

Polymers and rheology: A tale of give and take

Leire Sangroniz, Mercedes Fernández, Antxon Santamaria*

POLYMAT and Department of Polymers and Advanced Materials: Physics, Chemistry and Technology, Faculty of Chemistry, University of the Basque Country UPV/EHU, Paseo Manuel de Lardizábal, 3, 20018, Donostia-San Sebastián, Spain

ABSTRACT

Polymers and rheology were both born in the twenties of the last century, fruit of the disruptive and creative scientific atmosphere of this decade. The development of polymer science and technology in the last almost 100 years has been colossal, whereas rheology has been able to create its own route as a branch of Physics. In this review paper we describe the interactions between both scientific areas, demonstrating that many of the crucial aspects for the progress of one of them owes to contribution of the other and viceversa. This interrelationship is shown through a historical survey of the principal milestones, starting from the correlation of the molecular weight with the intrinsic viscosity. A pondered analysis of the contributions of rheology to polymer science and technology, lead us to assert that the role of the former is rather founded on 50 years old discoveries.

1. The tumultuous beginnings of polymers and the quiet birth of rheology

The idea of long-chain molecules involving only chemical bonds, introduced by Hermann Staudinger in 1924 and nowadays a fundamental concept in biology, chemistry and physics, was disregarded and even attacked by the chemists of the time. The reaction of the scientific community was logical in view of the apparent soundness of the notion of colloids as aggregates of small molecules, which was able to explain the high viscosity solution, gelation and other physical features of gums, cellulose and other substances currently defined as polymers. The offensive against the new disruptive idea was in many occasions unpleasant and aggressive to Staudinger, who suffered personally from this lack of consideration; this was recognized by the scientific community when the German scientist was awarded with the Nobel Prize for Chemistry in 1953 [1,2].

Some examples of what we now consider unfounded criticisms are reported in the literature. For instance, as remarked by Moravetz [3], the very influential organic chemist Paul Karrer dismissed Staudinger's idea considering it ridiculous that starch would consist of hundreds of glucose units joined by glucoside bonds, because "it is improbable that a plant in converting sugar to a reserve substance from which it might soon have to be recovered would perform such complex work". Moravetz refers also to an unpleasant episode in the farewell lecture given by Staudinger at the ETH Zurich in 1925, in which one of the speakers compared him and his concept of long-chain molecules, with a traveler in Africa that had seen a 400 m long zebra. In this list of disrespectful comments, it is also known [4] the friendly letter sent to Staudinger by

the Nobel Prize laureate in 1927 Wieland, with this central message: "Dear colleague, abandon your idea of long molecules, organic molecules with molecular weights exceeding 5000 do not exist. Purify your products such as rubber, they will crystallize and turn to be low molecular weight compounds".

As pointed out by Mulhaupt [1,2], a firm opposition to the concept of polymers came from the pioneering scientists in the field of incipient crystallography, who believed that it was impossible for long-chain molecules to fit in the crystallographic unit cell. Currently it is known that only chain segments are present in the unit cell. Paradoxically, crystallization of polymers remains a principal subject of study and discussion in polymers. According to the report of T.P. Lodge on the occasion of the 50th anniversary of the very influential journal *Macromolecules* [5], the theory of polymer crystallization is positioned in first place in the list of current challenges in polymers.

Compared to the heroic efforts of Staudinger to introduce the concept of polymer chains in 1920s, the birth of rheology in 1928 was humble and peaceful. Marcus Reiner remembered [6] the summer of 1928 when he arrived from Palestine to Easton Pennsylvania invited by Eugene Bingham who said to him: "Here you, a civil engineer, and I, a chemist, are working together at joint problems. With the development of colloid chemistry, such a situation will be more and more common. We therefore must establish a branch of physics where such problems will be dealt with". Reiner's response was: "This branch of physics already exists; it is called mechanics of continuous media or mechanics of continua". Bingham replied: "No, this will not do. Such a designation will frighten away the chemists". Then, he consulted a professor of classical languages at Lafayette College and arrived at the designation of

* Corresponding author.

E-mail address: antxon.santamaria@ehu.es (A. Santamaria).

the term Rheology, in concomitance with the sentence of Heraclitus “Panta rei” (Everything flows).

It can be said that, humbly and elegantly, rheology was born with the intention of pleasing and attracting the chemists (at least to not disturb them). The definition of rheology coined by Bingham was “Fundamental and practical knowledge concerning the deformation or flow of matter”. According to Doraiwamy [7], the foundations of the Society of Rheology were established in April 1929, at a meeting in Columbus (Ohio) attended by Herschel, Ostwald and other scientists, in addition to Bingham and Reiner. The Society of Rheology was officially founded on December 19, 1929 and became one of the five founding members of the American Institute of Physics. But, rheology was not free of criticisms and years later Truesdell [8] remembered that a negative definition of rheology was introduced at the time through the sentence: “Rheology concerns the fluids that fluid-dynamicists ignore”. Besides the fact that reflects a certain ignorance, since rheology also concerns solids, its malicious intention failed completely in view of the extraordinary perspectives open to rheologists with the development of materials of peculiar physical features, such as polymers. The development of rheology to become an independent science is soundly explained in the book of Tanner and Walters “Rheology: An historical perspective” [9], with precise details of the origins of rheological societies, congresses and journals.

In this paper we show the crucial role played by rheology in polymer science and technology and we recall that the principal advances in rheology, as non Newtonian flow behavior and viscoelasticity, owe to the study of polymers. This mutual devotion and stimulus between polymers and rheology, has been emphasized, among others, by Kausch-Blecken [10].

2. Intrinsic viscosity-molecular weight relationships: A great step for polymers

The high viscosities of polymer solutions, even at dilute concentrations, drew Staudinger’s attention who used this circumstance to consolidate the concept of polymers, and to face those who maintained the hypothesis of colloidal aggregates. Based on viscosity results of polystyrene/benzene solutions measured in an Ostwald capillary viscometer, Staudinger [11] observed a linear correlation between the molecular weight and the intrinsic viscosity $[\eta] = K_m M$, and so proposed an experimental method to deduce the molecular weight of polymers. The molecular weight considered by Staudinger is now defined as the viscous average molecular weight M_v , and lies between the number average molecular weight, M_n , and the weight average molecular weight, M_w . The intrinsic viscosity is obtained from the relative viscosities of polymers solutions of different concentrations:

$$[\eta] \equiv \lim_{c \rightarrow 0} \left(\frac{\eta - \eta_s}{c\eta_s} \right) \quad (1)$$

η being solution viscosity, η_s the solvent viscosity and c the concentration [12].

Staudinger’s experiments were followed by other authors, including, for instance, the 1975 Nobel Prize laureate P.J. Flory [13] who used the following correlation, established by Goldberg, Hohenstein and Mark for polystyrene [14]:

$$\log M_v = \frac{\log[\eta] + 4.013}{0.74} \quad (2)$$

M_v being the viscosity average molecular weight.

Later, linear equations for the relationship between intrinsic viscosity and molecular weight were substituted by a better approach, the power law correlation or Mark-Houwink equation [15,16]:

$$[\eta] = kM_v^a \quad (3)$$

K and a parameters depend on the polymer/solvent couple and temperature and their respective values are available in literature for

most polymers. M_v is the viscosity average molecular weight.

Molecular theories on dynamics of polymers, developed at the end of the forties, have explained the correlations found between intrinsic viscosity and molecular weight [17]. The study of the kinetics of monomeric units on the assumption that monomer units do not interact with each other and do not distort flow, lead Debye [18] to demonstrate Staudinger’s law. This was corrected by Debye and Bueche [19] and by Kirkwood and Riseman [20] who introduced the idea of the shielding effect of the peripheral monomers over interior monomers, using, respectively, different models for the internal structure of the polymer molecule. Interestingly, these molecular models give a physical meaning to the a exponent of the empirical Mark Houwink equation. The hydrodynamic shielding determines the value of a (between 0.5 and 1): when protection is complete, $a = 1$ (Staudinger law), whereas when the solvent freely penetrates the polymer, it drains all the monomers independently of their position, then $a = 0.5$. These models are valid for polymer coils, since in the case of rod-like polymers, which give rise to liquid crystal polymers, the exponent is $a > 1$ [21]. The development of models sustained on viscosity results of dilute solutions opened new routes for the study of the conformation of polymer chains, as reflected in Flory’s book “Principles of Polymers Chemistry” [22].

Although the implications of the rheology of polymer solutions in the field of the Molecular Biology are not in the scope of this review, it is compulsory to recall the work of Zimm et al. [23–25] on the viscoelastic behavior of chromosomal-sized DNA. Their rheological analysis proved that the DNA of an eukaryotic cell consists of just one, extremely big macromolecule ($M_w \approx 4 \times 10^9$ g/mol and contour length ≈ 2 cm).

In recent decades other techniques, like light scattering and, in particular, size exclusion chromatography (SEC), which allows determining M_n , M_w and higher averages of the molecular weight distribution, have gained ground. Notwithstanding, rheological evaluation of the intrinsic viscosity remains currently a cheap and very widely used tool to have a first approach to the molecular weight of the analyzed polymer. The rather tedious procedure of obtaining the intrinsic viscosity by means of Ostwald or Ubbelohde [26–28] viscometers is currently facilitated by the use of automated capillary and rotational viscometers.

3. The non-Newtonian flow and its implication in polymer processing: gathering scientists and engineers

In the opening session of a *General Discussion* on colloids organized by the Faraday Society in 1913, Ostwald [29] opined about the viscosity of these substances. He mentioned 10 factors affecting their flow properties. Flow rate or the associated shear rate was not among these factors.

The notion of the viscosity of a liquid being dependent on the applied shear rate was unknown until the end of the twenties and its discovery is the most important finding of the beginnings of rheology as a newly defined branch of physics. The analysis of colloidal dispersions carried out by Ostwald in 1925 [30] using the capillary viscometer designed by himself, revealed a dependence of the viscosity on flow velocity. The deviation from the so-called Newtonian flow behaviour, according to which the viscosity is independent of the applied shear rate, was clearly evidenced in the paper published by Reiner in November 1929, on the viscosity of rubber/benzene solutions [31]. The results showed a decreasing viscosity as the shear rate or shear stress is increased. Fig. 1 displays the summary of the viscosity data obtained by Reiner using a capillary viscometer in which the applied pressure and the flow rate are, respectively, directly proportional to the shear stress and the shear rate.

