

Gelling of Cellulose Nanowhiskers in Aqueous Suspension

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ABSTRACT: The gelling properties of a 0.46 wt % semi-dilute aqueous suspension of well-characterized nanocrystalline cellulose particles extracted from the tunic of marine animals were studied by measuring the time evolution of linear viscoelastic moduli at various frequencies. The results show the existence of a gel time characterized by a frequency-independent loss angle, which suggests that gelling is due to the growth of self-similar clusters, whose fractal dimension was determined. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2014, 131, 40676.

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INTRODUCTION

In the last decade, there was increasing interest in the development of high performance “green” nanocomposites derived from cellulose nanofibers, often referred to as nanowhiskers, coming from animal or plant resources.^{1–4} These review articles clearly show that the renewable, biodegradable, nontoxic, cellulose nanowhiskers have a high reinforcement potential of polymer matrices, due to their high Young’s modulus (between 100 and 160 GPa) and their high surface area. Moreover, because of their high aspect ratio, from about 10 to 100 depending on the source of cellulosic material, the reinforcing properties of nanowhiskers can be observed at low contents. An early study of composite reinforcement by cellulose nanowhiskers has clearly shown that dramatic reinforcements could be achieved when nanowhiskers form a percolating network.⁵

Besides, the ability of cellulose nanowhiskers to self-assemble and organize in polar and nonpolar solvents has been recently reviewed.⁶ When dispersed in water, the cellulose nanowhiskers, like many other rod-like or anisometric particles, form an isotropic phase in the dilute regime, and an anisotropic liquid crystalline phase in the semi-dilute regime. Moreover, the results obtained by Bercea and Navard strongly suggest that nanowhiskers’ anisotropic suspensions exhibit a texture similar to that of liquid crystalline polymer solutions.⁷

A better understanding of reinforcement effect of polymer matrices by cellulose nanowhiskers, also of self-assembling phenom-

ena exhibited by cellulose nanowhiskers in solvents, requires a better characterization of the microstructures that these rod-shaped nanoparticles can adopt.

As recently reviewed by Solomon and Spicer,⁸ rod-shaped particle dispersions exhibit common features regarding their microstructure, as well as their dynamical and rheological response. For example, at low-volume fractions, a great variety of rod-shaped particles have been shown to form a space-filling network, which imparts elasticity and gel-like rheological properties to rod suspensions; the volume fraction at which the gel forms depends on the intensity of pair interactions, and of the rod aspect ratio.⁸ In the case of nanowhiskers, their ability to form gels at low volume fractions in water is due to not only excluded volume interactions, but also electrostatic interactions induced by the presence of negative surface charges imparted during the acid hydrolysis step classically used to produce cellulose nanocrystals.⁹

In the gelation literature, the elastic modulus of a gel is often considered analogous to the electrical conductivity of a random network of conductors, and can therefore be described by percolation theory, as originally proposed by de Gennes.¹⁰ Thus, different percolation models have been used in the literature to describe both polymeric and particulate gel formation.¹¹ Within this theoretical framework, theories of gelation describe the finite fractal cluster growth process, which leads to the formation of an infinite cluster at the gel point, identified with the

percolation threshold.¹² At the gel point, for a great number of covalently and physically cross-linked polymeric systems^{13–15} but also for some particulate systems,^{16,17} the storage and loss moduli, which characterize the dynamic mechanical behavior of the material, were shown to obey a common power law as a function of frequency. This particular viscoelastic behavior is the signature of the self-similarity (or scale invariance) of the gel structure, as predicted by the critical gel model by Winter and Chambon.¹⁸

In the present work, we present a viscoelastic investigation of the gelling properties of a low concentrated aqueous suspension of tunicate cellulose nanowhiskers, which are known to exhibit a high average aspect ratio. From a fundamental point of view, the aim of the dynamic mechanical characterization performed in this work is to give a physical insight into the mechanism of the gel formation of cellulose nanowhiskers in aqueous suspensions, which was never studied in the literature. From a more applied point of view, a better knowledge of the gelation phenomenon, which can be encountered in nanowhiskers aqueous suspensions, can be useful to improve the sol–gel processing technique, which is one of the different processing methods used to prepare nanowhiskers-based nanocomposites.⁶

