

The Effect of Rheology in Polymer Processing: A Simulation Point of View

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ABSTRACT

Rheology is important in polymer processing as it dictates the way the material flows and deforms. Rheology has made great strides in the last years, both in the *experimental* and the *computational* fields. The present work reviews the current state of affairs, mainly in the computational field, where new and complex models have been developed to deal with the viscoelasticity of the polymer melts. The simulation of the various polymer processes offers a great challenge to the rheological community due to the interactions between material, machine, and operating conditions, that takes place in every polymer processing operation.

INTRODUCTION

Rheology deals with the flow and deformation of all matter¹. *Experimental rheology* deals with the development of new techniques and instruments to measure the rheological material functions, such as the shear viscosity (η_s), the first and second normal stress differences (N_1 and N_2), the 3 extensional viscosities in uniaxial (η_E), biaxial (η_B) and planar (η_P) extension, the storage modulus (G') and loss modulus (G''), etc. *Computational rheology* deals with the development and use of constitutive equations, which are able to predict correctly the above-mentioned rheological material functions.

On the other hand, in polymer processing there are *steady-state operations*, such as extrusion, wire coating, calendering, etc., and *batch operations*, such as injection and blow molding, thermoforming, etc. The complexity of the processes and the interaction of material (usually in the form of a polymer melt) and machine make the problem of analysis and design a formidable one. Human ingenuity has nevertheless made a variety of useful assumptions, and many processes are now amenable to analytical tools by such an approach. For example, in the standard textbooks on polymer processing²⁻⁴, many steady processes are analysed by considering *simple shear flow*, in which a shear-rate dependent viscosity, following the simplest power-law model, is required for the analysis and design. Such processes are extrusion, calendering, and coating operations (wire, cable, and roll coating). Other processes are considered as *extensional processes*, where a simple Newtonian model with a constant viscosity has been used to gain a better understanding of the operations and their variations. Such processes are film blowing, fiber spinning, and film casting. The analysis and design of *unsteady-state operations*, such as injection and blow molding, is understandably more difficult due to time variations and possibly three-dimensional effects, and hence less amenable to easy analytical tools.

The use of computers and the development of numerical methods has made possible in the last years the simulation of various polymer processes with more sophisticated rheological models, not purely viscous but *viscoelastic*. These models are able to fit well most of the rheological material functions of the polymer melts mentioned above, in shear and extensional flows under steady or transient conditions. Prominent among those have been integral constitutive equations of the K-BKZ type⁵, and differential constitutive equations, such as the Phan-Thien/Tanner model⁶, and more recently, based on molecular arguments, the “pom-pom” model⁷ and its variants⁸.

In all these cases, the argument goes that if a model is able to fit well all rheological experimental data in simple flows and deformations, then the model is a good representation of the polymer and it can simulate well its flow and deformation in polymer processing operations.

The current work shows some interesting new developments in the field of polymer processing away from the simple models found in textbooks, and considers the future for these simulations and the new challenges ahead.

MATHEMATICAL MODELLING

The flow of polymer melts inside processing equipment follows the general conservation equations of mass, momentum and energy. In full tensorial forms, these are written as⁴

$$\nabla \cdot \mathbf{v} = 0 \quad (1)$$

$$0 = -\nabla p + \nabla \cdot \boldsymbol{\tau} \quad (2)$$

$$\rho C_p \mathbf{v} \cdot \nabla T = k \nabla^2 T + \boldsymbol{\tau} : \nabla \mathbf{v} \quad (3)$$

where \mathbf{v} is the velocity vector, p is the scalar pressure, $\boldsymbol{\tau}$ is the extra stress tensor, ρ is the density, C_p is the heat capacity, k is the thermal conductivity and T is the temperature.

To close the system of equations it is necessary to consider a rheological constitutive model that relates the stresses to the velocities and their gradients. The choice of the rheological model is of major importance and makes all the difference in polymer processing simulations.

For *purely viscous models*, the generalized Newtonian model is adequate. In this case, the constitutive model is written

$$\boldsymbol{\tau} = \eta(\dot{\gamma})\dot{\gamma} \quad (4)$$

where $\dot{\gamma} = \nabla \mathbf{v} + \nabla \mathbf{v}^T$ is the rate-of-strain tensor and $\dot{\gamma}$ is its magnitude based on its second invariant. The viscosity function η can follow any of the models that capture well the shear-dependent behaviour of polymer melts, such as the power law, the Carreau, the Cross, etc.⁴ The Newtonian model is recovered from Eq. (4) by setting a constant viscosity $\eta = \mu$.

