SYNTHESIS AND PROCESSING OF POLYMERS AND POLYMERIC COMPOSITES

СИНТЕЗ И ПЕРЕРАБОТКА ПОЛИМЕРОВ И КОМПОЗИТОВ НА ИХ ОСНОВЕ

ISSN 2686-7575 (Online)

https://doi.org/10.32362/2410-6593-2021-16-4-337-344

UDC 678. 541.6



RESEARCH ARTICLE

Aqueous polyvinyl alcohol solution foaming at different molecular masses

Anastasiya A. Akimova^{1,@}, Viktor A. Lomovskoy^{1,2}, Igor D. Simonov-Emel'yanov¹

¹MIREA – Russian Technological University (M.V. Lomonosov Institute of Fine Chemical Technologies), Moscow, 119571 Russia

²A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Moscow, 119071 Russia

[®]Corresponding author, e-mail: akimova@mirea.ru

Abstract

Objectives. Investigation of aqueous polyvinyl alcohol (PVA) foaming process and the influence of its water solution structure, when possessed of different molecular weights and concentrations, on foaming multiplicity.

Methods. Solution foaming analysis was performed on the data of dynamic light scattering obtained on the Zetasizer Nano particle analyzer.

Results. In this work, the foaming ability and foaming multiplicity of aqueous PVA solutions (as a main component for obtaining special-purpose foams) have been studied. It is shown that PVA solutions in water are colloidal dispersed systems consisting of different-sized associates (from 4.8 to 68.1 nm), depending on the molecular weight of PVA. Dependencies of aqueous PVA solution foaming multiplicities on the concentration, molecular weight, and solution temperature were given. Optimal values of concentration and molecular PVA weight, as well as optimal foaming process conditions from aqueous PVA solutions, were established.

Conclusions. Increasing PVA concentrations in aqueous solutions cause foaming multiplicity to decrease for all molecular weights by 1.5 times, and increasing molecular weight increases foaming multiplicity by 2 times. The foaming ratio of aqueous PVA solutions with different concentrations and molecular weights (depending on a solution temperature characterized by a maximum of 30° C) is associated with decreased viscosity and surface tension.

Keywords: polyvinyl alcohol, molecular weight, aqueous solution, solution concentration, foaming multiplicity

For citation: Akimova A.A., Lomovskoy V.A., Simonov-Emel'yanov I.D. Aqueous polyvinyl alcohol solution foaming at different molecular masses. *Tonk. Khim. Tekhnol. = Fine Chem. Technol.* 2021;16(4):337–344 (Russ., Eng.). https://doi.org/10.32362/2410-6593-2021-16-4-337-344

НАУЧНАЯ СТАТЬЯ

Пенообразование растворов поливинилового спирта с разной молекулярной массой в воде

А.А. Акимова^{1,@}, В.А. Ломовской^{1,2}, И.Д. Симонов-Емельянов¹

¹МИРЭА – Российский технологический университет (Институт тонких химических технологий им. М.В. Ломоносова), Москва, 119571 Россия

²Институт физической химии и электрохимии им. А.Н. Фрумкина Российской академии наук, Москва, 119071 Россия

®Автор для переписки, e-mail: akimova@mirea.ru

Аннотация

Цели. Исследовать процесс пенообразования водных растворов поливинилового спирта (ПВС) с различной молекулярной массой и концентрацией и влияние их структуры на кратность их вспенивания.

Методы. Анализ пенообразования растворов проводили по данным динамического светорассеяния, полученным на анализаторе частиц Zetasizer Nano.

Результаты. В работе изучена пенообразующая способность и кратность вспенивания водных растворов ПВС как одного из основных компонентов получения пен специального назначения. Показано, что растворы ПВС в воде представляют собой коллоидные дисперсные системы, состоящие из ассоциатов с разными размерами (от 4.8 до 68.1 нм) в зависимости от молекулярной массы ПВС. Приведены зависимости кратности вспенивания водных растворов ПВС от концентрации, молекулярной массы и температуры раствора. Приведены значения оптимальной концентрации и молекулярной массы ПВС, а также установлены оптимальные условия процесса пенообразования из водных растворов ПВС.

Выводы. Установлено, что с ростом концентрации водных растворов ПВС кратность вспенивания снижается для всех молекулярных масс приблизительно в 1.5 раза, а с увеличением молекулярной массы она возрастает примерно в 2 раза. Кратность вспенивания водных растворов ПВС с разной концентрацией и молекулярной массой в зависимости от температуры раствора характеризуется максимумом при 30 °C, что связано с уменьшением вязкости и снижением поверхностного натяжения растворов.

