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RHEOLOGICAL BEHAVIOR OF LOW-DENSITY POLY(ETHYLENE) AND OF ITS COMPOSITES.

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ABSTRACT

This chapter reviews the current state of the art referring to the rheology of low-density Poly(ethylene)-based systems: undoubtedly, processing this commodity, alone or in combination of different micro- to nano-fillers, requires a deep knowledge of its rheological behavior, in order to be able to set up the process parameters. In particular, after an overview of the fundamentals of rheology of thermoplastics (also including the main rheological tests employed for this characterization), the chapter will discuss the specific rheological behavior of LDPE, and how fillers ranging from micro- to nano-scale may affect it.

1. Introduction

Rheology is a branch of physics that describes the mechanical behavior of materials during flow-induced deformation [1-2]. Rheological studies are not specifically focused on ideal elastic materials or ideal fluids, the behavior of which can be described by the well-known Hooke and Newton models, respectively. Conversely, rheology often focuses on materials that are able to exhibit elastic, viscous or both behaviors under different flow conditions [3-6]. This kind of materials, referred as *complex fluids*, include polymers, gels, emulsions, foods, biofluids or inks. For this reason, in the last decades the rheology has become an important field in materials engineering, food science and biotechnology [7].

As far as polymeric materials are concerned, in the melt state they exhibit a rather complicated and unusual flow behavior; unlike water, oil or organic solvents, polymers are non-Newtonian fluids [8-10]. By definition, fluids deform when a force is applied and continue to deform until the force is removed; in a Newtonian fluid, the rate of deformation is directly proportional to the applied force [11]. Conversely, polymers in the molten state do not exhibit a direct relationship between the rate of deformation and the stress applied to the melt, hence showing a non-Newtonian response [12]. More specifically, polymeric materials exhibit a so-called viscoelastic behavior, involving both a viscous and an elastic component; additionally, the response of a polymer upon deformation is time dependent [13-14]. All these issues make rheology a very useful tool for characterizing polymer systems.

Besides, rheological characterization has a primary role in polymer research, being a fundamental link between the production of polymers and their end-use properties. In fact, especially for thermoplastic polymers, the knowledge of the flow behavior is essential for all production processes, as they typically involve the melting of the material, its subsequent shaping through the flow in a die or the filling of a mold and, lastly, its solidification into the final product [15-17]. Since the fundamental part of the productive process occurs while the polymer is in the molten state, the processing of thermoplastics is determined by their flow behavior, which in turn depends on both polymer structure and selected processing conditions, in terms of applied temperatures, pressures and stresses [18-20]. In this view, the rheological characterization is firstly necessary for the design of the processing equipment; as an example, the evaluation of the dependence of viscosity as a function of the applied shear rate at different temperatures allows assessing the flow behavior of polymer melts [21]. In Figure 1, a typical viscosity curve of a linear polymer is shown, along with the different shear rate ranges corresponding to the common processing operations for thermoplastics [22-23]. It is evident that the rheological behavior of thermoplastics and their processing are strictly related; the knowledge of the polymer flow behavior is thus mandatory to model and design their processing. Besides, a deep understanding of the polymer rheological characteristics enables to solve process troubleshooting and to optimize the processing conditions [24].

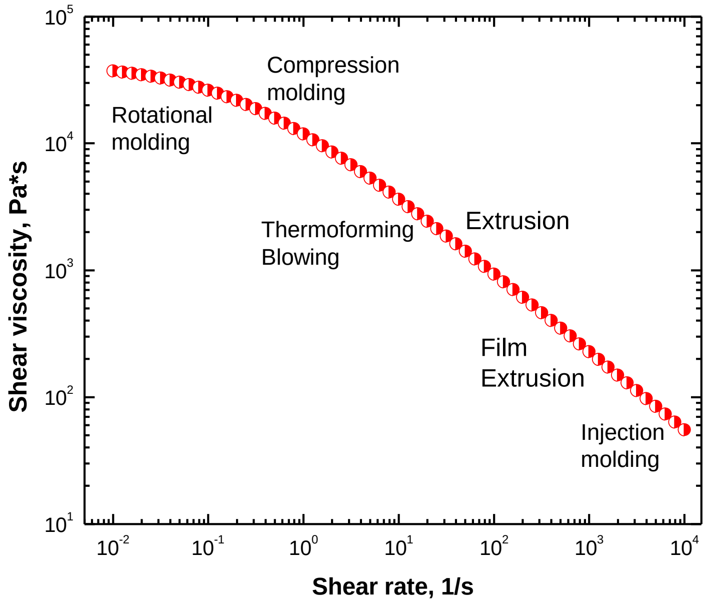

Figure 1. Processing shear rates

On the other hand, the rheological properties are very sensitive to the microstructural characteristics of polymers, such as molecular weight, molecular weight distribution and presence of either short or long chain branching [25-27]. More specifically, the flow behavior is strongly affected by the structural architecture of polymer chains, since the presence of high molecular weight chains or long branches is able to modify the motion dynamics of macromolecules, leading to changes in the polymer relaxation spectrum [28]. In this context, the study of the polymer rheological behavior can be profitably exploited to gain some insight into the chemical structure of the material and to characterize its branching structure that is difficulty assessed through classical spectroscopic or chromatographic techniques [29].

Additionally, as far as polymer-based composites and nanocomposites are concerned, the rheological characterization is a powerful tool to infer the state of distribution of micro- and/or nano-sized fillers, as well as the possible occurrence of strong polymer-filler and filler-filler interactions [30-31]. In fact, the rheological response of polymer-based complex systems reflects their intimate microstructure: more specifically, when the formation of interconnected structures of nanofillers, such as percolative networks, occurs, the motion of long polymer chain segments is restricted, thus resulting in a change in the relaxation spectrum of the material [32-34]. Rheological measurements are hence capable of revealing fundamental information as far as the microstructural evolution of filled polymers is concerned, being very sensitive to changes in composite internal structure and to the relaxation dynamics of polymer chains [35].

This chapter aims to thoroughly describe the rheological behavior of low-density Poly(ethylene) and the correlation occurring between its rheological properties, molecular structure and melt processing. Before detailing this part, the basic flow characteristics of thermoplastics and the typical rheological measurements performed on polymers will be discussed. Afterward, the focus will be devoted to the main rheological characteristics of LDPE, also considering the possible influence of micro- and nano-fillers on the polymer viscoelastic response.

2. Fundamentals of polymer rheological measurements

2.1 Shear flow

For the determination of the polymer viscosity in a shear flow field, the so-called two-plate model, sketched in Figure 2, is used. In this model, the polymer is trapped in between two parallel surfaces: the bottom plate is fixed, while the upper one moves at constant speed.

