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Polymer-Treated Graphite Nanocomposite for Sealing Applications in Geothermal

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ABSTRACT

With the potential to become a sustainable clean energy source in the future, geothermal energy is usually produced from geothermal systems. To extract a considerable amount of heat from underground, deep wells are usually drilled to reach a high-temperature production zone. The temperature surrounding a deep geothermal well is usually much higher than that surrounding oil and gas wells. At such a high temperature, constituent polymers of seals used for zonal isolation in geothermal wells may undergo cracking, degradation, and decomposition. To address this challenge, this study aims to develop a novel nano-reinforcement approach to preparing thermally resistant polymer nanocomposites that are adequate for sealing deep geothermal wells. The surface properties of small-size lamellar graphite (SFG15) particles were treated to form a strong bond between graphite and the polymeric matrix. The X-ray photoelectron spectroscopy (XPS) analysis of treated graphite particles showed that carboxyl (-COOH) groups are formed on the surface of treated particles and their oxygen contents are considerable. The bonding of -COOH groups to the surface of graphite is stable at high temperatures. We prepared polymeric nanocomposites by adding various contents of surface-treated SFG15 particles to ethylene propylene diene monomer (EPDM). Scanning Electron Microscopy (SEM) images of EPDM-graphite nanocomposites revealed intercalation and uniform dispersion of treated graphite within the polymeric matrix. The addition of treated graphite to EPDM significantly improves its high-temperature mechanical resistance. As is shown by dynamic mechanical analysis of prepared nanocomposites, 9 wt% of treated graphite could improve the high-temperature storage/elastic modulus and loss/viscous modulus of EPDM rubber by around 200% and 140%, respectively. Considering the markedly improved mechanical resistance of developed nanocomposites at high temperatures, they are a promising candidate for the constituent polymer of seals applicable in geothermal wells.

1. INTRODUCTION

To obtain clean energy from the subsurface while minimizing side effects on the environment, it is incredibly important to develop novel technologies that can bring better economics, improved safety, and low waste leakage risk by maintaining good wellbore integrity (Dahi Taleghani and Santos, 2023). In the past years, geothermal energy that is often produced from the so-called geothermal systems has gradually become one of the clean energy resources (Bertani, 2016; Liu and Dahi Taleghani, 2023a, b). To extract enough heat from geothermal reservoirs, drilling wells to a high-temperature production zone has been usually adopted. The environmental temperature surrounding a geothermal system can be very high. Polymers are extensively used as seal materials for providing zonal isolation in subsurface wellbore environments, such as oil and gas reservoirs as well as geothermal reservoirs. However, at high temperatures in geothermal reservoirs, constituent polymers of seals may experience cracking, degradation, and decomposition, in which case leaks of circulating working fluid in the wellbore might happen (Patel et al., 2019). According to Mackenzie and Garfield (2007), it is very challenging to seal with elastomers when the environmental temperature is higher than $250-300°$F. Hence, it is essential to improve the mechanical and thermal properties of the constituent polymers at elevated temperatures. In oil and gas wells, some ordinary polymers have been adopted, including Fluoroelastomers (FKM), Perfluorocarbon Elastomer (FFKM), Nitrile Butadiene Rubber (NBR), and Ethylene Propylene Diene Monomer (EPDM) (Patel et al., 2019). Compared with NBR and EPDM, FKM and FFKM have much higher prices and can be used in hotter environments. Nevertheless, FKM and FFKM present worse performances in low-temperature environments. Some inexpensive polymers like NBR show superior mechanical properties to fluoroelastomers; however, they fail to work at elevated temperatures, which limits their application (Patel et al., 2019).

In the past years, the idea of improving the physical properties of raw polymers by forming polymer-based nanocomposites containing nanoscale graphite platelets has been developed. Compared with raw polymers, these nanocomposites have presented improved mechanical, electrical, thermal, and optical properties (Yasmin et al., 2006; Afanasov et al., 2009; Safdari and Al-Haik, 2013). To initially explore the approach to developing economic sealing materials for geothermal wells, Liu et al. (2024) reinforced EPDM with low concentrations (1.5 wt% and 3 wt%) of surface-treated graphite and obtained promising improvements in the temperature resistance of EPDM. High-quality dispersion of an additive inside a polymer nanocomposite will result in a larger contact area between the additive and polymer matrix, thus promoting sufficient interactive force so that stress can be transferred effectively between the two components (Shokrieh et al., 2013). Also, to improve the mechanical strength of the polymer more effectively, it is beneficial to form good bonding between the additive and polymer matrix, which can be facilitated by proper surface treatment of additive particles. As reported by Malas et al. (2012), natural rubber filled with surface-modified expanded graphite shows better mechanical and thermal properties than that filled with expanded graphite without modification.

