Measurement 97 (2017) 218–225

Contents lists available at ScienceDirect

Measurement

journal homepage: www.elsevier.com/locate/measurement

# A special instrument for the defined modification of polymer properties in solutions and polymer layers

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ARTICLE INFO

*Article history:*
Received 17 June 2016
Received in revised form 1 November 2016
Accepted 4 November 2016
Available online 5 November 2016

*Keywords:*
Instrument
Heat transfer
Self-organisation
Fluid flow
Conformation
Condensation

ABSTRACT

A special apparatus allowing for the targeted modification of the physicochemical characteristics of dispersive systems via a self-organised liquid flow (Bénard-Marangoni or Railegh-Bénard instability) was constructed. The apparatus was tested by means of heat transfer rate and temperature distribution uniformity over a newly-designed composite heating plate. New types of a solidification cell and a condenser were developed for polymer solution solidification in temperature gradients, at low pressure or in a defined atmosphere. Two polysaccharide systems were used to demonstrate the abilities of the apparatus. The results demonstrate how significant an effect the self-organised liquid flow can have on the arrangement of macromolecular systems in solutions, at phase boundaries or in solidified polymer foils.

## 1. Introduction

Flow-induced conformation changes in flexible macromolecular systems have been repeatedly studied (and simulated) [1–3]. The action of such forces can result in irreversible changes in the tertiary and quaternary structures of macromolecular systems [4,5], thereby determining the physicochemical properties of individual chains and the system as a whole [5–8]. These changes can include the organisation of macromolecular segments and coils, their mean size [9–11], rigidity, ability to occupy a phase boundary [12–14], viscosity [3,15–18], temperature of phase transitions, etc. The effects of the preceding thermal exposure (thermal history) [6] or pH and ionic strength fluctuations in a solution [12,19–23] are also appreciable. The changes in polymer conformation have a direct impact on the behaviour of a macromolecular system at the phase boundaries [12,14,24,25], which plays an important role, e.g., in the response of a hosting biological system [26,27].

A typical example of a physicochemical phenomenon, where heat and mass transfers occur at a shear strain, is the self-organised flow of liquid represented by the Bénard-Marangoni convective cells or Railegh-Bénard rotational cylinders [28–31]. These non-equilibrium phenomena related with energy dissipation have been studied for over a century [28–30,32,33]. The initiatory stage of the process can be described with the Marangoni number, which is determined through an equation involving the basic parameters, Eq. (1), namely the temperature difference between the bottom layer and the open surface $\Delta T$, the thickness of the liquid layer $d$, dynamic viscosity $\eta$ and the coefficient of thermal diffusivity $\kappa$ [28].

$$Ma = \frac{(-\partial\gamma/\partial \mathrm{T})\Delta \mathrm{T}d}{\kappa\eta} \tag{1}$$

This thermo-capillary instability is driven by the temperature fluctuations in a liquid surface layer and is typical for slowly-evaporating systems with the thickness of the liquid layer in the order of millimetres [28–30], whereas in systems with the liquid layer thickness in the order of micrometres, the concentration – diffusion mechanisms play dominant roles [34–36]. The latter case is not discussed in this paper, given the nature of our systems (solvent, thickness of a liquid layer, etc.). The flow mechanism and related self-organised patterns (Bénard-Marangoni cells) in the polymer solution or solidified film are also affected by the properties of the dispersed polymeric phase, namely the rotation about the primary bonds, the molecular weight and its

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http://dx.doi.org/10.1016/j.measurement.2016.11.006
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**Nomenclature**

| | |
|---|---|
| 2-HEC | 2-hydroxyethyl cellulose |
| BM | Bénard-Marangoni |
| $d$ | thickness of the liquid layer |
| $dT$ | temperature differential between the heating plate and the air, cca 10 mm above the initial liquid level |
| $HA$ | sodium salt of hyaluronic acid |
| $Ma$ | Marangoni number |
| MW | average molecular weight |
| $T$ | temperature |
| $t$ | time |
| $w$ | mass fraction of a polymer in a solution |

*Greek symbols*

| | |
|---|---|
| $\gamma$ | surface tension |
| $\Delta T$ | temperature difference between the bottom layer and an open surface |
| $\eta$ | dynamic viscosity |
| $\kappa$ | thermal diffusivity |
| $\lambda$ | thermal conductivity |

distribution, extramolecular secondary bonds, etc. [37,38]. The surface properties of the substrate [39], the size and shape of the container [36,40–42], the thermal history of the material [6] and solvent evaporation [24,43,44] also contribute to the complexity of the system. Consequently, it is virtually impossible to predict the behaviour of such a complicated system on the base of some idealised model [45–48]. Thus, it is still necessary to rely on a perfectly-performed experiment [37,43,44], the results of which will provide information about the practical application of the self-organised processes for the targeted modification of (not only) polymeric systems.