If the no-slip boundary conditions are satisfied, the velocity of the fluid varies linearly from 0 at the bottom to V at the upper surface; the linear velocity profile generates a constant velocity gradient, known as shear rate ($\dot{\gamma}$) [36]. The shear viscosity (η) of the polymer is defined as the resistance that the fluid offers to the shear deformation, and can be derived from the ratio between the imposed shear stress τ (i.e. the force F tangentially applied, divided by the area A of the plate) and the shear rate $\dot{\gamma}$ [37]:

$$\eta = \frac{\tau}{\dot{\gamma}} \qquad (1)$$

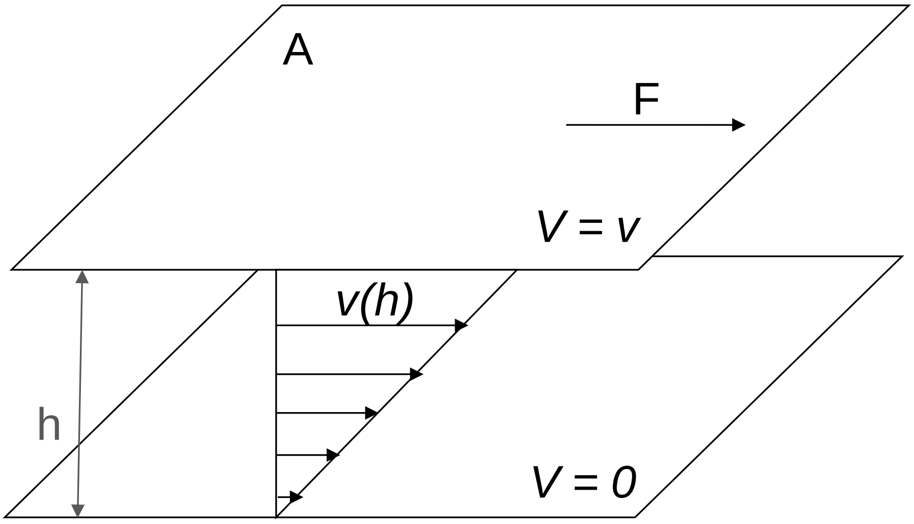

Figure 2. Schematic of simple shear flow between two parallel plates

This relation is known as Newton's Law of Viscosity; if the viscosity is independent from the shear rate, the fluid exhibits Newtonian behavior and its flow curve (i.e. the plot of the shear viscosity as a function of shear rate) is a straight line [38]. Conversely, molten polymers show a non-Newtonian behavior, involving a dependence of the viscosity from the applied shear rate. In particular, polymers are "shear-thinning" or pseudo-plastic fluids, since their viscosity decreases as the shear rate increases [39]. In Figure 3, the typical flow curves for Newtonian and shear-thinning materials are reported.

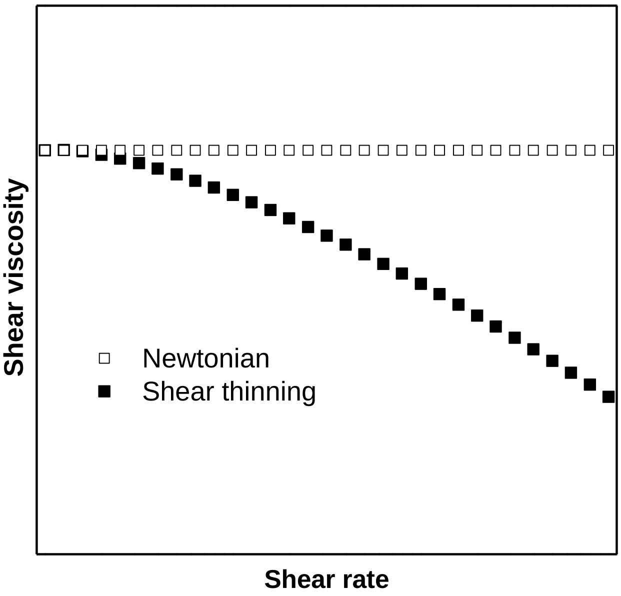

Figure 3. Flow curves for Newtonian and shear-thinning fluids

For thermoplastics, the shear viscosity approaches the ideal Newtonian behavior at low shear rate values: the region, in which the viscosity is constant, is called “Newtonian plateau” and the values of η in this zone is the *zero-shear* or *Newtonian* viscosity (η_0) [40]. As the shear rate increases, the viscosity starts to decrease, passing through a transition region towards the shear-thinning zone, in which a dramatic drop of the viscosity values can be observed. This decrease is due to the occurrence of two concurrent phenomena: the preferential alignments of the macromolecules along the flow direction and the disentanglements of the long polymer chains upon the applied deformation [41]. The higher the shear rate, the easier is the deformation of the polymer; this finding implies that the flow of the polymer through dies or other process equipment is facilitated at high shear rate values.

Different models are commonly employed for describing the flow behavior of pseudo-plastic fluids. The simplest viscosity model is the Power-law model, requiring two fitting parameters:

$$\eta = K\dot{\gamma}^{n-1} \qquad (2)$$

where K is the consistency of the fluid, accounting for the magnitude of the viscosity, and n is the power-law coefficient [42]. This model is able to describe only Newtonian plateau (n=1) or shear-thinning region (n<1), but is of less use for polymers showing a pseudo-plastic behavior.

An extension of the power law is the Cross model:

$$\eta = \frac{\eta_0}{1+(\lambda\dot{\gamma})^{1-n}} \qquad (3)$$

which introduces the following fitting parameters: η_0 = zero-shear viscosity; λ = characteristic relaxation time; n = power-law coefficient [43].

For certain thermoplastics, a better fit is achieved using the Carreau model, showing the same fitting parameters as the Cross model [44]:

$$\eta = \eta_0[1+(\lambda\dot{\gamma})^2]^{\frac{n-1}{2}} \qquad (4)$$

Rheological measurements in shear flow for thermoplastics are usually carried out using rotational or capillary rheometers (Figure 4). The first typology includes plate-plate and cone-plate configurations and the deformation of the material is performed through the mutual rotation of the two plates [45]. Rotational rheometers are able to work in strain-controlled or stress-controlled mode, depending whether the imposed variable is the strain rate or the stress, respectively. The polymer, in the form of granules or as a disk-shaped sample (preliminary obtained through compression or injection molding), is placed in between the plates and, after reaching the thermal equilibrium, is sheared while the torque or the deformation are collected as a function of the angular velocity of rotation or stress, respectively. Typically, these devices allow an accurate temperature control along with a high torque resolution, but they present a limitation about the maximum achievable deformation rates or stresses. Differently, the use of capillary rheometers enables to reach shear rate values similar to those experienced by the polymer during an injection molding or an extrusion process; for this reason, the capillary rheometers (Figure 4C) are usually used to measure the shear viscosity at high shear rate ranges [46]. To this aim, polymer granules or powder are firstly fed in a pre-heated barrel and then extruded through a capillary die at a specific piston speed; the viscosity function of the material is derived from the measurement of the melt pressure at the entrance and within the die. However, due to the complex flow field in the capillary, the obtainment of accurate viscosity values requires several corrections [47].

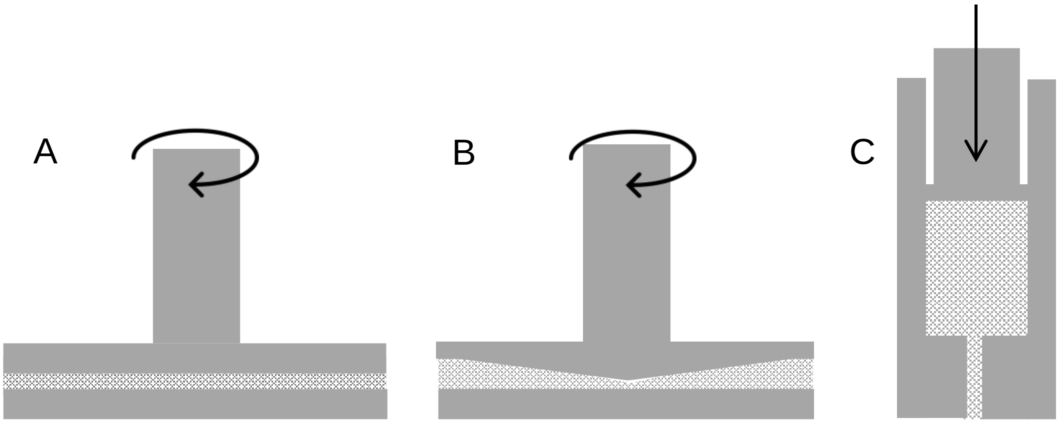

Figure 4. Schematics of plate-plate (A), cone-plate (B) and capillary (C) rheometers

2.1.1 Dynamic oscillatory shear tests

Dynamic oscillatory measurements represent the most common method to measure the flow behavior of a thermoplastic material using a rotational rheometer [48]. In this test, the material is subjected to a sinusoidal stress or strain and the resulting mechanical response is collected as a function of time. More specifically, the sample is oscillated about its initial equilibrium position in a continuous cycle: the amplitude (γ) of the applied oscillation corresponds to the maximum stress or strain and the angular frequency (ω) represents the number of oscillations per second. As regards an ideal elastic material, for which the stress is proportional to the strain, both strain and stress are in-phase; conversely, a purely viscous fluid shows 90° phase difference between stress and strain, since in this case the stress is proportional to the derivative of the strain. Polymer melts exhibit a viscoelastic behavior, i.e. partly elastic and partly viscous: therefore, their mechanical response falls between the two extremes, showing a phase difference between stress and strain ranging from 0 to 90° [49].

