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Viscosity and density measurement methods for polymer melts

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Abstract

In this article review of density and viscosity measurement methods is presented, including ultrasonic pulse echo methods, which are capable to measure these properties of polymer melts. The methods are presented according to measurement principles, methodology, accuracy and possibility to measure density and viscosity of polymer melts on-line during extrusion process. Such measurements are very important for process automation, process monitoring and control. The ultrasonic pulse echo methods are separated from other methods, because very often they are superior to other techniques. The advantage of this technique is that at the same time sound velocity and attenuation in a plastic melt may be measured, what gives more information. For this purpose polarized shear waves as well as longitudinal, torsional and other types of waves in a wide frequency range may be employed.

Keywords: Density, viscosity, extrusion, polymer melt, shear waves, longitudinal waves, ultrasonic measurements.

1. Introduction

The viscosity is the resistance of a substance to flow, e.g. is a measure of the resistance of a fluid to deformation under shear stress. There are two main types of the viscosity, the kinematic viscosity and dynamic viscosity. The dynamic viscosity, which sometime is referred as an absolute viscosity, is obtained by dividing the shear stress by the rate of shear strain. The kinematic viscosity is the measure of the rate at which momentum is transferred through a fluid. It may be obtained from the dynamic viscosity dividing it by the density of the substance.

Density is a physical property of matter that expresses a ratio of mass to volume. The density depends on the atomic mass of an element or compound. Since different substances have different densities, density measurements are very useful for identification and characterization of different substances.

The density and viscosity of polymer melts are very important physicochemical parameters in a polymer manufacturing process. They are very significant factors affecting the production cost and profitability of the manufacturing process. A reduction in the density reduces costs of raw materials and correspondingly costs of manufacturing [1].

1.1 The viscosity measurement methods

The viscosity is a very important physicochemical parameter in chemical engineering processes.

Many studies have been done on measuring viscosity by using different techniques. The main viscosity measurement methods are the following:

1. Viscometer methods:
   - 1.1. Rotational viscometric method.
   - 1.2. Capillary viscometric method.
   - 1.3. Vibratory viscometric method.
2. Ultrasonic pulse echo method.

In viscometer methods measurements are performed using various viscometers, in which different measurement principles are employed. For example, in one type, the time taken for a given volume of fluid to flow through an opening is recorded. In the capillary viscometer, the pressure needed to force the fluid to flow at a specified rate through a special tube is measured. Other types depend on measurements of the force needed to rotate the internal cylinder or the rate at which oscillations of a disk, vibrating in the fluid the viscosity of which is measured, decay [2].

The ultrasonic pulse echo method is very different from the mentioned above methods and is based on measurement of the time of flight of and attenuation of ultrasonic waves.

1.2 The density measurement methods

The density of solid or liquid substances usually is measured in laboratory conditions. For this purpose the following instruments are used:

3. Pycnometer.
4. Densymeter.
5. Areometer.
6. Ultrasonic pulse echo method.

The pycnometer is an instrument used for measuring fluid density, also known as a specific gravity bottle. Operation of pycnometer is based on the Archimedes' principle. The densymeter and aerometer are instruments for measuring the density or specific gravity of a solid or liquid substance.

As it was mentioned above, these instruments are usually used for measurements of a liquid materials density under laboratory conditions. The time delay between collecting the samples and obtaining the results can last from several minutes to several days, what is not suitable for monitoring manufacturing processes [4].

The density can be measured by using the ultrasonic pulse echo method. Advantage of this method is a high speed of measurements what enables to use it for on-line measurements and monitoring of a manufacturing process [7].

2. Measuring viscosity in polymer melt

The rheological behavior of most polymeric materials is very complex. A particularly difficult situation is in the case of polymer melts. Usually the viscosity must be measured in very complicated conditions- at high pressure (50-100) MPa and high temperature (about 150-300 ^0C). This reduces the accuracy and reliability of measurements. Often the polymer viscosity is measured off-line, where a sample of the polymer compound is melted and put into a special capillary tube (glass viscometer) [5] or by incorporating a capillary tube mounted parallel to the extruder for in-line measurements. The measurements performed by the glass viscometer require quite a lot of time to melt the sample and large volume of the samples [3]. Both techniques involve an additional time delay requested for the melt to flow through the transit lines and the capillary tube.

