Viscoelastic Behavior of Liquid-Crystal Polymer in Composite Systems

Andreea Irina Barzic and Silvia Ioan

Additional information is available at the end of the chapter

Abstract

Some basic concepts regarding the viscoelastic properties of polymers in solution phase, highlighting the effects of the some experimental variables, such as system composition, temperature or time, are reviewed. The main attention is given to experiments involving shear deformation of polymer solutions, since it provides the most significant data concerning the optimal processing of final product. The response of polymers to a mechanical perturbation involves several types of molecular motions, which are reflected in the microstructure changes. The elastic constants, which determine the motion of macromolecules, become anisotropic in case of liquid-crystal polymer (LCP). The state of art concerning the viscoelastic behavior of liquid crystal polymers in composite systems is described. The main aspects that are discussed include the effects on the viscoelasticity given by molecular orientation, system composition and interactions. Finally, some particular cases are presented to illustrate the potential applications of these principles to practical problems in the processing and use of the described materials.

Keywords: viscoelasticity, liquid crystals, applications, polymers, solutions

1. Introduction

The development of new products for current technologies demands close investigation of the properties variations in the presence of external forces. The mechanical performance arises from the viscoelastic features of the material [1]. In other words, mechanical features are time dependent, whereas perfectly elastic deformation and perfectly viscous flow are idealizations that are approximately reached in some limited conditions. Viscoelastic materials present, under mechanical stress, combined characteristics of these two behaviors, a "fading

memory", partial recovery, energy dissipation, etc. This type of dependence can be linear (stress – strain dependence is a straight line with a single slope) or nonlinear (stress – strain dependence presents many slopes) [2, 3].

Among the compounds with pronounced viscoelasticity, polymers are the most important in rubber and plastic industries [4, 5]. Their viscoelastic properties influence not only the mechanical reliability of the final products of these industries, but also the efficiency of processing methods at intermediate stages of production. In most cases, the designer aims to maintain the elastic deformations under a critical limit. The peculiar viscoelastic features of polymers arise from the complex dynamics of flexible chains [6]. For instance, above the glass transition temperature (T_g), the response of these materials to mechanical perturbation forces entails several types of molecular motions. The large freedom in the spatial arrangement of macromolecular compounds allows various types of motion according to the time and spatial scales. At big scales, the polymer chains present unique dynamic features that are not found in low-molecular-weight materials. These characteristics deal with motion in scales above the monomer size and are similar for polymer chains of various structures. The movement of macromolecules is reflected in various kinds of dynamic properties, including viscoelastic (rheological), dielectric and diffusion ones [6].

On the other hand, the special response to the deformation of macromolecular compounds arises from the fact that they have time- and temperature-dependent modulus, while for metals and ceramics, this property can be assumed to be constant at room temperature. The phenomenological theory of linear viscoelasticity of polymers is semiquantitatively clarified from the point of view of the effects induced by the molecular weight, temperature, concentration and other parameters [7]. However, there are still some aspects that are not entirely understood, such as the impact of molecular weight distribution or crystalline character. While not all polymers are viscoelastic to any important practical extent, the linear viscoelastic theory gives an engineering approximation for many applications in polymer and composites engineering. Even in cases that demand more elaborate approaches, the linear viscoelastic theory is a useful starting point in optimizing the mechanical performance of products containing liquid-crystal components that are used in certain devices. Particularly, liquid-crystal polymers (LCPs) present an interesting viscoleastic behavior [8, 9], which in combination with other materials can lead to composite systems with enhanced properties as demanded in modern applications [10–12].

This chapter describes the state of art in the field of LCPs in composite systems, highlighting the importance of viscoelasticity in designing advanced materials for recent technologies. Some fundamental notions, concerning the response given by these compounds under external fields, are discussed. The main attention is focused on experiments involving shear deformation of polymer solutions; generally, this is the state from which most materials are processed. The changes in viscoelastic characteristics after reinforcement of LCPs are reviewed in regard with some parameters, such as system composition, time or temperature. The practical importance of composite systems with LCPs phase is analyzed in agreement with the current demands on various industries.

2. Fundamentals on viscoelasticity in shear experiments

2.1. Viscoelastic behavior of polymers

Viscoelastic response is often used as a probe in polymer science, since it is sensitive to the material's chemistry and microstructure [13]. The response of such compounds with a viscoelastic component is complex and depends on several aspects of both experimental and structural nature.

Regarding the experimental procedure, it is known that the strain can be directly proportional to stress at any time and, in a similar manner, the stress at any particular moment in time is directly proportional to the strain depending upon which of these are considered the stimulus and corresponding response. This is generally noticed in the case of small stresses or strains. However, nonlinearities appear in the viscoelastic behavior because at increased strains the response does not range proportionally with applied field. Linear viscoelasticity can be included in general theory of mechanics of materials, and thus, macromolecular structures with viscoelastic components can be analyzed. In the dependence of modulus on normalized temperature (T/T_g), five regimes of deformation are noticed, particularly for linear amorphous compounds [14]:

- glassy regime with a large modulus (>3GPa);

- glass-transition domain in which the modulus drops from 3 GPa to 3 MPa;

- rubbery plateau with a low modulus around 3 MPa;

- viscous region when the polymer begins to flow;

- decomposition regime in which chemical breakdown occurs.