Although a considerable amount of work has been conducted to ameliorate the physical characteristics of polymers by graphite, there are still some research gaps on this topic. For example, few studies have been focused on improving the high-temperature mechanical performance of inexpensive polymers with nano additives to develop polymeric nanocomposites that can be used to seal deep hydrocarbon wells (Liu et al., 2022) along with geothermal wells. To fill current research gaps, we combined different concentrations of surface-treated graphite SFG15 particles with EPDM rubber separately and developed EPDM-graphite nanocomposites with enhanced high-temperature mechanical properties. Compared with plain EPDM, the prepared nanocomposites have much higher elastic/storage modulus at elevated temperatures, which provides a primary choice for seals in geothermal wells.

2. PREPARATION AND CHARACTERIZATION OF TREATED GRAPHITE PARTICLES

We used the technique of scanning electron microscopy (SEM) to analyze the geometric structure and dimensions of graphite SFG15 particles that will be utilized to reinforce EPDM rubber. The role of analyzing the geometry of graphite particles is to provide help for identifying graphite in the SEM images of polymer-graphite nanocomposites. The obtained SEM images of SFG15 particles are presented in Figure 1. From the images, we can see that graphite SFG15 particles generally possess a two-dimensional (2D) layered structure with a lateral dimension of around 1 µm to 10 µm.

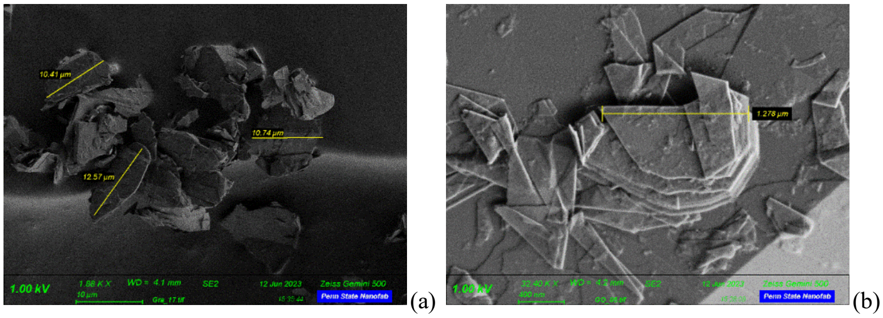


Figure 1: SEM images of graphite SFG15: (a) overall distribution of different flakes; (b) layered structure captured.

2.1 Surface Treatment Methodology

To benefit from the individual properties of any additives in enhancing the overall properties of a polymer, uniform dispersion of additives and effective bonding between them and the polymer matrix are a prerequisite. Therefore, we first developed surface treatment techniques to add functional groups, namely hydroxyl (-OH) and carboxyl groups (-COOH), to the surface of graphite particles.

Surface treatment with acid, like sulfuric acid (H_2SO_4), nitric acid (HNO_3), or their combinations, is a methodology to introduce oxygen-containing functional groups, including carboxylic and hydroxylic groups, onto the surface of graphite (Liu et al., 1998). Sulfuric acid and nitric acid are strong oxidizing agents. When graphite is treated with a mixture of these acids, the carbon atoms on the graphite surface undergo oxidation, causing carboxylic and hydroxylic groups to be formed. For the surface treatment of graphite, we have studied its efficiency regarding the dispersion and strength of bonding between surface-treated graphite and matrix (Tabatabaei et al., 2020a, b; Tabatabaei et al., 2021). We found that a combination of sulfuric and nitric acids with a ratio of 3:1 results in better dispersion and stronger bonding between surface-treated graphite and matrix as compared to other surface treatments, such as acid functionalization using a mixture of sulfuric acid and phosphoric acid with a ratio of 5:1, polymer wrapping using the poly acrylic acid (PAA), and the combination of polyvinyl pyrrolidone (PVP) and sodium dodecyl sulfate (SDS). Hence, we employed the steps illustrated in Figure 2 for surface treatment of graphite in the current work. First, graphite particles were introduced to a mixture of sulfuric acid (H_2SO_4) and nitric acid (HNO_3) with a ratio of 3:1. Then, using a hot plate, the mixture was heated up to 80℃ and stirred for four hours. Consecutively, the acid-functionalized particles were washed with deionized (DI) water and acetone until a colorless liquid was achieved. Lastly, we dried surface-treated graphite particles with a lab oven.