Sometimes the viscometers are mounted on the extrusion line and measure the stress on the die wall by measuring the pressure drop along a slit or capillary [6]. The flow rate is measured by an additional flow meter. These methods are more appropriate to the extrusion process, but there are some major drawbacks. The flow meter may disturb the melt flow and correspondingly to affect the original flow properties.

The presented methods do not satisfy requirements for on-line monitoring of polymer melts in the conditions characteristic during manufacturing process (high pressure, high temperature, the measurements in real time, aggressive environment). The melt viscosity can not be effectively monitored and measured with a good accuracy.

So, it can be assumed, that the most appropriate method to measure the viscosity of a polymer melt is ultrasonic pulse echo method. This method is analyzed separately from other methods, because it is in many aspects superior in comparison to other techniques.

The viscosity of polymer melts should be measured in real-time during extrusion process. The ability to measure the viscosity of polymer melts in-line during extrusion process provides the manufacturers with the ability to optimize their production [3].

2.1 The ultrasonic pulse echo method

Ultrasound has found applications in characterizing various polymers in solid and molten states [9]. This indicates that this technique may be a powerful tool for process monitoring. Using this technique the ultrasound velocity and attenuation of a polymer melt during extrusion is measured [15]. From these measurements the melt viscosity may be determined. As an example, we shall present the real experiment, which was carried out in Industrial Materials Institute, USA in the year 1998 [8]. The principle of ultrasonic measurement is shown in Fig. 1. The measurement method is based on exploitation of multiple reflections in buffer rods and plastic melt.

A longitudinal wave propagating at the frequency of 2 MHz is generated by a piezoelectric transducer (pulser). The ultrasound wave is transmitted to the polymer melt via a metallic buffer rod, which is made of stainless steel. The buffer rod protects ultrasonic transducers from a high temperature plastic melt. Acoustic impedances of the metallic buffer and the polymer are different, therefore part of the acoustic energy is partly transmitted and part is reflected back. The transmitted signals are then detected at the end of the second buffer rod by a second piezoelectric transducer (receiver). The sample is a polymer melt, thickness *l* of which is 30 mm.

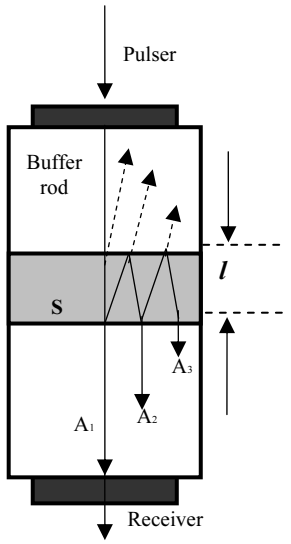

Fig. 1. **The principle of ultrasonic measurement: S is the polymer sample, l is the thickness of the sample**

This ultrasound technique based on the velocity and attenuation measurements of an ultrasonic wave propagating in the polymer melt.

The ultrasound velocity v is found from the polymer melt thickness l, and the measured time delay Δt between the neighbouring echoes A1, A2, A3 [8]:

$$v = 2l / \Delta t , \qquad (1)$$

where $(\Delta t = t_{n+1} - t_n)$, t_n - is the delay time of the *n*-th pulse.

The attenuation α is calculated from the ratio of the amplitudes of successive echoes and usually is given in dB/cm:

$$\alpha = -(1/2l)20\log\left[\left(1/\Gamma^2\right)\left(A_{n+1} - A_n\right)\right] , \qquad (2)$$

where Γ is the reflection coefficient through the polymer/buffer rod interface.

Then the ultrasonic viscosity η is calculated [8]:

$$\eta = \alpha \cdot 2\rho v^3 / \omega^2 , \qquad (3)$$

where ρ is the density and ω is the angular frequency ($\omega = 2\pi f$).

During the experiments the constant melt pressure is necessary, therefore the extruder was connected to a commercial process controller. The measurements were performed in a temperature range (130-180)°C. The viscosity of the polymer melt during measurements was in the range between (400-1300) Pa·s. The melt pressure and the melt temperature were measured also during the whole experiment [8].

