

# ACADEMIC RHEOLOGY AND INDUSTRIAL RHEOLOGY A PERSONAL REFLECTION [TO THE YEARS 1960-1970]

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## ABSTRACT

This paper is an attempt to highlight the problems faced by industrial rheologists. The problems are far more complex than subjects of usual academic pursuit. Because of the lack of scientific methods in both theory and instruments, the industrial rheologist often resort to empirical approach such as a use of the processing machines for processability evaluation. More fundamental approach is desirable. The examples are taken from high density polyethylenes and the period was 1960-1970. Although industry found solutions to the problems, the fundamental understandings have not been developed sufficiently.

## KURZFASSUNG

Der vorliegende Beitrag beleuchtet die von Industrierheologen erkannten Probleme. Sie sind komplexer als die Probleme, die in gewöhnlichen akademischen Arbeiten behandelt werden. Weil es an wissenschaftlichen Methoden sowohl in der Theorie als auch im Bereich der einsetzbaren Meßinstrumente mangelt, geht der Industrierheologe oft empirisch vor, und zwar durch den Einsatz von Verarbeitungsmaschinen selbst für die Bewertung von Verarbeitungsprozessen. Ein mehr fundamentales Verständnis ist demnach erwünscht. Die aufgeführten Beispiele betreffen den Bereich der Polyethylene hoher Dichte aus dem Zeitraum 1960-1970. Obwohl die Industrie Lösungsmethoden zu den technologischen Problemen gefunden hat, liegt für diese Materialien noch immer kein fundamentales Verständnis vor.

## RÉSUMÉ

Cet article tente d'évoquer les problèmes rencontrés par les rhéologues de l'industrie. Ces problèmes sont bien plus complexes que les problèmes abordés dans la recherche académique. A cause du manque de méthodes scientifiques, tant du point de vue expérimental que théorique, les rhéologues de l'industrie ont souvent recours à des approches empiriques comme l'utilisation de machines de production pour l'évaluation de la faisabilité. Une approche plus fondamentale est souhaitée. Les exemples donnés sont issus des polyéthylènes haute densité et la période traitée est 1960-1970. Bien que l'industrie ait trouvé des solutions aux problèmes, la compréhension de ces problèmes du point de vue fondamental n'a pas été suffisamment développée.

## 1 INTRODUCTION

This writer worked in polymer industries for 24 years, of which most of the time was spent at development centers. Major responsibility was problem-solving, for which a part concerned with manufacturing and the other part with processing of polymers. The ultimate objective was to relate processability back to polymerization conditions. Because he belonged to polymer manufacturer, many of the processing problems were those arose from customers.

Typically the development center was organized into two teams, the polymerization research team, supporting manufacturing and

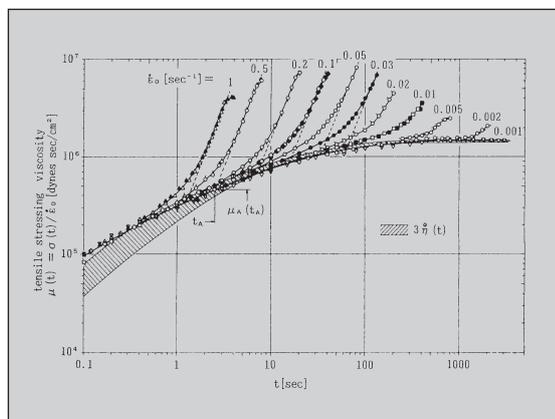
the technical service team for the customer relation. These teams were the first line problem solvers. Difficult problems, which could not be solved by them, were turned over to physics and analytical group "the second line defense" for which this writer was in charge.

A most difficult issue was the amount of time allowed for the problem solving. Usually much time had already been spent by the first line team, attempting to solve problems. By the time the problem was referred to the second line defense, no time was left for providing solution. Sometimes it was possible to come up with an answer or an advice after discussing the situation in a manner of consulting service. Other times, however, some

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Figure 10 :  
 Extensional stresses  
 viscosity,  $\mu(t)$ , and  
 comparison with the  
 (linear-viscoelastic) shear  
 stressing viscosity,  $\eta(t)$   
 (Melt,  $l$ ,  $T=150^{\circ}\text{C}$ ,  $\dot{\epsilon}_0 =$   
 constant extensional  
 strain rate).



## 7 ELONGATIONAL VISCOSITY

The elongational viscosity of Newtonian liquids had been known for some time as Trouton's viscosity, which was three times of shear viscosity. However, polymer rheologists in early 1960's did not remember it. Generally, the shear viscosity was called viscosity and regarded as a sole expression of viscous behavior of polymers. Gradually, however, the importance of elongational viscosity became recognized. This happened in conjunction with stretching films and monofilaments. The change of cross-sectional area in flow from barrel to capillary of a rheometer was recognized as equivalent to stretching a flowing melt [20].

For the measurements of steady state viscosity a constant shear rate was imposed and the steady value of shear stress was recorded. If a tensile machine was used to achieve a constant rate of deformation  $(dl/l)/dt = \text{constant}$ , machine speed must be exponentially increased. Meissner developed a winding device with gears to provide a constant rate of deformation at a constant speed of the machine [21]. Subsequent measurements of elongational behavior of low density polyethylene, LDPE, was an epoch-making discovery [22], Figure 10.

There were two important discoveries, (i) the elongational viscosity did not reach steady state and (ii) the viscosity increased progressively to exhibit strain-hardening.

Soon afterward there was a revision on the definitions of viscosity; not only shear viscosity and elongational viscosity were recognized as different material properties, but also steady state and non-steady state viscosities were differentiated.