Ключевые слова: поливиниловый спирт, молекулярная масса, водные растворы, концентрация растворов, кратность вспенивания

Для цитирования: Акимова А.А., Ломовской В.А., Симонов-Емельянов И.Д. Пенообразование растворов поливинилового спирта с разной молекулярной массой в воде. *Тонкие химические технологии*. 2021;16(4):337–344. https://doi.org/10.32362/2410-6593-2021-16-4-337-344

When creating highly porous filters for separating water from hydrocarbon fuels (kerosene, gasoline, etc.), polyvinyl alcohol (PVA) is used as the initial component, as it selectively absorbs water from hydrocarbon organic matter [1]. The filter technology includes a stage of obtaining foams from aqueous PVA solutions [2–4]. The structure and parameters of formed foams, foaming multiplicity, and foam stability over time are determined primarily by PVA molecular weight, the concentration of aqueous PVA solutions, and the technological parameters of solution production processes [5–9].

Of undoubted interest is the establishment of main regularities when forming foams with adjustable structure parameters and properties. The purpose of this work is to study the foaming process of aqueous PVA solutions and the influence of their structures (with different molecular weights and concentrations) as well as the power-speed and temperature parameters of foaming on their properties.

EXPERIMENTAL

PVA produced by *Mowiol* (Taiwan) with different molecular weights (M_w) was used as the object of this study: Mowiol 5-88 with $M_w = 22000$, Mowiol 18-88 with $M_w = 55000$, Mowiol 26-88 with $M_w = 68000$ and Mowiol 47-88 with $M_w = 81000$ with a 99.95% share of the base substance. It is impractical to take PVA with a M_w greater than 81000, since in the process of its dissolution in water, the partial flocculation of dissolved PVA particles occurs and forms large associates that cannot be separated [10, 11].

PVA solutions with given concentrations in water were prepared in a measuring flask with a volume of 1000 mL. PVA suspensions were placed and 800 mL of deionized water was poured. Deionized water was obtained using a Type 1 high water purification system, Milli-Q Integral 5 (Merck Millipore, Burlington, Massachusetts, USA), with a resistivity of 18.0 mOhm·cm. The flask was then placed in a thermostat at 80°C and the liquid was stirred constantly until the PVA was completely dissolved. The solution was then evaluated visually before being cooled to 25°C. The quality of complete dissolution and solution heterogeneity at different PVA concentrations in water was judged by the data of dynamic light scattering obtained using a Zetasizer Nano particle analyzer (Malvern Instruments, USA).

The method is based on the registration of scattered light fluctuations from particles in continuous Brownian motion [12]. A laser beam is passed through the analyzed sample and the intensity of light scattering by particles over time is recorded. When particles are irradiated with a laser, light is scattered in all directions. Observed scattered light comes from a set of scattering elements in a certain volume, depending on the angles at which registration is performed and the aperture characteristics. The observed intensity of scattered light under any conditions will be the result of light superposition scattered by each element, and thus depend on the relative positions of these elements. When the particles move, their relative positions change and fluctuations in scattered light intensity are observed. Since the particles move randomly under the influence of Brownian force and scattered light intensity fluctuations are random. For small fast-moving particles, fast fluctuations are observed, while larger and slower particles show slower fluctuations.

Analysis of intensity fluctuations makes it possible to determine the speed of Brownian motion and calculate the particle size using the Stokes-Einstein equation. The Zetasizer Nano photonic particle analyzer has a particle measurement range of 0.3 to 10000 nm. The operating temperature range is 2–120°C, the scattered light detection angle is 173°, a helium-neon laser with a wavelength of 633 nm is used as a light source, and the light source power is 5 MW. The device determines the particle size by measuring the rate of scattered light fluctuation by particles. Measurement is carried out in automatic mode according to the standard method.

Foams from aqueous PVA solutions with different Mw and concentrations were obtained via mechanical foaming [13] at different temperatures. A 250 mL measure of PVA solution in water was poured into a 500 mL measuring cylinder with a diameter of 50 mm and a height of 350 mm. A three-bladed rotor of an upperdrive laboratory agitator was placed in the cylinder in such a way that it did not touch the bottom of the cylinder (the distance to the bottom is ~50 mm) and the height of the liquid column was measured with a Vernier height gage before mixing. Depending on the experiment temperature, the cylinder with the solution was placed in a thermostat at a given temperature and thermostated for 30 min. The agitator was turned on and the foaming process was carried out at a speed of 1000 rpm for 5 min (it was experimentally determined that this amount of time is necessary to achieve maximum foaming multiplicity), after which the agitator was turned off and the column of liquid with foam was measured again.

