

Interrelationships between stream morphology and rheological response for multiphase systems based on polymer matrices

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Abstract Several versions of visualization of polymer stream morphology and structure were developed and tested. It was shown that in strong shear flow the regular instability consisting of concentric circle-like texture is formed. For filled polymer melts the alternating circles enriched with polymer or filler particles are realized. These observations initiated development of the new model explaining rheological behavior of polymer systems at high shear and extension rates when elastic response becomes dominating. Optical images of regular morphology were supplement with rheo-X-ray data allowing us to connect morphological and structural perturbations in liquid crystal polymer solutions containing crystalline clay particles. In the area of extension strain the novel spinning method of PAN solutions is proposed based on phase separation of solution in strong elongation flow registered by optical technique.

Keywords: rheology, visualization, shear and extension flow.

1 Introduction

This presentation is devoted to visualization of shear and uniaxial extension flows polymer solutions and melts as well as some multiphase systems on their base. Mainly, we will consider so-called “optical” visualization which in some cases will be supported with “X-ray visualization”. Such an approach allows us to withdraw rheology from position of “the black box” and convert it to the real structural science. Several examples will be considered in this paper including strong shear flow of the flexible-chain polyisobutylene (PIB) filled with solid particles of micro- and nano-size (clay, nanodiamonds) and polymer solutions used as dopes for fiber spinning, e.g. co-polyacrylonitrile (PAN) in livethylsulfoxide (DMSO). Special case presents rheo-X-ray method that requires structure active components, such as liquid crystal aqueous solutions hydroxypropylcellulose (HPC) filled with crystalline Na-montmorillonite.

2 Equipment

To start an activity with obtaining optical images we need to design and construct either new equipment or to modify the existing one. Some of instrumental companies already sail optical cells working in shear mode of deformation which are very useful for obtaining additional information for emulsions, foams, suspensions behavior at flow. But this equipment cannot cover all tasks coming from scientific practice with specific objects. That is why, all rheological groups need to create something new to look and see what happens with polymer system under flow. The same situation arises in our group when we start to work with heterophase polymer systems with unusual rheological response. Some versions of created equipment are shown in Fig. 1.

In the case (1) the flow proceeds in the gap between unmoved glass sphere and rotating plate. In the reflection mode (2) the metallic unmoved plate is replaced by 90o total reflection prism, and at rotating cone it is possible to see the stream morphology in the gap. The case (3) relates with X-ray flow in Quette cell at rotating inner cylinder. At last, the case (4) allows us to create interference patterns using coherent irradiation.

3 Results and discussion

The most exciting picture at strong flow of heterophase systems consisted in concentric circles formation. Such patterns were observed for mixture of isotropic solution of PIB in decaline and LC solution of HPC in water (Fig. 2). The main condition of such regular texturing of polymer blends is rather large difference in viscosity of solutions (LC solution has less viscosity than PIB solution) or melts.