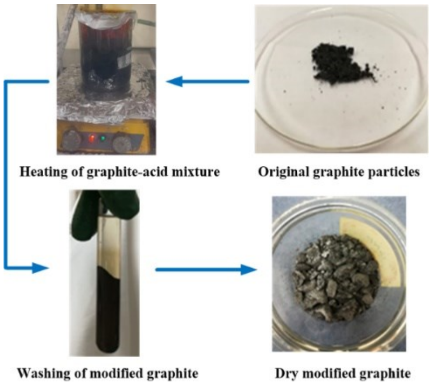
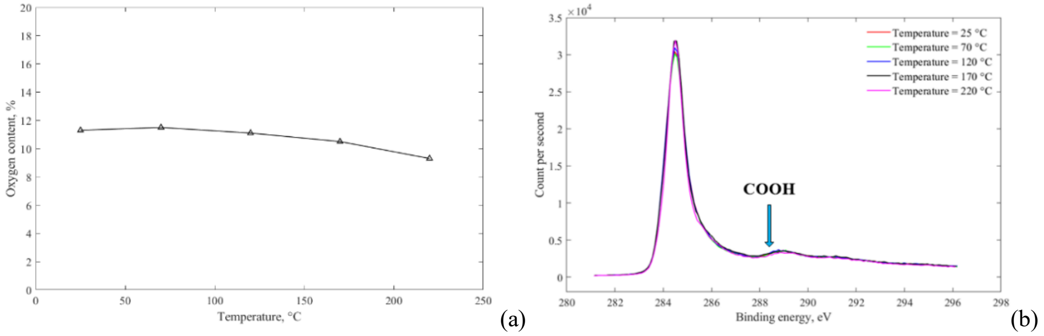


Figure 2: Procedure for surface treatment of graphite. Graphite is functionalized with a combination of sulfuric acid and nitric acid at 80 ℃, after which acid-functionalized graphite is washed continuously using deionized (DI) water and acetone.

2.2 Characterization: X-Ray Photoelectron Spectroscopy Analysis

The purpose of carrying out surface treatment is to oxidize and introduce functional groups to the surface of graphite SFG15 to achieve uniform dispersion of particles within the matrix. To examine the efficiency of developed surface treatment, XPS analysis was performed to identify functional groups and measure the content of oxygen formed on the surface of treated graphite particles. The XPS analysis was conducted inside a chamber at different temperatures up to 220℃. Results corresponding to SFG15 are presented in Figure 3. As it is seen from Figure 3a, an oxygen content of about 12% was detected on the surface of treated particles, which is reasonable as compared to the data available in the literature. For example, Bouleghlimat et al. (2013) prepared HNO_3-treated graphite particles and reported an oxygen content of about 14%. Figure 3b presents the C 1s spectra for the surface treated SFG15 heated at different temperatures from 25°C to 220°C. A peak is detected at the binding energy near 289 eV, corresponding to the formation of carboxylic acid functional groups (-COOH) on the surfaces of treated graphite SFG15 particles. It proves the efficiency of the acid functionalization method to oxidize graphite particles. Moreover, the -COOH peak intensity is still very considerable at high temperatures, despite its slight decrease as temperature increases. The -COOH groups on the surface of treated graphite are expected to promote strong bonding between the graphite particles and the polymeric matrix (Malas et al., 2012).



(a) (b)

Figure 3: (a) Oxygen content and (b) C 1s spectra for treated graphite SFG15 heated at different temperatures.