¹ Vilkova N.G. Colloidal-chemical properties of polyhedral foams and emulsions. Cand. Thesis (Chem.). Moscow: M.V. Lomonosov Moscow State University; 2007. 285 p. (in Russ.).

The foaming multiplicity (β) was calculated by

$$\beta = \frac{V_{\rm f}}{V_{\rm w}}$$

where $V_{\rm f}$ is the volume of the resulting foam; $V_{\rm w}$ is the volume of the initial PVA liquid solution.

RESULTS AND DISCUSSION

The homogeneity of aqueous PVA solutions was determined using the method of dynamic light scattering on the Zetasizer Nano particle analyzer. As an example, Fig. 1 shows the dependences of light scattering intensity for 4 vol % of aqueous PVA solutions of with minimum (1) and maximum (2) $M_{\rm w}$ of the associate diameters.

It has been established that PVA solutions in water are colloidal dispersed systems consisting of PVA associates in water, and the average associate diameter depends on M_w : for $M_w = 22000$, diameters

ranged from 4.8 to 50.8 nm, and for $M_w = 81000$, diameters ranged from 5.6 to 68.1 nm. The associative structure of aqueous PVA solutions influenced the foaming process.

Figure 2 shows the β dependences for aqueous PVA solutions based on concentration and $M_{\rm w}$.

With a concentration increase from 4 to 24 vol %, β decreased from 6.4–3.7 to 4.9–1.8 (i.e., by ~1.5 times) due to an increase in solution viscosity. On the curves of Fig. 2a, there is an inflection at a solution concentration of ~12 vol %; therefore, the dependence of β on M_w for solutions of 12 vol % concentration is of interest. The influence of PVA M_w on foaming is manifested to a lesser extent than the change in solution concentration (Fig. 2b), and an inflection is observed on the curve $\beta = f(M_w)$ at $M_w = 55000$, indicating an increase in the foaming efficiency when using PVA with a M_w greater than 60000. The maximum β (\approx 5.5) was achieved with PVA water solutions of 81000 M_w and a solution concentration of 4 vol %.

Temperature had a significant influence on the foaming process of aqueous PVA solutions, since temperature increases caused solution viscosity

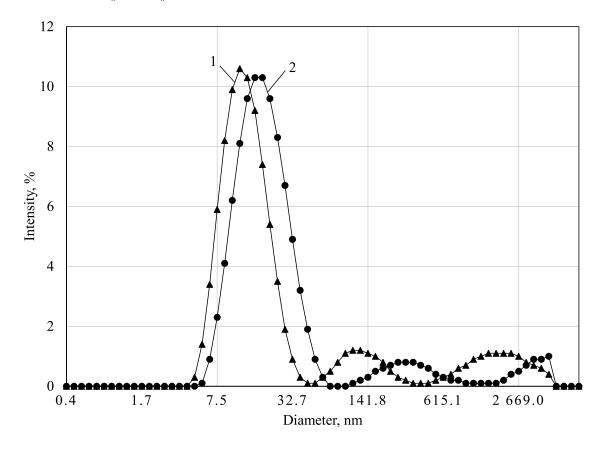
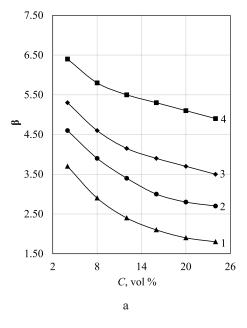


Fig. 1. Dependence of associate distributions by size in 4 vol % aqueous PVA solutions with different molecular weights (M_w) : (1) $M_w = 22000$, (2) $M_w = 81000$.

to decrease, an equivalent to a lower solution concentration. Figure 3 shows the dependences of β for aqueous PVA solutions at a 4 vol % concentration with measured $M_{_{\rm W}}$ and temperature.

Figure 3 shows that as M_w increases from 22000 to 81000, the β of the aqueous PVA solutions increases at almost all temperatures (10–60°C) by approximately 2 times. In Fig. 3a, the dependences

of β are close to each other at temperatures of 10°C and 60°C (they show the lowest β), yet there is also a sharp decrease in β at 60°C caused by decreased solution viscosity [13]. In Fig. 3b, it is possible to trace the influence of temperature on β , establishing that the maximum β is achieved at 30°C for almost all $M_{_{w}}$ values. As temperature continued to increase, β decreased.