Concerning the structural aspects, one may notice that application of a stress to a polymer can determine two different atomistic mechanisms of deformation [14]. The first one is related to the distortion of the lengths and angles of the chemical bonds that move the atoms to new positions of bigger internal energy. Such motions are small and require around 10^{-12} s. The second mechanism arises from the degree of flexibility of the polymer chains that lead to large-scale re-arrangements of atoms. Facile rotation of simple carbon bonds around the main chain can induce changes in the conformation of the molecule. For structures with high mobility, the polymer can extend itself along the applied stress, generating a reduction in conformational entropy.

On the other hand, the rearrangement of the macromolecular chains after cessation of external deformation force is reflected in different relaxation time scales. At the length scale of the repeating unit, this repositioning of chains may be very fast, involving cooperativity in the conformational transitions and even as the relaxation propagates along the backbones. This implicates a growing number of segments as the time passes. At very long times, disentanglements occur and the corresponding relaxation time is long and dependent on molecular weight and molecular architecture of the system. The disentanglements strongly influence the flow properties. Considering all these aspects, the molecular response of

polymers to deformation is complex, exhibiting a wide distribution of relaxation times that extend significantly in the time or frequency domain. The elastic character is mainly viewed at short time or long frequency, while at long time or short frequency, the viscous feature is prevalent.

To obtain information relevant to actual in-use conditions of viscoelastic polymer materials, mechanical characterization is often performed. Mostly, polymers are processed from solution phase or melt. The phenomena observed in such polymer systems as a result of viscoelastic deformation are mainly examined by means of dynamical mechanical spectroscopy (DMS) [15]. This is one fundamental rheological technique used to evaluate the viscoelastic properties of complex fluids and to investigate their microstructure [16]. For polymers in these states, the investigations are modified so as to enable observation of the time dependency of the material response. Although many such "viscoelastic tensile tests" have been used, one mainly encounters the following three tests:

- *Creep*: Such analyses allow measuring the time-dependent strain resulting from the application of a steady uniaxial stress. The test entails applying a constant shear stress onto a sample and observing the resulting elastic deformation and/or viscous flow. If the material has a linear behavior, stress-strain curve will be a straight line, with a slope that increases as the chosen time is decreased. The test enables to determine the following aspects:

  – a high-quality zero-shear viscosity value—by the sustained application of a shear stress that is taken at the linear viscoelastic limit for the sample;

  – the product behavior during long-term exposure to high level of stress that is still below the yield strength of the material, for example in draining, sagging, sedimentation or leveling cases;

  Creep compliance is the ratio of strain to stress in the case of time-varying strain arising from a constant stress. The dependence of creep compliance on time is described by various domains (**Figure 1a**), namely

  – Glassy: where the compliance is that of a glassy solid at short times, the latter variable having no influence;

  – Viscoelastic: observed at intermediate times, where compliance is time dependent;

  – Rubbery and flow: occurring at very long times, where compliance is typical for a rubber like solid and is independent of time;

- *Stress relaxation*: It consists of monitoring the time-dependent stress resulting from a steady strain. When instantaneous strain is applied to an ideal elastic solid, finite and constant stress will be obtained. For a linear viscoelastic solid, the instantaneous stress will be proportional to imposed strain and will decrease with time. For amorphous linear polymers at high temperatures, the stress may decay to zero, whereas in the absence of viscous flow, the stress decays to a finite value. Stress relaxation modulus dependence on time presents various regions (**Figure 1b**):

  – Glassy: found at very short times and the relaxation modulus is independent of time;

– Viscoelastic: placed at intermediate times, where relaxation modulus is time dependent;

– Rubbery and flow: noticed at very long times, relaxation modulus is similar to a rubber like solid and is independent of time;

- *Dynamic (sinusoidal) loading*: Both previous tests are convenient for the investigation of material response at long times (minutes to days), but less accurate at shorter times (seconds and less). Dynamic tests consist in determining the stress (or strain) resulting from a sinusoidal strain (or stress). This is more adequate for filling out the "short-time" range of polymer response. Application of sinusoidally stress to viscoelastic polymers determines the occurrence of a steady state. The recorded strain is also a sinusoidal signal with similar angular frequency but phase-shifted in regard with the imposed stress. This is analogous to the delayed strain observed in creep experiments. The strain lags the stress by the phase angle and this is true even if the strain rather than the stress is the controlled variable.
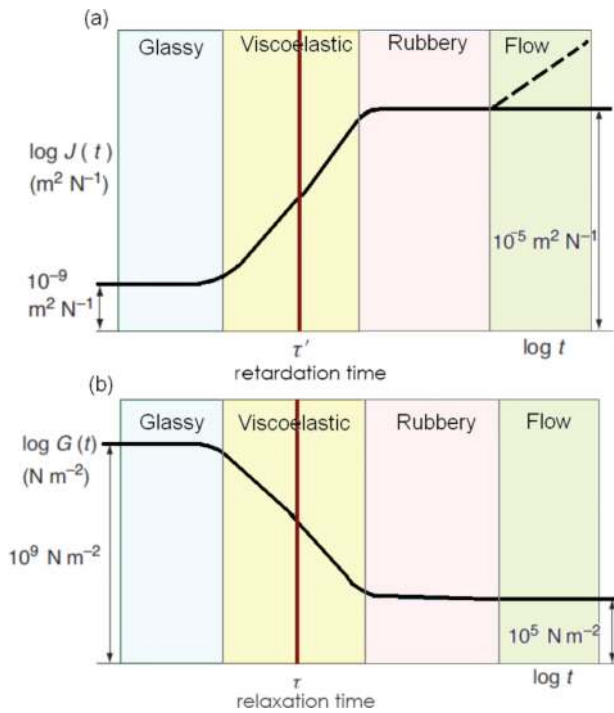
Figure 1. The dependence of creep compliance (a) and stress relaxation modulus (b) on time reflecting various behaviors of polymer systems.