3. PREPARATION OF POLYMERIC NANOCOMPOSITES AND DISPERSION QUALIFICATION OF TREATED GRAPHITE PARTICLES

3.1 Preparation Procedure for Polymeric Nanocomposites

The surface-treated graphite SFG15 additives prepared above are used to fabricate graphite-filled EPDM nanocomposites, named EPDM-SFG15. The detailed procedure for fabricating the EPDM nanocomposites consists of two consecutive steps as follows. In the first step, a blend of EPDM rubber, polyethylene-graft-maleic anhydride (PE-MA), and surface-treated graphite particles is first compounded at the temperature of 200℃ using a single screw extruder. Here, PE-MA is a compatibilizer that is compatible with EPDM due to the ethylene monomer existing in EPDM. The epoxy group in PE-MA will also react with the functional group (-COOH) in treated graphite (Tedesco et al., 2002). Hence, PE-MA can provide a good connection between EPDM and treated graphite. In the second step, the compounded mixture is hot pressed at 200℃ with a mold to fabricate the sample of a graphite-filled EPDM nanocomposite in desired dimensions and geometry.

3.2 SEM Characterization of Prepared Polymeric Nanocomposites

To examine the distribution of surface-treated graphite particles within prepared polymer nanocomposites, we conducted SEM analyses at the voltage of 5 kV and obtained SEM images at different scales, including 5 µm, 10 µm, and 100 µm. First, we imaged the cross-section of an EPDM-SFG15 sample and observed the intercalation of graphite plates into the polymeric matrix in different orientations, which is illustrated in Figure 4a. Then, the surface of the sample was imaged at the scale of 10 µm, through which graphite plates with lateral dimensions of several microns were detected, as shown in Figure 4b.

Additionally, we used SEM to analyze the dispersion of treated graphite particles in EPDM-SFG15 samples containing different contents of graphite, which is shown in Figure 5. We can observe from Figure 5a that, for the sample with 3 wt% of treated graphite, the whole domain is covered by graphite particles evenly without noticeable agglomeration of graphite particles. Figure 5b reveals that the surface of the sample with 9 wt% of treated graphite is not as smooth as that of the samples with a smaller graphite content, i.e., 3 wt%; Malas et al. (2012) observed similar phenomena in their study. Nevertheless, it is noteworthy that the sample with 9 wt% of graphite still possesses even dispersion of graphite particles. Therefore, it can be concluded that the current approach to surface treatment of graphite particles and the procedure for fabricating EPDM-SFG15 nanocomposites led to the formation of a generally uniform distribution of graphite particles within the polymeric matrix.

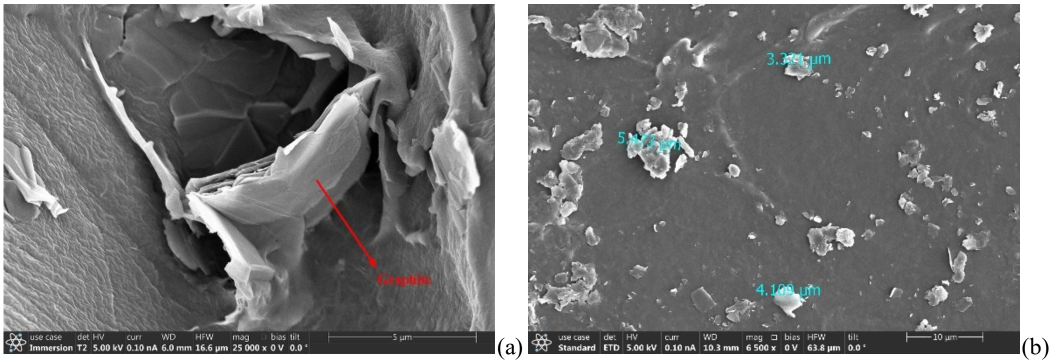


Figure 4: (a) Intercalation of graphite plates in EPDM matrix; (b) detection of graphite in prepared polymeric composite sample. (The content of treated graphite is 3 wt%.)