Ostwald’s analysis led to establish a power law between the stress and rate in a shear flow $\sigma_{21} = K\dot{\gamma}^n$, which is extended to a power law for the viscosity, $\eta = K\dot{\gamma}^{n-1}$, where K and n are characteristic parameters of the studied system. According to the Ostwald’s power law, when $n < 1$ the viscosity decreases as the shear rate increases; a behavior which has

Tabelle II.
Untersuchungen von Herschel und Bulkeley
an Gummi-Benzollösungen verschiedener Konzentrationen bei 30°C.

| p in g/qcm | Q/t in ccm/Sek. | $\eta' \cdot 10^6$ | $q' \cdot 10^{-3}$ | $\tau_w \cdot 10^2$ | Konstante $\frac{2}{5} \frac{f''(0)}{f''(0)}, \frac{f''(0)}{9}$ | $q_w \cdot 10^{-3}$ berechnet | $\Delta \varphi$ ber.—beob. | $\Delta \varphi$ in Proz. |
|---|--------------------|--------------------|--------------------|---------------------|--|----------------------------------|--------------------------------|------------------------------|
| 1. Konzentration 0,399, Viskosimeter Nr. 2. | | | | | | | | |
| 226,0 | 0,350 | 24,6 | 40,8 | 26,7 | 28,650 | 40,8 | ± 0,0 | ± 0,0 |
| 216,8 | 0,332 | 24,8 | 40,3 | 25,7 | | 40,6 | + 0,3 | + 0,7 |
| 208,0 | 0,314 | 25,1 | 39,8 | 24,5 | | 40,3 | + 0,5 | + 1,2 |
| 198,3 | 0,298 | 25,3 | 39,5 | 23,5 | | 40,0 | + 0,5 | + 1,3 |
| 189,2 | 0,281 | 25,6 | 39,1 | 22,3 | | 39,7 | + 0,6 | + 1,5 |
| 180,1 | 0,266 | 25,7 | 38,9 | 21,3 | 69,800 | 39,3 | + 0,4 | + 1,0 |
| 170,8 | 0,249 | 26,0 | 38,5 | 20,2 | | 39,0 | + 0,5 | + 1,3 |
| 160,4 | 0,233 | 26,1 | 38,4 | 18,9 | | 38,6 | + 0,2 | + 0,5 |
| 146,9 | 0,211 | 26,4 | 37,9 | 17,3 | | 38,0 | + 0,1 | + 0,3 |
| 133,4 | 0,190 | 26,7 | 37,5 | 15,8 | | 37,4 | - 0,1 | - 0,3 |
| 117,2 | 0,163 | 27,3 | 36,6 | 13,8 | -91,200 | 36,6 | ± 0,0 | ± 0,0 |
| 98,3 | 0,132 | 28,3 | 35,3 | 11,6 | | 35,5 | + 0,2 | + 0,6 |
| 79,3 | 0,105 | 28,7 | 34,8 | 9,4 | | 34,4 | - 0,4 | - 1,2 |
| 59,1 | 0,076 | 29,5 | 34,0 | 7,0 | | 33,1 | - 0,9 | - 2,7 |
| 20,1 | 0,023 | 33,1 | 30,3 | 2,4 | | 30,3 | ± 0,0 | ± 0,0 |

Fig. 1. Original table taken from the paper of Reiner [31]. The most significant data are those of the first and the second columns, which correspond, to the applied pressure and the flow rate, respectively. The results indicate that there is not a linear relationship between them, reflecting a non-Newtonian behaviour.

been termed as pseudoplastic or shear thinning. On the contrary, for $n > 1$ the viscosity augments with the shear rate, following a behaviour defined as dilatant or shear thickening. For $n = 1$ the viscosity remains constant at any applied shear rate, as was assumed by Newton, Hagen, Poiseuille, Couette and all scientists preceding the advent of rheology. The power law equation is very helpful to extend the dynamics of Newtonian liquids to the dynamics of polymer liquids, as it is demonstrated in the essential book of Bird, Armstrong and Hassager [32], which contains a great number of flow cases.

The progressive diffusion of the notion of non-Newtonian flow, and in particular the spread of the idea of shear thinning liquids, had an enormous relevance in polymer technology. It was possible to compare the processing ease and energy consumption of different polymers by measuring their characteristics parameter (k and n) at any temperature in home-made piston driven capillary extrusion rheometers which were developed in the 1940s [33]. This was the first step for the sound and fruitful relationship between rheology and polymers, as can be seen in the literature about polymer processing [34–37]. From the 11,320 total results found until July 2022 in the ISI Web of Knowledge [38] for the journal *Polymer Engineering and Science* edited by the very influential *Society of Plastics Engineers* (which was founded in 1942 and accounts for more than 20,000 affiliates currently), 4220 refer to the term *processing* and include, at a large or short extent, rheological data.

The interest of polymer rheologists to study the viscosity curves (i.e. viscosity versus shear rate) of polymer melts, has led to combine the results of rotational (plate-plate and cone-plate) and capillary extrusion rheometers. This allows covering a very wide interval of shear rates to obtain a fingerprint by shifting the viscosity curves at different temperatures to procure a master curve of each polymer, taking advance of the time-temperature superposition (TTS) method [39]. Fig. 2 shows the viscosity results for a low density polyethylene obtained at different temperatures [32,40]; similar results comparing the features of different polymers can be found abundantly in the literature. In order to show the relevance of this kind of rheological results to the processing of polymers, in this figure we have included the corresponding shear rates ranges involved in the most common processes like extrusion, injection etc. The shear rates range required for the more modern 3D printing procedure [41] are also included.

The aforementioned Ostwald’s law is only valid to fit the data in the shear thinning region that is to say above the critical shear rate which marks the end of the Newtonian flow. Currently the most used model to fit the viscosity data of polymers is the Carreau equation [32]:

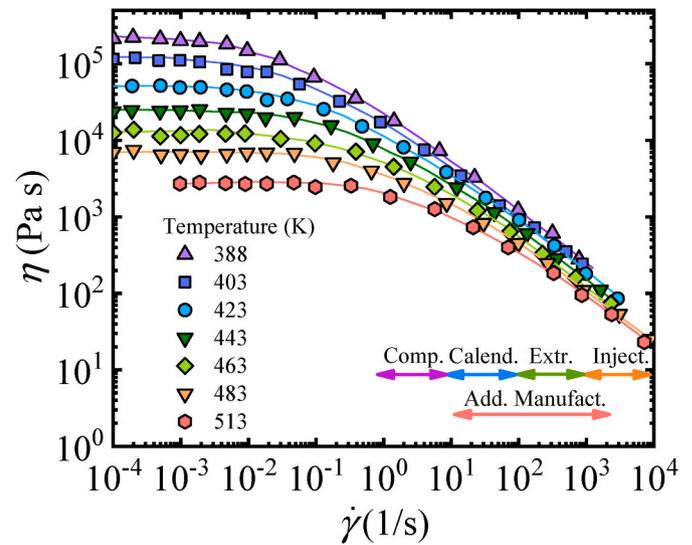


Fig. 2. Viscosity for a low density polyethylene at several temperatures measured with a capillary viscosimeter (high shear rates, above $5 \cdot 10^{-2} \text{ s}^{-1}$) and a Weissenberg Rheogoniometer (low shear rates). In the figure the shear rates corresponding to several processing techniques are shown [32,40]. The corresponding temperatures are included in the figure. The lines are drawn to guide the eye.

$$\eta = \eta_{\infty} + \frac{(\eta_0 - \eta_{\infty})}{[1 + (\alpha \dot{\gamma})^a]^{(1-n)/a}} \quad (4)$$

where η_0 is the so-called Newtonian viscosity, η_{∞} the viscosity plateau at high shear rates, α a characteristic time whose inverse is the critical shear rate for the onset of the non-Newtonian behavior, and n is the flow index. Generally, the contribution of η_{∞} is neglected.

The actual use of computer aided tools for polymer processing, such as the simulation software Moldflow for injection and compression molding, requires the inevitable loading of viscosity data. In doing so, the effect of shear rate, temperature and pressure on viscosity can be expressed through the equation:

$$\eta(\dot{\gamma}, T, P) = \frac{\eta_0 \exp\left(\frac{E_a}{RT}\right) \exp(\beta P)}{[1 + (\eta_0 \exp\left(\frac{E_a}{RT}\right) \exp(\beta P) \dot{\gamma} / \tau)^a]^{(1-n)}} \quad (5)$$

In this equation there is an Arrhenius like dependence of the viscosity on both, temperature and pressure: E_a is the activation energy of flow and β the viscosity-pressure coefficient. The parameter τ is the critical stress level at the transition to shear thinning ($\alpha = \eta_0/\tau$). Instead of the exponential dependence of the viscosity on temperature, the well known William-Landel-Ferry equation [42,43] can be also used.

$$\log a_T = \frac{-C_{1g}(T - T_g)}{C_{2g} + T - T_g} \quad (6)$$

The physical meaning of these parameters is linked to the theory of “free volume” [43] which is very relevant to the physical chemistry of polymers. The relative iso-free volume state $f_g = V_f/V = 0.025$, where V_f is the free volume and V the total volume, is the same for all polymers at the corresponding glass transition temperature T_g . For a typically flexible polymer like polyethylene the T_g is -120 °C, that corresponds to a relatively low thermal energy to reach $f_g = 0.025$. More energy is necessary, for instance, to reach this value in the case of a more rigid chain, like polystyrene, which gives rise to a higher glass transition temperature, $T_g = 100$ °C [12]. It has been observed [43] that the higher the glass transition temperature, the higher is the activation energy of flow.

In order to face industrial polymer processing, the coordinated work of polymer chemists who create polymers, and rheologists is crucial and constitutes one of the most interesting advances for both, polymers and rheology. Currently it is known how the basic features of polymers, such as chemical structure of monomer, average molecular weight, polydispersity of the molecular weight distribution and eventual presence of short and long branches, affect the parameters of equation (5). As an example of the effect of some polymer parameters on viscosity, in Fig. 3 [44] the combined effect of the molecular weight, M_w , and the molecular weight distribution broadness, expressed in terms of the polydispersity index M_w/M_n , is observed for two polystyrene samples: the effect of M_w is noticed on η_0 , while the influence of the polydispersity is reflected in the critical shear rate for the onset of non-Newtonian behaviour. For the benefit of polymer scientists and engineers the viscosity dependency on shear rate, closely linked to the processing conditions, can be controlled monitoring the polymerization conditions. The paradigmatic relationship *polymerization-rheology-processing* has been consolidated with the eruption of new polymerization methods,

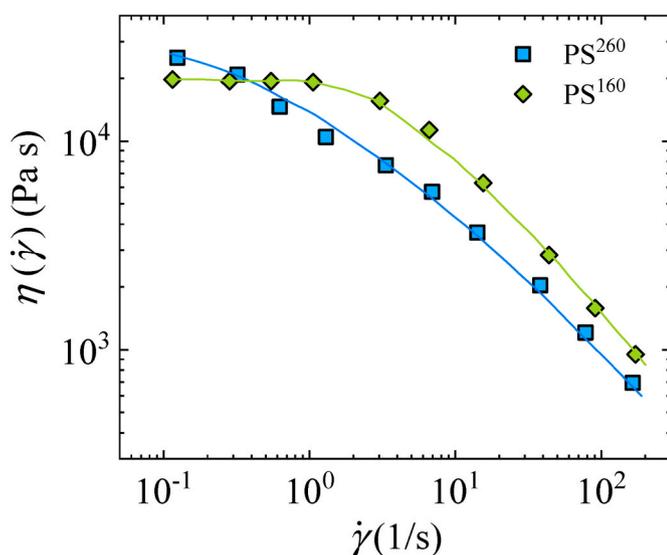


Fig. 3. Master curve of viscosity as a function of shear rate for two polystyrenes [44], PS²⁶⁰ $M_w = 260,000$ g/mol, $M_w/M_n \approx 2.4$, and PS¹⁶⁰ $M_w = 160,000$ g/mol, $M_w/M_n < 1.1$. The respective effects of molecular weight and molecular weight distribution broadness (polydispersity) are observed (see text). The lines are drawn to guide the eye.

like metallocene catalyst polymerization, atom transfer radical polymerization (ATRP) [45], reversible addition–fragmentation chain transfer (RAFT) [46], ring opening polymerization (ROP) [47], ring opening metathesis polymerization (ROMP), controlled anionic/cationic polymerization [48] and the progressive advance of polymers obtained from biological sources that has led to new polymers and complex topologies.

4. Newtonian viscosity and polymer chain entanglements: the imaginative tube and reptation model

The aforementioned molecular theories that explain the relation between molecular weight and intrinsic viscosity are based on the individuality of macromolecules, disregarding interactions between them. This is an acceptable reasoning, since obtaining $[\eta]$ implies measuring the viscosity of very diluted polymer solutions. However, in the case of concentrated solutions and polymer melts this individual response of polymer chains becomes questionable. Using the concept of temporary crosslinks or entanglements between chains [49–51], introduced to explain the elastic behaviour of polymer melts, Graessley [52] proposed a simple and intuitive model for the shear rate dependence of the viscosity. According to the model, during flow, polymer chains disentangle and entangle in a dynamics governed by the applied shear rate. At sufficiently low shear rates, that is to say below the critical shear rate, $\dot{\gamma}_c$, for the inception of shear thinning, the chains have enough time to disentangle and entangle again, because there is a low relative velocity between them. Therefore, the density of entanglements remains constant, giving rise to the Newtonian viscosity. However, at shear rates above $\dot{\gamma}_c$, the entanglements density begins to decrease, because the contact time between macromolecules is too short to bring about effective interactions. As shear rate is increased the entanglements density decreases proportionally, which is reflected in the viscosity reduction observed in Fig. 3.