In the following paragraphs, particular attention will be given to viscoelastic characterization by means of oscillatory rheology testing. The sinusoidal shear deformation, $\gamma(t)$, applied to polymer materials during such experiments, is described by the following relation (1):

$$\gamma(t)=\gamma_0\sin(\omega t) \tag{1}$$

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

The shear rate, namely rate at which a progressive shearing deformation is applied to a material, is given by the relation (2):

$$\dot{\gamma}(t)=\gamma_0\omega\cos(\omega t) \tag{2}$$

The material stress response is measured and, by the utilization of adequate theoretical models, it is correlated with the features of the polymer system under analysis. There are two different types of rheology tests, depending on the amplitude of the applied deformation [16–18]:

- Small amplitude oscillatory shear (SAOS): It is a robust, widely used rheology technique, where the amplitude of applied strain is small enough to induce a linear response of the sample. The stress is proportional to the oscillatory deformation and is represented by a sinusoidal wave with the same frequency;

- Large amplitude oscillatory shear (LAOS): It is a recent method involving large deformation to give a nonlinear response. The stress is still periodic, but not sinusoidal and can be deconvoluted in terms of a fundamental harmonic and its odd multiples. Stress is often examined in the Fourier space leading to the so-called Fourier transform rheology. Nonlinear experiments are, obviously, more complex than linear ones. However, they provide supplementary information about the morphology of microstructured polymer systems.
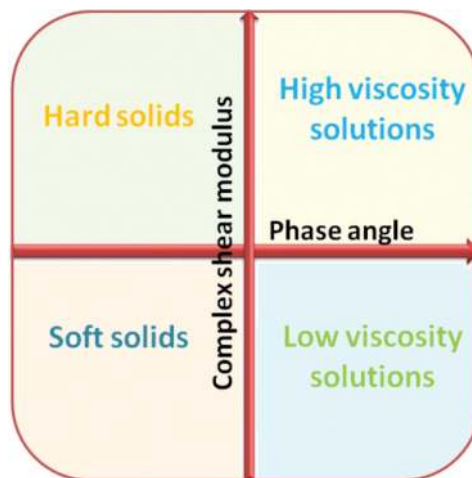

Figure 2. The viscoelastic map constructed based on phase angle and complex modulus.

Oscillatory shear testing is useful to analyze and quantify the rigidity and integrity of a polymer's internal structure as a result of a variety of phenomena, for example, flocculation and interaction of dispersed particles or droplets, or compatibility, crosslinking and entanglement of dissolved macromolecules. In most cases, oscillation rheology experiments are performed at very low applied stresses and strains, often significantly below the yield point of the polymer material. Typically, measured parameters include complex modulus (G^*), elastic (or storage) modulus (G') and viscous (or loss) modulus (G''), phase angle (δ) and tangent of the phase angle (tan δ). The viscoelastic map can be constructed based on phase angle and complex modulus (see **Figure 2**) thus allows one to distinguish between elastic solids and viscous liquids (left to right) and high to low rigidity or viscosity (top to bottom).

2.1.1. Linear viscoelastic behavior

Linear properties of viscoelastic polymer solutions have been investigated along with the mechanical behavior in this regime. Fundamentals on these aspects are documented in several textbooks [19–21]. SAOS measurements have been employed to characterize a very large number of complex fluids from polymer melts [22] to liquids crystalline [23] and from gels [24] to polymer blends [25, 26].

The linear domain of viscoelastic behavior can be easily determined from oscillation stress sweeps and strain sweep tests (**Figure 3**). Oscillation stress and strain sweeps offer easy-to-interpret information about the soft-solid rigidity and yield stress [4, 6]. These tests provide a deep insight into the rigidity and strength of the soft-solid polymer structures that render basic quality attributes in many manufactured products. The oscillation stress or strain sweep measurements consist in exposing the sample to small amplitude oscillatory (i.e., clockwise then counter clockwise) shear. In the beginning stages of the test, stress is sufficiently low to maintain structure. However, as the test continues the incrementing applied stress causes the ultimate disruption of structure—the yield process. The resulted structural change is manifested as a reduction of elasticity (phase angle increases) and an accompanying decrease in rigidity (complex modulus).
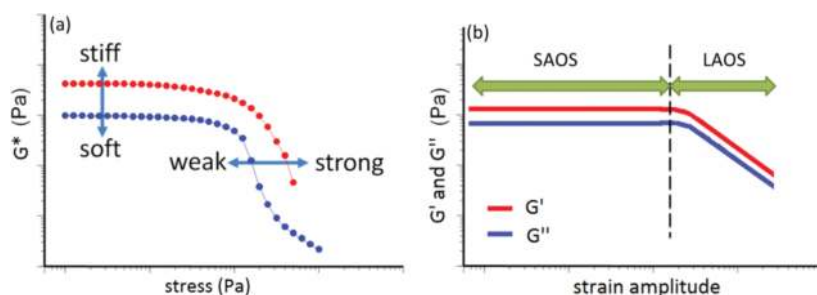
Figure 3. Schematic representation of (a) typical oscillation stress sweeps test and (b) strain sweep test at a fixed frequency, the latter determining the linear and nonlinear viscoelastic regions.

