; Heping et al. 2008). Silica started to agglomerate at higher concentration of TEOS and the biggest silica size that was form was 469 nm. Micrographs in Figure 4 were supported with the pendulum hardness test and scratch test. Mechanical properties increases until 30 phr

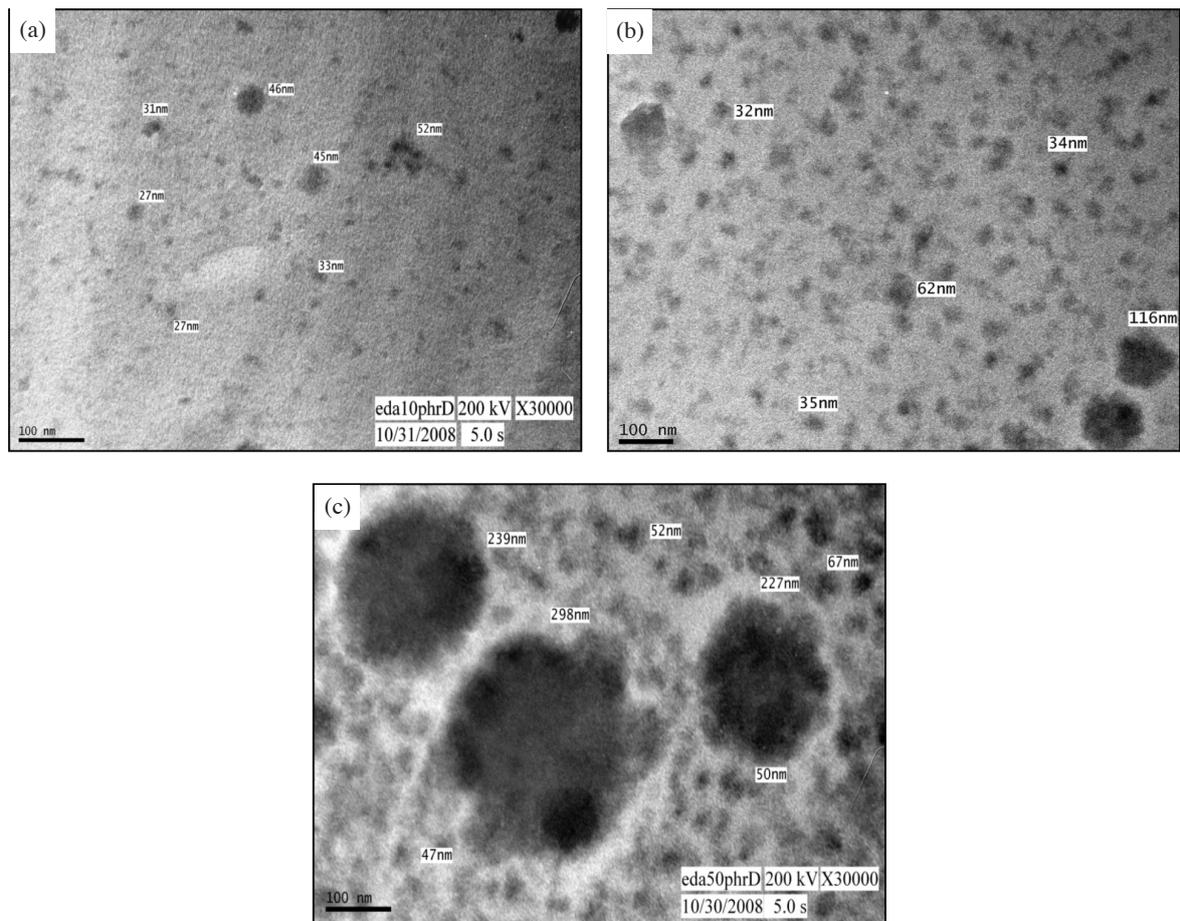


FIGURE 3. TEM micrograph for the high molecular weight; (a) LENRA/Si 10 phr TEOS, (b) LENRA/Si 30 phr TEOS, (c) LENRA/Si 50 phr TEOS