For *viscoelastic models*, a plethora of models have been introduced with varying degrees of success⁵. We focus here our attention to the integral K-BKZ model, since this model has been used more than any other in polymer processing simulations for real polymers. It is, however, understood that any other model with enough degree of sophistication, that can capture well the rheology of polymer melts, is also a good candidate for simulations of polymer processing.

The K-BKZ model in its usual form for simulations is written as⁵

$$\boldsymbol{\tau} = \frac{1}{1-\theta} \int_{-\infty}^t \sum_{k=1}^N \frac{a_k}{\lambda_k} \exp\left(-\frac{t-t'}{\lambda_k}\right) H_k(I, II) \left(C_t^{-1}(t) + \theta C_t(t') \right) dt' \quad (5)$$

where N is the number of relaxation modes, λ_k and a_k are the relaxation times and relaxation modulus coefficients at a reference temperature, θ is a material constant, and II , I are respectively the first invariants of the Cauchy-Green tensor C_t

and its inverse $C,^{-1}$ the Finger strain tensor. These appear in the strain-memory (or damping) function $H_k(I,II)$. The θ -parameter relates the second normal stress difference N_2 to the first one N_1 according to $N_2/N_1=\theta/(1-\theta)$. The damping function is of major importance as it dictates the nonlinear response of the material in strong shear and extensional flows. Various damping functions have been used in the past, with the most popular being the PSM damping function⁹

$$H_k(I, II) = \frac{\alpha_k}{(\alpha_k - 3) + \beta_k I + (1 - \beta_k) II} \quad (6)$$

where α and β are material parameters to be determined from shear and uniaxial extension, respectively. The above damping function allows for independent behaviour of the melt viscosity in uniaxial extension, but in planar extension, the viscosity follows the shear viscosity, which is not true for all polymer melts. To correct this, Olley¹⁰ proposed another damping function

$$H_k(I, II) = \frac{\alpha_k}{\alpha_k + \beta_k(I - 3) + (1 - \beta_k)(I - 3)^{3/2}} \quad (7)$$

The values of the material parameters are found by a regression analysis on available rheological experimental data, steady or transient.

An example of how the rheology is affected by the constitutive equation is given for a standard LDPE melt, the IUPAC-LDPE melt A. Data on G' and G'' (see Fig. 1) are used to obtain the relaxation spectrum (λ_k, a_k) of 8 relaxation modes, with the parameters of Table 1. Then depending on the damping function, hence the model used, different fitting for the extensional viscosities is obtained while the shear viscosity remains the same. Such differences in rheological behaviour are bound to affect the flow behaviour of the polymer and hence its behaviour in polymer processing.

Table 1. Material parameters obtained by the K-BKZ/PSM model for the IUPAC-LDPE melt A at 150°C ($\theta=-0.111$).

k	λ_k (s)	a_k (Pa)	α_k	β_k
1	10^{-4}	$1.29 \cdot 10^5$	14.38	0.018
2	10^{-3}	$9.48 \cdot 10^4$	14.38	0.018
3	10^{-2}	$5.86 \cdot 10^4$	14.38	0.08
4	10^{-1}	$2.67 \cdot 10^4$	14.38	0.12
5	10^0	$9.80 \cdot 10^3$	14.38	0.12
6	10^{+1}	$1.89 \cdot 10^3$	14.38	0.16
7	10^{+2}	$1.80 \cdot 10^2$	14.38	0.03
8	10^{+3}	$1.00 \cdot 10^0$	14.38	0.002

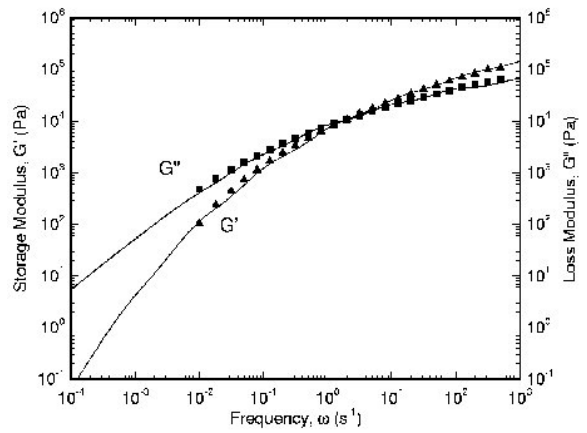


Figure 1. Rheology data (symbols) for the LDPE melt and its best fit (lines) with the K-BKZ model (Eq. 5).