The ultrasound velocity as a function of intrinsic viscosity is shown in Fig. 2 [8].

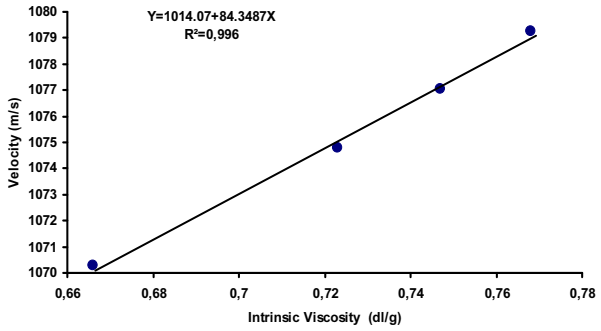

Fig. 2. **The ultrasonic velocity as a function of intrinsic viscosity**

The ultrasound velocity can be measured with a good accuracy (the error less than 0.4 m/s) and intrinsic viscosity variations 0.005dl/g could be detected on-line [8].

The technique was adapted for in-line monitoring (Piche et al., 1995) by measuring the ultrasound velocity and attenuation in the flowing melt [12]. The melt temperature and the pressure profile of the flow were measured correspondingly by thermocouples and pressure sensors. The results of ultrasonic measurements were compared to the results obtained by a capillary rheometer. [8].This technique is important tool for monitoring of the polymer melt extrusion process. The technique is non-invasive, measurements are performed in real time. This is a high accuracy system, which can be widely used in industry [13]. The measurements can be performed at high pressure and high temperature, what is very important for polymer melt measurements.

3. Measuring density in polymer melt

Density is a very important physical parameter in polymer engineering processes [10]. The density is a very significant factor affecting a production cost and profitability of the manufacturing process. A reduction in a density reduces the raw material cost and therefore decreases the manufacturing costs [1]. So, it is very important to measure the density of polymer melt with a good accuracy during the extrusion processes.

The density of a polymer melt can be measured by densymeters, pycnometers and mass flow meters. The most commonly used densymeters and mass flow meters are based on the principle of vibrating tubes, for example Coriolis flow meters [11]. These meters have major drawbacks. They are limited to pipe diameters below 60 mm and high pressure losses during the measurements occur. These meters are expensive and not stable, particularly when measurements in polymer melts must be performed at high pressure and temperature.

So, it can be suggested, that the most appropriate method to measure the density in polymer melt may be ultrasonic pulse echo method.

3.1 The ultrasonic pulse echo method

The ultrasonic pulse echo method overcomes limitations of the densitometers and mass flow meters. The measurements may be carried out in large pipes and without pressure losses, what is very important for polymer melts.

For measurement the density ultrasonic longitudinal and shear waves can be used.

The longitudinal wave reflection method is used to measure the time of flight of ultrasonic waves and the ultrasound velocity in polymer melt. These data are used to calculate the density. A thermocouple sensor and a mercury capillary transducer are necessary to acquire the respective temperature and the pressure during the measurements. The principle of ultrasonic measurement is shown in Fig. 3 [4].

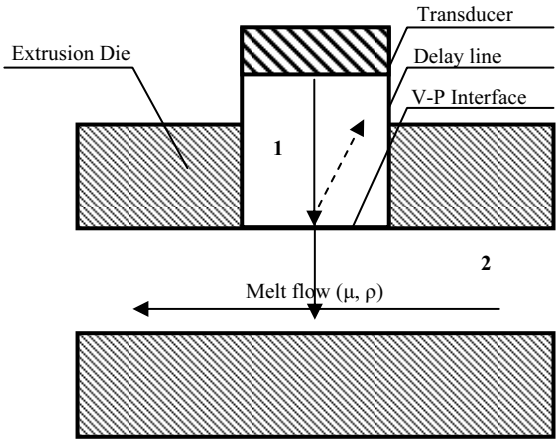

Fig. 3. **The principle of ultrasonic measurement: 1-buffer rod, 2-plastic melt**

The ultrasonic longitudinal waves propagating at a frequency of (2-4) MHz. Due to mismatch of acoustic impedances between the delay line and the melted polymer, the acoustic signals are partly transmitted and another part of the signals are reflected from the end of the delay line(buffer rod). The transmitted through the melt and reflected back ultrasonic signals are picked up by a piezoceramics transducer (pulser/receiver). The transmitted and reflected back longitudinal waves are shown in Fig 4.