EXPERIMENTAL

Production of Cellulose Nanowhiskers

The cellulose resource used in this work comes from the tunic of marine animals (*Phallusia mammilata*), provided by the Roscoff biology station. The proteins were extracted from washed pieces of the tunics by three successive bleaching treatments, alternating a treatment with a 5% potassium hydroxide solution at ambient temperature for 3 h, and a treatment with chlorite at 70°C for 4 h. The tunicate nanowhiskers were prepared by acid hydrolysis of the cellulosic residue dispersed in water at a concentration of about 10 wt %, using 96 wt % sulfuric acid, following a two-step procedure: in the first step, sulfuric acid is added drop by drop under continuous vigorous stirring of the mixture, and the temperature of the mixture is maintained at 32°C; then, in a second step, the reaction mixture is kept at 70°C for 45 min.

Preparation of Nanowhiskers Suspensions

The cellulose nanowhiskers were dispersed in deionized water and the suspension was dialyzed until the pH of the suspension reaches pH = 7, then it was sonicated for 10 min in order to disperse the cellulose nanoparticles. The suspension was then treated with a mixed-bed ion-exchange resin (Reference TDM-8 from Sigma Aldrich), and 0.02 wt % sodium azide, which acts as a bacteriostatic agent, was added to the suspension. The resulting 0.3 vol % (or 0.46 wt %) nanowhiskers suspension was stored at 4°C.

Titration

A total of 10^{-4} mol/L sodium hydroxide was added to a 0.17 vol % nanowhiskers aqueous suspension in order to titrate the charged sulfate groups resulting from the reaction of the sulfuric acid with the hydroxyl groups of cellulose. The number of sulfate groups at the surface of nanowhiskers per glucose unit was inferred from the overall number of sulfate groups per glu-

cose unit (derived from the titration measurements), divided by the ratio of surface chains to total chains in a nanowhisker, which can be calculated from the average dimensions of a nanowhisker and from the crystallographic characteristics of the cellulose crystal.¹⁹

Transmission Electron Microscopy

Transmission electron microscopy was used in order to determine the geometrical characteristics of cellulose nanowhiskers. A 0.2 vol % nanowhiskers aqueous suspension was placed on a copper grid, and stained with uranyl acetate. Transmission electron micrographs were acquired with JEOL JEM-1230 microscope at 80 kV, and analyzed using SigmaScan Pro 5.0.0.

Rheometry

All rheological measurements were carried out in oscillatory simple shear with a controlled strain rheometer ARES from TA Instruments, equipped with a parallel plate geometry of diameter 5 cm, at a gap of 1 mm. The sample temperature was fixed at 20°C using a thermostatic bath. Low viscosity silicone oil was used to prevent water evaporation during rheometrical tests, and waterproof abrasive paper with roughness of about 80 μm was used in order to prevent slippage at the surface of both plane geometries.

An optimized dispersion protocol was systematically applied prior to any rheometrical test, in order to reach a good reproducible initial dispersed state of the nanowhiskers in water, the dispersion state being characterized by viscoelastic measurements. This protocol will be presented and discussed in the Results section of the article. Two types of tests were performed: first, strain sweep tests in order to determine the extent of the linear viscoelastic regime at all frequencies tested (0.0316 Hz, 0.147 Hz, 0.215 Hz, 0.464 Hz, 0.618 Hz); then, with a new sample, the time evolution of the storage modulus G' and loss modulus G'' at the above-mentioned frequencies, in the linear regime, was studied.

RESULTS AND DISCUSSION

Geometrical Characteristics of Nanowhiskers

Figure 1(a,b) shows TEM images of a 0.2 vol % dispersion of cellulose nanowhiskers. These figures clearly confirm that cellulose nanowhiskers are long rigid rods. From such micrographs, the length (from Figure 1a) and diameter (from Figure 1b) of about 400 nanowhiskers were measured. Figure 2(a,b) presents histograms of the length and diameter distribution of the rod-like cellulose nanocrystalline particles. The average rod length $L = 960$ nm, and the mean rod diameter $D = 16$ nm, leading to a mean aspect ratio $p = L/D = 60$, with a rather large dispersity; these geometrical characteristics are in rather good agreement with those given in the literature for nanowhiskers produced from tunicate sources.²⁰