In the case of thermoplastics, the ratio between the applied stress (or strain) and the measured strain (or stress) gives the complex modulus G*, a quantitative measure of the polymer resistance to the deformation [50]. The complex modulus can be decomposed into the in-phase and out-of-phase components, representing the elastic and the viscous characteristics of the polymer, respectively.

More specifically, G* can be calculated as:

$$G^{*} = G'(\omega) + iG''(\omega) \qquad (5)$$

where G’ (storage modulus) is the in-phase and G” (loss modulus) is the out-of-phase component of the polymer viscoelastic behavior. G’ represents the elastic part, being related to the energy stored in the material, while G” stands for the viscous feature of the polymer response and refers to the energy dissipated in the deformation [51].

The ratio between the two moduli is the loss factor

$$tan\delta = G''/G' \qquad (6)$$

where δ is the phase angle between stress and strain.

Furthermore, the complex viscosity of the polymer can be derived through a dynamical measurement as follows:

$$\eta^{*} = \sqrt{(\eta')^2 + (\eta'')^2} = \sqrt{(G'/\omega)^2 + (G''/\omega)^2} = G^{*}/\omega \qquad (7)$$

Dynamic oscillatory shear tests can be performed either in the linear or nonlinear viscoelastic region of the polymer. Figure 5 schematically depicts the results of an isothermal strain sweep test, in which the response of the material is recorded as a function of the strain amplitude and a fixed frequency [52]. At low strain amplitude values, the linear viscoelastic regime can be detected: it is characterized by the independence of both moduli from strain amplitude. In the linear region, the applied stress or deformation are low enough to cause structural breakdown, and the oscillatory response remains sinusoidal. As the applied strain amplitude is increased, a transition from linear to nonlinear regime occurs, indicated by the dramatic drop of both moduli. In the nonlinear region, the moduli are strain amplitude-dependent; besides, the resulting periodic response is distorted and diverges from a sinusoidal wave [53].

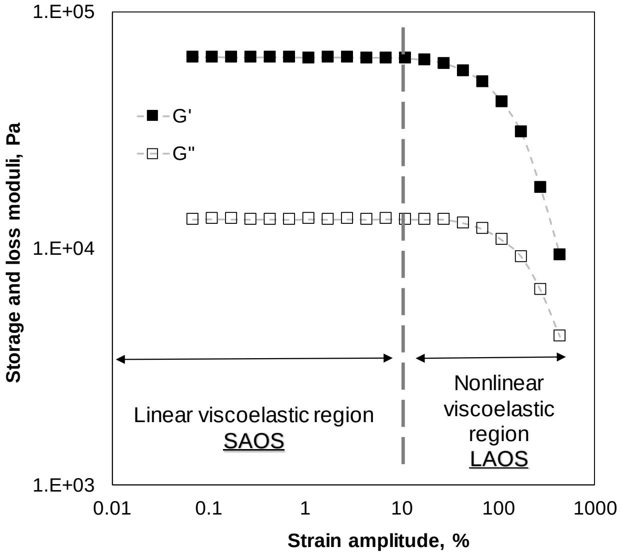

Figure 5. Storage and loss moduli measured in a typical strain sweep measurement

Small amplitude oscillatory shear (SAOS) measurements are carried out within the linear viscoelastic region of the material, providing useful information about the microstructure of polymers and polymer-based complex systems [54]. In Figure 6, the typical results of a SAOS test for a thermoplastic are reported; the measurement is performed at constant temperature and strain amplitude (low enough to be in the linear viscoelastic region of the material), by varying the frequency in the range 10^{-2} - 10^{2} rad/s. From the analysis of the complex viscosity curve, the Newtonian plateau at low frequencies can be observed, followed by the shear thinning region, characterized by a rapid decrease of the viscosity values as a function of the oscillation frequency. As far as the moduli curves are considered, a monotonic increasing trend as a function of frequency can be observed; in the low frequency range (the so-called terminal region), the polymer melt is predominantly viscous (G” > G’) and both storage and loss moduli curves exhibit a frequency dependence typical of a liquid-like rheological behavior (G’α ω^2 and G” α ω). In this region, the rheological response of the material is governed by the relaxation processes of long chain macromolecules. As the frequency increases, the polymer behavior becomes mainly elastic (G’ > G”) and the viscoelastic response is governed by the fast dynamics of short polymer chains [55].

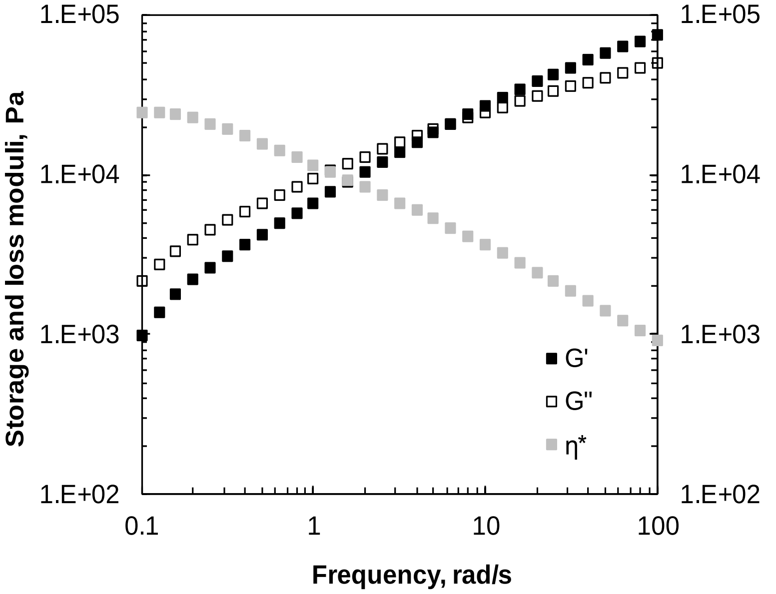

Figure 6. Typical results of a SAOS measurement

Although a SAOS test is able to accurately describe the flow behavior of a complex fluid, being based on a rigorous theoretical foundation, the linear viscoelastic region extends for quite small strain amplitude values. However, in a typical process operation, the polymer is subjected to large and rapid deformation; SAOS characterization is not hence sufficient to fully evaluate the flow behavior of the polymer in practical applications and it is necessary the study of the viscoelastic response of complex fluids in the nonlinear region through large amplitude oscillatory shear (LAOS) tests [56]. The measurement typically used to describe the type of nonlinear behavior is the strain sweep, depicted in Figure 7. Generally, four kinds of strain amplitude dependence can be observed: type I or strain softening, in which both moduli decrease as a function of strain amplitude; type II or strain hardening, in which both moduli increase; type III or weak strain overshoot, in which G" shows an overshoot; type IV, or strong strain overshoot, in which both moduli show overshoot. Type I behavior is typical of unfilled polymer melts, where the macromolecules tend to align along the flow direction for high strain amplitude; otherwise, the overshoots present in type III and IV are usually related to the formation of weakly interacting structures in gels or composites [57]. Additionally, the strain dependence of the rheological functions in the nonlinear region is helpful in characterizing the branching degree of polymer chains.