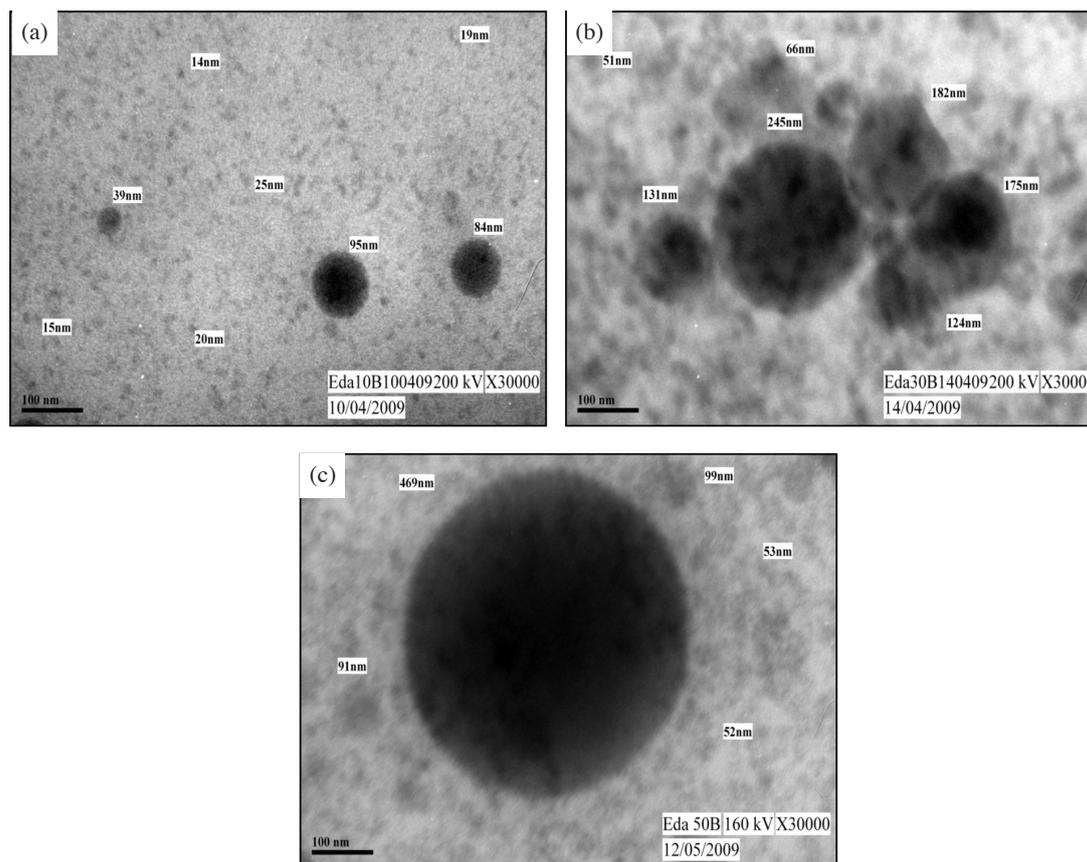


FIGURE 4. TEM micrograph for the low molecular weight; (a) LENRA/Si 10 phr TEOS, (b) LENRA/Si 30 phr TEOS, (c) LENRA/Si 50 phr TEOS

TEOS loading because of good dispersion and distribution of silica particles and decreases because of the agglomeration. High molecular weight showed a smaller size of silica particles and a very good dispersion and distribution of silica particles. Polymer matrix with low molecular weight could not entangle with silica particles (He et al. 2007). Therefore interaction between silica particles that were form in the matrix was higher than the interaction between silica particles and polymer matrix. Polymer matrix with high molecular weight could get entangled with silica particles (He et al. 2007). The interaction between polymer matrix and silica are stronger than the interaction between silica particles. Therefore, silica size formed in the high molecular weight polymer matrix are smaller and distributed well in the matrix than silica that form in the low molecular weight polymer matrix.

CONCLUSIONS

LENRA/silica hybrid composites were prepared successfully by sol-gel technique. Silica content increases as the TEOS content increase in the composites. From the pendulum hardness and scratch test results, LENRA/silica hybrid composites with high molecular weight of LENR showed a better mechanical properties than LENRA/silica hybrid composites with low molecular weight of LENR. TEM

micrographs showed good distribution and dispersion of silica in the LENRA/silica hybrid composites with high molecular weight. Silica size in the high molecular weight are smaller that low molecular weight.

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