Surface Charge

The number of sulfate groups, SO_3^- , per glucose unit, determined by titration, was found to be about 0.04. When the extent of acid hydrolysis is low, substitution occurs essentially at the surface of the nanowhiskers, so that the number of charged sulfate groups per glucose unit at the surface, DS_s , is higher, and can be deduced from the ratio of surface chains to total

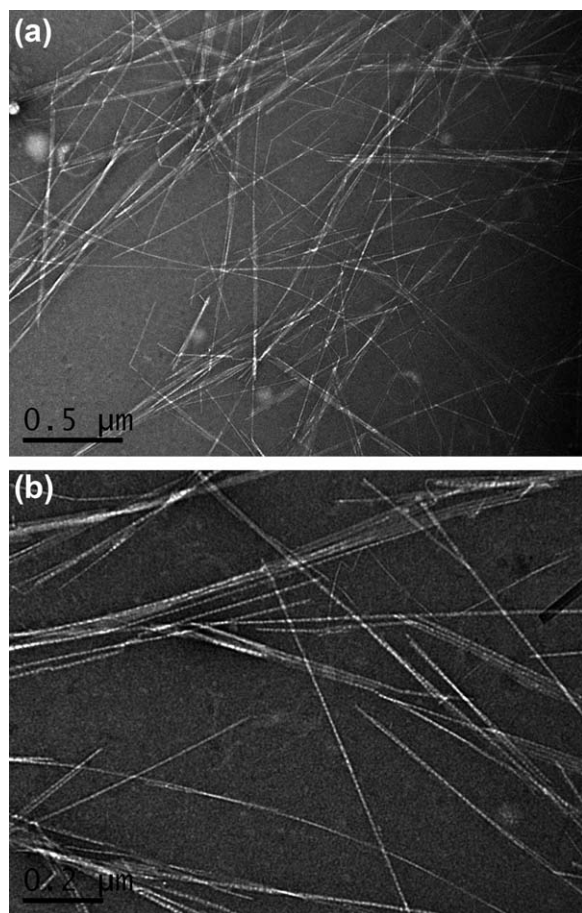


Figure 1. (a) Example of TEM image of a 0.2 vol % aqueous suspension of cellulose nanowhiskers, used for the determination of nanowhiskers length. (b) Example of TEM image of a 0.2 vol % aqueous suspension of cellulose nanowhiskers, used for the determination of nanowhiskers diameter.

chains in a nanowhisler,¹⁹ which is equal to 0.23 in our case, leading to $DS_s = 0.17$. This result means that 17% of accessible OH groups have been substituted by sulfate groups bearing a negative elementary charge on glucose units at the nanowhiskers surface by acid hydrolysis of cellulose.

Rheological Study

Optimization of the Dispersion Procedure. Prior to any rheological test, rheological experiments were first performed in order to determine the dispersion protocol leading to the best reproducible initial dispersed state of the nanowhiskers in water. A 50 W sonicator (Vibra cell from Bioblock Scientific) was used with different sonication times and the time evolution of the storage modulus was followed over 20 min just after the sonication step. The results, plotted in Figure 3, show that the sonication time mainly influences the initial G' values. This effect can be attributed to different initial degrees of dispersion of nanowhiskers in water after different sonication times. The lowest initial G' value, which is quite reproducible, is obtained for a 40-minute sonication time; it is worth noticing that a longer sonication time does not seem to have any additional effect on G' level. This result tends to show that 40 minutes would be the

best sonication time, that is, the time required to get the best and reproducible degree of nanowhiskers dispersion, at least with the sonication equipment used in this study. This optimized dispersion protocol was used before any rheometrical characterization performed in this study.

Evidence of Long-Time Structuration Kinetics. Figure 4 presents the time evolution of both viscoelastic moduli, G' and G'' , over 6 hours, for a 0.3 vol % cellulose nanowhiskers aqueous suspension, after the dispersion protocol presented above. This figure shows that both viscoelastic moduli initially increase rapidly, and go on increasing albeit weakly over many hours. This result is reminiscent of results obtained with Laponite clay suspensions, which have been shown to form gels under certain concentration and ionic strength conditions, without finding any equilibrium state over days.²¹ We think that this analogy makes sense, because both rod-like cellulose nanowhiskers and disk-like Laponite particles are anisometric charged nanoparticles.