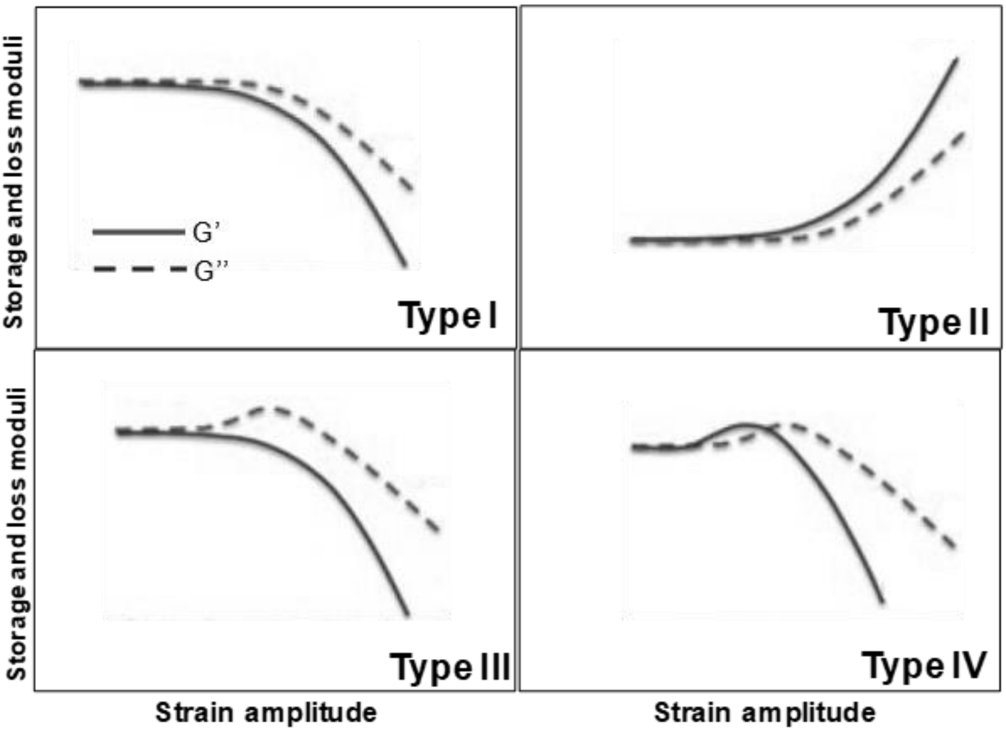

Figure 7. Different kinds of nonlinear rheological behavior

2.1.2 Stress relaxation tests

A typical stress relaxation test involves the application of an instantaneous deformation to the polymer sample, and the successive monitoring of the stress decay as a function of time [58]. This kind of measurement, that is called also step strain, allows evaluating the shear modulus, defined as:

$$G(t, \gamma_0) = \frac{\sigma(t, \gamma_0)}{\gamma_0} \qquad (8)$$

Therefore, shear modulus is a function of time and strain amplitude; however, if the strain amplitude value is low enough to be in the polymer linear viscoelastic region, the dependence of G(t) from γ_0 is negligible, and the modulus depends only on time. In this case, the shear modulus is called relaxation modulus and represents the decay of the stress as a function of time, after the deformation of the polymer. For unfilled polymers, G(t) tends to reach a value of equilibrium equal to zero after a certain time; materials showing this behavior are viscoelastic liquids, which dissipate all the energy provided with the deformation. Differently, materials with nonzero equilibrium modulus are defined as viscoelastic materials, since they are able to partly store the energy applied on the sample [59].

Stress relaxation modulus can be exploited to classify polymeric materials depending on their relaxation dynamics. Polymer melts usually shows the aforementioned terminal behavior, typical of liquid-like systems. For these materials, the stress relaxes completely, and G(t) approaches zero after a certain time once the stress is applied. Conversely, crosslinked materials or polymer-based nanocomposites, in which the formation of a percolative network of nanofillers occurs, exhibit a solid-like rheological behavior. For these systems, the presence of bridges between the macromolecules or the establishment strong polymer/filler and filler/filler interactions, make more difficult the motion of the polymer chains, slowing down their dynamics and avoiding their complete relaxation [60].

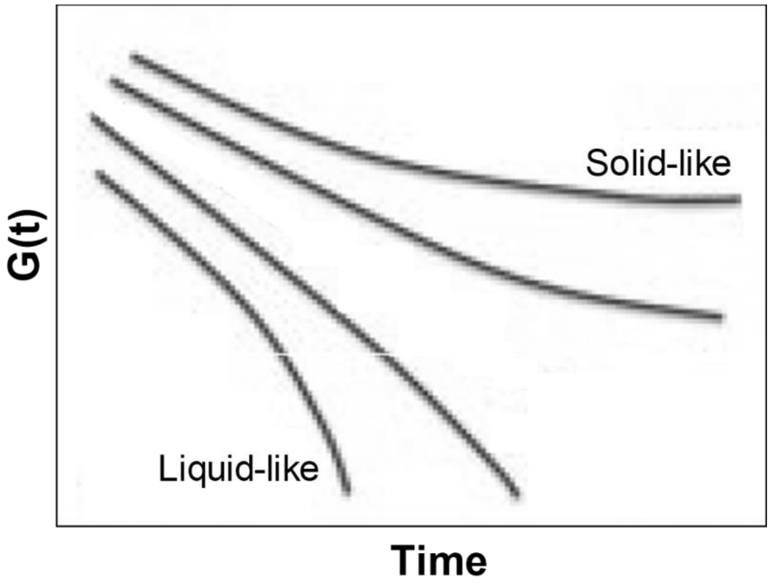

Figure 8. Stress relaxation behavior of different classes of polymers

2.2 Elongational flow

In many relevant processing operations, polymer melt is subjected to the elongational flow, i.e. a stretching deformation that, depending on the specific process, can be uniaxial or biaxial [61-63]. As an example, elongational flow plays a key role in fiber spinning, blow molding, film blowing or foaming. Additionally, the elongational deformation of the melt also occurs in some processes dominated by shear, such as extrusion and injection molding; the change of the die diameters or the injection of the polymer into the mold gate, represent some examples in which the melt experiences stretching deformations [64].

In analogy to the shear flow, the elongational viscosity (μ) is defined as the ratio between the applied stress and the deformation rate [65]:

$$\mu = \frac{\sigma}{\dot{\varepsilon}} \qquad (9)$$

In Figure 9, the typical trend of the uniaxial elongational viscosity as a function of time is reported for different values of deformation rate. In steady-state conditions, if the system is in its linear range of deformation, the so-called Trouton law applies, and the time-dependent elongational viscosity is three times the time-dependent shear viscosity [66]:

$$\mu_0(t) = 3\eta_0(t) \qquad (10)$$

Looking at the curves shown in Figure 9, the elongational viscosity increases as a function of time, reaching a plateau corresponding to the Trouton value for low deformation rates. Differently, at higher rates, the elongational viscosity exhibits a steep upturn that occurs at progressively shorter times as the deformation rate increases. This peculiar behavior, due to the growth of the stress as a result of the strain increase, is called strain hardening and is beneficial for the homogeneous deformation of the polymer in processing operations like film blowing or foaming [67-68].