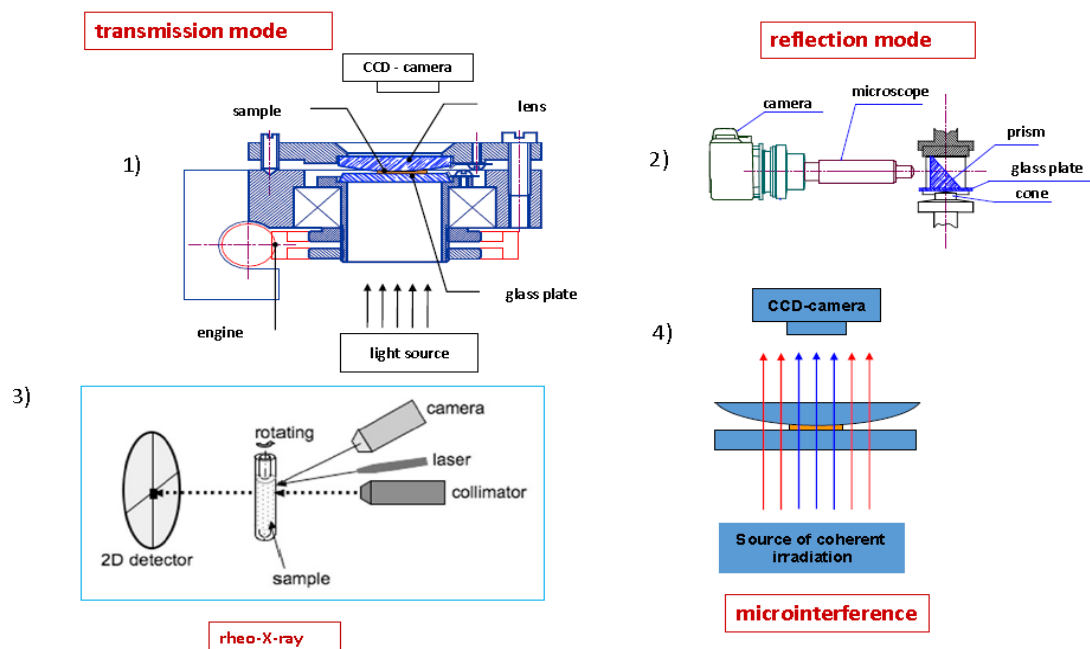


Fig.1 Equipment used for visualization of shear stream

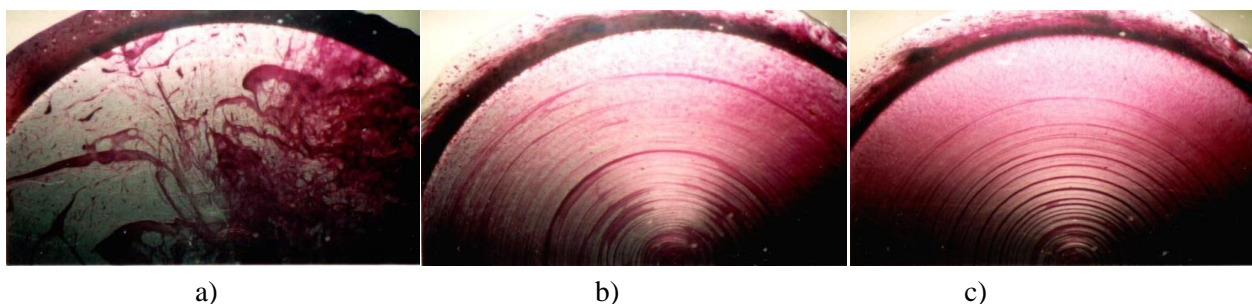


Fig. 2 Formation of concentric circles by HPC solution (pink) in PIB solution matrix, obtained at shear rate more than 10 s^{-1} with increase of strain from 0 (a) to 4000 units (c) in the reflection mode.

The same situation was observed for PIB melt containing $\sim 5\%$ of clay (Fig.3). With increase of total strain at shear rate of 15 s^{-1} the formation of regular circles proceeds during 5 min or strain of the order of 1000 (right part of the figure where arrows show increase of strain).

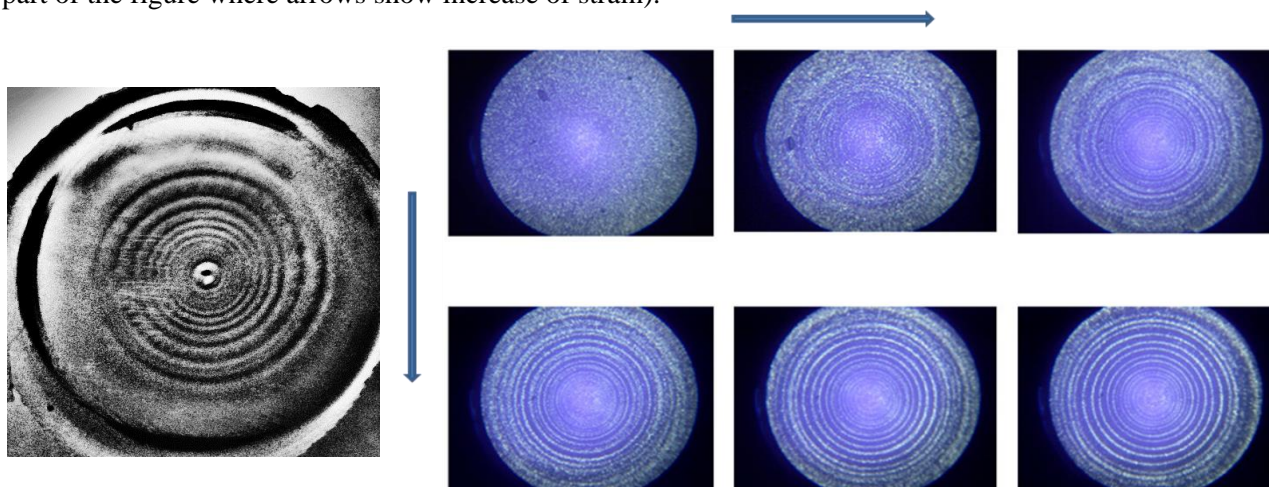


Fig. 3 Texture formation in the filled PIB solution containing 5% of clay (right part). The left picture reflects similar texture obtained at the same conditions for unfilled PIB [1]