Paradoxically, the discovery of the non-Newtonian viscosity of polymers led to increase the scientific interest on the Newtonian or shear independent viscosity, η_0 , of polymer melts. The correlation of the Newtonian viscosity with the length of the polymer chain raised scientific expectations, opening the route to the models for physical polymer chain interactions.

Experimental evidences of the correlation between Newtonian viscosity and molecular weight were reported more than 50 years ago, leading to results similar to those displayed in Fig. 4 taken from the paper of Berry and Fox [53]. It is worth noting that in a great majority of the reported Newtonian viscosity-molecular weight correlations the data refer to the weight average molecular weight M_w . Interestingly enough, it has been observed over the years that the double logarithmic η_0 - M_w plots of flexible polymers show the same trend, which is expressed by the equations:

$$\eta_0 = kM_w \quad (\text{for } M_w < M_c) \quad (7)$$

And

$$\eta_0 = KM_w^{3.4} \quad (\text{for } M_w > M_c) \quad (8)$$

where k and K are constants that reflect the effect of other factors than molecular weight, like temperature and the molecular structure of the monomer, and M_c is a critical molecular weight that depends on each polymer. It is assumed that for $M_w < M_c$ the chains are not sufficiently long to entangle. Actually, the Rouse model [54] was the first molecular theory predicting $\eta_0 = k M_w$ on the basis of no interaction between polymer chains.

Noticeable M_c differences are found for different polymers; for instance, between polyethylene, $M_c = 3500$ Da, and polystyrene, $M_c = 31,000$ Da [44], reflecting a greater easiness to entangle of the former. In 1986 Graessley and Edwards [55] found a correlation between M_c and the microstructure of the monomer, in terms of the bond average length,

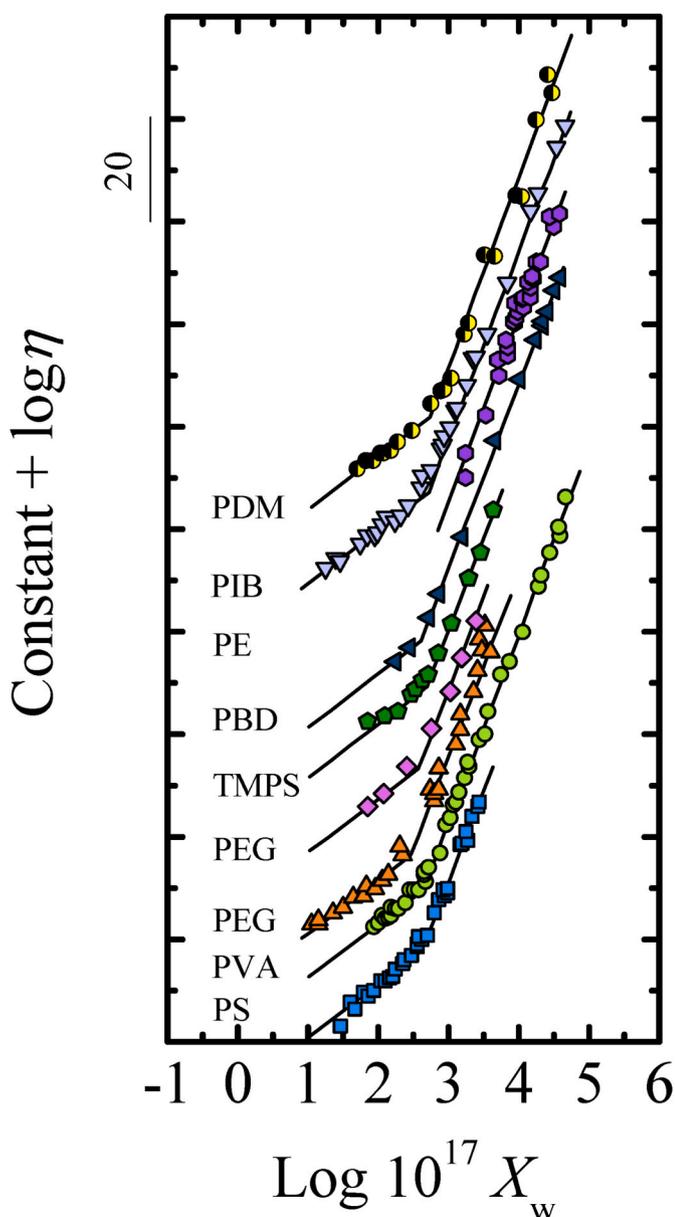


Fig. 4. Corrected viscosity, $\log \eta_s$, considering the constant friction factor ξ as a function of $\log X_w = \log [((s^2)_0/M)Z_w/v_2]$ for several linear polymers, being X_w a parameter that characterizes polymer coil dimension. The lines show a slope of 1.0 and 3.4. The curves have been shifted in the ordinate scale [53].

the monomer molecular weight and the characteristic ratio C_∞ which stands for the rigidity of the chain.

According to more exhaustive analysis of the relation between η_0 and M_w above M_c , carried out with a great number of polymers, the value 3.4 of the exponent should be considered as an approximation, since actually values between 3 and 4 have been found. In any case, the universality of the scaling law $\eta_0 = k M_w^a$, with $3 < a < 4$, is out of question, since it is followed by all investigated polymers, including biopolymers [56–58].

To highlight the relevance of this result we consider it from the polymer characterization perspective. The Newtonian viscosity becomes the physical parameter most susceptible to molecular weight changes, thus it is used as a control parameter in many processes like thermo-mechanical degradation during flow, post-polymerization processes, physical ageing and others [59]. For instance, considering a value for the power law of $a = 3.4$, a molecular weight change of only 5% is reflected in a η_0 change of near 20%.

The experimentally observed unique behaviour of polymer melts attracted the interest of relevant physicists. Advancing on the concept of physical chain interactions, Edwards [60,61] introduced the tube model for entangled state of monodisperse polymers ($M = M_n = M_w$) on the following hypothesis: the motion of a polymer chain is restricted by surrounding chains, so it is pictured to be confined to a tube-like region. The Nobel Prize for Physics (1991) Pierre Giles de Gennes envisaged that polymer linear chains are constrained to *reptate* in the tube [62] and defined a *reptation* or disengagement time, τ_d , as the time it takes the chain to diffuse out of the tube, which is proportional to N^3 being N the polymerization degree. This leads to the scaling law $\eta_0 = k M^3$, which is weaker than the experimentally found $\eta_0 = k M_w^a$ with $3 < a < 4$, being $a = 3.4$ the most often observed. This difference between experimental and reptation model exponent was considered to be due to tube length fluctuations [63]. Other hypothesis for this discrepancy are given, for instance, in the book of Doi and Edwards [64].

Initially the tube-reptation model was envisaged for linear polymer chains, but in the last decades it has been adapted to more complex architectures [65–69], like long chain branched, star polymers, cyclic polymers and physical polymer gels [70], increasing the scientific interest of this model for viscosity and diffusion related phenomena.

According to the analysis fulfilled by T.P. Lodge among the papers published in *Macromolecules* since its beginning [5], the theory of polymer chain reptation is among the six most relevant achievements in polymer science in the last 50 years, revealing the transcendence of this rheological contribution to polymers. Actually, the tube and reptation model includes the study of the diffusion of polymer chains, which is carried out experimentally by microscopy and neutron scattering. For instance, Nobel Prize winner for Physics 1997 Steven Chu provided experimental evidences of the key assumptions of tube and reptation model, using fluorescence microscopy to analyze the dynamics of fluorescently labelled molecules of DNA [71]. As an interesting corollary for the confluence of polymers and rheology, we remark that the mentioned Nobel laureate, Chu, also proved experimentally (through elongational flows) [72] the chain coil-stretch transition, which was predicted by another Nobel laureate, Pierre Giles de Gennes [73].

5. Viscoelasticity: polymers, the paradigm of viscoelastic materials

In non-polymeric liquids and solids respective deviations from viscous and elastic behaviour are negligible, because they are composed by small molecules which are only able to respond in a simple mode in a field of force. On the contrary, polymers are viscoelastic materials, owing to the capacity of the chains to offer mechanical responses at different length scales, from short-range to long-range, when a force is applied. When a mechanical force is applied to a polymer, then, local, segmental and complete motions of the chain can be induced, depending on the magnitude of the force, the temperature and the application time. This is schematically expressed in Fig. 5, taken from the aforementioned fundamental book of Ferry [43].

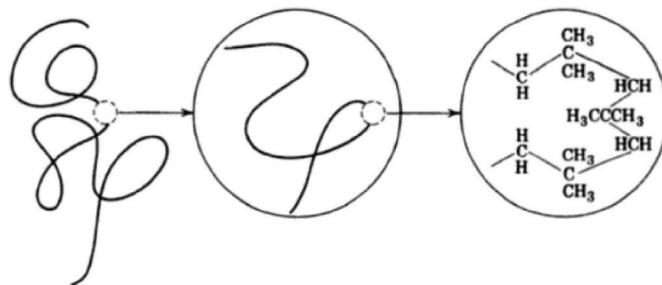


Fig. 5. Motions induced along time under stress are depicted for polyisobutylene in the scheme [43]: segmental, local and complete chain level (from right to left).

In addition to the dynamics of an individual polymer chain envisaged in this figure, entanglements among chains, which give rise to temporary elastic networks, create a unique and inherently viscoelastic framework.

Introducing the concept of viscoelasticity, Maxwell described gases as viscoelastic fluids with viscosity and elasticity and proposed the first equation for viscoelasticity [32,74], which can be adapted as:

$$\sigma_{21} + \frac{\eta_0}{G} \frac{d\sigma_{21}}{dt} = \eta_0 \dot{\gamma}_{21} \quad (9)$$

where σ_{21} is the shear stress, $\dot{\gamma}_{21}$ is the strain rate, η_0 is the Newtonian viscosity and G the Hookean elastic modulus.

A simple mathematical analysis of this equation shows that it is able to represent the two extremes: the purely viscous response in the steady state flow where $d\sigma/dt = 0$, or the purely elastic behaviour in a sudden change of stress for which $\sigma = 0$.

The term η_0/G is actually defined as the relaxation time λ and can be obtained experimentally by applying the Maxwell equation to a stress relaxation after a sudden strain implementation. The relaxation time $\lambda = \eta_0/G$ is used to evaluate the Deborah number, De , introduced by Reiner in the beginnings of the rheology, as was explained in 1964 [75]: $De = \text{time of relaxation}/\text{time of observation}$. This is a fundamental concept of rheology which situates solids and liquids under the same physical concept, since the greater is De , the more solid (elastic) is the material, whereas as De is smaller the material is more fluid. Ideally, for $De = \infty$ the material is purely elastic and for $De = 0$ is merely viscous.

Certainly, the idea of polymeric chains giving rise to a single relaxation time is in apparent contradiction with the polymer dynamics expressed in Fig. 5, and the Maxwell model should be extended with a certain number of relaxation times to fit experimental results of polymers. This leads to an integral form of the generalized linear viscoelastic model [32]:

$$\sigma(t) = \int_{-\infty}^t G(t-t') \frac{d\gamma(t')}{dt'} dt' \quad (10)$$

where $G(t-t')$ is the relaxation modulus which allows determining a continuous spectrum of relaxation times $H(\lambda)$.

The approach offered in preceding paragraphs is particularly helpful to introduce the concept of viscoelasticity to polymer chemists and engineers. But we have to remark that Coleman and Noll [76] showed their criticism on the lack of physical rigor of the springs and dashpot model. Instead, they assert that the integral form of the viscoelasticity (Eq. (10)) can be deduced from the Boltzmann [77,78] superposition principle, according to which the stress at any time can be described as a function of the history of the rate of change of strain.

The aforementioned excellent treatise on polymer dynamics written by Bird, Armstrong and Hassager [32], as well as the book of Tanner on engineering rheology [79] bring many examples of the application of this equation to different viscoelastic experiments.