The typical shear stress response of a SAOS test is given as follows:

$$\sigma(t)=\sigma_0 \sin(\omega t+\varphi)$$ (3)

The frequency of oscillation (ω) of stress does not change in regard with the imposed deformation, but it is shifted by an angle $\varphi\in[0, \pi/2]$. The value of φ is equal to 0 for elastic solids, and hence, the stress is not phase shifted in relation to the strain. For viscous liquids, the value of φ is equal to $\pi/2$; therefore, in this case, the stress is in phase with the shear rate. In the linear regime, the phase angle is mainly influenced by strain frequency, while amplitude of applied strain is not reflected in the elastic or viscous components [4, 17]. Equation (3) is usually written in the following way:

$$\sigma(t)=\gamma_0\left[G'\sin(\omega t)+G''(\cos(\omega t)\right]$$ (4)

where:

$$G'=\frac{\sigma_0}{\gamma_0}\cos(\varphi)$$ (5)

$$G''=\frac{\sigma_0}{\gamma_0}\sin(\varphi)$$ (6)

The term G' is in phase with the strain, while the term G'' is in phase with the shear rate.

Oscillatory frequency sweep allows evaluating the nature of the structuring mechanisms present in a polymer solution or melting. The sample is subjected to small-deformation oscillations of various frequencies to estimate the structural response to shear of longer or shorter timescales. The technique can differentiate between the "relaxable" structures and those characterized by permanent elasticity, being a useful tool when trying to match textures and flow behaviors in thickened polymer systems [4]. **Figure 4** displays some typical frequency sweep tests for polymer samples.

As stated earlier, in linear regime, the amplitude of the stress is proportional to the amplitude of the imposed deformation, consequently G' and G'' do not depend on amplitude of applied strain, but on frequency only. The storage and loss modulus for typical "liquid-like" and "solid-like" fluids are shown in **Figure 4**. For the "liquid-like" sample, the elastic modulus is much lower than the viscous one and it has a frequency dependence of type: $G' \propto \omega^2$, whereas the viscous modulus is linear in frequency, namely $G''\propto \omega^1$ [4]. In materials with "solid-like" behavior, like polymer gels, the elastic shear modulus overcomes the viscous one, and almost no dependence on angular frequency is observed. Real complex fluids often present an intermediate viscoelastic behavior.
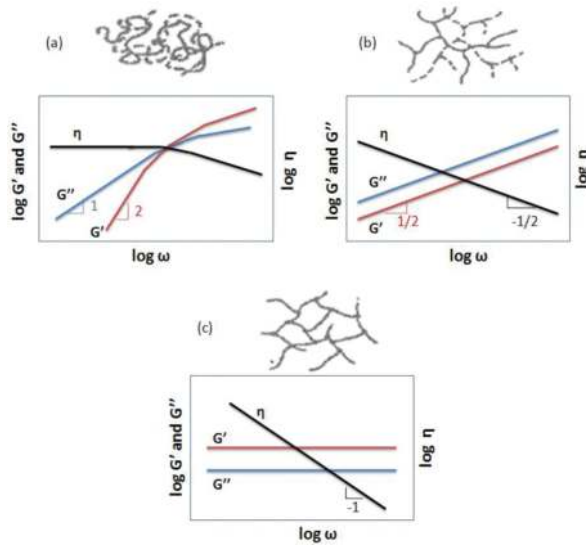
Figure 4. Typical frequency sweeps for polymer solutions (liquid-like) or melts (a), gelation or (b) and curing finished or "solid-like" materials.

2.1.2. Nonlinear viscoelastic behavior

Nonlinear viscoelastic behavior of polymer systems is intrinsically more complex than linear one, from both the experimental and the theoretical point of view. The interest for this aspect of viscoelasticity is very high because many polymeric systems are processed in the nonlinear regime. Therefore, LAOS experiments can provide essential information on the material characteristics in that specific range. Furthermore, nonlinear experiments are able to describe in detail the complex fluids microstructure. The first experimental works on nonlinear measurements were reported in the seventies [27], but only in the last two decades, they are significantly increased [28–30], owing to the significant development of experimental devices and software programs.

The shear stress response of a LAOS test is still periodic, with the same frequency ω of the imposed oscillation, but not sinusoidal [17]. It can be described by a Fourier series of odd harmonics:

$$\sigma(t)=\sum_{\substack{k=1\\k,odd}}^{\yen} a_k\cos(k\omega t)+\sum_{\substack{k=1\\k,odd}}^{\yen} b_k\sin(k\omega t) \tag{7}$$

where a_k and b_k represent the amplitude of the cosine and sine terms of the k-th harmonic and depend on both frequency and strain amplitude. They can be obtained as follows:

$$a_k = \frac{2}{T} \int_0^T \sigma(t) \cos(k\omega t) dt \tag{8}$$

$$b_k = \frac{2}{T} \int_0^T \sigma(t) \sin(k\omega t) dt \tag{9}$$

where T is the period of the imposed strain oscillation.

The utilization of the Euler notation leads to another form of Eq. (7):

$$\sigma(t) = \sum_{\substack{k=-\infty \\ k,\text{odd}}}^{\infty} I_{k\omega} e^{jk\omega t} \tag{10}$$

$$I_k = \frac{2}{T} \int_0^T \sigma(t) e^{-jk\omega t} dt \tag{11}$$

In expression (10), the term $Ik\omega$ is the complex coefficient of the k-th harmonic in the Fourier domain, $I_{k\omega} = a_k - jb_k$. It should be remarked that shear stress is an odd function of the strain. Therefore, only odd terms of the Fourier series are taken in consideration for in Eqs. (7) and (10).

An important aspect that one should remark is that during a LAOS test, the system is deformed with a single frequency, while the stress presents more than one frequency, so the collected signal expresses several time scales, thus providing detailed data about the analyzed polymer material. LAOS technique involves the following aspects [17]:

- a sophisticated experimental apparatus;

- an elaborated data manipulation;

- a theoretical model that allows interpretation of nonlinear results.