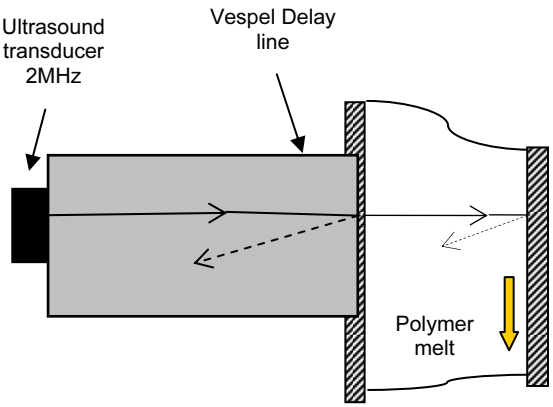

Fig. 4. **The transmitted and reflected back longitudinal wave**

The ultrasound velocity is determined by dividing the travel distance l by the measured time-of-flight of the signal in the melt τ:

$$c = \frac{l}{\tau}. \quad (4)$$

The amplitude reflection coefficient R_{12} is given by [4]:

$$R_{12} = \frac{Z_2 - Z_1}{Z_2 + Z_1}, \quad (5)$$

where Z_2 and Z_1 are the acoustic impedances for longitudinal wave of the polymer melt and the Vespel delay line.

The acoustic impedances of a polymer melt and delay line given by:

$$Z_2 = \rho_2 \cdot c_2 \; ; \; Z_1 = \rho_1 \cdot c_1 \quad (6)$$

The density of the delay line ρ_1 is known. The ultrasound velocities c_1 and c_2 are calculated:

$$c_1 = \frac{l_1}{\tau_1} \; ; \; c_2 = \frac{l_2}{\tau_2}. \quad (7)$$

Finally, the density of the polymer melt ρ_2 is calculated:

$$\rho_2 = \frac{\rho_1 c_1}{c_2} \cdot \frac{(1 + R_{12})}{1 - R_{12}} \quad (8)$$

The melt density measured by ultrasound is compared to the in a laboratory measured foam density. The correlation between these measurements is particularly linear with a correlation coefficient over 96% [4]. The correlation between the ultrasound measured melt density and the laboratory measured density is shown in Fig. 5 [4].

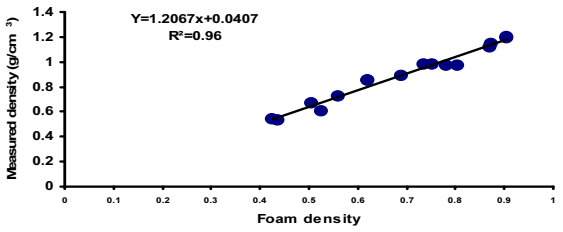

Fig. 5. **Correlation between ultrasound measured melt density and laboratory measured density**

The measurements are performed in the temperature range (165-188^{0}C). The measured density was in the range (0.4-1.4) gm/cm^3 [4]. The accuracy of measurements is dependent from several factors: the condition of the ultrasound transducers, stability of the process, variations of the acoustic performance of the ultrasonic transducers [18]. Note that the different transducers may have different acoustic characteristics [16]. The temperature of polymer melt and pressure must be constant, because they will have an effect on the acoustic properties of the melt and will reduce the accuracy of the measurements [4].

For density measurements polarized shear waves may be used as well as longitudinal waves. As an example, we would like to analyze the real experiment, which was carried out in University of Wisconsin-Milwaukee in the year 2004 [4]. The principle of ultrasonic measurement is shown in Fig. 6. The shear wave is transmitted through the Vespel delay line, partly transmitted and partly reflected from the opposite side of the delay line.