For a historical survey of viscoelastic methods in polymers we turn to the following witty comment of Plazek [80]: “Whereas Leaderman was considered to be the King of Creep during the 40’ and 50’, Arthur V. Tobolsky was the King of Stress from the 40’ through the 60’ and John D. Ferry was the King of Dynamic Mechanical Properties from the 50’ through the 70’”. A summary of the physical parameters and viscoelastic functions that can be determined in linear viscoelastic measurements using shear and extensional deformation is shown in Table 1, taken from the paper of Dealy on rheological nomenclature [81].

All the mentioned methods have indeed contributed to the development of the study of the viscoelasticity of polymers, but we are compelled to recognize that dynamic or oscillatory tests leading to determine storage and loss moduli, G' and G'' , constitute the most relevant and enriching rheological procedure in polymer science.

Considering the variety of eventual mechanical responses of

Table 1
Nomenclature for linear viscoelasticity from Society of Rheology [81].

| Quantity | Symbol | S.I. units |
|--|------------------|------------------|
| Simple shear | | |
| Shear strain | γ | — |
| Shear modulus (modulus of rigidity) | G | Pa |
| Shear relaxation modulus | $G(t)$ | Pa |
| Shear compliance | J | Pa ⁻¹ |
| Shear creep compliance | $J(t)$ | Pa ⁻¹ |
| Equilibrium shear compliance | J_e | Pa ⁻¹ |
| Steady-state shear compliance | J_s^0 | Pa ⁻¹ |
| Complex viscosity | $\eta^*(\omega)$ | Pa s |
| Dynamic viscosity | $\eta'(\omega)$ | Pa s |
| Out-of-phase component of $\eta^*(\omega)$ | $\eta''(\omega)$ | Pa s |
| Complex shear modulus | $G^*(\omega)$ | Pa |
| Shear storage modulus | $G'(\omega)$ | Pa |
| Shear loss modulus | $G''(\omega)$ | Pa |
| Complex shear compliance | $J^*(\omega)$ | Pa ⁻¹ |
| Shear storage compliance | $J'(\omega)$ | Pa ⁻¹ |
| Shear loss compliance | $J''(\omega)$ | Pa ⁻¹ |
| Tensile extension | | |
| Strain (True strain) | ϵ | — |
| Young’s modulus | E | Pa |
| Tensile relaxation modulus | $E(t)$ | Pa |
| Tensile compliance | D | Pa ⁻¹ |
| Tensile creep compliance | $D(t)$ | Pa ⁻¹ |

polymers, and the effect of time and temperature in terms of the dimensional scales of these responses, the combined effect of both parameters was considered, bringing about one of the milestones of polymers viscoelasticity: The time-temperature superposition (TTS) method. The issue at stake was whether in polymer viscoelasticity, temperature change is equivalent to a shift of the logarithmic time scale. Pioneering works on the effect of temperature were carried out by Leaderman [82], analyzing creep results of plasticized polyvinyl chloride, and by Tobolsky and Andrews [83] studying relaxation and creep results of rubber gum. From these results a route was opened to achieve a reduced or viscoelastic master curve by shifting to superpose data obtained at different temperatures along a logarithmic time or frequency axis. This procedure was explained and popularized in the essential book of Ferry “Viscoelastic Properties of Polymers” [43]. An example of the application of TTS method to obtain a master curve which allows extending hugely the time scale of stress relaxation data is shown in Fig. 6, thanks to the use of a shift factor which is shown in the inset.

The application of TTS method is not obvious for all kind of polymers. Actually, it is only valid for “thermorheologically simple” polymers, as was coined by Schwarzl and Staverman [39]. TTS fails in complex and multiphasic polymeric systems, like immiscible polymer

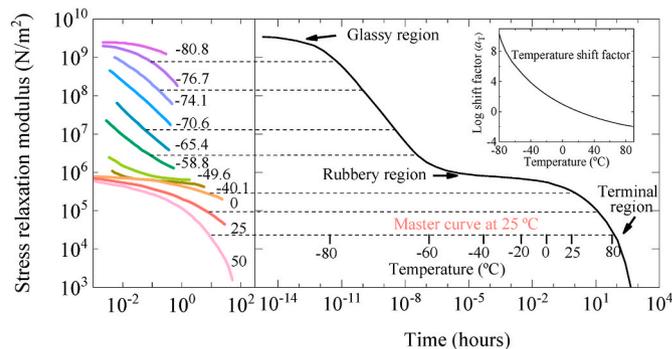


Fig. 6. In the left, stress relaxation modulus of an uncrosslinked polyisobutylene (PIB) sample measured at 11 different temperatures from -80 to 50 °C is shown. On the right the master curve obtained by shifting stress relaxation curves horizontally along the time axis at a reference temperature of 25 °C is shown [84]. The shift factor, a_T varies with temperature as shown in the inset at upper right. Stress and time units are depicted as defined in the reference.

blends and phase separated block copolymers and master curves cannot be accomplished.

Similar, to the procedure shown in Fig. 6, master curves can be obtained with creep and dynamic or oscillatory viscoelastic data. When a proper time span is reached three characteristic zones, which reflect the uniqueness of polymers as viscoelastic materials, are defined: glassy state, rubbery state and terminal or flow region. However, in the case of crosslinked polymers, like cured elastomers, only two regions are detected, since the terminal or flow region is suppressed due to the impossibility of polymer chains to diffuse. Instead of a continuous decrease of $G(t)$ as time increases (Fig. 6), an equilibrium modulus, G_e , is observed. The equilibrium modulus is proportional to the molecular weight M_x between two chemical cross-links:

$$G_e = \frac{\rho RT}{M_x} \quad (11)$$

where ρ is the density, R is the gas constant and T the temperature.

This equation, which denotes the entropic character of the elasticity of crosslinked polymers, is derived from the network theory of the rubber elasticity [85]. The practical relevance of this simple equation in every day polymer technology is huge, in particular for thermosets, which include relevant industrial fields like rubbers and adhesives.

The three regions depicted in Fig. 6 are interpreted on the basis of the various length scale dynamics of polymer chains, within the framework of the general concepts of the physics of polymers. The intermediate plateau, which corresponds to the so-called rubbery zone, is assumed to arise from polymer chain entanglements [43,86]. Consistently, not any other material but polymers show this plateau zone. The value of the stress relaxation modulus at the intermediate plateau zone is called the entanglement modulus, G_N^0 , and is concomitant to the equilibrium modulus, G_e , of crosslinked polymers. This parallelism between cross-links leading to a permanent network and entanglements which lead to temporary networks, has brought about a relationship between G_N^0 and the molecular weight between entanglements, M_e :

$$G_N^0 = \frac{\rho RT}{M_e} \quad (12)$$

The liaison between the entanglements involved in viscosity results and the viscoelastic pattern of Fig. 6, is understood assuming that for large times the terminal or flow zone is reached, as entanglements slippage occurs. Therefore, two characteristic molecular weights of entanglements are defined in polymer rheology: The aforementioned critical molecular weight, M_c , for the dependence of the Newtonian viscosity on molecular weight and the molecular weight between entanglements, M_e . As it is asserted in the book of Vinogradov and Malkin "Rheology of Polymers" [86], independent determinations of these molecular weights have shown that $M_c \approx M_e$. The physico-chemical considerations made about the effect of the microstructure of the monomer on the critical molecular weight, M_c , which marks the limit between the linear and the power law dependence of η_0 on M_w , are also valid for the molecular weight, M_e , obtained from the plateau modulus G_N^0 . A list of G_N^0 values with their corresponding M_e values for different polymer species is given, for instance, in the treatise of Graessley [44].

Besides its uniqueness and fundamental physical relevance, G_N^0 , which determines the density of entanglements $G_N^0 = \rho N_A / M_e$ (where ρ and N_A are respectively the density and the Avogadro's number), is also functionally relevant in the mechanical properties of polymers, as is remarked by Hans-Henning Kaustch [10] in his review commemorating 80 year of polymers. For instance, this author extols the results of Wu [87] demonstrating the close correlation between the entanglements density and crazing, precursor to fracture, of polymer solids. Also, the entanglement modulus is linked to the diffusion of macromolecules in polymer-polymer blends interfaces [88,89] and to tackiness or immediate adhesion of adhesives [90,91]. Chain interdiffusion is also crucial to reach a good welding in layer by layer additive manufacturing process

[92].

In the glassy state, which corresponds to very short times or low temperatures (see left side of Fig. 6), the motion of the chains is very local corresponding typically to a few monomers, as is depicted in Fig. 5. Increasing time or temperature, a transition from the glassy state to the rubbery state is observed. This transition is defined as the glass transition temperature, T_g , when the isochronal relaxation modulus is plotted as a function of temperature giving rise to $G(T)$ which is equivalent to $G(t)$. The transcendence of the glass transition temperature, which can be also determined by dilatometry and calorimetry, is enormous in polymer science and technology. Many physico-chemical studies of polymers are centered on the glass transition temperature, as can be noticed in any of the existing general books of polymers. Referring again to the paper of T. P. Lodge on 50 years of *Macromolecules* [5], we remark that the theory of the glass transition appears as the second most relevant challenge in polymer science, only after the theory of polymer crystallization. The theory of the free volume, which sustains the concept of T_g as an iso-free volume state, has been soundly developed in polymer science in consonance with rheological results. On the other hand, from the perspective of polymer engineering, it is worth recalling that the glass transition temperature marks to a great extent the processing conditions of amorphous polymers. Whereas in the case of semi-crystalline polymers, extrusion, injection and other processing methods should be, obviously, carried at temperatures above the melting temperature, T_m , for amorphous polymers the recommended temperature is $T_g + 100$ °C [36]. An interesting link between the glass transition temperature and the rheology of polymer processing is that, in general, the higher is T_g the bigger is the activation energy of flow, E_a [43], which stands for the effect of temperature on viscosity depicted in Equation (5). The implications of these results in the energy consumption during fabrication of plastic parts, a subject of increasing interest, are evident.

6. Dynamic viscoelastic measurements: A powerful tool to characterize polymers

The application of alternating stresses or strains for fundamental research in materials was initiated in the middle of the past century. In particular, the use of dynamic measurements as a tool for investigation in metals was reviewed by Zener in 1948 in his book "Elasticity and Anelasticity of Metals" [93]. In the same year, Nolle [94] described several methods for the determination of the dynamic viscoelastic properties of rubber solids and rubber solutions under very small sinusoidal strains. In 1952 dynamic viscoelastic results of polyisobutylene solids and liquids were reported by Markovitz et al. [95]. The works of Ferry [43], integrated already in the first edition (1960) of his aforementioned book, represent a fundamental step to consolidate the research on dynamic viscoelasticity of polymers. Also, the tremendous development of electronics and computing science in the last decades of XXth century, facilitating data acquisition, has strongly contributed to the spread of rheology, like in any other branch of science. We have to recall, for instance, that in contrast with the powerful calculation systems employed nowadays by contemporary rheometers, nomographs were used by Nolle in 1948 to calculate the real and imaginary parts of Young or tensile modulus, E' (storage) and E'' (viscous) of rubbers under variation of frequencies from 0.1 to 1 cycles/s and temperatures from -60 to 100 °C. The development of experimental methods to obtain the dynamic viscoelastic functions of polymers has led to the following preferential strain modes: Bending, bar torsion and simple extension, to obtain the tensile storage (elastic) modulus, E' , and the tensile loss (viscous) modulus, E'' , of polymer solids. Torsion in coaxial cylinders, cone-plate and plate-plate, to determine the shear storage (elastic) modulus, G' , and the shear loss (viscous) modulus, G'' . Oscillatory compression experiments to obtain the compression storage (elastic) modulus, K' , and the compression loss (viscous) modulus, K'' , are much less employed, although they are of great interest in the field of physical gels, for instance hydrogels for medical purposes [96,97].

As is explained in Ferry's book [43], the simplest way to introduce the physical basis of dynamic or oscillatory viscoelastic functions is to consider a sinusoidal shear strain γ :

$$\gamma = \gamma_0 \sin \omega t \quad (13)$$

where γ_0 is the strain amplitude and ω is the angular frequency of oscillation.