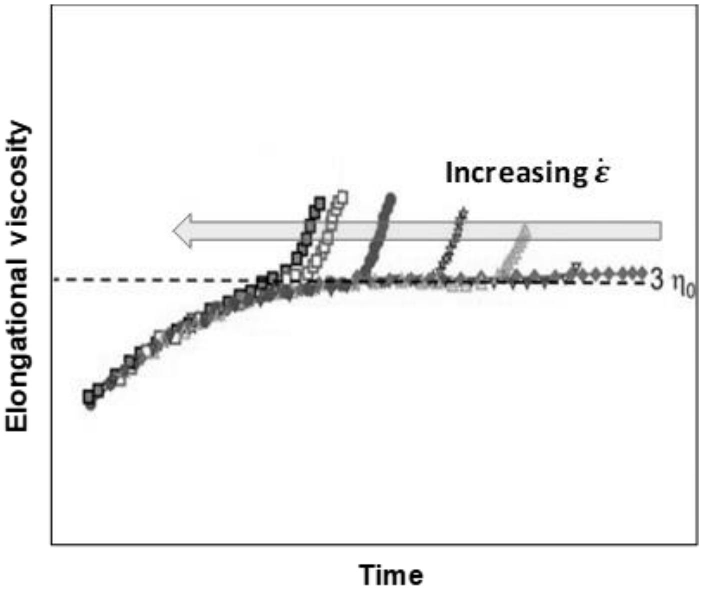

Figure 9. Elongational viscosity at different rates of deformation

Elongational viscosity can be used to describe the extensional behavior of polymers in isothermal conditions; however, during the most common processing operations, in which elongational flow is involved, the temperature of the material changes while processing. Therefore, to fully evaluate the flow behavior of polymers in practical real applications, rheological characterization in non-isothermal elongational flow is performed [69]. The commonly used equipment is provided with a series of pulleys, which grab the hot polymer filament coming out from an extruder, and deliver it into a final pulley rotating at steady acceleration, while a load cell measures the force on the filament [70]. At the breaking of the filament, the current force and the speed of the final pulley are recorded. The fundamental properties derived from such an experiment are the melt strength (MS) and the breaking stretching ratio (BSR). MS refers to the force in the molten polymer at breaking, while BSR represents the maximum elongation of the melt and is calculated as the ratio between the drawing speed at breaking and the extrusion velocity [71].

3. Rheological behavior of LDPE

As stated in the Introduction, the rheological properties of a polymeric material, both in shear and in elongational flow, strictly depend on the structure of the polymer, in terms of molecular weight, distribution of molecular weight and presence of short and long branches. In the following, the main feature of the flow behavior of low density poly(ethylene) will be discussed, considering the relationships between the rheological functions and the macromolecular structure of this polymer.

3.1 Shear flow behavior

3.1.1 Effect of the molecular weight

The shear viscosity as a function of the shear rate of a series of LDPE with different molecular weight (M_w) has been evaluated by Acierno et al. [72] ; the molar mass distribution of the investigated samples and their degree of branching are very similar, while their weight average molecular weight significantly differ, ranging from $67*10^3$ to $166*10^4$. Two different effects can be observed as a result of the increase of the polymer M_w: a significant growth of the zero-shear viscosity (η_0) values in the low shear rete region, and a progressively more pronounced shear thinning behavior. In other words, the zero-shear viscosity becomes remarkably higher as M_w increases, but the differences in the viscosity values tend to diminish at high shear rate.

Generally, as far as the enhancement of the zero-shear viscosity is concerned, the well-known Mark-Houwink equation can be used to predict the effect of the polymer M_w [73-74]:

$$\eta_0 = K_1 M_w \quad for \quad M_w < M_C \tag{11}$$

$$\eta_0 = K_2 M_w^{\alpha} \quad for \quad M_w > M_C \tag{12}$$

where K_1 and K_2 are parameters depending on the kind of polymer and temperature, α lies between 3.4 and 3.6 and M_c is the critical molar mass. In Figure 10, this relation is applied to determine the critical molecular weight of a series of LDPE with different M_w [75].

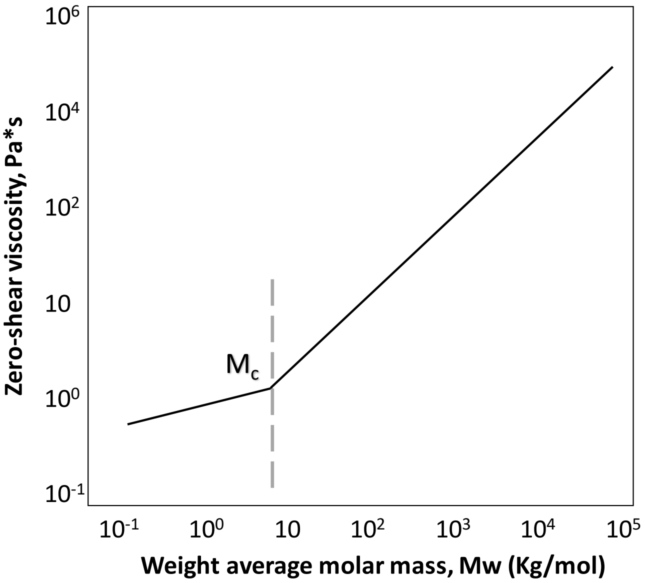

Figure 10. Flow curves of different LDPE samples with different M_w (A) and zero-shear viscosity as a function of M_w (B)

Several reports discuss about the possible dependence of the Mark-Houwink equation on the molar mass distribution [76-78]. In this context, Stadler et al. [79] evaluated through linear viscoelastic measurements, the zero-shear viscosity of twenty-four LDPE samples with different M_w, characterized by polydispersity index ranging from 1.8 to 16. The obtained data were represented in a η_0 vs. M_w plot, in order to verify the applicability of the Mark-Houwink equation for all materials. The results showed that all the experimental data follow the trend predicted by the power-law relation, indicating its independence from molar mass distribution. This finding allowed using the plot of zero-shear viscosity as a function on the molar mass to discriminate polymers with different macromolecular architectures; in fact, as the Mark-Houwink equation is independent from the polydispersity index of the polymer, any deviation from this relationship can be attributed to the existence of complex molecular architectures, such as tree-like or star-like structures [80].

Wood-Adams et al. [81] performed SAOS measurements of seven samples of LDPE with the aim to investigate the effect of the molecular weight on the polymer linear viscoelastic behavior. The M_w of the selected samples ranges from $38*10^3$ to $33*10^4$, while their polydispersity index is approximately 2. From the analysis of the flow curves, an increase of the zero-shear viscosity values and an amplification of the shear thinning as a function of M_w occur. Due to the high molecular weight of the selected materials, the calculation of η_0 from the viscosity curves was not possible, and the viscosity values were determined using discrete relaxation spectrum. The fitting of the experimental data with the Mark-Houwink equation confirmed the validity of the used procedure, as the fitting parameters coincide with those already reported in literature for LDPE [82]. Additionally, the effect of the molecular weight on the loss angle was studied, documenting a significant influence of the polymer molar mass on the frequency, at which the elastic feature of the LDPE viscoelastic behavior becomes prominent. Furthermore, important information about the calculation of the molecular weight between entanglements were obtained from the analysis of the storage modulus G' as a function of M_w with increasing the polymer molar mass, a progressive disappearance of the terminal behavior was observed, due to the higher number of entanglements in the high molecular weight LDPEs.

As far as the influence of the molar mass distribution on the flow behavior of LDPE is concerned, it has been shown that the breadth of the distribution has a quite irrelevant effect on the flow curve shape. In fact, LDPE samples characterized by different polydispersity index, exhibited a very similar trend of the complex viscosity as a function of frequency, and the differences in the molar mass distribution caused a slight broadening of the transition zone of the curve, at intermediate frequencies between the Newtonian plateau and the shear thinning region [83-85].

