MINISTRY OF EDUCATION AND SCIENCE OF THE RUSSIAN FEDERATION

Federal State Autonomous Education “Ural Federal University named after the first President of Russia B.N. Yeltsin”

Institute of New Materials and Technologies

Signed and Approved

Vice-rector for Research

\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ V.V. Kruzhaev

«\_\_\_» \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ 2018 г.

DISCIPLINE PROGRAM

**THERMODYNAMICS OF POLYMER SYSTEMS**

|  |  |  |  |
| --- | --- | --- | --- |
| **EP code** | **direction** | **Direction (profile) of the postgraduate program** | **Qualification** |
| 04.06.01 | chemical sciences | High-molecular compounds | Researcher. Research-teacher |

1. **GENERAL CHARACTERISTIC OF DISCIPLINE**

1.Special discipline "Thermodynamics of polymer systems" promotes mastering of the main professional competences and their components and is aimed at in-depth study of basic sections in the field of phase transitions and thermodynamic properties of polymer systems.

1.3As a result of mastering this discipline, the graduate student must master the following competencies:

**general professional competence:**

* the ability to independently carry out research activities in the relevant professional field using modern research methods and information and communication technologies (OPK-1);
* readiness to organize the work of the research team in the field of chemistry and related sciences (OPK-2);

**- professional competencies:**

**research activities:**

* the ability to independently conduct research and to obtain scientific results that meet the established requirements for the content of dissertations for the academic degree of the candidate of sciences in the field of orientation (scientific specialty) 02.00.06 - High-molecular compounds (PC-1)
* readiness to present scientific results on the topic of dissertational work in the form of publications in peer-reviewed scientific publications, reports at scientific conferences, review and edit scientific articles on the direction (scientific specialty) 02.00.06 High-molecular compounds (PC-2)

**2 STRUCTURE AND DISTRIBUTION OF TRAINING TIME**

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Names of the discipline | semester | The amount of time devoted to mastering the discipline | | | | | | |
| Auditory lessons hour | | | | Independent work hour | Certification in discipline (test, exam) | Total hours/exams |
| Total | lectures | practical lessons | laboratory works |
| Thermodynamics of polymer systems | 6 | 4 | 4 |  |  | 104 | Examination, 6 semester | 108/3 |
| Total for development | | 4 | 4 |  |  | 104 |  | 108/3 |