The first two points are widely analyzed in the literature [28, 31], while the third point is less investigated [30]. The fundamental modifications of traditional rotational rheometer to correctly implement the nonlinear DMS are reported [31]. It is essential to improve the signal-to-noise ratio of the achieved experimental signals. If appropriate practical contrivances are made, one may obtain highly sensitive detection. Since experimental data are analyzed in the Fourier domain, the technique is usually named Fourier transform rheology (FTR).

There are many advantages concerning data analysis in the Fourier rather than in the time domain. First of all, the appearance of nonlinearity is better noticed [32]. FTR can detect the nonlinear contribution at about 10 times lower strain amplitude compared to linear oscillatory measurements [31]. The resulted files of the experimental data concern only the intensity of the odd peaks, and therefore, they require a low amount of memory on the computer.

Furthermore, the Fourier coefficients are less affected by experimental noise. Generally, only the third and fifth overtones and, in particular, their absolute value are analyzed. There are not many reports concerning the separation of the real and imaginary part of the harmonics [30, 32]. The fundamental lack of FTR is the absence of theoretical models, which can correlate experimental points with the morphology of the polymers.

Regardless the viscoelastic domain in which experiments are performed, there are several inherent parameters that influence the viscoelastic behavior of polymeric systems. The primary ones are the following:

- chemical structure;

- molecular architecture;

- molecular weight and crosslinking;

- copolymers and blends;

- effect of plasticizers;

- molecular orientation;

- fillers and fibers.

2.2. Viscoelastic behavior of LCPs

The linear viscoelastic response to shear deformation was investigated for many LCPs by checking the dependence of rheological moduli on frequency. The range of strain amplitudes corresponding to linear viscoelastic domain is broad for side-chain LCPs in nematic phase, similarly to common flexible polymers. This is not maintained for main chain nematic polymers. For those in smectic phase, the range of linear viscoelasticity is narrower.

Viscoelastic behavior of LCPs depends on temperature at which the sample is subjected during oscillatory testing. For example, aqueous solutions of methylcellulose present changes in elastic modulus during the heating process from 20 to 80°C that consist in several stages, depending on concentration [33]. In the range of 20–35°C, the storage modulus increases slowly. In the following stage, G' has a more pronounced increase with temperature to about 50°C, and then, the rate of increase slows down. Above about 60°C, the polymer solutions with different concentrations show different rheological behaviors. For the samples with lower concentrations (c<4.0 g/L), elastic modulus eventually reaches a plateau value. For more concentrated solutions of 8 and 10 g/L, a third remarkable increase in G' is noticed as a result of formation of a mature gel. As for the solutions with medium concentrations, 4–6 g/L, a third appreciable increase in G' is remarked at about 66°C as a result of the occurrence of a weak gel. At higher temperatures (>65°C), the strength of the gel increases with the concentration. However, while the values of storage modulus increase monotonically with temperature, the values of this parameter do not increase monotonically as a function of concentration, as expected for normal polymer solutions. A discontinuity of change in G' at several temperatures with the concentration of cellulosic polymer in solution occurs. A similar behavior was reported for other LCP solutions in lyotropic phase [34].

The viscoelastic properties of thermotropic LCPs that have mesogenic pendant groups to flexible main chain were found to be sensitive to smectic-nematic and smectic isotropic transitions. However, they are less affected by nematic isotropic transition as time-temperature superposition applies across this transition. In contrast to main chain LCPs, the nematic side chain ones present linear viscoelastic behavior over a large range of strain amplitudes that is independent of thermal and shear histories. At very low frequencies below than the reverse of diffusion time, side chain LCPs in their nematic state have a terminal response, which is typical for viscoelastic liquids. In their smectic phase, they are still viscoelastic in the same frequency domain and approach the terminal response of a viscoelastic solid at the lowest frequencies [35].

Another report [36] concerns the comparison of viscoelastic properties of two polymers in isotropic and anisotropic phases. The poly(p-phenylene terephtalamide) (PPD-T) and HPC present similar rheological features in isotropic solutions. However, the nematic PPD-T and cholesteric HPC present different rheological row responses in that the yield stress of HCP remained almost constant with increasing concentration, whereas that of PPD-T increased significantly. At 1 rad/s both LCPs present an increase of the ratio of elastic modulus to twice loss modulus with increasing concentration. At 100 rad/s, HPC exhibits monophonic decrease in $G'/2G''$ with concentration, whereas in case of the other LCP, the ratio increase at the concentration higher than the saturated concentration. There is certain sensitivity of elastic modulus of nematic PPD-T to strain level, while for HPC, there is almost no dependence to this experimental parameter.

The evolution in time of shear moduli after flow cessation is a useful to analyze structural relaxations on LCPs. Upon flow cessation, the flow-induced orientation is lost. The variation of the moduli of a cellulose derivative with time was proved to be caused by the reformation of a chiral nematic phase that had become nematic under flow [37].

2.3. Viscoelastic behavior of LCPs in composite systems

The literature concerning the viscoelastic properties of LCPs in composite systems is not so abundant in regard with LCPs. Some reports involve oscillatory shear investigations on systems prepared from hydroxylpropyl cellulose (HPC) in lyotropic phase blended with different polymers, such as polyimide [38] and cellulose acetate phthalate [39]. Other studies concern reinforcement of LCPs with carbon nanotubes [40]. Such multiphase systems concern also blends of thermotropic LCP with commercial polymers [41].