The shear wave acoustic impedance of a polymer melt is given by:

$$Z_{melt} = \sqrt{i\rho\mu\omega}, \quad (9)$$

where $i = \sqrt{-1}$, ρ is the plastic melt density, μ is the melt viscosity and $\omega = 2\pi f$ is the excitation frequency.

The density of the plastic melt is calculated from Eq. 9:

$$\rho = \frac{Z^2_{melt}}{\mu\omega}. \quad (10)$$

It means that in order to determine melt density, the melt cinematic viscosity μ must be known in advance, or it must be measured by an independent method.

4. Measuring density and viscosity in polymer melt

By using the ultrasonic pulse echo method it is possible to measure density and viscosity of polymer blends simultaneously in real-time during extrusion process [14]. This is of a very high importance in polymers industry. The information about polymer properties can be obtained by measuring ultrasound velocity or by measuring the wave's attenuation. It is necessary to keep in mind that velocity measurements can be done with a higher precision than the attenuation.

As an example, we would like to analyze the real experiment, which was carried out in University of Pennsylvania in the year 1989 [19]. The used ultrasonic technique is based on a measurement of the velocity of a torsional stress waves propagating through the metallic waveguide immersed in polymer melt.

The torsional wave reflection method is used to measure the time of flight of ultrasonic waves. The flight time of the torsional wave depends on the polymer's density ρ_f and shear viscosity μ.

Two separate waveguides with different cross-sectional geometries were used in this experiment. They are shown in Fig. 6 [19].

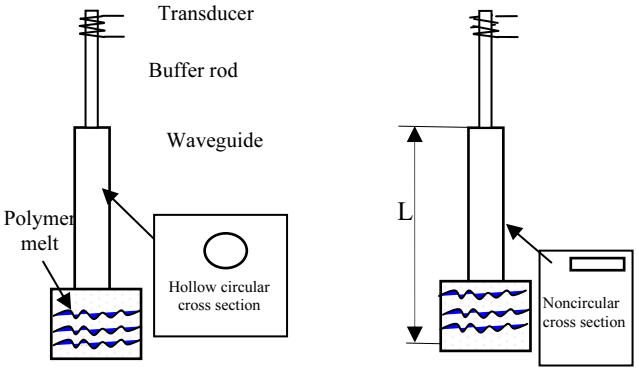

Fig. 6. **Schematic description of the torsion-wave sensors consisting of a waveguides with a different cross-sectional geometry (hollow circular cross section and noncircular cross section).**

The waveguides are made of an elastic material density of which is ρ_S. Inside one waveguide is a hollow circular cross section, in another one there is a noncircular

(rectangular) cross section. The propagation velocity of torsional stress waves depends on the waveguides' cross-section geometry, the polymer's density and its viscosity. The both waveguides are submerged in a polymer of the density ρ_f and the shear viscosity μ (Fig.6).

The torsional stress waves are generated by using magnetostrictive phenomenon. One waveguide with the length L=300mm and with the rectangular cross section is made of stainless steel. The second waveguide with the hollow circular cross section and the length L=300mm is made of aluminum. The buffer rod is made of Remendur (Co-Fe-V) of length about 1000 mm [19]. Due to mismatch of acoustic impedances, part of the wave is reflected at the waveguide interface. Another part propagates in the waveguide and is reflected from its another end. The transmitted through the melt and reflected back ultrasonic signals are recorded by a transducer (transmitter/receiver). The signals are viewed on an oscilloscope screen. The time of flight of a torsional stress waves depends on the densities of the waveguide and the polymer blend, on the polymer's viscosity and the shape of the waveguide.

The density and viscosity of polymer are obtained from the time of flight of a torsional stress waves.

Then the torsional wave velocity c is calculated from the equation [19]:

$$c = K(G/\rho_s)^{1/2} \cdot (1 + \rho_f I_f / \rho_s I_s)^{-1/2}, \qquad (11)$$

where I_S is the solid waveguide's inertia, I_f is the measurement polymer inertia, G is the shear modulus of the solid waveguide, $K = \sqrt{(D^*/I_s)}$, where ρ_f is the density of polymer, ρ_S is the density of waveguide and D* is the torsional rigidity.

$$D_t = t - t_0 \qquad (12)$$

where t_0 is the time of flight in the waveguide in air and t is the time of flight in the waveguide submerged in polymer at the same temperature.