It was unexpected to observe similar ring-like morphology for pure PIB matrix. This fact initiated the novel model of polymer melts behavior at high shear rates. It is based on position of development in strong flow of high elastic deformation. Moreover, in the limiting case polymer melts or solutions deform as rubber with total elastic response. According to proposed model [2], the melt in elastic approximation is a system non-penetrable grains (elastic ellipsoids) contacting each other and capable to interact sterically – be deformed and rotated relatively centers of masses. There exists free volume, enough high for rotational motions. The shape of ellipsoids will be characterized by the eccentricity ε , and their projections $S = (S_i, S_j, S_l)$. The space position is determined by the vector coincided with the direction of the main principle axis (). Two items should be considered. The first one is related to the energy of steric interactions in a system of elastic ellipsoids. Centers of mass of particles are localized in the nodes of a lattice and particles have only a rotational degree of freedom. We will suggest that elastic deformation can be characterized by single parameter – modulus of elasticity E . Deformation behavior of particles was modeled by computer simulations in the *Comsol Multiphysics* medium by the finite differences method. This allows us to find the energy of collisions between grains w_1 depending on E , eccentricity ε and the angle between principal directions of ellipsoids φ :

$$w_1 = -\beta E (1 + |S_n| |S_{n+1}|) \lg \frac{1 + S_n \cdot S_{n+1}}{1 + |S_n| |S_{n+1}|}$$

The second item reflects the turn of particles under the action of the external dynamic field. Obtained results for the specific energy of particle deformation due to the turn of ellipsoidal particles in a shear field are approximated by the equation:

$$w_2 = -\alpha \tau \lg(1 + h_e \cdot S_n)$$

where τ is the shear stress, h_e is an unit vector showing the direction of shear. The parameters α and β in basic equations are numerical factors of the order of 1.

The total energy of deformed system expressed by Hamilton function H , is a sum of these two constituents of elastic energy:

$$H = -\alpha \tau \sum_{i,j}^N \lg(1 + S_{i,j} \cdot h_e) - \beta E \sum_{i,j}^N (1 + |S_n| |S_{n+1}|) \lg \frac{1 + S_n \cdot S_{n+1}}{1 + |S_n| |S_{n+1}|}$$

Classical equations of dynamics allow us to formulate the law of vectors evolution for this Hamilton function, i.e., equation of motion:

$$\frac{\partial}{\partial t} S_{i,j} = \frac{\alpha \tau}{1 + h_{i,j} \cdot S_{i,j}} h_{i,j} \times S_{i,j} + \frac{\beta E}{1 + S_{i,j} \cdot S_{i\pm 1, j\pm 1}} S_{i,j} \times S_{i\pm 1, j\pm 1}$$

So, the model contains four main parameters: vector of the shear field h , susceptibility to the action of shear stresses $1/k$ (where k is a relative angle at the iteration step), the value of a local field E , and a possibility to be rotated in the field of a neighboring particle, $1/m$. At $E/h > 1$ (Weissenberg number analog) - structure formation!

Calculations carried out with using this model and experimental results allowed us to propose the following scheme of texture formation in matrix polymers in vicinity of unstable shear flow regime (“spurt” [3]) shown in Fig. 4. Under action of high reversible deformation homogeneous polymer melt transforms to a system of strongly oriented wires growing in a spiral manner from the point of maximal shear stresses (apex of cone or lens) (Fig. 4a). In the zone a) model predicts accumulation of high extension deformation initiating elastic turbulence. The spiral b) far from the apex converts to concentric circles (c), and then at increasing the gap and decreasing the shear stress the texture does not form (d). The inner structure of the spiral sleeves presents cylindrical surfaces of the equal normal stresses (Fig. 4b) вложенных друг в друга. The filler particles are forced to be concentrated in weak places of such texture, contracting the main picture as tracers.