A system consisting of HPC/polyimide presents a combination of viscoelastic behavior of each counterpart. The polyimide solutions present frequency sweep curves similar to those presented in **Figure 4(a)**. So, at the low frequencies, the loss modulus is higher than the storage modulus, with no plateau appearing in G'. At a specific frequency, this changes and rheological modulus cross each other, thus elastic modulus becoming higher [38]. The HPC in the liquid crystalline phase, the crossover frequency is higher comparatively with the case of the isotropic solutions. The dependence of the rheological moduli on frequency has slopes below unity. For HPC/polyimide composites, in the low-frequency range, the slopes are smaller comparatively to the pure components and are reduced as the lyotropic phase becomes predominant. The

overlap frequency is influenced by the chemical structure of the individual polymers and by the blend composition. If the flexible counterpart is diminished, transition from the viscous to the elastic flow is delayed and the moduli crossover occurs at higher frequencies.

The HPC/cellulose acetate phthalate composites present similar behavior to those previously described. The exponents from the dependence of shear moduli versus frequency decrease on one hand, at lower values of polymer concentrations and, on the other, at lower HPC compositions in the system. In addition, the frequencies corresponding to the crossover point, which marks the transition from viscous flow to the elastic one, become higher with increasing the cellulose acetate phthalate content in composite [39].

A thermotropic liquid crystal polyester (TLCP) was reinforced with a very small quantity of modified carbon nanotube (CNT). The rheological properties of the composite are influenced by the uniform dispersion of CNT and the interactions between the CNT and TLCP, which can be enhanced by chemical modification of the filler [40]. The values of shear moduli of TLCP nanocomposites are significantly enhanced with increasing frequency and filler content. This enhancing effect was more pronounced at low-frequency region. The behavior is similar to the relaxation of typically filled polymer composite system, namely if polymer chains are fully relaxed and exhibit a characteristic homopolymer-like terminal behavior, the flow curves of polymers can be expressed by a power law with slopes like those from **Figure 4(a)**. The variations of terminal zone slopes of TLCP nanocomposites revealed the nonterminal behavior with the power law dependence of shear moduli on frequency. The decrease in the slope of for TLCP nanocomposites with the introduction of filler is based on the fact that the nanotube-nanotube or nanotube-polymer interactions produce the formation of the interconnected or network-like structures. This leads to the pseudosolid-like behavior more elasticity of TLCP nanocomposites in regard with TLCP matrix. As the shear frequency increased, the interconnected or network-like structures were disrupted by high levels of shear force and TLCP nanocomposites presented almost similar or slightly higher G' and G'' values than that of pure matrix at high-frequency region. The nanocomposites containing modified CNT have higher values of rheological moduli of TLCP, suggesting the increased interactions between modified CNT and TLCP matrix. Similar results were reported for thermotropic LCPs reinforced with a commercial polymer [41].

3. Applications

The viscoelastic features of polymer systems with self-alignment features are explored in several applications, including in tissue engineering or in display industry.

Tissues engineering represents a large subdomain of biomedicine and consists in improvement or replacement of biological functions of a damaged part of organism by utilization of a scaffold for the formation of new viable tissue. Biocompatible polymers are good candidates for cell growth substrates. In addition, the partial organization of LCPs, such as the natural derived macromolecules, is useful in preparation of cytocompatible supports with guided growth ability [42]. For example, polymer systems with chiral phase are able to direct anisotropic cell

growth and play a crucial role in formation of patterns noticed in mammalian tissues [42]. The use of biologically derived polymers as LC layers for *in vitro* material production opens novel design perspectives because of the innate cellular response of these materials *in vivo*. Moreover, it was proved that the support morphology and viscoelasticity influences cell behavior [43]. If the scaffold surface has on its surface deep valleys and wide grains, then it is expected to have a greater effect on cell spreading and arrangement than alteration of the elastic modulus. Particularly, it was shown that valley depth plays a leading role in contact guidance of endothelial cells on microtextured silicone elastomer. In other words, at lower grain widths and in shallower valleys, the modulus of the substrate it appears to exhibit an essential role comparatively with rough and different nanocomposite surfaces. So, it can be stated that cell attachment, proliferation, and differentiation could be optimized by controlling the surface roughness and stiffness of the biocomposite scaffold [43].

Another important application of LCPs in composite system is the preparation of polymer dispersed liquid crystals (PDLCs) or nematic alignment layer for display purposes. The PDLC is a light-scattering material that operates on the principle of electrically modulating the refractive index of the liquid crystal in an optical isotropic, transparent solid [44]. The electro-optic material is placed between two polarizers, and its corresponding droplets, with dimensions varying between 0.1 and 10 μm, have positive dielectric anisotropy. PDLC displays demand a driving transistor array with high driving voltages, more current and less leakage. In OFF state, the polymer network follows the planar cholesteric helix and maintains its memory in previous stages by anchoring the director in suitable configuration. The helical birefringent texture reflects electromagnetic radiation from visible domain in a selective manner. In ON state, the director tends to align along the external field, but it is prevented by bulk anchoring on the polymer network. Thus, it results a scattering conical texture. Increasing the field intensity allows full alignment of director and PDLC composite becomes transparent. However, the memory regarding the initial cholesteric arrangement is permanently retained in the polymer network and on switching the field off, the optical features came back to their original state. The randomly inhomogeneous PDLC with a dilute rigid polymer network should be contrasted with liquid crystalline gel network. Cross-linking polymer chains do not phase separate from the LCP, the latter being considered as an anisotropic solvent in a homogeneous gel with a weak rubber-elastic polymer network.