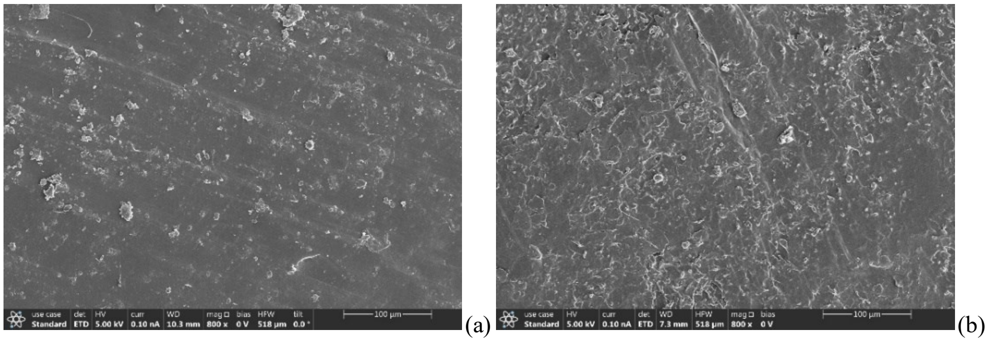


Figure 5: Dispersion of graphite particles in prepared polymeric composite samples filled with (a) 3.0 wt% and (b) 9.0 wt% of treated graphite.

4. MECHANICAL PROPERTIES OF NANO-REINFORCED POLYMER: DYNAMIC MECHANICAL ANALYSIS

The mechanical properties of a polymer are a key factor affecting its deformation and functionality when subjected to external forces. As a well-developed mechanical test method, dynamic mechanical analysis (DMA) has been extensively applied to examining the mechanical behavior of polymer materials dependent on temperature (Saba et al., 2016). Critical mechanical properties of a polymeric material could be acquired from DMA, such as viscous/loss modulus and elastic/storage modulus. The overall resistance to deformation, namely complex modulus, of the polymeric material has the expression of

$$G = G' + G''i \tag{1}$$

in which G' refers to the material's storage modulus; G'' denotes its loss modulus; $i^2 = -1$. We conducted DMA using the TA Instruments Q800 Dynamic Mechanical Analyzer to evaluate the mechanical properties of the prepared EPDM-SFG15 nanocomposites. We prepared test specimens (films) with dimensions of 20 mm (length) × 5 mm (width) × 1.4 mm (thickness). A pair of tension clamps, including an upper fixed clamp and a lower movable clamp, were used to apply a dynamic load to the film in the direction of its length. The controlled strain mode was adopted, with the amplitude being 10 µm. The adopted single frequency of the dynamic load was 1 HZ. Before dynamic loading started, a preload force of 0.01 N was applied to the test specimen to make it completely straight. During DMA, the film was heated to increase its temperature from 30 ℃ to 120 ℃ at a heating rate of 3 ℃/min.

We tested nanocomposite samples filled with different contents of treated graphite particles, including 1.5 wt%, 3.0 wt%, 6.0 wt%, and 9.0 wt%. DMA results of all tested samples are shown in Figure 6, with storage modulus and loss modulus included. For a comparison purpose, we also included the test result of a plain EPDM sample. Figure 6a shows that compared to the plain EPDM situation, the addition of treated graphite to EPDM markedly alleviates the decline of storage modulus due to an increase in temperature. The explanation for this phenomenon is that graphite has high stiffness, and it imparts this property to the nanocomposite. Surface treatment of graphite enhances its compatibility with the EPDM matrix with the help of the compatibilizer. This improved interaction at the graphite-polymer interface promotes better stress transfer between the polymer and graphite, resulting in increased stiffness and modulus. The addition of 1.5 wt.% of treated graphite leads to significant enhancement in the storage modulus of EPDM. Increasing the concentration of treated graphite from 1.5 wt.% to 3.0 wt.%, the enhancement in the storage modulus is still considerable. The storage modulus of plain EPDM decreases to 0.62 MPa as temperature increases to 120℃. After 1.5 wt% and 3 wt% of treated graphite particles are added to EPDM, storage modulus is raised by 77.9% and 152.5%, respectively. When graphite concentration continues to increase to 6 wt% and 9 wt%, the enhancement in storage modulus compared to plain EPDM increases to 176.6% and 191.2%, respectively. Hence, with graphite concentration increasing from 3 wt% to 9 wt%, considerable improvement in storage modulus is still achieved.