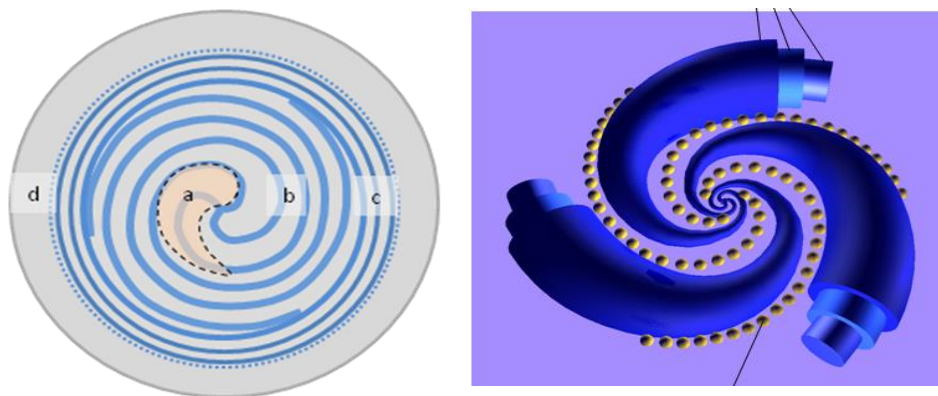


Fig. 4 Schematic image of the spiral texture formation (a) and the inner structure and distribution of strong polymer sleeve and filler particles (b)

Thus, visualization of homophase and heterophase polymer melts strong flow gave food to development of novel constitutive model in conditions of prevailing elastic strain.

In the case of rheo-X-ray the aqueous liquid crystalline (LC) HPC solutions have been chosen as matrices [4]. As for all lyotropic LC systems based on stiff-chain polymers, they are suffered the following sequence of transitions with increase of polymer concentration: isotropic solution (I) – mixture of isotropic and anisotropic phases (I+LC), totally anisotropic phase (LC) and additive compound of a polymer and a solvent – crystal solvate (CS). The diffusion interaction between HPC and water was studied by **microinterference method** (interferograms at two temperatures are shown in Fig. 5a), and these data allowed us to construct the phase diagram (Fig. 5b). 50 (biphasic) and 60% totally LC) solutions were chosen for experiments.

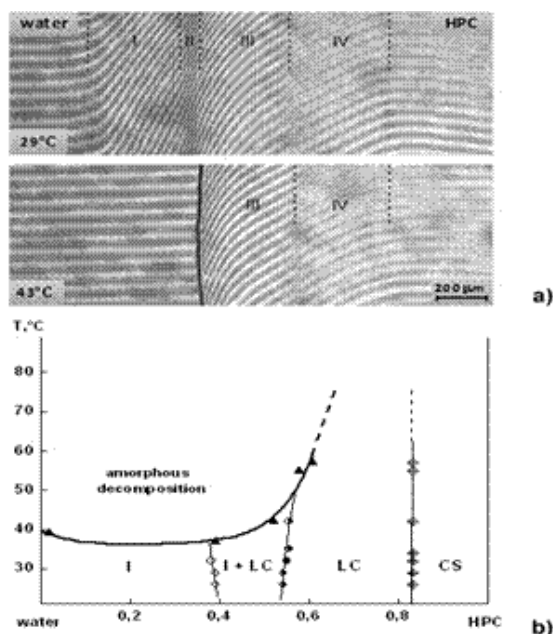


Fig 5. (see explanation in text)

As is seen from Fig.6, after loading nanocomposites in Couette cell HPC is oriented transversally to the further shear, but immediately after applying shear it reorients along the shear stream. In 60% solution the clay reflection remains in equator with some oscillation around this direction at fast deformation. For 50% solution this situation preserves up to highest shear rates, while for 60% solution beginning with shear rate $\sim 300 \text{ s}^{-1}$ the clay reflection splits between equator and meridian forming 4-spots diffractogram.