## 8 ELONGATIONAL VISCOSITY AND CHARACTERIZATION

Important requirements for rheological characterization in industry are: (i) to determine processability difference in a laboratory with rheological instrument. It should do away with more expensive evaluation by using actual processing machine. (ii) One should be able to explain the processability difference in terms of molecular make-up such as molecular weight distribution and branch-pattern.

A characterization with the melt flow curve (shear flow) was quite inadequate in some of the critical applications such as a high speed blow-molding [23]. For selecting suitable resin for the process the actual machine had to be used for screening [24]. The flow curve, linear viscoelastic data and GPC data did not provide screening capability [23].

There were not many published data of elongational viscosity. However, variations among samples appeared to be magnified at large deformation. At processing conditions the behavior of melt is usually non-steady state and a combination of both shear and elongation. The use of both shear and elongational measurements for characterization of gum rubbers was developed later. The method was capable for relating molecular structure to processability [25].

## 9 VISCOELASTICITY AND MEMORY BEHAVIOR

Memory behavior is very often a part of the processing problem. An elastic body retains either, 100% memory or none. For a viscoelastic body it is very complex. At any given time a memory possessed by a body is related to the sum of all experience in the past minus sum of the forgotten ones. The recovery of the memory is also complex, because it does not occur instantaneously. That is, the swelling of extrudate occurs faster with some resins and slower with others.

Even in the linear viscoelastic behavior the memory is very complex to describe. In actual processing the material behavior is usually nonlinear. Further difficulty is to explain the memory behavior from both processing condition and molecular make up. The works in this area are mostly empirical and fundamental knowledge is lacking [26].

## 10 MELT FRACTURE

When the extrusion rate through a capillary rheometer is increased, at certain high rate the extrudate shape changes from smooth cylinder to irregular shapes. It may start from the roughness of the surface, or take a shape of twisted rope, screw and many other irregularities. Although the causes may be different for each case, they are all called "melt fracture".

The shear rate at which the melt fracture occurs is called critical shear rate (or critical shear stress in terms of stress). Usually a higher value of the critical shear rate is preferred for the high speed processing. However, the HDPE extrudates from capillary at very high shear rate past the critical zone of melt fracture becomes cylindrical again. Therefore, sometimes a lower value of the critical shear rate is preferred [24]. A problem here was that the critical shear rate could not be predicted from the flow curve nor from linear viscoelastic properties.

## 11 CONCLUSION

This paper is an attempt to highlight the problem faced by industrial rheologists. The problems are far more complex than subjects of the usual academic pursuit. Industrial rheologists often resort to empirical approach such as uses of the processing machines for the processability evaluation. More fundamental approach is desirable, but the basic knowledge is lacking in many cases. Examples were taken from the period, 1960~70. Some progress has been made since then, but the problem remains by-and-large.

## REFERENCES

- [1] Nakajima, N., *J. Appl. Polym. Sci.*, 14, 2643 (1970)
- [2] Bueche, F., *Chem. Phys.*, 22, 1570 (1954)
- [3] Pao, Y-H., *J. Chem. Phys.*, 25, 1294 (1956)
- [4] Bueche, F., Harding S.W., *J. Polym. Sci.*, 32, 177 (1958)
- [5] Sabia, R., *J. Appl. Polym. Sci.*, 7, 347 (1963)
- [6] Kepes, A., *J. Polym. Sci.*, 22, 409 (1956)
- [7] Nakajima, N., *J. Polym. Sci.*, A-2, 5, 101 (1966)
- [8] Nakajima, N., Wong P.S.L., *Trans. Soc. Rheol.*, 9, 3 (1965)
- [9] Kraus, G., Gruber J.T., *J. Polym. Sci.*, A, 3, 105 (1965)
- [10] Nakajima, N., Casper, F.S., Hoffman, R.D., *Trans. So. Rheol.*, 15, 647 (1971)
- [11] Nakajima, N., *J. Polym. Sci.*, C, 21, 153 (1968)
- [12] Nakajima, N., *Separation Sci.*, 6, 275 (1971)
- [13] Nakajima, N., *J. Appl. Polym. Sci.*, 15, 3089 (1971)
- [14] Wales, J.S.L., *Pure Appl. Chem.*, 20, 331 (1969)
- [15] Nakajima, N., *Adv. In. Chem. Ser.*, 125, 98 (1973)
- [16] Nakajima, N., *J. Appl. Polym. Sci.*, 14, 14 (1970)
- [17] Nakajima, N., Shida, M., Wissburn, K.F., Abstract 26th Int. Cong. Pure Appl. Chem., Session V., 1309 (1977)
- [18] Cox, W.P., Merz, E.H., *J. Polym. Sci.*, 28, 619 (1958)
- [19] Shida, M., Shroff, R.N., *Trans Soc. Rheol.*, 14, 605 (1970)
- [20] Nakajima, N., Shida, M., *Trans. Soc. Rheol.*, 10, 299 (1966)
- [21] Meissner, J., *Rheol. Acta.*, 19, 230 (1971)
- [22] Meissner, J., *Trans. Soc. Rheol.*, 16, 405 (1972)
- [23] Miller, J.C., *Trans. Soc. Rheol.*, 19, 341 (1975)
- [24] Schaul, J.S., Hannon, M.J., Wissburn, K.F., *Trans. Soc. Rheol.*, 19 (1975)
- [25] Nakajima, N., *Polym. Intern.* 36, 105 (1995)
- [26] Nakajima, N., *Reorojii Gakkaishi*, 18, 5 (1990)