For this reason, a new experimental apparatus was designed and constructed, extending the range of the original device [37] in order to generate a broader range of temperature gradients, the ability to modify polymer solutions without their solidification, and the capability of preparing thin polymer foils in an environment with a defined pressure and atmosphere. The function of the apparatus is demonstrated on two polysaccharide systems: 2-hydroxyethly cellulose and sodium salt of hyaluronic acid.

## 2. Experimental apparatus

The experimental apparatus for the defined modification and solidification of polymer solutions (hereafter referred to as *apparatus*) is especially designed for changing the physicochemical properties of polymer solutions and for the preparation of thin (polymeric) foils, films and membranes. It works on a similar principle as a condensation drier. The treated material is further exposed to defined temperature gradients (the temperature difference between the top and bottom plates).

The *apparatus* consists of one control and power unit and up to eight working sub-units; see Fig. 1. Each working unit consists of a supporting steel frame, an antivibration base block, a stand with four threaded steel rods for positioning two heating/cooling plates fitted with Pt100 temperature probes (class A), a cooler (heat-pipe technology) and a ventilation tunnel. The heating/cooling plates are equipped with 150 W Peltier elements (40 × 40 mm). The ventilation tunnel supports the heat dissipation from the top plate via the cooler, when it operates in cooling mode. Each working unit is powered with a stabilized laboratory supply 0–15 V, 0–60 A (Maas).

The essential function of the *apparatus* is creating a defined temperature gradient in the area confined between the top and bottom plate. A Peltier element attached to a copper heatsink serves as both a heating and cooling device and is responsible for even temperature distribution over the whole contact plate.

The *apparatus* (Fig. 1) can be utilized for modifying the physicochemical properties of a polymer solution, if the plastic spacer (Fig. 2) is removed. In such a case, the polymer solution is inserted between the top and bottom plates in a suitable way, e.g., in an open-surface container (Petri dish) or in a sealed plastic bag. Moreover, the *apparatus* can also be used for the solidification of polymer solutions. In this case, a plastic spacer, Fig. 2, stainless steel condenser, Fig. 3, silicone gasket and a stainless steel contact sheet are inserted between the top and bottom plates. The polymer film is then solidified on a suitable support plate (a surface treated polymer or glass plate), positioned at the lower part of the polymer spacer, as portrayed in Fig. 2, position 2.

Each sub-unit is capable of working autonomously, regardless of the other units. This means that all sub-units can work in the modification or solidification mode. Each unit can work with a different temperature set-up to allow for the rapid optimization of the process parameters. The *apparatus* was deliberately constructed as modular and universal. The heating/cooling performance can be modified by the power rating of the Peltier element and by the mutual positions of the top and bottom plates and their orientations, which can be adjusted with the help of the threaded steel rods.

The key parts of the control unit are the temperature controller and the utility software (B.L.I. Treg16), developed at the Department of Physics and Materials Engineering, Tomas Bata University in Zlín, Czech Republic. The controller operates up to 16 channels, each either in cooling or heating mode, with a maximum current load of 10 A for each channel. The temperature is controlled and monitored with the software program, via standard commands – ramp (up and down) and hold.

Homogenous temperature distribution over the whole active area of the cooling/heating plates is essential for the successful and well-defined process of polymer modification/solidification. Various plate designs were tested, starting with a simple sheet of aluminium (dimensions 120 × 120 × 3 mm, $\lambda = 235\ \mathrm{W\,m^{-1}\,K^{-1}}$) or copper (dimensions 150 × 150 × 3 mm, $\lambda = 401\ \mathrm{W\,m^{-1}\,K^{-1}}$), with the Peltier element situated in the middle of the metal sheet. To improve the heat dissipation from the relatively-small Peltier element over the larger area of the active heating/cooling plate and to ensure homogenous temperature distribution, an updated design was used, consisting of two copper plates (thickness 3 mm), separated by an thin insulating layer (1–1.5 mm) made from a silicone based polymer with $\lambda = 1.5\ \mathrm{W\,m^{-1}\,K^{-1}}$ (Lukopren N6681, Lučební závody Kolín, Czech Republic); see Fig. 4. The metal frame assures the shape stability of the whole plate, while the plastic frame helps to insulate metal constructions from the copper plates. The thin polymer layer, the thermal diffusivity of which is much lower than that of copper (approx. 250 times), serves as a thermal barrier and helps to evenly distribute temperature over the top copper plate. Such a construction proved effective for even temperature distribution over the whole contact