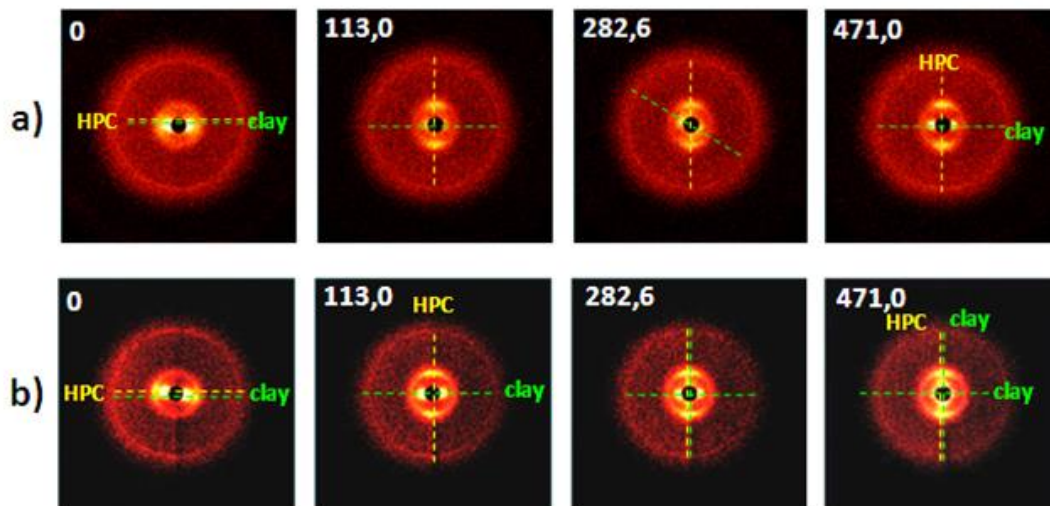


Fig. 6 2D diffraction patterns for filled systems based on 50 (a) and 60% HPC solutions (b) at different average shear rates (indicated in figure)

Prolong deformation changes a situation and the most drastic changes were observed for the biphasic LC matrix: the clay reflex turns on 90° from equator to meridian while for 60% HPC matrix the splitting preserves during whole observation time. This fact allowed us to propose the following hypothesis: clay platelets form at shear the columnar-like mesophase structure, which at definite strain in strong flow conditions completely (biphasic matrix) or partially (LC matrix) converts to discotic-like structure (Fig. 7).

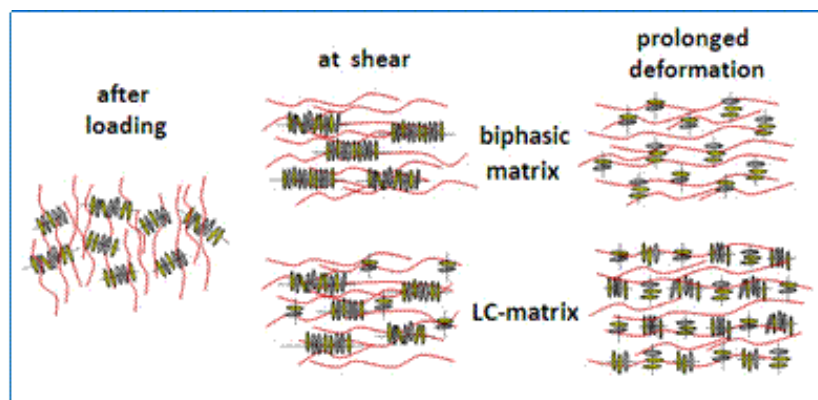


Fig. 7 The approximate scheme of the clay particles arrangement and orientation of compositions based on biphasic and fully LC solutions

All above mentioned cases relates with strong shear strain, but structural and phase transitions take place at extension flow. As an example, we consider an extension of PAN solution in DMSO as dopes for fiber spinning [5-7]. The visualization technique consists of camera and elongated solution jet. At high extension rates the phase separation of solution proceeds with evaluation of solvent on the fiber surface. This process was named as mechanotropic spinning since at extension practically all amount of solvent going away of jet and real solid fiber forms. The process of the phase separation can be understood only via visualization. The version of jet extension is shown in Fig. 8.

This process does not require the coagulation bath and sooner it is a version of the dry spinning with subsequent washing and drying. The diameter of filaments can be varied from hundreds nanometers to 5-10 μ . The skin-core effect is virtually absent for such fibers, i.e., their cross sections have homogeneous structure.

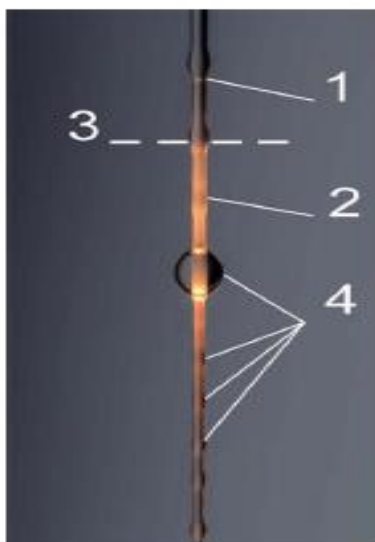


Fig. 8 Solvent evaluation from extended solution jet: 1 – fluid part of a filament; 2 – solidified part of a filament; 3 – boundary of the phase separation; 4 – large and small solvent droplets spread over the filament surface

4 Conclusion

Some versions of the visualization of polymer melts and solutions in shear and extension deformation are considered. All of them give very useful information about physical processes taking place at flow. In several cases the visual images initiate development of new models and mechanisms in polymer physics.

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