Provided that the viscoelastic behavior is linear, it is found that the shear stress σ also varies sinusoidally, although out of phase with strain:

$$\sigma = \sigma_0 \sin(\omega t + \delta) \quad (14)$$

where δ is the phase angle between the stress and the strain.

Using the generalized integral equation of the linear viscoelastic model (Eq. (10)) the storage or elastic shear modulus and the loss or viscous shear modulus are respectively defined:

$$G' = \frac{\sigma_0}{\gamma_0} \cos \delta \quad (15)$$

$$G'' = \frac{\sigma_0}{\gamma_0} \sin \delta \quad (16)$$

From these functions the loss tangent is determined:

$$\tan \delta = \frac{G''}{G'} \quad (17)$$

To ensure that the results are obtained in the linear regime, i.e. same respective moduli independently of the applied stress or strain amplitude, low amplitudes are requested. This has led to coin the term Small Amplitude Oscillatory Shear (SAOS) measurements, standing for linear dynamic tests, whereas the name LAOS (Large Amplitude Oscillatory Shear) is used for non-linear measurements.

Probably the most outstanding results of the dynamic viscoelastic behavior of polymers are those which display the respective master curves of storage and loss moduli and $\tan \delta$ as a function of frequency, in measurements carried out at different temperatures. An example is shown in Fig. 7 [98]. The evident resemblance of the $G'(\omega)$ function with the relaxation modulus, $G(t)$, considering the inverse proportion between frequency and time, has led to many researchers to use this type of plots to define the three viscoelastic zones. Compared to the information that can be reached from $G(t)$ plots, simultaneous plots of $G'(\omega)$ and $G''(\omega)$ allow understanding the viscoelastic character of each viscoelastic

zone in a more intuitive way. The chain dynamics in the terminal zone (low frequencies or large times/temperatures) is characterized by the motion of the polymer chain as a whole (Fig. 5), which implies more energy dissipation than storage. This is reflected in Fig. 7 by $G'' > G'$, which also leads to loss tangent values of $\tan \delta > 1$. The rubbery zone, observed at intermediate times in $G(t)$ measurements and characterized by the entanglements modulus, G_N^0 , is noticed in Fig. 7 by an intermediate frequency interval at which the elastic modulus is practically independent of frequency and $G' > G''$, with a consequent $\tan \delta$ minimum. This denotes the elastic character of the entanglements network, whose modulus is determined typically by the constant value of G' at the intermediate frequency interval or the value of G' at the G'' minimum. Other procedures to obtain G_N^0 from dynamic viscoelastic measurements have been proposed in literature [99], showing that SAOS measurements allow determining G_N^0 in an easier and more accurate way than stress relaxation experiments.

The ease of use and the relative low price, as compared to other polymer characterization techniques, has led to a great popularity of SAOS tests to investigate the terminal and rubbery zones of polymer solutions and melts. The application of the general linear viscoelastic model [32] offers the possibility of linking low frequency G' and G'' results to steady state flow parameters, like the Newtonian viscosity, η_0 , and the steady state or recoverable compliance, J_e^0 , which can be typically obtained from creep and recovery tests and represents the elasticity of a polymer liquid during flow.

$$\eta_0 = \lim_{\omega \rightarrow 0} G'' / \omega \quad (18)$$

$$J_e^0 = \lim_{\omega \rightarrow 0} G' / G''^2 \quad (19)$$

These results imply that according to the linear viscoelastic model G' should be proportional to ω^2 and G'' proportional to ω as frequency is reduced.

Since the Newtonian viscosity depends on the molecular weight following a power law equation (see above) and J_e^0 increases with the molecular weight for monodisperse polymers [44], as well as with the broadness of the molecular weight distribution and long chain branching [100–102], the terminal zone becomes very sensitive to any molecular change in polymer chains architecture. Taking advance of this feature, approaches on the correlation between SAOS results in the terminal zone and molecular weight distribution have been made in literature [100,103] correlating each time from the spectrum of relaxation times $H(\lambda)$ to a certain molecular weight. Numerical methods to determine relaxation spectra from storage and loss moduli are available in the classical book of Tschoegl "The Phenomenological Theory of Linear Viscoelastic Behavior" [104] and in the more recent book of Cho "Viscoelasticity of Polymers. Theory and Numerical Algorithms" [105], among others. For instance, the following equation, proposed by Tschoegl, can be used to obtain the relaxation spectra [43]:

$$H(\tau) = \frac{dG'}{d \ln \omega} + \frac{1}{2} \frac{d^2 G'}{d(\ln \omega)^2} \Big|_{\omega = \sqrt{2\tau}} \quad (20)$$

However, the procedure for obtaining relaxation spectra from the appropriate results (creep data bring about discrete or continuous retardation spectra, whereas stress relaxation and oscillation data give relaxation spectra) requires advanced mathematical methods to avoid experimental errors, as those developed by Honerkamp and Weese [106, 107] included in the software currently available in some commercial rheometers.

Actually, besides polymer architecture, any factor which affects mobility of the chain as a whole, like microphase separation in a polymer blend or a block copolymer, alters significantly both, the elastic and loss moduli, in the terminal zone, reducing considerably the respective dependences $G' \propto \omega^2$ and $G'' \propto \omega$. An example of this is given in Fig. 8 taken from the paper of Bates [108] which shows the rheological

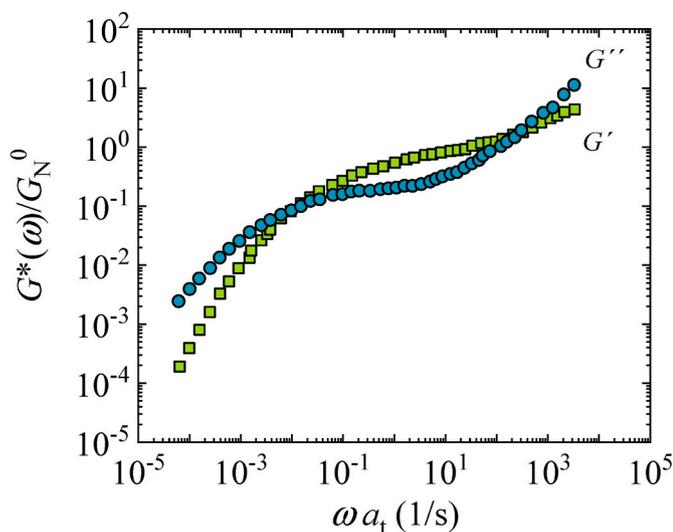


Fig. 7. Master curve of G' and G'' for polystyrene at a reference temperature equal to 150 °C. The moduli were actually measured in the frequency range 10^{-3} to 10^2 1/s at different temperatures and then superposition method was applied [98].

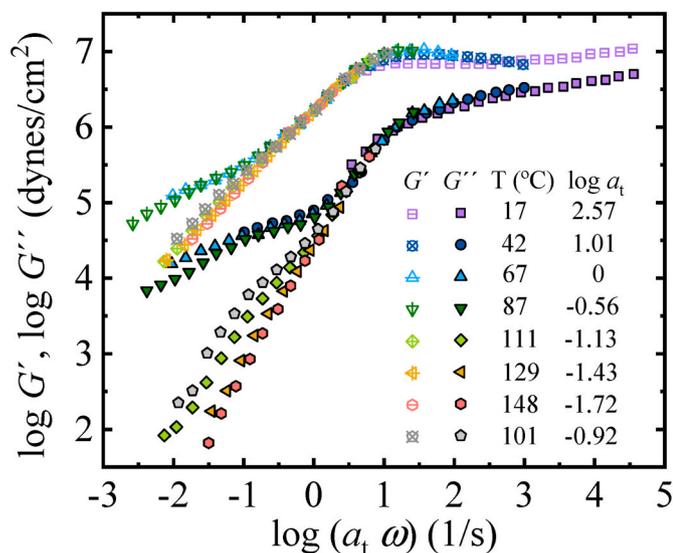


Fig. 8. Reduced elastic and loss moduli for 1,4-polybutadiene-1,2-polybutadiene diblock copolymer. The loss moduli data has been shifted 1 order of magnitude in the vertical axis [108]. At a temperature of 111 °C and above the sample is in a disordered state and a behavior typical of homopolymers is observed. However, at 87 °C and below the response corresponds to that of a microphase separated copolymer. Moduli units are depicted as defined in the reference.

behavior in the ordered state (microphase self-assembly) and in the disordered state above a certain critical temperature.

On the other hand, in the context of what we can call practical routine rheology, the analysis of the terminal zone of industrial polymer products is used for quality control; typically, a G' and G'' versus frequency footprint of each sample is obtained through SAOS tests and compared to the model results of the sample taken as a reference.

The most extended dynamic viscoelastic tests in polymer science are the ones performed increasing the temperature from the glassy state, at a constant strain amplitude and frequency (isochronal). The most usual measurements are performed in bending mode at a frequency of 1 Hz to determine E' , E'' and $\tan \delta$ as a function of temperature. The purpose of the so-called Dynamic Mechanical Analysis or DMA tests is to determine the glass transition temperature or glass transition temperatures of any polymer system. There is, therefore, a rivalry between this rheological technique and differential scanning calorimetry, DSC, which is often used to obtain T_g . Indeed, the advantage of the later technique compared to DMA lies more on its great capacity for the analysis of the crystalline phase. But, avoiding any passionate favoritism for rheology, it should be recognized that DMA is more accurate for determining glass transitions in complex polymer systems, such as semicrystalline and crosslinked polymers, polymer blends, random and block copolymers and polymer composites, among others.

The sensibility of dynamic viscoelastic measurements to detect the transition from the glass to the rubbery state, is observed in Fig. 7 which shows typical G' and G'' results as a function of frequency for a homopolymer: In the transition zone a maximum in G'' , which gives rise to a $\tan \delta$ maximum (not shown), is noticed. When instead of frequency scans, temperature scans are performed, like in DMA, the results are the opposite in terms of x axis, since on the basis of time-temperature equivalence temperature is equivalent to the inverse of frequency. Then, the glass transition temperature, T_g , is determined as the temperature at which the maximum on E'' or $\tan \delta$ takes place.

In the first edition of the Ferry's book (1960), as well as in the very useful book for beginner rheologists of Murayama "Dynamic Mechanical Analysis of Polymeric Materials" [109] mentions to papers on T_g determined by DMA, published already in the sixties of the past century,

are included [110,111]. So far, the number of papers referring to this kind of measurements, under the name of "Dynamic Mechanical Analysis" (DMA) or "Dynamic Mechanical Thermal Analysis" (DMTA), is substantial. And, in view of the large number of equipment purchased by industrial polymer companies, a sizable quantity of temperature scans of $\gamma = \gamma_0 \sin \omega t$ are carried by polymer engineers every day. It is worth mentioning the extraordinary information given by Bell and Murayama 50 years ago [111] in their paper about DMA results of nylons and polyethylene terephthalate. As an example, Fig. 9 taken from Murayama's work, shows the effect of the degree of crystallization on the glass transition temperature (defined as α transition) and sub-glass transition temperatures of a Nylon 6.

The observed capacity of this rheological technique to detect local motions, like side-motions and crankshaft rotation, besides segmental motions which stand for T_g , is absolutely remarkable. In polymer science DMA results are often combined with other results obtained by dielectric and NMR methods to study the effect of microstructure on dynamics of polymer chains.

Considering the physical basis of the dynamic viscoelastic experiments, tests involving strain amplitude scans are also relevant. First, because they mark the way to determine the linear viscoelastic region, at which the viscoelastic functions are independent of the applied strain or stress amplitude. Also, studies of the effect of strain amplitude outside the linear region are particularly interesting for polymer systems which contain physical interactions, like interactions among crystallites or secondary bonds, as is the case of polymers prone to interchain hydrogen bonds. This is the case of thermoreversible polymer gels whose transition from weak solids to liquids depends on temperature and the applied stress. It is generally assumed that the vanishing of the gel network takes place when G'' overcomes G' in an isothermal and isochronal strain amplitude scan. However, the prominent paper of Winter and Chambon [112] (1879 citations until July 2022), which proposes a sound viscoelastic criterion for the gel point of crosslinked polymers, discloses the effect of frequency on $G'' > G'$ rule.