The ratio D_t/t_0 can be expressed as [19]:

$$D_t / t_0 \cong \rho_f I_f / 2\rho_s I_s . \qquad (13)$$

The waveguides density ρ_S is known. By measuring D_t/t_0 for waveguides with circular and rectangular cross sections the density ρ_f of the polymer may be obtained from Eq. (13).

The apparent inertia for a waveguide with cross-sectional radius a is given by [19]:

$$I_f / I_s = (8\eta / \omega a^2)^{1/2}, \qquad (14)$$

where η is the kinematics viscosity and ω is the wave's frequency. Hence, it is possible to obtain kinematic viscosity from Eq.14

The liquid density is varied by changing the fluid concentration. The kinematic viscosity was varied in the range $\eta = 50 - 180 \cdot 10^{-6}$ m^2/s [19]. The propagation time of the torsional stress wave can be measured with an uncertainty 5 ns [19].

Measurements were performed in the temperature range (20- 50)^{0}C. The dispersion of the experimentally measured ratio (D_t / t_0) was smaller than 0.15%. By using this method, the density can be resolved with uncertainty about 0.5%. The shear viscosity can be resolved with uncertainty about 1% [19].

This method may be used for measurements of density and viscosity of liquids or high-pressure gases and is very attractive for industrial users. It means that it is possible to measure density and viscosity of polymer melts simultaneously, however measurements are performed in a rather low temperature range (20- 50)^{0}C, which is not sufficient.

5. Conclusions

In this paper density and viscosity measurement methods, suitable for measurements in polymer melts, are presented. In polymer industry the viscosity and density must be measured in very complicated conditions- at very high a pressure (about (50-100M Pa)) and high temperature (up to (150-350) ^{0}C). This reduces accuracy and reliability of measurements and these parameters can not be effectively monitored. So, majority of methods analyzed in this review can not be used for measurement of the polymer melt parameters, except ultrasonic methods.

The ultrasonic measurement methods are discerned from other methods. This technique is a powerful tool for polymer melt extrusion process monitoring [17]. The advantage of the ultrasonic techniques is that they are non-invasive, what is very important for process automation in industry. The ultrasonic pulse echo method can be used to measure the melt density inside the extrusion die. Also, ultrasonic methods may be used for simultaneous measurement of the density and viscosity of polymer melts on-line. They are characterized by a high reliability and a good accuracy. The resolution of density measurements may be up to 0.5 %, resolution of the shear viscosity is 1 %.

References

1. **Abu-Zahra N.** In- process density control of extruded foam PVC using wavelet packet analysis of ultrasound waves. Mechatronics. 2002. Vol. 12. P. 1083- 1095. http://dx.doi.org/10.1016/S0957-4158(02)00016-8

2. **Coates P. D., Barnes S. E., Sibley M. G., Brown E. C.** In-process vibrational spectroscopy and ultrasound measurements in polymer melt extrusion. Polymer. 2003. Vol. 44. P. 5937-5949. http://dx.doi.org/10.1016/S0032-3861(03)00544-5

3. **Abu-Zahra N**. Real-time viscosity and density measurements of polymer melts using dielectric and ultrasound sensor fusion. Mechatronics. 2004. Vol. 14. P. 789-803. http://dx.doi.org/10.1016/j.mechatronics.2003.11.001

4. **Abu-Zahra N**. Measuring melt density in polymer extrusion processes using shear ultrasound waves. Int. J. of Adv. Manufac. Tech. 2004. Vol. 24. No. 9-10. P. 661-666. http://dx.doi.org/10.1007/s00170-003-1743-6

5. **Mekawy M., Afifi H. and El-Nagar K.** Comparison between different methods for viscosity measurements. 15 th Symp. for Thermophysical properties. USA(NIST).2003. P. 22-27.

6. **Padmanabhan M**. Measurement of extensional viscosity of viscoelastic liquids foods. J. Food Eng. 1992. Vol. 25. No 3. P. 311. http://dx.doi.org/10.1016/0260-8774(94)00016-3

7. **Chiu S., Yiu H., Pong S.** Development of an in-line viscometer in an extrusion molding process. John Wiley and Sons Inc.1997. P.919-924.