On the other hand, viscoelasticity also counts when constructing polymer alignment layers for nematics. The LCP surface interaction is essential for the device reliability. The nature of this interaction is complex and is a combination of van der Waals interactions, dipolar interactions, steric factors, chemical and hydrogen bonding. Also, surface topography and mechanical features of polymer layer affect the mechanism of nematic orientation. It was assumed that anisotropic liquid crystal orientational elasticity in connection with rubbing-induced microgrooves on polymer surface could be the key factor in designing display devices. Berreman [45] proposed that the director field adapts itself to the morphology of the polymer to reduce as much as possible the elastic strain energy arising from the distortions of the director field [45]. Introduction of soft polymers in a LCP matrix subjected to shear can determine a specific texture onto the surface of the resulted mixed alignment layer. Depending on the composite

system composition, one can tune the surface texture and viscoelasticity and implicitly the ability to align uniformly nematic molecules.

4. Conclusions

This chapter describes the viscoelastic properties of polymers. The size and the large aspect ratio of these materials cause high elasticity and viscoelasticity. High elasticity is related to the ability of flexible chain macromolecules to recover from large strains, a property unique to rubber. Viscoelasticity denotes a time-varying reaction to a transient perturbation, unaccompanied by any modification in the material. Viscoelastic polymers both dissipate and store energy during deformation. These two characteristics underlie most applications of rubbery materials. The chapter provides an overview of the viscoelastic behavior during shearing of LCP solutions and also in composite systems highlighting the local and segmental motions, the chain dynamics, and also the influence of temperature, composition and time.

Acknowledgements

Author details

Andreea Irina Barzic and Silvia Ioan[*]

*Address all correspondence to: ioan_silvia@yahoo.com

Department of Physical Chemistry of Polymers, "Petru Poni" Institute of Macromolecular Chemistry, Iasi, Romania

References

[1] Christensen RM. Theory of Viscoelasticity. 2nd ed. Mineola: Dover Publications Inc; 1982.

[2] Findley WN, Lai JS, Onaran K. Creep and Relaxation of Nonlinear Viscoelastic Materials. Revised ed. New York: Dover Publications; 2011.

[3]   Lakes R. Viscoelastic Materials. Cambridge: Cambridge University Press; 2009. DOI: 10.1017/CBO9780511626722

[4]   Ferry JD. Viscoelastic Properties of Polymers. 3rd ed. New York: Wiley; 1980.

[5]   Hyuna K, Wilhelm M, Klein CO, Cho KS, Nam JG, Ahn KH, Lee SJ, Ewoldt RH, McKinley GH. A review of nonlinear oscillatory shear tests: analysis and application of large amplitude oscillatory shear (LAOS). Prog Polym Sci. DOI: 10.1016/j.progpolymsci.2011.02.002, 36,1697–1753, 2011

[6]   Watanabe H. Viscoelasticity and dynamics of entangled polymers. Prog Polym Sci. DOI: 10.1016/S0079-6700(99)00029-5, 24, 1253–1403, 1999

[7]   Roland RM. Viscoelastic Behavior of Rubbery Materials. Oxford: Oxford University Press; 2011.

[8]   Acierno D, Brostow W. Rheology and Processing of Liquid Crystal Polymers. London: Springer; 1996.

[9]   Baek SG, Magda JJ, Cementwala S. Normal stress difference in liquid-crystalline hydroxypropylcellulose solutions. J Rheol. DOI: 10.1122/1.550404, 37, 935–945, 1993

[10] Cosutchi AI, Hulubei C, Stoica I, Ioan S. A new approach for patterning epiclon-based polyimide precursor films using a lyotropic liquid crystal template. J Polym Res. DOI: 10.1007/s10965-011-9653-z, 18, 2389–2402, 2011

[11] Dobos AM, Onofrei DM, Tudorachi N, Ioan S. Structural orientations of cellulose acetate phthalate/ethyl cellulose blends in solution. J Macromol Sci Part B. DOI: 10.1080/00222348.2015.1078625, 54, 1092–1104, 2015

[12] Dutta D, Fruitwala H, Kohli A, Weiss RA. Polymer blends containing liquid crystals: a review. Polym Eng Sci. DOI: 10.1002/pen.760301704, 30, 1005–1018, 1990

[13] Roylance D. Engineering viscoelasticity. Courses of Massachusetts Institute of Technology.   http://ocw.mit.edu/courses/materials-science-and-engineering/3-11-mechanics-of-materials-fall-1999/modules/visco.pdf; 2001.

[14] Cerrada ML. Introduction to the Viscoelastic Response in Polymers. In: RA Diaz, editor. Thermal Analysis. Fundamentals and Applications to Material Characterization. Coruña: Universidade da Coruña, Servizo de Publicacións; 2005. p. 167–182.

[15] Menard KP. Dynamic Mechanical Analysis: A Practical Introduction. 2nd ed. Boca Raton: CRC Press; 2008.

[16] Shaw MT. Introduction to Polymer Rheology. New York: Wiley; 2012.

[17] Carotenuto C. Advanced mechanical spectroscopy to investigate the microstructure of complex fluids. Doctoral Thesis submitted to Napoli University, 2006.

[18] Cho KS. Viscoelasticity of Polymers Theory and Numerical Algorithms. New York: Springer; 2016.

[19] Macosko CW. Rheology: Principles, Measurements and Applications. New York: VCH; 1994.

[20] Larson RG. Constitutive Equations for Polymer Melts and Solutions. Washington: Butterworth; 1988.