Advanced electronics and computational techniques applied to current rheometers has led to a progressive popularization of Large Amplitude Shear Oscillatory, LAOS, measurements in polymers rheology. In the last ten years (2013–2022) 230 papers on LAOS have been published. But, despite the increasing proportion of LAOS papers with respect to SAOS papers, the new outcomes obtained by these

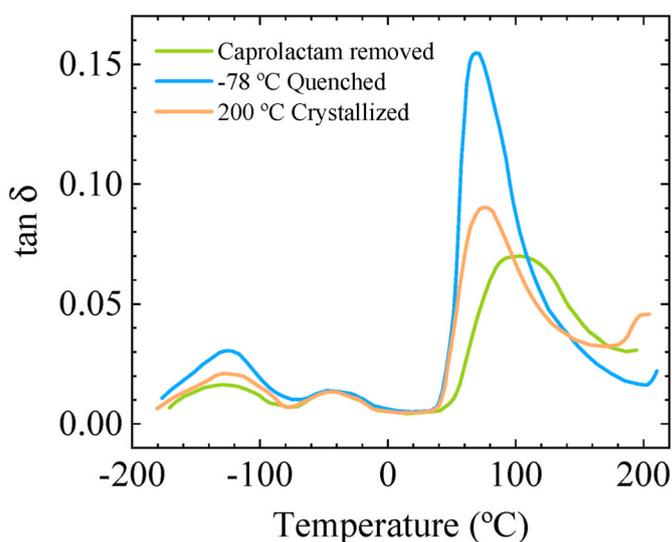


Fig. 9. $\tan \delta$ vs temperature for Nylon 6 obtained employing different procedures at 100 Hz [109]. The effect of the degree of crystallization is noted in the α transition, close to 100 °C: the highest peak corresponds to the least crystalline sample. Transitions at lower temperatures, called γ (lowest temperature) and β , correspond to local motions of the chains.

techniques are sparse, as despite being mathematically robust, the interpretation of the measurements is still an active area of research. The LAOS provides an experimental procedure to reliably reproduce non-linear flow conditions by independently controlling the strain amplitude and oscillatory frequency. The most common analysis used is the Fourier transform of the time-domain stress responses to determine the spectrum of the Fourier harmonics [113]. Other Fourier-based frameworks include stress decomposition [114] and the Chebyshev description of the stress decomposition parameters [115]. These analyses provide a macroscopic response averaged over one cycle of strain, so structural rearrangements that occur on time scales shorter than a full period of oscillation (yielding, crystallization, plastic events ...) require a different approach [116–118]. For these cases, as an alternative, the use of a physical process sequence (SPP) framework, which determines the instantaneous moduli of the elastic and viscous properties, G'_t and G''_t , has been proposed [119,120].

Among the most interesting contributions of the aforementioned work, we can highlight the identification of new nonlinear parameters in the LAOS regime that will help to better understand the rheological response of polymers as a function of their structural properties. A clear example is the Q nonlinear parameter, based on the intensity of the third harmonic, which has proven to be very sensitive to molecular architecture, e.g. branching of long chains, even at very low branching contents. Also noteworthy is the contribution of the analysis of Lissajous curves, whose quantification in terms of intra- and inter-cycle non-linear parameters (stiffness/strain softening, shear thinning/adhesion), is useful for determining the characteristic rheological fingerprints of soft materials, biopolymers and hydrogels.

In general terms the study of nonlinear viscoelasticity using the LAOS technique focuses on studies of topology, morphology, concentration in a variety of polymeric systems, such as melts and polymer solutions

[121,122], nanocomposites [123], immiscible blends [124–126], suspensions [127], and hydrogels [128,129].

In last decades the kinetics of important polymer processes, such as crystallization, crosslinking and physical gelation, are typically monitored through the analysis of the time evolution of dynamic viscoelastic functions under constant strain amplitude and frequency. The procedure envisaged by Winter and Chambon [112], that can be used for crosslinking and physical gelation, implies actual frequency scans at different times of conversion. In the case of crystallization kinetics, SAOS experiments have been used to monitor the isothermal crystallization of polymers. During this process polymer melts evolve to form complex solid structures, which results in an increase of several order of magnitudes of the storage modulus [130–134].

Fig. 10 displays a scheme of the applications of the dynamic viscoelastic measurements for the characterization and processing of polymer systems.

7. Elastic polymer liquids

Oldroyd's paper entitled "On the formulation of rheological equations of state" [135], which discusses the invariant forms of rheological equations of state suitable for application to all conditions of strain and stresses, is a milestone in the theory of rheology. Suffice it to say that it is one of the most quoted paper in rheology, with 1439 citations until July 2022, which has aided to spread the name of this branch of science to fluid mechanics and mathematics. As remarked by Oldroyd himself, one of the equations derived from the *converted differentiation with respect to time* allows predicting specifically that "If the liquid, initially in steady motion constrained to be two-dimensional, were suddenly given a free horizontal surface, the free surface of material A would begin to rise near the outer cylinder and fall near the inner cylinder, but the material B

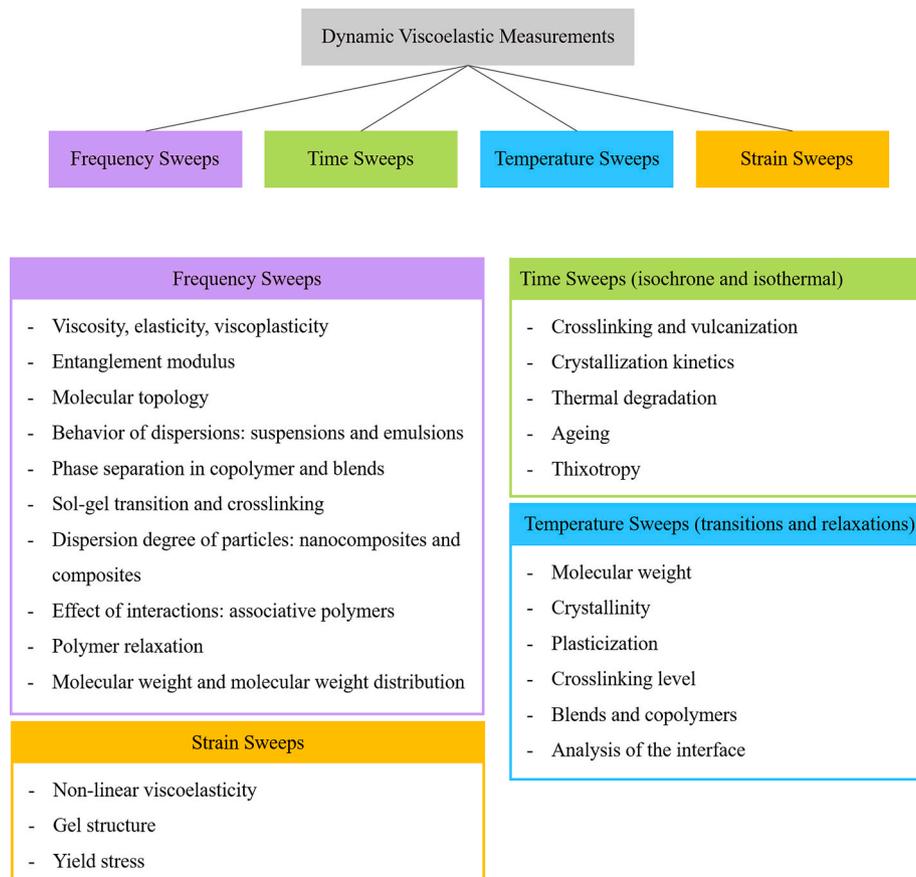


Fig. 10. Scheme of the applications of the dynamic viscoelastic measurements for the characterization and processing of polymer systems.

would show the opposite effect, tending to ‘climb up’ the inner cylinder”.

Certainly, this theoretical assessment was experimentally discovered by Weissenberg three years before [136]. The so-called Weissenberg or rod-climbing effect, responds to the eventual climbing of the liquid in the rod that rotates creating a shear flow. This spectacular and unexpected phenomenon is shown for a polyacrylamide solution in glycerin and a polyisobutylene/polybutene mixture and in respective photographs of the beautiful book “Rheological Phenomena in Focus” [137].

When subjected to a shear flow non-Newtonian fluids develop not only a shear stress σ_{21} , which corresponds to component 21 of the stress tensor, but also normal stresses σ_{11} , σ_{22} , σ_{33} which correspond to the diagonal components of the stress tensor. Based on this assumption, the rheological functions employed to characterize a shear flow of a polymer liquid are:

$$\text{Viscosity } \eta = \frac{\sigma}{\dot{\gamma}} \quad (21)$$

$$N_1 \text{ First Normal Stress Difference } N_1 = \sigma_{11} - \sigma_{22} \quad (22)$$

$$N_2 \text{ Second Normal Stress Difference } N_2 = \sigma_{22} - \sigma_{33} \quad (23)$$

The Weissenberg effect is the result of the first normal stress difference, which, as a corollary, can be measured in a cone-plate flow from the vertical force, F , which tends to separate both elements of the geometry:

$$N_1 = \sigma_{11} - \sigma_{22} = \frac{2F}{\pi R^2} \quad (24)$$

The first normal stress difference is of great importance for polymer rheology, although less than viscosity. On its part, the second normal stress difference $N_2 = \sigma_{22} - \sigma_{33}$, which is usually considerably lower than N_1 , is not very relevant for polymer scientist and engineers. Based on the results of the book “Dynamics of Polymeric Liquids” [32] it can be demonstrated that, in the linear regime, $N_1 = 2 J_e^0 (\sigma_{21})^2$, where J_e^0 is the steady state or recoverable compliance that is obtained from creep and recovery tests. Taking into account the aforementioned dynamic results on linear viscoelasticity a correlation can be established between dynamic viscoelastic, creep and N_1 data, which allows studying the viscoelastic response of polymer liquids.

The term “elastic liquid” became rather popular thanks to two paradigmatic rheology books: Reiner’s “Deformation, strain and flow. An elementary introduction to Rheology” [138] and A.S. Lodge’s “Elastic Liquids” [139]. In the latter the expression “rubber-like liquids” appears as a counterpart to “rubber-like solids”. Besides of the Weissenberg effect, other elastic effects have been reported, such as tubeless siphon and elastic recoil, which are shown in photographs in the books of Bird et al. [32] and Boger and Walters [137]. The viscoelastic behavior of polymer liquids in flow deserved this amusing poem of Bird [32] which refers to the striking features of polymer liquids:

A fluid that’s macromolecular
Is really quite weird-in particular-
The abnormal stresses
The fluid possesses
Give rise to effects quite spectacular

But the most important elastic effect derived from first normal stress difference is the so-called extrudate swell, also called erroneously die swell, which reflects the increase of the diameter of a fluid, with respect to the diameter of the capillary, when it leaves the capillary die. The value of the extrudate swell is given by d_e/D , where d_e and D are, respectively, the diameters of the extrudate and the die. An interesting debate on the origin of the first report of extrudate swell is posed in the book of Tanner and Walters [9]. Extrudate swell is also known as Barus effect (913,000 results in Google until July 2022) or Merrington effect

(146,000 results). Actually, the first reported picture of this phenomenon was presented by Merrington in Nature [140] with a rubber solution. An example of this phenomenon can be seen in Fig. 11 for a hydrolyzed polyacrylamide solution [141]. Merrington refers to extrudate swell as an elastic capillary ends effect and concludes that d_e/D is a measure of the elastic property of the material that increases with the applied shear stress. The popularization of the extrusion capillary rheometers since the 70s of the last century has led to an extensive observation of extrudate swell for polymer thermoplastics, which typically give rise to values of $d_e/D > 1.5$. Needless to say, the relevance of extrudate swell in polymer processing is extraordinary, because the real dimensions of any object obtained in a method involving extrusion, are at stake. This issue deserved attention in books that highlighted the importance of viscoelastic flow in polymer processing in the last third part of XX century [34,36,37,79].