**3 Contents**

**3.1 Contents and learning hours**

|  |  |  |  |
| --- | --- | --- | --- |
| №  п/п | Section, Topic | Hours/credits | |
| hour. | Credits. |
| 1 | **Section 1. Introduction.** Basic concepts of thermodynamics of polymer solutions. Thermodynamic affinity of the solvent to the polymer. Ideal and imperfect solutions. Osmotic pressure of polymer solutions. Swelling pressure. The second virial coefficient. Enthalpy, internal energy and entropy of mixing, combinatorial and noncombinatorial contributions to entropy. Volume change during dissolving of polymers. Criteria of orientation and balance of processes. Partial values. Thermodynamic affinity and methods for its evaluation. Thermodynamic stability of systems. Resistance to diffusion. Stability and critical phenomena**.** | 1 |  |
| 2 | **Section 2.** Theories of polymer solutions. Thermodynamic theory of solutions of non-electrolytes. The theory of regular Hildebrand solutions. Solubility parameter, methods for its determination. Solubility parameter concept. Statistical theories of liquids and liquid solutions. Lattice theories of liquids and solutions. The theory of free volume. The theory of strictly regular Huggenheim solutions. Flory-Huggins theory. Barker's theory. Theories of solutions, based on the law of the respective states .. The theory of Prigozhin's solutions and its development. New theory of Flory solutions, its advantages. Group theory of solutions. UNIQUAC equation. Model UNIFAC.  The effect of chain flexibility and chain packing density on the thermodynamics of polymer dissolution and swelling. Thermodynamics of polymer dissolution and critical dissolution temperatures. The volume of mixing systems polymer - solvent. Combinatorial and noncombinatorial entropy of mixing. The influence of the glassy state of the polymer on the thermodynamics of its dissolution. Features of the glassy state of polymers. Structural contribution to the enthalpy of mixing a glassy polymer with a solvent. The enthalpy of mixing solutions of glassy polymers with the upper critical temperature of dissolution. Gibbs energy and entropy of mixing a glassy polymer with a solvent. The influence of the degree of crystallinity of the polymer is not the thermodynamics of its dissolution. Thermodynamics of aqueous solutions of polymers. | 24 |  |
| 3 | **Section 3.** Thermodynamics of polymer blends.  Compatibility of polymers in solution. Dobri method. Kriegbaum and Wall method. Determination of mutual solubility of polymers. Works by V.N.Kuleznev. Scott theory of polymer blends. Gibbs energy and polymer interaction parameter estimate. Phase separation in polymer - polymer systems. Non-thermodynamic methods for assessing compatibility. Evaluation of compatibility for glass transition temperatures. Using electron microscopy to assess the compatibility of polymers. Limitations and limitations of the methods. Thermodynamic compatibility of polymers. Stable, metastable and unstable polymer-polymer systems. Thermodynamics of mixing. Gibbs energy of polymer mixing. Using the thermodynamic cycle to determine the value of ΔG. Determination of Gibbs energy by the sorption method. Enthalpy and entropy of mixing. Ways to enhance the compatibility of polymers. Specific interactions and compatibility. Connection of macromolecules by chemical bonds as a way to increase the stability of polymer systems. Block copolymers. Vulcanized rubber compounds. Interpenetrating grids. Copolymerization as a way to improve the compatibility of polymers. Various uses of copolymerization to increase the stability of mixtures. Compatibilizers - interfacial additives that promote compatibility**.** | 29 |  |
| 4 | **Section 4.** General questions of phase equilibrium of polymer systems. Types of phase diagrams of polymer - solvent systems. The influence of the size and shape of solvent molecules on phase transitions. Classification of phase transitions. Liquid crystal state of substances. Phase diagrams of solutions of rigid-chain polymers. The influence of the molecular weight of the polymer on the position of the boundary curves. The influence of the chemical structure of the polymer on the phase liquid crystal transitions. The influence of the nature of the solvent on the phase liquid crystal transitions. | 1 |  |
| 5 | **Section 5.** Phase diagrams and structure of polymer systems with amorphous, crystalline and liquid-crystal phase transitions. Phase transitions in polymer solutions induced by a mechanical field. Dynamic structure formation in polymer solutions. Phase transitions in melts and solutions of crystalline polymers caused by a mechanical field. Effect of deformation on phase transitions in solutions of amorphous polymers. Phase transitions in deformable gel-forming systems. Compatibility of components of rubber-containing mixtures and solutions in static conditions and in a mechanical field. Phase diagrams of rubber compounds under static conditions. Phase transitions in deformable mixtures of rubbers. Phase transitions in polymer - polymer - solvent systems. Theoretical substantiation of the phase separation of polymer solutions caused by a mechanical field. Amorphous delamination. Crystalline phase separation. Phase transitions in polymer blends caused by a mechanical field. Experimental data. Systems with amorphous delamination. Systems with crystalline phase separation. Theoretical representations. Phase transitions in gels of cross-linked polymers - non-electrolytes, caused by a mechanical field. Phase diagrams. The pulsating mechanism of the phase decomposition of gels. Effect of deformation on thermodynamic stability and phase transitions of polymer gels. The influence of external pressure on the phase behavior of polymer systems. Effect of pressure on the solubility of amorphous substances. The effect of pressure on the solubility of crystalline substances. Effect of pressure on critical temperatures of polymer systems. The effect of negative pressure on the phase behaviour of polymer solutions. Phase and structural transitions of polymer systems in an electric field. Effect of precipitating agents on the phase equilibrium of polymer solutions near the upper and lower critical temperatures of dissolution. Self-organization of macromolecules in solutions of rigid polymers. The influence of the magnetic field on the sizes of supramolecular particles in solutions of cellulose ethers. Phase and structural transitions of liquid crystal systems in mechanical and magnetic fields. | 18 |  |
| 6 | **Section 6.** Methods for constructing phase diagrams, values of the critical and θ - temperatures of polymer systems. Methods based on measuring optical characteristics. Cloud point method. The method of light scattering at large angles. The method of critical opalescence. Pulsed induced light scattering method. Measurement of optical density and turbidity. Turbidimetric titration method. Refractometric method. Interventional micromethod. The method of polarization microscopy. Spectral methods. The method of infrared spectroscopy. Pulsed NMR method. Paramagnetic probe method. The spin label method. Dielectric method. Thermophysical methods. Dilatometric method. DTA and DSC methods. Methods that fix the mass transfer of components. Viscometric methods. Diffusion method. Reverse gas chromatography method. Centrifugation method. Method for determining the composition and volume ratio of coexisting phases. Thermodynamic methods. Experimental methods for determining the Gibbs energy and mixing enthalpy. Method for determining the second virial coefficients. The method of limited swelling. Determination of interfacial surface energy. Determination of vapor pressure. Determination of solubility parameters. The method of dynamic osmometry. The method of temperature diffractometry and neutron scattering method.  Methods for calculating boundary curves, critical and θ-temperatures. Comparison with experiment. Calculations based on the Flory-Huggins theory. Calculations based on the Prigozhin-Patterson theory and the new Flory theory. Phase diagrams and thermodynamic parameter of the interaction between the components of deformable polymer solutions. | 18 |  |
|  | total | 108 | 3 |