An interesting study by La Mantia et al. [86] was addressed to derivate a relationship between the LDPE molecular weight and the so-called die-swell, i.e. the property related to the swelling ratio of a polymer filament coming out from a capillary. From a technological point of view, the die-swell is of fundamental importance to predict the diameter of a polymer filament exiting from an extrusion die, being the ratio between the actual diameter of the extrudate and the die diameter. The existence of this swelling phenomenon in thermoplastics is due to the elastic component of their viscoelastic behavior, since the polymer is able to expand at the exit of a capillary because of the stored normal stresses. Usually, the experimental measure of the die-swell is difficult, as the extrudate may freeze at the exit of the die, before reaching its maximum recovery; additionally, in the case of low viscosity polymers, the falling of the exiting strand under its own weight needs to be considered. Therefore, a prediction of this property from the polymer rheological behavior should help in solving many practical issues. Six different LDPE samples, differing for M_w and polydispersity index were selected and characterized through shear measurements. The obtained data showed an increase of the swelling ratio with increasing both molecular weight and molecular weight distribution. Besides, an analytical expression for the calculation of die-swell was found, taking into account the effect of the polymer molecular structure, the geometrical characteristics of the used dies and the operating conditions, as well.

Besides die-swell, a further issue commonly encountered during the extrusion of high molecular weight LDPE is the occurrence of the so-called sharkskin phenomenon, i.e. the appearance of instabilities during the processing resulting in periodic irregularities on the extrudate surface [87]. The sharkskin phenomenon is usually observed for extrusions at high shear rate (high production rates) and is attributed to the cohesive rupture of the polymer at the die exit, due to the rearrangement of the velocity profile at the die tip. More specifically, if the imposed tensile stress exceeds the cohesive strength of the polymer, a rupture of the extrudate surface occurs; for this reason, this phenomenon is also called melt-fracture [88]. Several reports documented the effect of the molecular characteristic of the polymer on the appearance of this phenomenon, showing an increase of the critical shear stress as a function of the breadth of the molecular weight distribution [89-91]. Furthermore, Yamaguchi et al. [92] documented a decrease of the critical stress for the onset of sharkskin as a function of the increased molecular weight between entanglements. Interestingly, Ansari et al. [93] found a relationship between the onset of the sharkskin and the plateau modulus, implying that LDPEs with higher modulus experience this phenomenon at higher shear rates and stresses.

The described relationships between linear viscoelastic functions and LDPE molecular weight were often used as an alternative to the classical chromatographic methods, to obtain some information concerning the polymer M_w and molecular weight distribution [94-95]. The use of rheology instead of gel permeation chromatography has some advantages: first, as many commercial LDPE samples with high M_w do not dissolve in solvents at room temperature, only the devices operating at high temperature are able to perform the analysis. Furthermore, rheological functions such as viscosity or storage modulus can be measured in a more convenient way than GPC elution curve. For all these reasons, several procedures have been proposed, such as viscosity methods, involving the use of Mark-Houwink equation [96], or empirical correlations using storage modulus [97], among a few to mention.

3.1.2 Effect of the macromolecular architecture

The topology of the macromolecular chains, in terms of presence of short or long branches anchored to the main polymer backbone, has a relevant effect on the rheological functions of thermoplastics in general, and particularly for LDPE [98]. In general, there are three different kinds of branch architectures: star structure, with a certain number of branches radiating from a center; comb structure, with uniformly spaced side-chains and random branching structures, which is the most probable architecture for LDPE obtainbered through radical polymerization [99]. For LDPE containing random distributed branches, a further classification between short and long chains branching needs to be taken in account, since it is of fundamental importance as far as their influence on the viscoelastic properties of polymer is concerned. In fact, from a rheological point of view, long chain branching (LCB) are the side-chains long enough to improve the entanglement number of the polymer [100]. In this case, the introduction of LCB is hence able to introduce novel relaxation modes related to the motion of these long chains, which in turn can bear further minor ramifications, leading to an amplification of the non-Newtonian feature of the polymer flow behavior [101]. On the other hand, the presence of LCB can also reduce the hydrodynamic volume of the polymer [102]; therefore, these two concurrent phenomena having an opposite effect on the polymer rheological behavior need to be considered to fully understand the effect of the macromolecular architecture in affecting polymer viscoelastic properties. Conversely, the presence of short chain branching (SCB) has less impact on the rheological functions, as the density of entanglements remains almost unchanged with respect the correspondent linear polymer [103].

Numerous investigations have been performed concerning the effect of SCB and LCB on the rheological properties of several LDPE samples having different chain topology. Several investigations [104-106] report a lower melt viscosity for LDPE as compared to a linear polyethylene with similar M_w, although usually an impressive increase of the viscosity values was observed for LDPEs having low density of LCB and high molecular weight. Bersted at al. [107] documented a different effect of LCB depending on the branching mechanism; in particular, a more pronounced effect on the polymer rheological behavior was found for LCB introduced through peroxide-initiated reactions with respect to those by thermal initiation. Different samples of LDPE characterized by different densities of LCB, similar M_w and narrow molecular weight distribution, were synthetized by Yan et al. [108] using a high temperature/high pressure process and a titanium-based catalyst. Compared to a linear polymer having the same molecular characteristics, LDPE samples exhibited progressively higher zero-shear viscosity and lower viscosity at higher shear rates as a function of LCB content. Furthermore, the increase of the LCB content caused an amplification of the elastic feature of the polymer viscoelastic behavior, with an increase of the relaxation time and a higher level of die-swell.

Wood-Adams et al. [81] demonstrated a remarkable effect of the LCB density on storage modulus and loss angle. More specifically, the storage moduli curves as a function of frequency showed the presence of a shoulder in the low frequency region, associated with the appearance of a new well-defined relaxation regime in the branched polymer that is not present in the linear counterpart. Furthermore, they found that loss angle is a very sensitive indicator of the LCB presence. As far as the loss angle trend is concerned, linear sample exhibits the typical terminal behavior, approaching loss angle = 90° at low frequencies; conversely, in the curve of LDPE sample, a plateau at intermediate frequencies appears, the extension and magnitude of which depend on the LCB density.

Stadler et al. [109] analyzed the viscosity functions of several LCB polyethylenes, fitting the obtained data with a Carreau-like model involving 6 fitting parameters to determinate the characteristic relaxation time of selected polymers. They pointed out that a proper evaluation of the dependence of the rheological functions on LCB level is possible only if both M_w and LCB concentration were exactly known, since in many cases the influence of long-chain branches and the molar mass could not be separated.

The rheological behavior of a LDPE suitable for film-blowing was investigated and compared with that of linear and SCB polyethylenes [110]. According to other reports, the presence of LCB enhanced the non-Newtonian features in the trend of the viscosity curve (i.e. disappearance of the Newtonian plateau and amplification of the shear thinning behavior). Besides, the LDPE sample exhibited higher values of die-swell as compared to the others materials, because of its more prominent elastic behavior.

Valenza et al. [111] presented a set of rheological data for a series of LDPE polymerized in presence of different comonomers, differing in M_w and in the length of grafted branches. The general trend of the collected data suggested that the non-Newtonian behavior in shear flow is significant dependent on the length and on the density of LCB. Furthermore, the critical shear rate, at which surface irregularities (sharkskin) appear during extrusion was evaluated, showing that the activation energy for this phenomenon is strongly affected by both M_w and LCB structures.

The presence of LCB also affects the thermorheological behavior of thermoplastics, i.e. the temperature dependence of the relaxation mechanisms occurring in polymers. In this context, Stadler et al. [112] analyzed the thermorheological behavior of various LDPE samples, proving their thermorheological simplicity; this finding implies that the flow activation energy for these samples is independent from the relaxation time. Furthermore, activation energies were measured from the relaxation spectra of selected materials, in good agreement with the literature.