To our knowledge, the first attempt to link extrudate swell to elasticity is owed to Spencer and Dillon [142] who assumed a linear relation between the strain related to d_e/D and the shear elastic modulus G' . Several equations were proposed in the first 70s of the last century [143, 144] relating the first normal stress difference, N_1 , to extrudate swell d_e/D . According to our own experience we can say that Tanner’s equation [145,146] has been quite widely used in polymers industry, being $\left(\frac{N_1}{2\sigma}\right)_w$ the stress ratio at the capillary wall:

$$\frac{d_e}{D} = 1 + \frac{1}{2} \left(\frac{N_1}{2\sigma} \right)_w^{1/6} + 0.13 \quad (25)$$

Obtaining the melt elasticity of polymers in terms of N_1 , which can be performed directly from cone-plate tests or indirectly by creep experiments, and SAOS measurements, is not only an academic task but a crucial factor for a sound analysis of polymer processing. The usefulness of this and similar equations to link the job of polymer chemists to those of rheologists is large. In that respect, correlations between shear compliance, J_e^0 , (related to the first normal difference by $N_1 = 2 J_e^0$



Fig. 11. Swelling of a partially hydrolyzed polyacrylamide solution in water and NaCl (20 g/L) when emerges from the capillary. Polymer concentration 6000 ppm at a flow rate of $20 \text{ mm}^3/\text{s}$ ($\dot{\gamma}_w = 1200 \text{ 1/s}$). The outer diameter of the die is 0.89 mm [141].

$(\sigma_{21})^2$) and molecular weight distribution were established more than sixty years ago [147]:

$$J_e^0 = \frac{2}{5} \rho RT \frac{M_z M_{z+1}}{M_w} \quad (26)$$

where M_z and M_{z+1} are, respectively, the third and the fourth moments of the molecular weight distribution.

Among other purposes, controlling and tailoring the molecular distribution is a fundamental key to work in the framework of the well established relationship *structure-rheology-processing*.

Melt elasticity and in particular normal stresses in unidirectional shear flows can give rise to an important technological consequence: The appearance of flow instabilities in capillary dies and slits, which bring about extrudate distortions. Needless to say, this is enormously detrimental to polymer extrusion, which is the processing technique employed with more than 50 % of all polymers.

Probably the first allusions to extrudate distortions in capillary flows were made in late 40' of the last century. Spencer and Dillon [148] found that above a critical stress at the capillary wall the extruded filament buckles into a spiral. By his part Reiner [149] referred to this phenomenon posing the hypothesis of a fracture of the viscoelastic liquids when the applied stress reaches a limit which corresponds to the strength of the liquid. The first photograph of evident irregularities in the surface of extrudates corresponds to the case of a polystyrene sample extruded at 200 °C, presented in the paper of Spencer and Dillon [148]; this is shown in Fig. 12. The authors observe that above a critical stress at the wall, the extruded filament buckles into a spiral. Similar and even grosser irregularities were reported by Tordella [150] for polymethylmethacrylate at 170 °C and were explained considering Reiner's hypothesis of rupture taking place when stress reaches the limit of the strength of the melt. In the contribution of Tordella to the book edited by Eirich "Rheology Theory and Applications" [151], a vast set of photographs of polymer

melt instabilities is offered. These mentioned extrudate irregularities correspond to what we currently call "melt fracture", in the framework of the classification of M. Denn [152]: a) Stable (smooth surface) b) Sharkskin c) Slip-stick (alternating smooth and sharkskin) d) Wavy and e) Melt fracture.

The practically ignored (only 26 citations) paper of Benbow et al., published in Nature in 1961 [153], clarifies synthetically fundamental concepts on shear flow instabilities of polymers. The phenomenon of "shark skin" is defined as consisting of ridges at a small separation as compared to the diameter of the extrudate. On the other hand, as explained by the authors, at larger shear stresses the extrudate may take a helicoidal or irregular, distorted, form, which is attributed to a "melt fracture". The hypothesis of these instabilities being associated with stick-slip phenomenon at the die wall was probably posed for the first time in the referred Nature's paper. Along the years it has prevailed the thought of shark-skin being associated to stick-slip, whereas melt fracture was rather related to the flow at the entrance of the die, where both shear and elongational flows take place (see next section). In particular, strain inhomogeneities at the converging flow at the entry die above a critical shear stress, would cause recovery inhomogeneities and extrudate distortion because of non-uniform swelling. The latter consideration on melt fracture was contemplated by Bagley and Schreiber in a paper [154], also published in 1961, which had more repercussion than that of Benbow et al. Accepting stick-slip is implied in capillary flow instabilities, Wang et al. [155] consider also the elongational stresses generated by the diverging flow at the die exit. On these bases they propose a sound model which correlates the onset of sharkskin with an entanglement-disentanglement state; on their own words: "Sharkskin formation arises from a stress-induced *molecular instability* that is related to the unsteady nature of the overall chain conformation in the high stress die exit region where the adsorbed chains oscillate between the entangled and disentangled states". As an example of the controversial origin of sharkskin instability, we have to mention that the same author, Wang [156], dismissed later that sharkskin is a slip-stick phenomenon. Also, in 2002 direct velocimetry results obtained during sharkskin, lead Migler et al. [157] to disdain the hypothesis of sharkskin being linked to stick-slip. The relevance of wall slip in the context of polymer shear flow instabilities is discussed in depth in the review paper of Denn [152], and in the book edited by Hatzikiriakos and Migler Polymer processing instabilities: control and understanding [158].

In comparison to the phenomenon of sharkskin, which is rather observed in polyethylenes, melt fracture is more relevant in polymer processing, because it affects to practically all thermoplastics polymers, including biopolymers [159–162].

Critical stress values for the onset of instabilities in polyethylenes were discussed by Hatzikiriakos and Dealy [163]; as a general rule it is assumed that shear stresses above around 2×10^5 Pa give rise to the so-called *sharkskin*. Earlier, Vlachopoulos and Alam [164] reported critical shear stress values for the onset of melt fracture of linear and branched polyethylenes, as well as polystyrene. From the work of these authors the following norm, which is still acceptable, is deduced: The critical shear stress for melt fracture decreases as both, M_w and polydispersity of the molecular weight distribution, increase.

Knowing this critical value for any of the studied thermoplastic is a key for polymer processing, since it marks the shear rate maximum to obtain smooth (instabilities free) extrudates and so predict industrial extrusion adequate conditions. Certainly, reducing viscosity by rising extrusion temperature allows increasing the shear rate window, but energy consumption perspective should be always kept in mind. Today different strategies are at stake to avoid flow instabilities which hamper capillary and slit extrusion processes. The most widespread method is based on the alteration of the flow velocity profile in the capillary, creating a flat profile which avoids elastic energy storage. In this way, capillaries with slippery surfaces allow eliminating extrudate distortion, as is explained in the review of Piau et al. [165]. Also, fluoropolymer agents added to the polymer migrate from the matrix, creating a

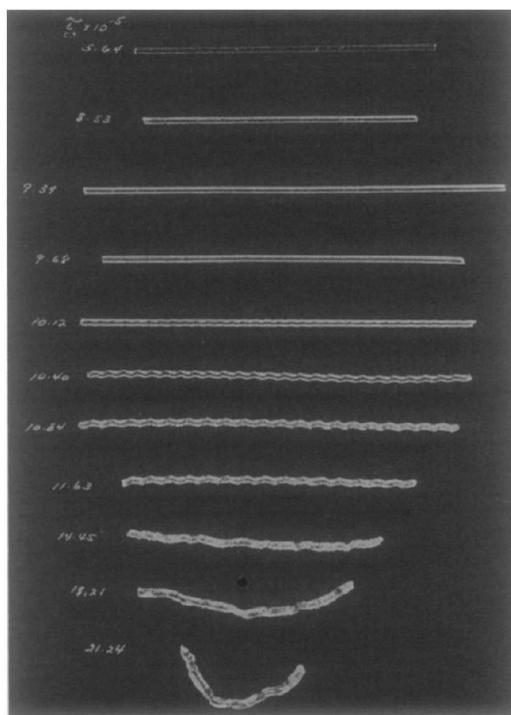


Fig. 12. Extrudate irregularities for polystyrene obtained applying several shearing stresses at 200 °C. The wall shearing stresses from top to bottom are: 5.64, 8.53, 9.39, 9.68, 10.12, 10.40, 10.84, 11.63, 14.45, 18.21, 21.24 $\times 10^5$ dyne/cm² [148]. Note that the unit for stress and the decimal values are those given in the reference.

fluoropolymer-coated surface which favors slippage [152]. Another strategy is based on a molecular modification of the polymer, reducing its M_w and polydispersity index. But, we have to consider the likely impoverishment of the mechanical properties of the sample that this polymer chain alteration can cause. On the other hand, an interesting approach, based on the usefulness of polymer blending, is reported in a paper of the group of J. Martínez-Salazar: Sharkskin of metallocene-catalyzed polyethylenes is eliminated by the addition of small amounts of a high molecular weight sample [166].

The role played by rheology to help avoiding the industrial problem of polymer extrusion instabilities has led to join together the efforts of academia and industry rheologists. This is the case of the project entitled “Postpone polymer processing instabilities (3PI)” financed by the European Commission, which gathered several universities and the most important European polyolefin producing companies.

8. Shearfree flows

An easily understandable mathematical treatment of flows that do not involve shear, i.e. shearfree flows, is given in the book of Bird et al. [32] where the following equations of the velocity field are presented:

$$v_x = \frac{-1}{2}\dot{\epsilon}(1+b)x \quad (27)$$

$$v_y = \frac{-1}{2}\dot{\epsilon}(1-b)y \quad (28)$$

$$v_z = +\dot{\epsilon}z \quad (29)$$

Particular choices of b parameter bring about the following definitions:

Elongational flow: ($b = 0, \dot{\epsilon} > 0$)

Biaxial stretching flow: ($b = 0, \dot{\epsilon} < 0$)

Planar elongational flow: ($b = 1$)

Elongational flow, which has been more studied than the other flows, is also called *uniaxial extensional flow* (see for instance Appendix 1 of the book of Tanner and Walters [9]) or *tensile extensional flow* [81]. The elongational viscosity is defined as $\eta_E = \sigma_E/\dot{\epsilon}$ where σ_E stands for the tensile stress.

A majority of the papers on the rheology of liquid polymers deals with shear flow and in particular with steady state shear flow, called also viscometric flow [9,32]. Notwithstanding, shearfree flows are especially relevant because these flows are involved in very important industrial polymer processing methods, such as fiber spinning, calendaring and additive manufacturing, which require elongational flow, and film blowing, blow molding and foaming in which planar elongational flow is involved. For polymer solutions, the relatively modern technique of electrospinning [167], used in academic laboratories, rather than in industry, to produce very thin fibers, implies an elongational flow. The rheological analysis is basically centered on the critical concentration for entanglements of the polymer solution that ensure jet stability [168].

The studies carried out by Petrie on extensional flows and in particular his book “Elongational Flows” [169] and his review [170] written on the occasion of 100 years of the first paper on the extensional viscosity published by Trouton in 1906 [171], constitute a good basis for a general understanding of extensional flows.

Referring particularly to extensional viscosity of polymer melts it is mandatory to mention the experimental contribution of Meissner [172–174]. Current results on extensional viscosity are based in two devices envisaged by this author decades ago: The tensile tester for polymer melts and the extensional rheometer for constant strain rate. The first instrument consists in an extruder with a capillary die and a drawdown device (a pair of gears) which stretches the polymer melt: the measured parameters are the drawdown force and the velocity of

rotation of the gears. The design of the original extensional rheometer for constant strain rate is based in two rotational clamps located at a certain distance; the sample is a rod floating in silicone which is stretched by the clamps.