Dynamic Mechanical Characterization of Gel Formation. Figure 5(a,b) presents the time evolution of the storage modulus and the loss modulus of a 0.3 vol % nanowhiskers aqueous suspension, at different frequencies in the linear response regime. These figures show that, after a more or less rapid initial increase, the continuous increase of both viscoelastic moduli, G'

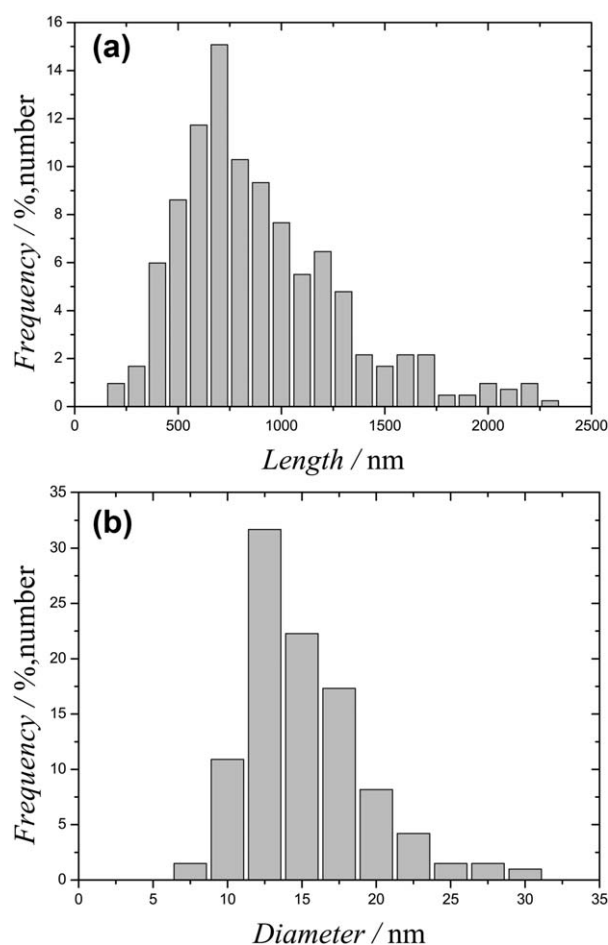


Figure 2. (a) Length distribution of nanowhiskers and (b) diameter distribution of nanowhiskers.

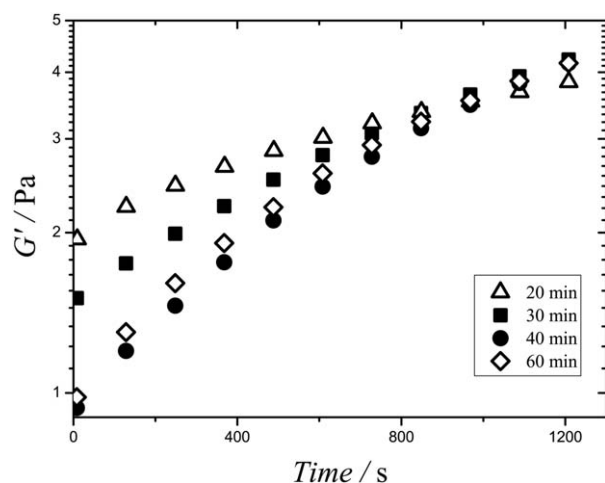


Figure 3. Time evolution of the storage modulus G' , at 1 Hz frequency and 3% strain amplitude, for a 0.3 vol % nanowhiskers aqueous suspension after different sonication times.

and G'' , with time is observed at all frequencies investigated. Moreover, they also show that, at any given time, the storage and loss moduli increase with frequency. The time evolution of the loss angle, $\tan \delta = G''/G'$, is plotted in Figure 6.