**3.2. Distribution of learning/teaching hours**

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **№ п/п** | **Section, topic** | | **Estimated learning hours for study credits/hours** | | | | | |
|  | **Face-to-face hours** | | | | | **Self-study** | **Total on topics and sections** |
| **total** | | **lectures** | **Seminars/ practices** | **Lab hours** |
| 1 | Section 1. Introduction. | 1 | | 1 |  |  |  | 1 |
| 2 | Section 2. Polymer solution theory | 1 | | 1 |  |  | 23 | 24 |
| 3 | Section 3.Thermodynamics of polymer blends | 1 | | 1 |  |  | 28 | 29 |
| 4 | Section 4.General issues of phase equilibrium in polymer systems | 1 | | 1 |  |  |  | 1 |
| 5 | Section 5. Phase diagrams and the structure of polymer systems with amorphous, crystalline and liquid crystalline and phase transitions. |  | |  |  |  | 27 | 27 |
| 6 | Section 6. Methods of designing phase diagrams, values of critical and θ –temperatures in polymer systems |  | |  |  |  | 26 | 26 |
| **total** | | **4** | | **4** |  |  | **104** | **108** |

**3.3 Self-study**

|  |  |  |  |
| --- | --- | --- | --- |
| Sections and topics for self-study | Types of works for self-study (reports, translations, callculations, experiment designs etc.) | Study hours | |
| hours. | credits. |
| **Section 2.** Lattice theories of liquids and solutions. The theory of free volume. The theory of strictly regular Huggenheim solutions. Flory-Huggins theory**.** | Readaing the recommended literature, analysis of abstracts of journals and electronic sources, taking into account the content of the discipline (writing notes). | 23 |  |
| **Section 3.** Thermodynamic compatibility of polymers. Stable, metastable and unstable polymer-polymer systems. Thermodynamics of mixing. Gibbs energy of polymer mixing. Using the thermodynamic cycle to determine the value of ΔG. Determination of Gibbs energy by the sorption method. Enthalpy and entropy of mixing. Ways to enhance the compatibility of polymers .. | Analysis of abstracts of journals and electronic sources subject to content of the discipline (report). | 28 |  |
| **Section 5.** The effect of external pressure on the phase behaviour of polymer systems. Effect of pressure on the solubility of amorphous substances. The effect of pressure on the solubility of crystalline substances. Effect of pressure on critical temperatures of polymer systems. The effect of negative pressure on the phase behaviour of polymer solutions.Phase and structural transitions of polymer systems in an electric field. Effect of precipitating agents on the phase equilibrium of polymer solutions near the upper and lower critical temperatures of dissolution**.** | Reading the recommended literature, analysis of abstracts of journals and electronic sources, taking into account the content of the discipline (writing notes). | 27 |  |
| **Section 6.** Methods for calculating boundary curves, critical and θ-temperatures. Comparison with experiment. Calculations based on the Flory-Huggins theory. Calculations based on the Prigozhin-Patterson theory and the new Flory theory. Phase diagrams and thermodynamic parameter of the interaction between the components of deformable polymer solutions**.** | Reading the recommended literature, analysis of abstracts of journals and electronic sources, taking into account the content of the discipline (writing notes). | 26 |  |
| **Total** | | **104** |  |