8. **Tatibouet J., Hamel A., Piche L.** Ultrasound as monitoring tool for polymer degradation and reactive extrusion. Canada: Industrial Materials Institute, National research council. 1999. Vol.75. P. 3-5.

9. **Piche L., Hamel A., Gendron R., Dumoulin R., Tatibouet J.** US Patent 5. (July 18) 1995. P.433.

10. **Puttmer A., Hauptmann P., Henning H.** Ultrasonic density sensor for liquids/ IEEE transactions on ultrasonics, ferroelectrics and frequency control. 2000. Vol. 47. P. 85-91. http://dx.doi.org/10.1109/58.818751

11. **Jasiūnienė E.** Ultragarsinė medžiagotyra: Mokomoji knyga. Kauno Technologijos Universitetas. 2007.

12. **Piche L., Sahnoune A.** Ultrasonic study of anharmonicity in amorphous polymers: temperature, pressure and molecular weight effects. Journal of polymer science.1996. P. 665.

13. **Franco E., Adamowski C., Buiochi C.** Ultrasonic viscosity measurement using the shear-wave reflection coefficient with a novel signal processing technique/ IEEE transactions on ultrasonics, ferroelectrics and frequency control. 2010. Vol. 57. P. 1133-1138. http://dx.doi.org/10.1109/TUFFC.2010.1524

14. **Wu K., Jen C.-K., Kobayashi M., Zhao L.** Ultrasonic probes simultaneously producing one longitudinal and two shear waves and their potential applications. Natural Sciences and Engineering Research Council of Canada, Boucherville, Canada. 2009. P. 630-632.

15. **Assia O., Hakim D.** Propagation of ultrasonic waves in viscous fluids. Faculty of Physics, University of Sciences and Technology Houari Boumedienne. 2010.

16. **Henning B., Daur P., Prange S., Dierks K., Hauptmann P.** In-line concentration measurement in complex liquids using ultrasonic sensors. Ultrasonics. 2000. Vol. 38. P. 799-803. http://dx.doi.org/10.1016/S0041-624X(99)00190-0

17. **Coates D., Barnes E., Sibley G., Brown C., Edwards G., Scowen J.** In-process vibrational spectroscopy and ultrasound measurements in polymer melt extrusion. Polymer. 2003. Vol. 44. P. 5937-5949. http://dx.doi.org/10.1016/S0032-3861(03)00544-5

18. **Abu- Zahra N., Seth A.** In-process density control of extruded foam PVC using wavelet packet analysis of ultrasound waves. Mechatronics. 2002. Vol. 12. P. 1083-1095. http://dx.doi.org/10.1016/S0957-4158(02)00016-8

19. **Jin O., Bau K. and H.** Instrument for simultaneous measurement of density and viscosity. Review of scientific instruments. 1989. Vol. 60(6). P.1111-1115. http://dx.doi.org/10.1063/1.1140325

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Skystųjų polimerų klampos ir tankio matavimo metodai

Reziumė

Šiame straipsnyje aptarti klampos ir tankio matavimo metodai. Išskirti ultragarsiniai matavimo metodai, kuriais galima išmatuoti minėtus parametrus skystuosiuose polimeruose realiuoju laiku. Metodai sugrupuoti pagal matavimo principus, metodiką ir gebėjimą išmatuoti tankį ir klampą skystuosiuose polimeruose realiuoju gamybos laiku. Tai ypač svarbu gamybos proceso automatizavimui, kontrolei ir stebėjimui. Ultragarsiniai matavimo metodai iš kitų klampos ir tankio matavimo metodų išsiskiria tuo, kad ultragarso bangos greitis gali būti matuojamas tuo pačiu metu, kai ultragarso banga slopinama, o tai gerokai praplečia matavimo galimybės. Skersines ir sukininės (torsinės) bangos sėkmingai gali būti naudojamos matavimuose kaip ir išilginės. Matavimuose gali būti naudojamas labai platus dažnių diapazonas.

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