3.2 Elongational flow behavior

The rheological behavior of LDPE in elongational flow has been widely investigated, being this polymer largely processed through different processing operations, such as film-blowing or thermoforming, in which uniaxial or biaxial deformation is prominent. Results from extensional experiments performed on a standard LDPE at constant elongational rate $\dot{\varepsilon}_0 = 0.1\, s^{-1}$ [113] demonstrated the typical elongational behavior of LDPE, characterized by a steep increase of the stress at the beginning of the measurement, followed by a region, in which the stress-strain curve shows a growing slope (strain hardening behavior) and then a plateau for $\varepsilon_H > 4$.

Wolff et al. [114] studied the elongational properties of a commercial LDPE sample through creep and creep-recovery experiments, aiming at assessing the differences in the flow behavior between linear and non linear range of deformations. First, they found that the breadth of the linear range of LDPE is higher in elongational than in shear flow; besides, the experimental results indicated that, in the linear range, the Trouton law is fulfilled, implying that the value of the elongational viscosity is three times higher the value of the zero-shear viscosity. In the nonlinear range of deformations, as expected for long branched polymers, LDPE exhibited strain hardening behavior, with a rapid growth of the elongational viscosity as a function of stress. Münstedt et al. [115] formulated several blends based on LDPE in order to improve the film blowing properties of a series of linear polyethylenes. Virgin LDPE shown the usual strain hardening behavior as a function of time and the increase of viscosity was found more pronounced for the higher elongational rate probed. Conversely, for linear polyethylene samples the strain hardening was not observed, and the viscosity values, after a nearly constant regime, decreased. The addition of 10 wt.% of LDPE to the linear polymer resulted in the appearance of a defined strain hardening at high elongational rates; though at low rates this behavior was not detected, the elongational viscosity values do not drop down, indicating that the sample remains homogeneous during deformation. Furthermore, the homogeneity of the produced blown films was assessed through the measurement of the film thickness at 32 positions along the bubble take-up direction, and the calculation of an “inhomogeneity index”. The virgin LDPE film showed a very low value of the index, which remained constant during the entire duration of the characterization, reflecting the general favorable effect of strain hardening on the uniformity of deformation; conversely, for the linear polymer, higher values of the index were obtained, with significant data scattering during the measurement. The blend containing LDPE exhibited an improved stability of the film thickness, although it did not reach the performance of virgin LDPE.

Aiming at assessing the relationship between elongational viscosity and molecular structure, Münstedt et al. [116] characterized three LDPE samples differing for M_w, molecular weight distribution and LCB content. In the linear range of deformation, all the investigated samples exhibited a very similar behavior, and the values of their elongational viscosity coincided with the Trouton value. Differently, in the nonlinear range the viscosity curve is shifted towards higher values as a result of the increase of Mw and of a broadening of the molar mass distribution. In a similar way, also the presence of LCB affected the shape of the elongational viscosity curve, causing a progressive increase of the viscosity maximum in the nonlinear range of deformation, as a function of the degree of branching.

Two samples of LDPE were synthesized in a laboratory-scale autoclave under high pressure, and their elongational behavior was compared to that of two commercial materials [117]. Preliminary GPC analyses performed on the synthesized LDPEs revealed the presence of high molecular weight tails, resulting in a bimodal molar mass distribution. Rheological characterization in elongational flow shown that these samples exhibit improved strain hardening behavior as compared to the commercial samples, because of the longer characteristic relaxation time of the fraction of high molecular weight macromolecules.

As far as the rheological behavior in non-isothermal elongational flow is concerded, La Mantia et al. [118] evaluated the MS and BSR of different LDPE samples having different M_w and polydispersity index. Additionally, to evaluate the influence of the chain topology, one sample of LDPE was obtained in a vessel reactor, showing "three-like" branching, while all the other samples were synthesized in a tubular reactor. An increase of the polymer M_w is found to cause an increase of the melt strength and a decrease of the polymer deformability for all LDPE samples, except for the polymer with three-like branching, which exhibited higher MS and lower BSR as compared to the expected values. Therefore, the presence of a different chain topology caused a decrease of the polymer stretchability and an increase of the melt resistance. This behavior was explained considering that the presence of three-like structures makes more difficult the orientation of the macromolecules along the flow direction, causing a drastic reduction of the polymer extensibility and an increase of the melt resistance.

4. Effect of fillers on the rheological behavior of thermoplastics: general remarks and some applications to LDPE

The scientific literature reports several papers dealing with the rheological behavior of filled thermoplastics, but only few are specifically focused on LDPE-based systems.

4.1 Nanoclays

Clay nanofillers (i.e. nanoclays) are nanoparticles of layered mineral silicates. It is well-known [119] that their inclusion in a polymer matrix can lead to different morphologies, which derive from the aptitude of macromolecular chains to enter the clay galleries (the so-called *intercalation* phenomena) or even to collapse the stacked structure of clays by delaminating their sheets (*exfoliation* phenomena). Besides, when no interactions take place between the organic and inorganic constituents, phase separation occurs and the resulting composite structure is considered as *separated* *phase*: as a consequence, the so-derived polymer/clay composites are classified in the range of traditional micro-composites.

Generally speaking, the rheological behavior of clay composite systems that do not exhibit intercalation or exfoliation phenomena is similar to that of the polymer matrix, due to the low filler loadings and the weak interactions taking place between the two phases [120,121]. Conversely, the nanocomposites exhibiting intercalated or exfoliated morphologies are primarily prone to develop a particular rheological behavior [122] that comprises the following phenomena:

- a very low nanoclay loading (usually below 5 wt.%) is enough for promoting a transition between quasi-liquid and quasi-solid behavior. This transition determines a significant increase of G’ in the low frequency region
- the protracted application of large deformations produces a significant decrease in the linear viscoelastic module and the disappearance of the quasi-solid state of the nanocomposite system.

The transformation from a quasi-liquid to an almost solid behavior has been mainly interpreted on the basis of the formation of a percolation network, which occurs at very low nanoclays loadings because of their high anisotropy [123,124].

Some of the advances on the rheology of LDPE-clay systems will be summarized in the following. The rheological effects of LDPE containing Cloisite Na^+ (i.e. a typical montmorillonite clay), first modified with octadecyl ammonium chloride and then with equimolar amounts of octadecylamine (with respect to the pristine modified clay) were thoroughly investigated and correlated with the level of intercalation achieved as a consequence of the nanoclay modifications. Besides, a commercially-available organo-modified clay (namely Cloisite 30B) was treated with the same modifiers and compounded with LDPE in a Brabender mixer unit at 3 wt.% loading [125]. The complex viscosity of the systems based on LDPE and its nanocomposites was not affected by the presence of the modified nanoclays, because of the occurrence of limited intercalation phenomena. Conversely, when the modified nanoclays were added to LDPE-EVA (14 w/w of vinyl acetate) compounds, higher basal spacing values were achieved, hence increasing the complex viscosity of the nanocomposite system with respect to the unfilled counterpart.

Two different clays (namely, montmorillonite and kaolinite) were compounded in LDPE, using a twin-screw extruder and two screw configurations with different shear intensities. In particular, one configuration was set for intensive mixing and high residence time, while the other for more conventional, lower residence time compounding processes [126]. The state of nanoclay dispersion was also investigated through rheological analyses carried out with a rotational rheometer: in particular, at low frequencies, none of the tested samples, comprising unfilled LDPE, showed a

Newtonian plateau. Besides, the complex viscosity trends were found to depend on several experimental factors, namely: the screw profile, the clay nature and the possible presence of a compatibilizer. The most significant differences between the rheological curves were observed at low angular frequencies, for which the nanocomposites, according to the high degree of intercalation–exfoliation, showed the highest complex viscosity and G' values. Besides, using the power law expression ($\eta=A\omega^n$), it was possible to calculate the shear thinning exponents n for the nanocomposites extruded with the configuration for intensive mixing and high residence time in the low frequency region (i.e. from 0.1 and 1 rad/s): it is worthy to underline that while the presence of the clay alone did not affect the shear thinning behavior, this latter was significantly changed in the presence of a compatibilizer, capable for increasing the clay dispersion within the polyolefin.