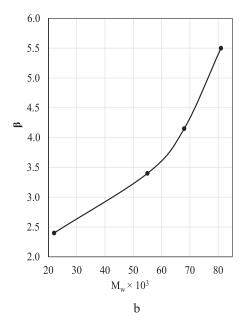
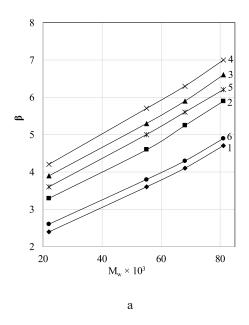


Fig. 2. Dependence of β for aqueous PVA solutions with different M_w at 20°C: (1) $M_w = 22000$, (2) $M_w = 55000$, (3) $M_w = 68000$, (4) $M_w = 81000$; (a) concentrations, (b) M_w for a concentration of about 12 vol %.



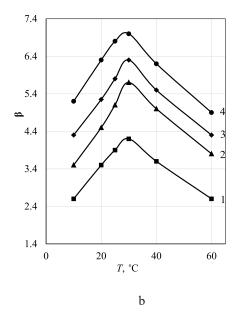


Fig. 3. Dependence of β for aqueous PVA solutions at a concentration of 4 vol %: (a) on the M_w at different temperatures: (1) 10°C, (2) 20°C, (3) 25°C, (4) 30°C, (5) 40°C, and (6) 60°C; and (b) on temperature at different M_w : (1) $M_w = 22000$, (2) $M_w = 55000$, (3) $M_w = 68000$, (4) $M_w = 81000$.

CONCLUSIONS

This study obtained data on the processes of mechanical foaming from aqueous PVA solutions with different $M_{\rm w}$ (from 22000 to 81000) and solution concentrations (from 4 to 24 vol %) at different temperatures (10–60°C). It was found that the maximum foaming ability was possessed by PVA solutions with a $M_{\rm w}$ of 81000 and a concentration of 4 vol %. However, to increase the PVA concentration in aqueous solutions and obtain more stable foams (i.e., the ability to maintain initial structure parameters, since foam is a structured dispersed system), foaming can be carried out at an optimal temperature of 30°C and a PVA concentration equal to 12 vol %. In such cases, the maximum β = 4.2 is

achieved, which was previously obtained at 4 vol %. The β of aqueous PVA solutions with different concentrations and M_w , depending on solution temperature, is characterized by a maximum at 30°C, which is associated with decreased viscosity and solution surface tension.

Authors' contribution

- **A.A. Akimova** planning and conducting research, processing research materials, writing the text of the article;
- **V.A.** Lomovskoy scientific consulting and assistance in processing the results obtained;
- **I.D. Simonov-Emel'yanov**—general management of research processes and preparation of material for publication.

The authors declare no conflicts of interest.

REFERENCES

- 1. Ushakov S.N. *Polivinilovyi spirt i ego proizvodnye: v 2 t. (Polyvinyl alcohol and its derivatives: in 2 v.).* Moscow, Leningrad: Izd. Akad. Nauk SSSR; 1960.V. 1. 552 p. (in Russ.).
- 2. Panov Yu.T. Nauchnye osnovy sozdaniya penoplastov vtorogo pokoleniya: monografiya (Scientific basis for the creation of second-generation foams). Vladimir: Vladimir Gos. Univ. 2003. 176 p. (in Russ.). ISBN 5-89368-379-X.
- 3. Lysakov V.N., Sedunov S.G., Taraskin K.A., Spiridonova M.P. Methods of obtaining and studying the properties of foam compositions, promising for creation sound-proof coatings. *Molekul. Tekhnol.* = *Molecul. Technol.* 2008;2:61–79 (in Russ.).
- 4. Lomovskoy V. A., Abaturova N. A., Lomovskaya N. Yu., Khlebnikova O. A., Sakov D. M., Galushko T. B., Barteneva A. G. Influence of the porosity of the polyvinylformal structure on its sorption characteristics. 5th Scientific Conference "Physical Chemistry of surface phenomena and adsorption." July 1–6, 2013 Ples: Proceedings of the conference. FGBOU VPO Ivan. Gos. Khim.-Tekhnol. Univ. Ivanovo, 2014. p. 52. (in Russ.)
- 5. Vilkova N.G., Mishina S.I., Dorchina O.V. Stability of foams containing diesel fuel. *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.* 2018;61(6):48–53 (in Russ.). https://doi.org/10.6060/tcct.20186106.5361
- 6. Manzhai V.N., Fufaeva M.S. Dispersity and stability of foams obtained from poly(vinyl alcohol) solution and the properties of resulting formed foams cryogels. *Colloid J.* 2014;76(4):495–499. https://doi.org/10.1134/S1061933X14040097
- 7. Tikhomirov V.K. Peny: teoriya i praktika ikh polucheniya i razrusheniya (Foams: theory and practice of their production and destruction). Moscow: Khimiya; 1983. 265 p. (in Russ.).