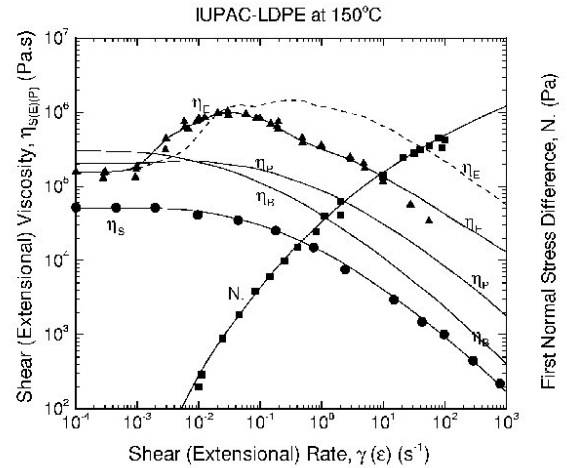


Figure 2. Rheology data (symbols) for the LDPE melt and its best fit (lines) with the K-BKZ model (Eq. 5) and the PSM damping function (Eq. 6). The dashed line corresponds to a single $\beta=0.018$.

RESULTS AND DISCUSSION

Extrusion through dies

A test case often encountered in polymer processing is the extrusion through a die. If the die is *axisymmetric* (production of rods or pipes) then the uniaxial elongational viscosity η_E is important as well as the shear properties of the melt. For this case, simulation results for the IUPAC-LDPE melt A are in very good agreement with experiments both for the vortex growth and the extrudate swell¹¹. Typical results are shown in Fig. 3.

However, when the same melt is extruded through a slit die (*planar geometry*, production of plastic sheets), then it is the planar extensional viscosity that is important as well as the shear properties of the melt. In this case, the K-BKZ/PSM model predicts a planar extensional viscosity η_P that follows the shear viscosity (see Fig. 2), showing always a strain-thinning behaviour. Then, no vortex growth appears in the simulations, instead the vortex diminishes in direct contrast with experiments.

In this case, it is important that the damping function is modified according to Eq. (7) to predict the same behaviour in planar extension as in uniaxial extension. The relaxation spectrum of Table 1 remains the same, but the α_k and β_k parameters are now changed to fit the data. The new parameters are given in Table 2 and the rheology results are shown in Fig. 4. It is now obvious that with the new damping function, the response is similar in all cases of extensional flow, and this will affect the flow behaviour as well.

The flow behaviour is shown in Fig. 5, where the simulation results are compared with recent experimental flow patterns in a 14:1 planar contraction¹². The vortex is now large, in qualitative agreement with the experiments. The lack of quantitative agreement shows that still more work is needed to fully understand the rheology (in this case in planar extension) and how this

influences the flow behaviour and hence the processing of the polymer melt.

Table 2. Material parameters obtained by the K-BKZ/Olley model for the IUPAC-LDPE melt A at 150°C ($\theta=0$).

k	λ_k (s)	a_k (Pa)	α_k	β_k
1	10^{-4}	$1.29 \cdot 10^5$	4.7	1.0
2	10^{-3}	$9.48 \cdot 10^4$	4.7	1.0
3	10^{-2}	$5.86 \cdot 10^4$	4.7	$1.03 \cdot 10^{-1}$
4	10^{-1}	$2.67 \cdot 10^4$	4.7	1.0
5	10^0	$9.80 \cdot 10^3$	4.7	$2.46 \cdot 10^{-2}$
6	10^{+1}	$1.89 \cdot 10^3$	4.7	$2.75 \cdot 10^{-1}$
7	10^{+2}	$1.80 \cdot 10^2$	4.7	$5.92 \cdot 10^{-3}$
8	10^{+3}	$1.00 \cdot 10^0$	4.7	$1.46 \cdot 10^{-4}$