**4 Assessment criteria**

Objective assessment of the level of compliance of learning outcomes with the requirements for the development of EP.

|  |  |  |  |
| --- | --- | --- | --- |
| **competencies** | **Level of achievement** | | |
| **threshold** | **advanced** | **proficient** |
| **knowledge** | A PhD student demonstrates knowledge-acquaintance, knowledge-transfer: recognizes objects, phenomena and concepts, finds differences in them, shows knowledge of sources of information, can independently perform reproductive actions on knowledge through self-reproduction and application of information. | A PhD student demonstrates analytical knowledge: confidently reproduces and understands the knowledge gained, assigns them to one or another classification group, independently organizes them, establishes relationships between them, and productively applies them in familiar situations. | A PhD student can independently extract new knowledge from the outside world, creatively use it to make decisions in new and non-standard situations. |
| **skills** | A PhD student is able to correctly perform prescribed actions on instructions, an algorithm in a familiar situation, independently performs actions to solve typical tasks that require a choice between the accepted methods, in a predictably changing situation | A PhD student is able to independently perform actions (techniques, operations) on solving non-standard tasks that require a choice based on a combination of accepted methods in an unpredictably changing situation. | A PhD student is able to independently perform actions related to solving research problems, demonstrates the creative use of skills (technologies) |
| **Personal characteristics** | The PhD student has a low motivation for learning activities, shows an indifferent, irresponsible attitude to study, the assigned task | The graduate student has a pronounced motivation for learning activities, demonstrates a positive attitude to learning and future work, is active. | The PhD student has a developed motivation for study and work, shows perseverance and enthusiasm, hard work, independence, and creative approach. |

**information and reference systems and search systems:**

ScienceDirect: <http://www.sciencedirect.com>;

Web of Science: <http://apps.webofknowledge.com>;

Scopus: <http://www.scopus.com>;

Reaxys: <http://reaxys.com>

<http://lib.urfu.ru/course/view.php?id=141>

**6.2 Electronic educational resources**

<http://lib.urfu.ru>

<http://lib.urfu.ru/course/view.php?id=76>

<http://opac.urfu.ru/>

<http://lib.urfu.ru/mod/resource/view.php?id=2330>

<http://lib.urfu.ru/course/view.php?id=75>

<http://lib.urfu.ru/mod/data/view.php?id=1379>

**The list of issues to offset (audited competences OPK-1, OPK-2, PK-1, PK-2):**

1. Enthalpy, internal energy and entropy of mixing, combinatorial and non-combinatorial contributions to entropy.

2. Thermodynamic affinity and methods for its evaluation. Thermodynamic stability of systems.

3. Solubility parameter, methods of its determination. The concept of solubility parameter.

4. Thermodynamic classification of phase transitions. Stable and metastable phases. Binodal, spinodal, liquidus curve.

5. The new theory of solutions Flory, her dignity.

6. Volumes of mixing polymer-solvent systems.

7. Thermodynamic compatibility of polymers. Stable, metastable and unstable polymer-polymer systems.

8. Methods of enhancing the compatibility of polymers. Specific interactions and compatibility.

9. Phase diagrams of solutions of rigid-chain polymers. Effect of the molecular weight of the polymer on the position of the boundary curves. Influence of chemical structure of polymer on phase liquid crystal transitions.

10. Dynamic structure formation in polymer solutions.

11. Phase transitions in deformable gel-forming systems.

12. Gibbs energy of mixing polymers. Use of the thermodynamic cycle to determine the value of ΔG.

13. Effect of deformation on phase transitions in solutions of amorphous polymers.

14. Effect of pressure on the solubility of amorphous substances. Effect of pressure on the solubility of crystalline substances.

15. Effect of pressure on the critical dissolution temperature of polymer systems.

16. Phase transitions of liquid-crystal systems in mechanical and magnetic fields.

17. Methods for constructing phase diagrams, based on measuring the optical characteristics of solutions.

18. Methods for constructing phase diagrams: DTA and DSC methods