Besides, Figure 6b indicates that the loss moduli of prepared nanocomposites significantly increase as compared to the plain polymer having no treated graphite. The improvement can be explained as follows. Loss modulus reflects energy dissipation in the viscoelastic

EPDM nanocomposite and is related to its damping characteristics. The surface treatment of graphite introduces functional groups and modifies the surface, which could enhance internal friction within the nanocomposite. This increased friction during dynamic loading and unloading cycles contributes to higher energy dissipation, leading to an increase in loss modulus. The loss modulus of the plain EPDM sample at 120 °C is 0.510 MPa, and 1.5 wt% and 3 wt% of graphite lead to improvement in loss modulus by 57.3% and 112.2%, respectively. With the graphite content increasing from 3 wt% to 9 wt%, enhancement in loss modulus compared to the case of plain EPDM becomes 136.08%, not much higher than that brought by 3 wt% of graphite given that graphite concentration has been increased significantly. The loss modulus represents the viscous part of the complex modulus, related to the ability of a polymeric material to dissipate stress through energy loss in the form of heat. Therefore, the prepared nanocomposites with a higher loss modulus than the plain EPDM present a stronger ability to resist external forces through energy dissipation.

In summary, treated graphite SFG15 particles effectively enhance the storage modulus and loss modulus of EPDM at different levels of high temperature, and the enhancement may not keep increasing markedly with graphite concentration increasing to beyond 9 wt%. The prepared EPDM-SFG15 nanocomposite has a much higher resistance to external forces as compared to plain EPDM used in oil and gas wells.

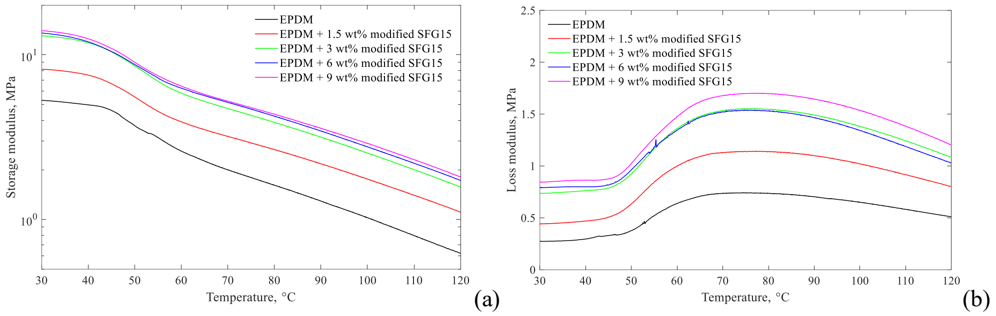


Figure 6: Effect of the content of treated graphite SFG15 on (a) storage modulus and (b) loss modulus of EPDM samples at different temperatures.

5. CONCLUSIONS

In this paper, a novel methodology is proposed to prepare high-performance polymeric nanocomposites adequate to seal geothermal wells, by dispersing surface-treated graphite SFG15 into low-cost raw EPDM. First, surface treatment of nanosized graphite SFG15 is conducted using acid functionalization. XPS analysis of treated graphite particles is used to assess the performance of conducted surface treatment. Then, surface-treated graphite particles are used for the nano-reinforcement of EPDM. The intercalation and dispersion of treated graphite in the EPDM matrix are examined by SEM analysis. We then test the high-temperature mechanical resistances of prepared polymeric nanocomposites utilizing DMA. The main outcomes of this study are as follows:

Considerable functional groups (–COOH) are generated on the surfaces of graphite particles via surface treatment, and generated -COOH groups have a stable connection with graphite at high temperatures. Treated graphite particles are intercalated into the EPDM matrix effectively, and uniform dispersion of treated additive particles is achieved. The addition of treated graphite particles enhances the high-temperature mechanical resistance of EPDM significantly. Results of temperature-related DMA show that 9 wt% of treated graphite could increase EPDM's elastic/storage modulus by around 200% and elevate its viscous/loss modulus by up to about 140%. Hence, EPDM nanocomposites containing treated graphite have a stronger ability to resist external forces through energy dissipation than plain EPDM. From the above outcomes, it is concluded that the developed EPDM-graphite nanocomposites, especially the one containing 9 wt% of treated SFG15, have significantly enhanced the temperature resistance and mechanical properties of inexpensive EPDM. Hence, it is recommended that the nanocomposite with 9 wt% of treated SFG15 be adopted as a superior choice for the constituent polymer of seals used in geothermal wells.

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