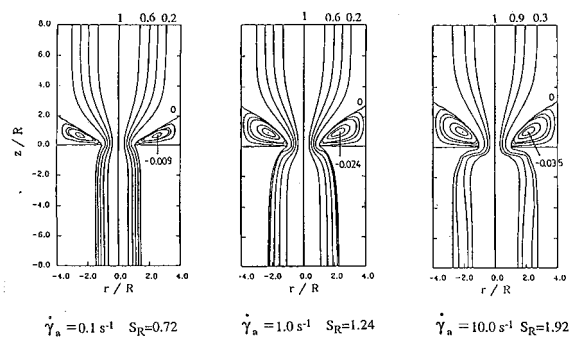


Figure 3. Flow patterns of the IUPAC-LDPE melt through an orifice die¹¹. Note the vortex growth and enhanced extrudate swell as the flow rate increases.

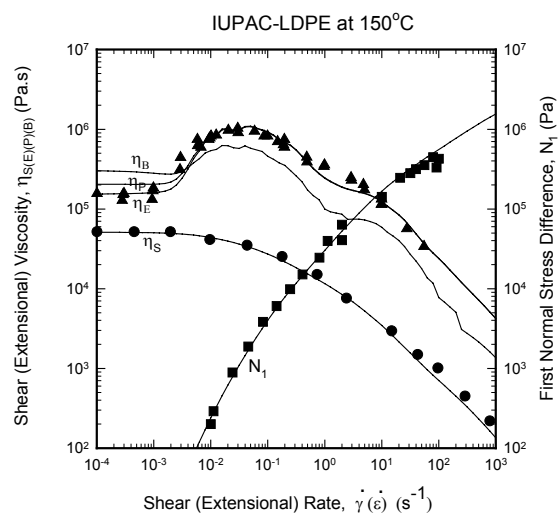


Figure 4. Rheology data (symbols) for the LDPE melt and its best fit (lines) with the K-BKZ model (Eq. 5) and the Olley damping function (Eq. 7).

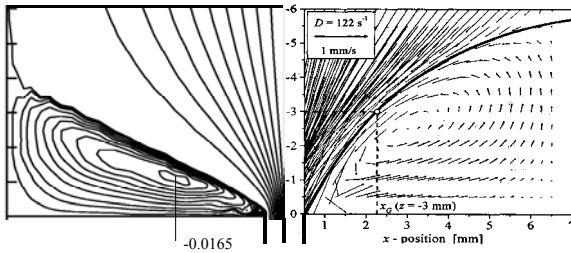


Figure 5. Flow patterns of the IUPAC-LDPE melt through a 14:1 planar contraction: (left) simulation results with the K-BKZ/Olley model, (right) experimental flow pattern¹².

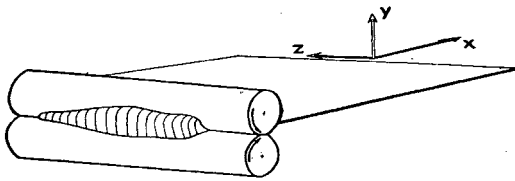


Figure 6. Schematic representation of molten polymer sheet passing through a calender.

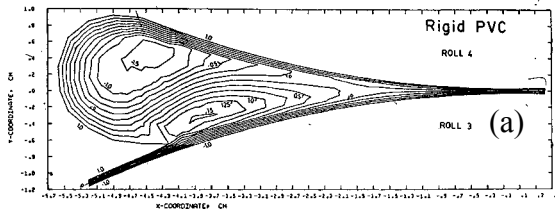


Figure 7. Calendaring of rigid PVC with slip: (a) streamline pattern from simulations¹³, (b) experimental pattern¹⁴.

Calendering

In the process of calendering, a polymer melt passes in the nip region between two corotating rolls to produce a thinner plastic sheet (see Fig. 6). Because of the *shear-dominated flow* in the nip region, a purely viscous model obeying Eq. (4), with a shear-rate and temperature-dependent viscosity, is able to capture well the behaviour of polymer melts. This is evidenced in Fig. 7 for calendaring of rigid PVC sheets^{13,14}.