Home-made “tensile testers” (according to Meissner’s nomenclature) for polymer melts have been used by polymer engineers to determine two essential parameters of fiber spinning: the melt strength or maximum force before filament breaking and the drawdown ratio, V_1/V_0 where V_1 is the velocity of rotating clamps and V_0 the velocity of the polymer at the exit of the die. In general terms, both parameters define what is called the spinnability of a polymer, allowing to select adequate samples for industrial fiber spinning process. Han’s book [175] offers a nice approach to the subject including some remarkable results, obtained almost fifty years ago. In any case, issues that arise from the proper concept of spinnability have been discussed by Petrie [170].

Currently, commercial rheometers based on Meissner’s tensile tester have spread the study of elongational flows. The most popular is the Goettfert Rheotens™ device, launched in 1976, which has been widely used for the analysis of the spinnability of polyolefin fibers. The ideal polymer for melt spinning should have moderate melt strength and the highest possible drawdown ratio, V_1/V_0 , to obtain the finest fibers. The effect of molecular parameters, such as molecular weight distribution and branching, on melt strength and V_1/V_0 has been investigated [160, 176] to fix the targets of polymerization and avoid false trial-and-error strategies. This has resulted in an important advance of fibers industry which represents 15 % [177] of the whole polymer industry.

The rheological parameters melt strength and drawdown ratio, obtained in laboratory experiments with Goettfert Rheotens™ and similar devices, have shown also to be useful to anticipate the adequacy of polymer samples for film-blowing processes. The difference of what is sought for fiber spinning (a high drawdown ratio), in this case large melt strengths are desirable to avoid breaking the polymer bubble when it is stretched towards the nip rolls [178,179]. Differing also from spinning, the film-blowing process implies a planar or biaxial elongational flow, defined above.

On the other hand, an important practical problem that affects industrial production of fibers by melt spinning and films by film-blowing, is the phenomenon of “draw resonance”, which consist in a periodical change of the diameter of the fiber or the thickness of the film. The latter produces a bubble instability that must be avoided peremptorily. A set of results and discussion of draw resonance in melt spinning and film-blowing was presented in Han’s and Midlemann’s respective books, “Rheology in Polymer Processing” [34] and “Fundamentals of Polymer Processing” [37]. The paper of Minoshima and White [180], published in 1986, remains one of the most cited on the subject with 83 citations, so far. Actually, these instabilities have not received much attention in scientific literature in XXI century and are rather considered a technical problem to be solved practically by trial and error method.

Interesting efforts have been made to calculate the steady state elongational viscosity, η_E , from Goettfert Rheotens™ and similar instruments [65,181–185]. The starting point was the generation of Rheotens grandmastercurves for simple thermorheological polymer melts [183] which simplified the description of the material behaviour at the spin line, providing the rheologically correct basis for a direct and quantitative comparison of the extensibility of polymer melts under processing conditions. This analytical model, developed and improved by Wagner et al. [184], is included in the Rheotens software and allows the calculation of the elongational viscosity.

But, mistakes are often made, because the flow is non-isothermal, unless a chamber is employed; as well, V_z velocity profile is not necessarily linear, which results in a z depending $\dot{\epsilon}$, impeding to determine steady state values of η_E .

Some years ago, the aforementioned original extensional rheometer for constant strain rate designed by Meissner for polymer melts, was modified to avoid using annoying silicone baths. Instead, a conventional air oven can be used to reach thermostatic conditions, thanks to a fixture

with dual wind-up drums to ensure a uniform extensional strain that can be adapted to the environmental chamber of any commercial rotational rheometer. A well known instrument for polymer melts is the so-called Sentmanat Extensional Rheometer (SER) [186,187]. Also, the so-called Extensional Viscosity Fixture (EVF) [188,189] popularized by TA Instruments, is quite widely used in the series of ARES rheometers. Three years ago a new system, called Horizontal Extensional Rheometry (HER) which allegedly combines the advantages of both, SER and EVF devices, has been presented [190].

Extensional rheometers that allow measuring the transient and steady state elongational viscosities constitute a reliable tool for polymer characterization and processing. Actually, different polymer samples that cannot be distinguished in shear flow measurements, are often detected through extensional rheometry. This gives satisfaction to the scarce rheologists devoted to this technique. The case of long chain branched is quite paradigmatic.

Indeed, over the years, the comparison with the transient response in simple shear has been used as a reference to investigate the extensional rheological characteristics of low-density polyethylene (LDPE) [178, 191–193]. The term “strain hardening” was introduced to recognize the essential differences noticed in Fig. 13.

The transient shear viscosity at a finite rate is always lower than that obtained in the zero-rate limit, whereas the transient extensional viscosity can deviate upward from the zero-rate elongational viscosity. This upward deviation is known as strain hardening (SH), whereas the downward trend is known as strain softening (SS). It is usually thought that this feature of strain hardening is due to long chain branching (LCB) in LDPE, because linear polyethylene such as high density polyethylene (HDPE) fails to display such upward deviation. Actually, extensional rheology and in particular the SH nonlinear factor is very sensitive to branching architecture [194] and, what is also very remarkable, it correlates with the ability of melts to sustain high extensional stresses developed during fast extensional flows [195], which occur in many industrial processing operations (e.g. film blowing, thermoforming, fibre spinning, etc). Currently, rheology-processability studies extend to the case of biobased and biodegradable polymers, which are degradable materials obtained from renewable sources that have been studied as promising alternatives to partially or totally replace packaging based on synthetic polymers. Also in these materials, the extensional rheology can aid the strategies of polymer processing which involve shear free flows, like those mentioned above. The presence of strain hardening increases the stability of blowing domain of PLA-PBAT blends [196] and the melt

strength of bionanocomposites is determinant in film blowing processing [197].

The emphasis for highlighting the performances of extensional rheometers that allow measurement of the transient and steady state elongational viscosities, has led to some dubious conclusions. For instance, it has been claimed that strain hardening helps to avoid cell coalescence in foaming of thermoplastics by chemical and physical blowing agents [198–200]. However, this statement has been soundly rebutted recently [201].

As pointed out by Petrie [170] the most important flows that combine shear and extension are converging and contraction flows. Based on the assumption that extensional stresses exceed considerably shear stresses in converging flows, Cogswell [202] proposed a method to calculate the extensional viscosity. A corollary of converging flows developed at the entrance of capillary dies is the generation of crystallization in semicrystalline polymers, like polyethylene terephthalate [203]. The relevance of this phenomenon has not been sufficiently highlighted in the literature, but it has a great importance in extrusion and spinning processes.

9. Final observations

Table 2 shows what we consider the most significant pillars where rheology and polymers have feed each other. Our selective point of view, which avoids mentioning any milestone of polymers rheology in the last 50 years, can be striking for many rheologists and, indeed, is proposed as a subject of debate. For instance, it can be argued that recent numerical simulation methods and the use of theoretical dynamic models for the study of novel polymer systems, like nanocomposites, hydrogels, physically and chemically reversible self-healing polymers, bio-based recyclable polymers, 3D-printable soft materials, cyclic polymers for biomedical applications, drive the progress of polymers rheology. But, actually, no new disruptive theories have been proposed, beyond of adaptations and extensions of the tube and reptation model.

As in all branches of knowledge, the contemporary presence of electronics and computer science has enormously facilitate the task of rheologists to take advantage of the discoveries remarked in Table 2, rather than to propose new findings. Think in the scenario of software programs, like Moldflow[®] for injection and compression molding of polymers. The scientific basis for this software are rheological features mentioned in Table 2 and discovered more than five decades ago. An example of the advantages of the computerization of rheology is the case of large amplitude oscillatory shear (LAOS) research, which in the framework of the oscillatory deformation and flow studies dating from

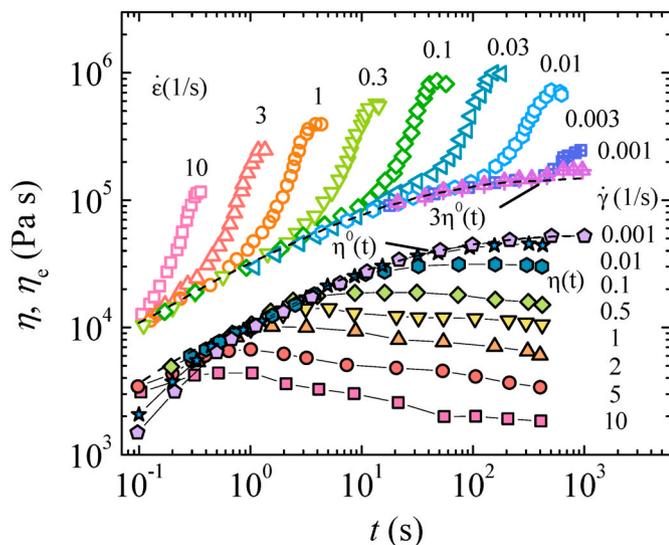


Fig. 13. Shear viscosity and elongational viscosity as a function of time at several deformation rates for LDPE at 150 °C [191].

Table 2
Milestones in rheology and its relevance to polymer science and engineering.

| MILESTONES IN RHEOLOGY | | RELEVANCE TO POLYMER SCIENCE AND ENGINEERING |
|------------------------|---|--|
| 1928 | Deborah number | First conceptual approach to viscoelasticity |
| 1929 | Non Newtonian flow | Foundations of polymer processing |
| 1931 | Intrinsic viscosity | Polymers molecular weight determination |
| 1932–1946 | The concept of temporary networks | Elastic polymer liquids and reversible gels |
| 1943–1960 | Time-temperature superposition | Viscoelastic spectrum associated with polymers physical features |
| 1947 | First Normal stress difference and Weissenberg effect | Extrudate swell in polymer processing |
| 1948 | Oscillatory deformation and flow | Characterization, processing, properties and applications of polymers in general |
| 1967 | The tube and reptation model | Diffusion of polymer chains and universal scaling law for the viscosity of polymer melts |
| 1972 | Transient elongational rheometry | Characterization of LCB polymers; fibers and films processing |

1948, has brought about interesting progresses in developing physical mathematics approaches to analyze non-newtonian rheological features including pseudoplasticity, viscoelasticity, thixotropy and yielding, from reliable measurements of nonlinear flow conditions by independently controlling the strain amplitude and oscillatory frequency.

In fact, in the last decade more than 50 papers on LAOS of polymers have been published in referential journals like *Journal of Rheology*, *Rheologica Acta* and *Macromolecules*. But, we have to admit that the relevance of LAOS outcomes in polymer science and technology is, by far, less significant than that of SAOS results.

It can be noticed that in recent years research on polymers is progressively tending to multidisciplinary, often gathering polymer laboratories of several institutions with different and complementary objectives. Considering the numbers from the journal *Macromolecules*, for the 20 most cited papers in 1990, in 15 of them the number of laboratories involved was just one. However, in 2021 for the 20 most cited papers only in 5 the authorship corresponded to one laboratory.

As a corollary, nowadays more and more papers cover the paradigm “polymerization-characterization-properties-applications”, in a socially demanding context of sustainability, which involves, among other aspects, the development of bio-based polymers and recent processing techniques like additive manufacturing. Certainly, the role played by rheology is very relevant in the framework of the aforementioned paradigm. Notwithstanding, the fundamentals of the tools used by rheologists in this context (e.g. characterization of biopolymers; flow and adhesion in 3D printing) derive directly from findings previous to the seventies of the last century.

As we have stated in the beginning, rheology was born to help scientists, particularly chemists, in the study of deformation and flow of materials and substances, with the intention of imply them directly in the use of this “more friendly” branch of mechanics. Currently, almost 100 years after the emergence of both, polymers and rheology, the latter has become popular among polymer scientist and engineers, overcoming the practically total rheology ignorance of decades ago. In the last years the contribution of rheology to polymer science has expanded, but not on the basis of novel rheological procedures. The development of accessible commercial rheometers with extraordinary electronic and software features, in hands of daring, but often unconscious, polymer scientists, has led T.P. Lodge [5] to remark that, rheological measurements currently have been democratized to the point where their application is routine. This depreciation of rheology by scientist who do not have a clue on the matter must be fought: Avoiding the trivialization of polymer rheology, deepening the existing corpus and creating new theoretical and experimental instruments is at stake.

Data availability

Data will be made available on request.

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