СПИСОК ЛИТЕРАТУРЫ

- 1. Ушаков С.Н. *Поливиниловый спирт и его производные: в 2 т.* М.-Л.: Изд. АН СССР; 1960. Т. 1. 552 с.
- 2. Панов Ю.Т. *Научные основы создания пенопластов второго поколения: монография.* Владимир: Ред.-издат. комплекс ВлГУ; 2003. 176 с. ISBN 5-89368-379-X.
- 3. Лысаков В.Н., Седунов С.Г., Тараскин К.А., Спиридонова М.П. Методы получения и исследования свойств пенных составов, перспективных для создания звуко-изоляционных покрытий. *Молекулярные технологии*. 2008;2:61–79.
- 4. Ломовской В.А., Абатурова Н.А., Ломовская Н.Ю., Хлебникова О.А., Саков Д.М., Галушко Т.Б., Бартенева А.Г. Влияние пористости структуры поливинилформаля на его сорбционные характеристики. 5-ая Научная конференция «Физическая химия поверхностных явлений и адсорбции». 1–6 июля 2013 г. Плес: Труды конференции. ФБГОУ ВПО Иван.гос.хим.-технол. ун-т. Иваново, 2014. с.52.
- 5. Вилкова Н.Г., Мишина С.И., Дорчина О.В. Устойчивость пен, содержащих дизельное топливо. *Изв. ВУЗов. Серия: Химия и химическая технология.* 2018;61(6):48–53. https://doi.org/10.6060/tcct.20186106.5361
- 6. Манжай В.Н., Фуфаева М.С. Дисперсность и устойчивость пены, полученной из раствора поливинилового спирта, и свойства сформированных пенокриогелей. Коллоидный журнал. 2014;76(4):495–499. https://doi.org/10.7868/S0023291214040090
- 7. Тихомиров В.К. Пены: теория и практика их получения и разрушения. М.: Химия; 1983. 265 с.
- 8. Özarmud Ö., Steeb H. Rheology properties of liquid and particle stabilized foam. *J. Phis.: Conf. Ser.* 2015;602(1):012031. https://doi.org/10.1088/1742-6596/602/1/012031

- 8. Özarmud Ö., Steeb H. Rheology properties of liquid and particle stabilized foam. *J. Phis.: Conf. Ser.* 2015;602(1):012031. https://doi.org/10.1088/1742-6596/602/1/012031
- 9. Bondarenko Zh. V., Adamtsevich N. Yu., Brutskaya I. O. Foaming in aqueous solutions of binary mixtures of anionic and nonionic surfactants. *Trudy BGTU. Ser. 2. Khimicheskie tekhnologii, biotekhnologiya, geoekologiya = Proceedings of BSTU. Ser. 2. Chemical technologies. Biotechnology. Geoecology.* 2017;2(199):127–131 (in Russ.).
- 10. Nagarkar R., Patel J. Polyvinyl Alcohol: A Comprehensive Study. *Acta Scientific Pharmaceutical Sciences*. 2019;3(4):34–44.
- 11. Muppalaneni S., Omidian H. Polyvinyl Alcohol in Medicine and Pharmacy: A Perspective. *J. Develop. Drugs.* 2013;2:112. http://dx.doi.org/10.4172/2329-6631.1000112
- 12. Khlebtsov B.N., Khanadeev V.A., Pylaev T.E., Khlebtsov N.G. Dynamic light scattering in studies of silicate and gold nanoparticles. *Izvestiya Saratovskogo universiteta*. *Novaya seriya. Seriya: Fizika = Izv. Saratov Univ. (N.S.). Ser.: Physics.* 2017;17(2):71–84 (in Russ.). https://doi.org/10.18500/1817-3020-2017-17-2-71-84
- 13. Tager A.A. *Fiziko-khimiya polimerov (Physical chemistry of polymers)*. Moscow: Nauchnyi mir; 2007. 575 p. (in Russ.). ISBN 978-589-176-437-8