Then, the rheology of polyethylene-montmorillonite (Cloisite Na^+) nanocomposites prepared by means of a water-assisted melt-intercalation process performed in a twin-screw extruder was thoroughly investigated, working in small amplitude oscillatory frequency sweep mode [127]. It was found that the changes in the rheological behavior strictly depend on the level of dispersion of the nanoclay within the polymer matrix. In particular, for well-intercalated systems, in the terminal region, a rise in complex viscosity and elastic modulus, as well as a decrease in phase angle values was observed: these findings pointed out the existence of solid-like or pseudosolid-like rheological behavior in the investigated systems.

4.2 Particles

When inorganic particles are incorporated into a thermoplastic matrix, the resulting material shows a complex rheological behavior, quite different from the rheology of unfilled homopolymers.

From an overall point of view, the addition of particles to a molten polymer usually increases the melt viscosity and decreases the melt elasticity. Different factors, comprising the volume fraction of the particles, their shape, size and size distribution, as well as the level of dispersion are well-known to affect the bulk rheological properties of particulate-filled polymer melts.

Some of the advances on the rheology of LDPE filled with different particles will be summarized in the following.

LDPE-Fly ash composites at different filler loadings (ranging from 4.2 to 28.6 vol.%) were prepared using a Two Roll Mixing Mill [128]. Fly ash is a by-product derived from the combustion of coal in thermal power plants; more specifically, it is a mixture of oxides rich in silica, Fe_2O_3 and alumina. As assessed by rheological tests, both shear stress and shear viscosity increased with increasing the filler loading. Besides, two regions of shear thinning were observed at 200°C for the prepared composites. The first normal stress difference was found to decrease with increasing the fly ash loading and the temperature. Conversely, this parameter remained almost unchanged at low shear.

Quite recently, Cobalt/Aluminum and Nickel/Aluminum layered double hydroxide (LDH) were intercalated with dodecylsulphate, laurate, stearate and palmitate and then compounded in LDPE at different loadings, ranging from 0.2 to 7.0 wt.% [129]. Low LDH loadings (i.e. below 2 wt.%) did not substantially affect LDPE shear moduli; conversely, with increasing the filler loading, the rheological curves showed a decrease of G' and G" moduli: this finding was ascribed to phase separation phenomena, occurring between LDH and LDPE regions. Besides, as revealed by the master curves of the unfilled polymer and its compounds with LDH, built using a vertical shift factor obtained at high frequency range (~100 rad.s^{-1}), no crossing between G' and G" was observed, and G" was always higher than G' throughout the frequency sweep: these findings confirmed the absence of transient networks in the molten state for the LDPE at the working temperature (190 °C).

Liang investigated the effects of temperature, elongation strain rate, die extrusion velocity, and nano-ZnO loading on the rheological properties of LDPE-ZnO nanocomposites prepared through a melt spinning technique [130]: this allowed understanding the rheological behavior mechanisms occurring in the composites during the melt elongation flow. To this aim, different LDPE-ZnO compounds (filler concentration: 0.2 to 4 wt.%) were designed, extruded in a twin-screw extruder and analyzed in a constant rate type of capillary rheometer. It was found that the effect of the nano-ZnO loading and elongation strain rate on the rheological behavior of composite melts was irregular. In particular, the melt elongation viscosity decreased with increasing the temperature, approximately following the Arrhenius equation. Furthermore, the melt elongation viscosity of the prepared composites containing low amounts of ZnO (within 0.4 and 0.8 wt.%) was lower in the whole composite system and showed the "roller effect". In particular, at elongation strain rates below 0.3 s^{-1}, the melt elongation viscosity raised and then lowered with the increasing elongation strain rate; meanwhile, the melt elongation stress reached a maximum around an elongation strain rate of 0.3 s^{-1}. This finding was ascribed to stress hardening effects.

Lin and co-workers investigated the rheological behavior of LDPE-MgO nanocomposites at different filler loadings (from 0.25 to 20 wt.%), using a rheometer working in oscillatory mode [131]. Notwithstanding a typical shear thinning behavior observed for all the nanocomposite systems, the complex viscosity was further reduced for the compounds incorporating low ZnO amounts (i.e. up to 1 wt.% of nanofiller). This finding was ascribed to the increase of free volume between the macromolecular chains and the nanoparticles, i.e. to an interface effect.

Recently, the rheological properties of LDPE composites incorporating LDH modified with disodium

2,2’-((1,1’-biphenyl)-4,4’-diyldivinylene)bis(benzenesulphonate), employed as fluorescent whitening agent, i.e. as a chemical compound that absorbs light in the ultraviolet region and re-emits in the blue region, were thoroughly investigated [132]. In particular, it was found that G’ and G” moduli showed constant values in a wide range of strain; besides, G” values were higher than G’, and when the temperature was raised, a decrease of the elastic and viscous moduli was observed. Finally, as assessed in frequency sweep tests, both G’ and G” were slightly affected by the incorporation of the modified LDH.

4.3 Carbon-based fillers

Several carbonaceous materials (such as carbon black, carbon nanotubes, graphene, fullerenes, among a few to mention) have been incorporated into different thermoplastic and thermosetting matrices, aiming to study the thermal, rheological, electrical, mechanical and barrier properties of the resulting materials. However, only few papers deal with the rheological behavior of LDPE-carbon based filler composites, which will be summarized in the following.

Gaska and co-workers prepared LDPE-based composites filled with different amounts of graphene nanoplatelets (ranging in between 1 and 7.5 wt.%) [133]. The rheological behavior of the obtained nanocomposites was investigated using a rheometer with plate-plate geometry; linear and nonlinear viscoelastic oscillatory shear tests were carried out, aiming at identifying the rheological percolation thresholds. As far as G’ and G” dependence in the terminal region is considered, a slight increase with the increasing graphene nanoplatelets loading in the whole angular frequency range was observed; however, it was not possible to prove the existence of an additional elastic contribution in the lower limit of the angular frequency range. Finally, the rheological percolation was observed for the systems containing 7.5 wt.% of the nanofiller.

Finally, in a recent work, LDPE-based nanocomposites containing different amounts of graphene (namely, 0.5, 1 and 3 wt.%) were prepared by melt compounding, using a mini-lab twin-screw mixer [134]. The Newtonian behavior shown by LDPE at very low frequencies totally disappeared for the nanocomposites containing the highest graphene loading, which exhibited shear thinning behavior unchanged with respect to the unfilled matrix. Besides, the viscosity change from liquid-like to solid-like at low frequencies was attributed to the formation of interlocked network structures in the nanocomposites, ascribed to hindered motion of macromolecular chain segments.

5. Conclusions and future perspectives

Though low density poly(ethylene) is a very well-established and cheap commodity, its processing is strictly related to the whole comprehension of the rheological behavior: therefore, the setup of such process parameters as temperature and shear rate is very important in order to obtain the most performing components or parts. For sure, the processing parameters depend on the architecture of the polyolefin, its molecular weight and molecular weight distribution, as well as on the branching degree. Therefore, a deep knowledge of all these parameters is really a key issue: rheological tests, performed according to different experimental conditions, can effectively help the designers and the manufacturers, leading to optimized conditions. Besides, as the use of neat LDPE homopolymers is somehow limited to specific applications (mainly including packaging and biomedical applications), a deep understanding of the effects of micro-to-nanofillers at different loadings on the polymer processability is undoubtedly of high importance, especially for high-tech advanced applications. In fact, the sensitivity of the rheological features with the structure and morphology of filled LDPE systems can help to discriminate the different morphologies that the standard characterization techniques are not able to elucidate.

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