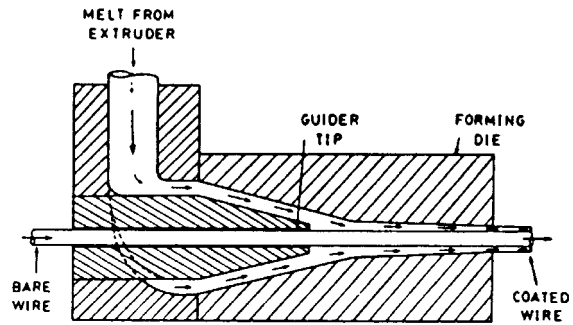


Figure 8. Schematic representation of molten polymer sheet passing through a wire-coating die.

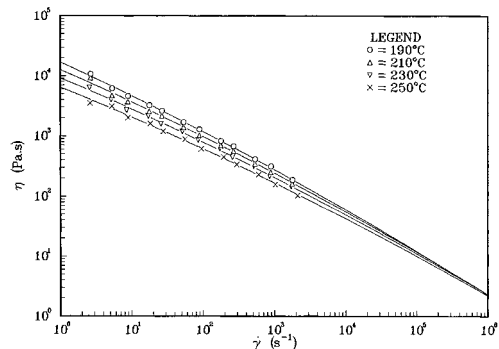


Figure 9. Experimental data for shear viscosity for a wire-coating LDPE melt (ALATHON 3535) and their best fit by using a purely viscous model¹⁵.

Wire Coating

In the process of wire coating, a polymer melt passes from the extruder head into the die and flows under pressure around a moving wire, so upon exiting the die the wire is coated (see Fig. 8). Again as before, because of the *shear-dominated flow* in the flow channel, a purely viscous model obeying Eq. (4), with a shear-rate and temperature-dependent viscosity, is able to capture well the behaviour of polymer melts. For example, for a wire-coating LDPE melt (ALATHON 3535) good experimental data for the shear viscosity are needed as shown in Fig. 9 (from¹⁵). Then the simulations are able to predict correctly the pressure drop in the system as a function of wire speed, as evidenced in Fig. 10. This is what the industry is interested in in high-speed wire-coating operations¹⁵.

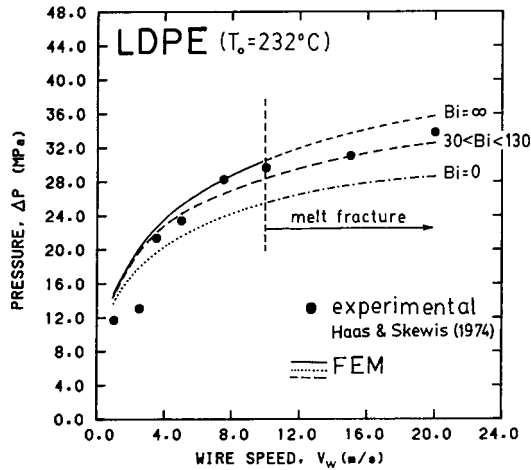


Figure 10. Wire coating of LDPE melt. Comparison of pressure drops between experiments and simulations¹⁵.

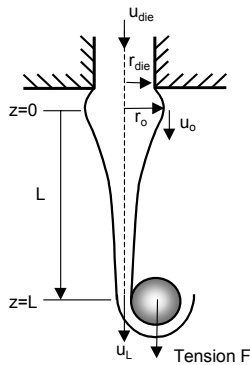


Figure 11. Schematic representation of fiber spinning.

Fiber Spinning

In the process of fiber spinning, a polymer melt passes through the spinneret and is spun out under tension to form a thin fiber (see Fig. 11). Here unlike before, the flow of the polymer melt is *dominated by uniaxial extension*, and therefore shear properties are of no interest. Viscoelasticity and flow-induced crystallization are of particular importance. In isothermal melt spinning, the K-BKZ model appears to be able to predict well the radius and speed of the fiber as shown in Fig. 12 (from¹⁶). A new model including flow-induced crystallization has also appeared and shown great promise¹⁷.