- 9. Бондаренко Ж. В., Адамцевич Н. Ю., Бруцкая И. О. Пенообразование в водных растворах бинарных смесей анионного и неионогенного поверхностно-активных веществ. Труды БГТУ. Сер. 2. Химические технологии, биотехнология, геоэкология. 2017;2(199):127–131.
- 10. Nagarkar R., Patel J. Polyvinyl Alcohol: A Comprehensive Study. *Acta Scientific Pharmaceutical Sciences*. 2019;3(4):34–44.
- 11. Muppalaneni S., Omidian H. Polyvinyl Alcohol in Medicine and Pharmacy: A Perspective. *J. Develop. Drugs*. 2013;2:112. http://dx.doi.org/10.4172/2329-6631.1000112
- 12. Хлебцов Б.Н., Ханадеев В.А., Пылаев Т.Е., Хлебцов Н.Г. Метод динамического рассеяния света в исследованиях силикатных и золотых наночастиц. *Изв. Сарат. ун-та. Нов. сер. Сер.: Физика.* 2017;17(2):71–84. https://doi.org/10.18500/1817-3020-2017-17-2-71-84
- 13. Тагер А.А. *Физико-химия полимеров*. М.: Научный мир; 2007. 575 с. ISBN 978-589-176-437-8.

About the authors:

Anastasiya A. Akimova, Senior Lecturer, Department of Management Issues Institute of Cybernetics, MIREA – Russian Technological University (78, Vernadskogo pr., Moscow, 119454, Russia). E-mail: akimova@mirea.ru. https://orcid.org/0000-0001-9882-4005

Viktor A. Lomovskoy, Dr. Sci. (Phys. and Math.), Professor, Department of Chemistry and Technology of Plastics and Polymer Composites Processing, M.V. Lomonosov Institute of Fine Chemical Technologies, MIREA – Russian Technological University (86, Vernadskogo pr., Moscow, 119571, Russia); Head of the Laboratory of Structure Formation in Dispersed Systems, A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences (31, Leninskii pr., Moscow, 119071, Russia). E-mail: lomovskoy49@gmail.com. Scopus Author ID 38361576700, ResearcherID J-5229-2018, https://orcid.org/0000-0002-6116-1209

Igor D. Simonov-Emel'yanov, Dr. Sci. (Eng.), Professor, Head of the Department of Chemistry and Technology of Plastics and Polymer Composites Processing, M.V. Lomonosov Institute of Fine Chemical Technologies, MIREA – Russian Technological University (86, Vernadskogo pr., Moscow, 119571, Russia). E-mail: simonov@mitht.ru. Scopus Author ID 6603181099.

Об авторах:

Акимова Анастасия Александровна, старший преподаватель кафедры проблем управления Института кибернетики ФГБОУ ВО «МИРЭА – Российский технологический университет» (119454, Россия, Москва, пр-т Вернадского, д. 78). E-mail: akimova@mirea.ru. https://orcid.org/0000-0001-9882-4005

Ломовской Виктор Андреевич, д.ф.-м.н., профессор кафедры химии и технологии переработки пластмасс и полимерных композитов Института тонких химических технологий им. М.В. Ломоносова ФГБОУ ВО «МИРЭА – Российский технологический университет» (119571, Россия, Москва, пр-т Вернадского, д. 86); заведующий лабораторией структурообразования в дисперсных системах, Институт физической химии и электрохимии им. А.Н. Фрумкина Российской академии наук (119071, Россия, Москва, Ленинский проспект, 31, корп. 4). E-mail: lomovskoy49@gmail.com. Scopus Author ID 38361576700. ResearcherID J-5229-2018. https://orcid.org/0000-0002-6116-1209

Aqueous polyvinyl alcohol solution foaming at different molecular masses

Симонов-Емельянов Игорь Дмитриевич, д.т.н., профессор, заведующий кафедрой химии и технологии переработки пластмасс и полимерных композитов Института тонких химических технологий им. М.В. Ломоносова ФГБОУ ВО «МИРЭА – Российский технологический университет» (119571, Россия, Москва, пр-т Вернадского, д. 86). E-mail: simonov@mitht.ru. Scopus Author ID 6603181099.

The article was submitted: July 03, 2020; approved after reviewed: September 25, 2020; accepted for publication: August 07, 2021.

Translated from Russian into English by N. Isaeva Edited for English language and spelling by Enago, an editing brand of Crimson Interactive Inc.