This figure clearly shows that, at all frequencies, the loss angle decreases with time, and that, at a well-defined time, $t_g \sim 1$ hour, it is independent of the frequency, at least over some limited frequency range, which means that G' and G'' exhibit the same frequency dependence at t_g . This result is in agreement with the prediction of the critical gel model by Winter and Chambon,¹⁸ at the gel point, which suggests that t_g might be considered as the gel time. It is interesting to notice that, following the same approach, the gel time of a 0.27 wt % surfactant-stabilized carbon nanotubes in aqueous suspension was shown to be about 2 h,²² whereas that of a 1 wt % Laponite aqueous suspension at an ionic strength of 0.001 M was shown to be about 3 h.¹⁶

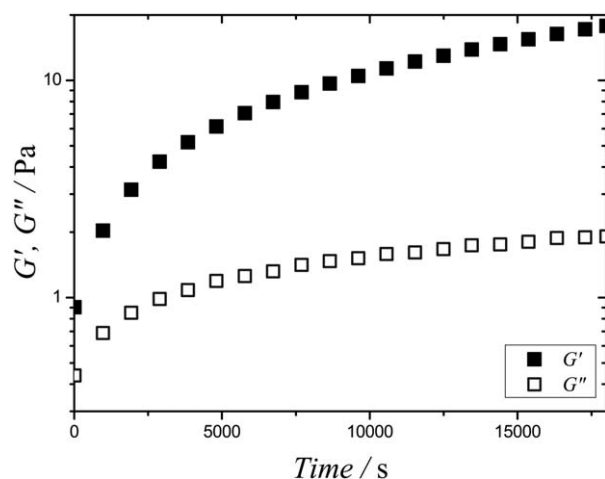


Figure 4. Storage modulus G' and loss modulus G'' as a function of time, at 1 Hz frequency and 3% strain amplitude, for a 0.3 vol % nanowhiskers aqueous suspension.

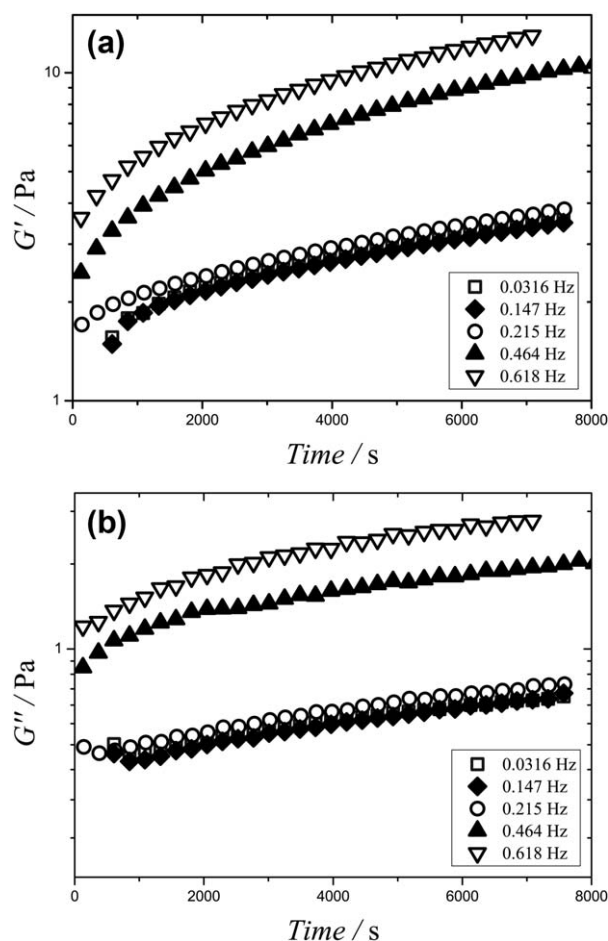


Figure 5. (a) Time evolution of the storage modulus G' , at different frequencies and 3% strain amplitude, for a 0.3 vol % nanowhiskers aqueous suspension. (b) Time evolution of the loss modulus G'' , at different frequencies and 3% strain amplitude, for a 0.3 vol % nanowhiskers aqueous suspension.