[21] Collyer AA, Clegg DW. Rheological Measurements. London: Chapman and Hall; 1998.

[22] Laun HM. Description of the non-linear shear behaviour of a low density polyethylene melt by means of an experimentally determined strain dependent memory function. Rheol Acta. DOI: 10.1007/BF01567859, 17, 1–15, 1978

[23] Acierno S, Grizzuti N. Measurements of the rheological behaviour of a crystallizing polymer by an "inverse quenching" technique. J Rheol. DOI: 10.1122/1.1545080, 47, 563–576, 2003

[24] Winter HH, Chambon F. Analysis of linear viscoelasticity of a crosslinking polymer at the gel point. J Rheol. DOI: 10.1122/1.549853, 30, 367–382, 1986

[25] Tucker CL, Moldenaers P. Microstructural evolution in polymer blends. Annu Rev Fluid Mech. DOI: 10.1146/annurev.fluid.34.082301.144051, 37, 177–210, 2002

[26] Onofrei MD, Dobos AM, Stoica I, Olaru N, Olaru L, Ioan S. Lyotropic liquid crystal phases in cellulose acetate phthalate/hydroxypropyl cellulose blends. J Polym Environ. DOI: 10.1007/s10924-013-0618-7, 22, 99–111, 2014

[27] Krieger IM, Niu TF. A rheometer for oscillatory studies of nonlinear fluids. Rheol Acta. DOI: 10.1007/BF01525599, 12, 567–571, 1973

[28] Zaman AA. Techniques in Rheological Measurements. London: Chapman and Hall; 1993.

[29] Debbaut B, Burhin H. Large amplitude oscillatory shear and Fourier transform rheology for a high-density polyethylene: experiments and numerical simulation. J Rheol. DOI: 10.1122/1.1495493, 46, 1155–1176, 2002

[30] Neidhöfer T, Wilhelm M, Debbaut B. Fourier-transform rheology experiments and finite-element simulations on linear polystyrene solutions. J Rheol. DOI: 10.1122/1.1608954, 47, 1351–1371, 2003

[31] Wilhelm M, Reinheimer P, Ortseifer M, Neidhöfer T, Spiess HW. The cross-over between the linear and nonlinear mechanical behaviour in polymer solutions as detected by Fourier-transform rheology. Rheol Acta. DOI: 10.1007/s003970000084, 39, 241–246, 2000

[32] Reimers MJ, Dealy JM. Sliding plate rheometer studies of concentrated polystyrene solutions: large amplitude oscillatory shear of a very high molecular weight polymer in diethylphthalate. J Rheol, 40. DOI: 10.1122/1.550738, 40, 167–186, 1996

[33] Yin Y, Nishinari K, Zhang H, Funami T. A novel liquid-crystalline phase in dilute aqueous solutions of methylcellulose. Macromol Rapid Commun. DOI: 10.1002/marc. 200600099, 27, 971–975, 2006

[34] Lee HC, Brant DA. Rheology of concentrated isotropic and anisotropic xanthan solutions. 2. A semiflexible wormlike intermediate molecular weight sample. Macromolecules. DOI: 10.1021/ma011527e, 35, 2223–2234, 2002

[35] Colby RH, Gillmor JR, Galli G, Laus M, Ober CK, Hall E. Linear viscoelasticity of side chains liquid crystal polymers. Liq. Cryst. 13(2), 233–245, 1993.

[36] Hwang SS, Kim BC, Kim KU, Hong SI. Rheological implications of mesomorphic order in lyotropic liquid crystalline polymers. Korean J Rheol, 9(1), 200–205, 1997.

[37] Appaw C. Rheology and microstructure of cellulose acetate in mixed solvent systems. Dissertation submitted at Graduate Faculty of North Carolina State University, 2004.

[38] Cosutchi AI, Hulubei C, Stoica I, Ioan S. Morphological and structural-rheological relationship in epiclon-based polyimide/hydroxypropylcellulose blend systems. J Polym Res. DOI: 10.1007/s10965-009-9342-3, 17, 541–550, 2010

[39] Dobos AM, Onofrei MD, Stoica I, Olaru N, Olaru L, Ioan S. Rheological properties and microstructures of cellulose acetate phthalate/hydroxypropyl cellulose blends. Polym Compos. DOI: 10.1002/pc.22350, 33 2072–2083, 2012

[40] Kim JY. Carbon nanotube-reinforced thermotropic liquid crystal polymer nanocomposites. Materials. DOI: 10.3390/ma2041955, 2, 1955–1974, 2009

[41] Weiss A, Wansoo HUH, Nicolais L. Novel reinforced polymers based on blends of polystyrene and a thermotropic liquid crystalline polymer. Polym Eng Sci. DOI: 10.1002/pen.760270913, 27, 684–691, 1987

[42] Kirkwood JE. Liquid crystalline collagen: matrices for oriented cell growth. Dissertation submitted to Stanfort University, 2008.

[43] Hosseini MS, Katbab AA. Effects of surface viscoelasticity on cellular responses of endothelial cells. Rep Biochem Mol Biol, 3(1), 20–28, 2014.

[44] Chang SJ, Chiao S, Lai WJ, Lin CM, Fuh AYG. Polymer dispersed liquid crystal display device for projection high definition television application. Macromol Symp. DOI: 10.1002/masy.19940840119, 84, 159–166, 1994

[45] Berreman DW. Solid surface shape and the alignment of an adjacent nematic liquid crystal. Phys Rev Lett. DOI: 10.1103/PhysRevLett.28.1683, 28, 1683–1686, 1972