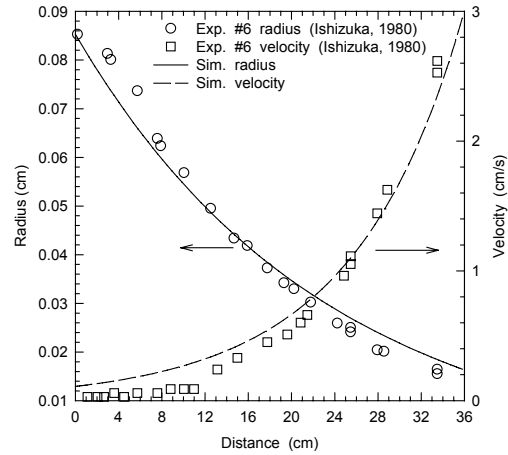


Figure 12. Isothermal fiber spinning of PP melt at 200°C. Comparison of fiber radius and speed between experiments and simulations¹⁶.

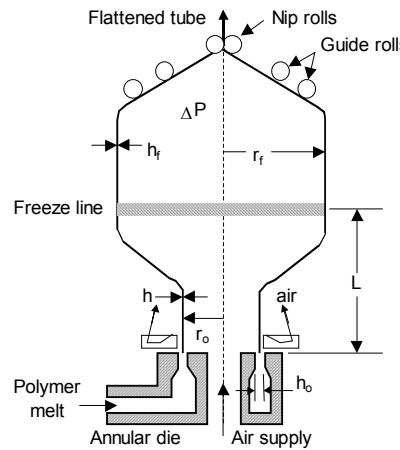


Figure 13. Schematic representation of film blowing.

Film Blowing

In the process of film blowing, a polymer melt passes through an annular die and then is blown and drawn upwards to form a bubble and hence a thin film for making plastic bags or sheets (see Fig. 13). Again here unlike before, the flow of the polymer melt is *dominated by biaxial extension*, and therefore shear properties are of no interest. On top of viscoelasticity and flow-induced crystallization, of particular importance is the *cooling process* that is taking place by a sophisticated design and arrangement of cooling rings. Therefore, isothermal film-blowing does not seem to be of interest, while the interaction of outside

blowing air and heat transfer to the film are of particular importance. Thus, a new model taking into account these interactions has been developed¹⁸, and taking the bubble shape as given, it finds the heat transfer from the air to the bubble. Obviously, this is a very difficult process to analyse, and a full simulation is still lacking. This is an example that a lot of work is still needed to fully understand some processes from the rheological as well as the mechanical point of view, before design can be based on pure simulations.

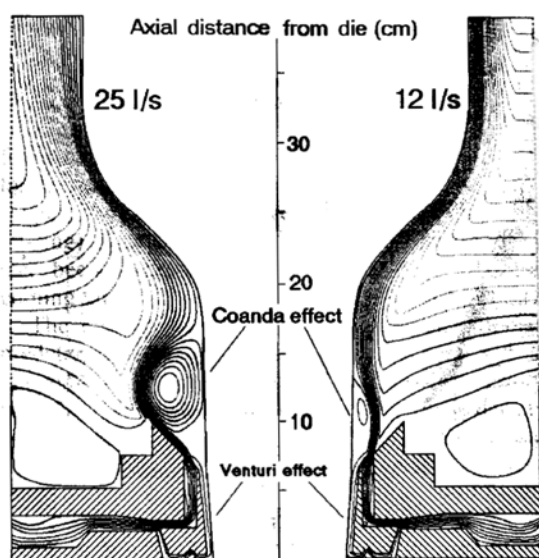


Figure 14. Cooling air streamlines around a high neck bubble in film blowing of HDPE polymer melts. Streamlines for a high air flow rate (left) and a moderate air flow rate (right). The shape of the bubble is given and the melt is considered as Newtonian with a temperature-dependent viscosity¹⁸.

CONCLUSIONS

The present work has attempted to show the effect that rheology has on some polymer processes. From the simple case of extrusion through a die to the sophisticated and complex process of film blowing, rheology is always important and one needs to know the process well and the effect of forces in it. For *shear-dominated flows*, as in calendering, wire coating, and flow through

long dies, good shear viscosity data as a function of shear rate and temperature, are sufficient for most simulations to be successful. For *extension-dominated flows*, as in fiber spinning, film casting and film blowing, the effect of extensional viscosity remains a difficult task to resolve, due to inadequacies in measurements of extensional properties. Finally, the synergistic effect of rheology and mechanical operating conditions still presents us with a formidable task to tackle, and will keep busy the polymer-processing simulation community for some time.

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