Assuming that G' and G'' have the same power law frequency dependence at all frequencies, as predicted by Winter and Chambon¹⁸ at the gel point, the common power exponent Δ can be calculated from the value of the loss angle at t_g , which is 0.23 in our case, which gives: $\Delta = 2\delta/\pi = 0.15$. For most polymer gels^{23,24} but also for Laponite nanoparticle gels¹⁶ at the gel point, the power exponent Δ was shown to lie between 0.5 and 0.7, in agreement with percolation theory.²⁵ However, other, much less numerous, critical gels are characterized by a much lower Δ value. For example, Δ was shown to lie between 0.1 and 0.2 for the critical gel induced by the crystallization of an elastomeric poly(propylene)²⁶ but also for the critical gel formed by rod-like virus particles.¹⁷ A relationship established by Muthukumar²⁵ allows to explain that Δ can take any value between 0 and 1:

$$\Delta = d(d+2-2d_f)/2(d+2-d_f) \quad (1)$$

where d is the space dimension ($d=3$), and d_f is the fractal dimension characterizing the self-similar structure of the clusters that form a three-dimensional network at the gel point.

Knowing Δ for a 0.3 vol % nanowhiskers aqueous suspension, eq. (1) allows to determine the fractal dimension d_f of the

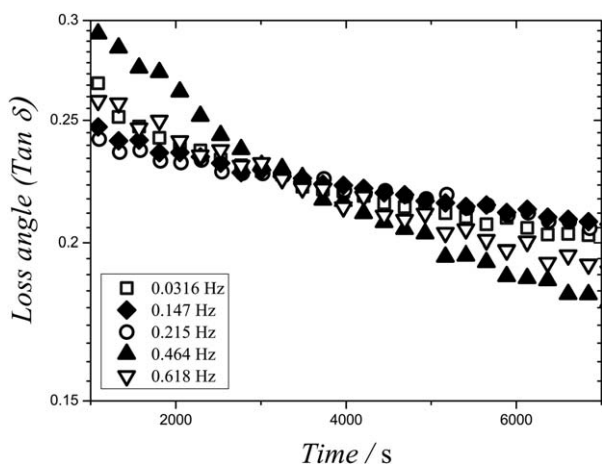


Figure 6. Time evolution of the loss angle, $\tan \delta = G''/G'$, at different frequencies and 3% strain amplitude, for a 0.3 vol % nanowhiskers aqueous suspension.

cellulose nanocrystalline clusters: $d_f = 2.4$. Such a large value is in good agreement with the fractal dimension deduced from a recent modeling of the viscosity of suspensions of highly anisometric nanoparticles.²⁷ Indeed, the fractal dimension of clusters of rod-like colloidal particles is higher than that of clusters of spherical colloidal particles, and all the more as the aspect ratio of the rods is higher.²⁸

Influence of Nanowhiskers Concentration Regime on Gelation. Following exactly the same approach, we studied the time-dependent dynamic mechanical properties of a 0.2 vol % nanowhiskers aqueous suspension. The results (not shown here) did not show the existence of any gel time over 10^4 seconds. This highlights the influence of nanowhiskers concentration on the gel formation: a minimum volume fraction is needed for gelation to occur. We suggest that this minimum concentration can be roughly estimated as the semi-dilute limit, from which pair interactions cannot be neglected. This limit, for rigid rods interacting only through excluded volume interactions, is given by¹¹:

$$\Phi_* = 24/p^2 \quad (2)$$

where p is the rod aspect ratio. Using eq. (2) with $p = 60$, which is the average aspect ratio of the rod-like cellulose nanowhiskers studied in this work, leads to $\Phi_* = 0.6\%$. This value is expected to overestimate the real semi-dilute limit of the nanowhiskers suspensions, because nanowhiskers interact not only through excluded volume interactions, but also through long-range electrostatic interactions. Our results suggest that the onset of semi-dilute regime, needed for gelation to occur, lies between 0.2 vol % and 0.3 vol %, for the nanowhiskers suspensions studied in the present work.

CONCLUSION

The study of the time evolution of linear viscoelastic moduli at various frequencies of a 0.3 vol % tunicate cellulose nanowhiskers semi-dilute aqueous suspension, submitted to 50 W sonication for 40 minutes, was performed. The dynamical

mechanical characterization shows that, after about 1 hour, the suspension can form a critical gel, resulting from the percolation of self-similar nanowhiskers clusters, whose fractal dimension is 2.4. The results of this study also show that, for gelation to occur, a nanowhiskers volume fraction between 0.2 vol % and 0.3 vol %, corresponding to the onset of semi-dilute regime, is needed. Finally, the results suggest a strong analogy between nanowhiskers gels and other rod-like, or disk-like, anisometric particle gels.

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