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RESEARCH ARTICLE

Physicochemical fundamentals of processing solutions of thermoplastic poly(ether urethane)s to obtain fibrous-porous polymer composite materials

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Abstract

Objectives. *To study the structure and properties of solutions of thermoplastic poly(ether urethane)s (PEUs) to inform their potential use in the production of fibrous-porous polymer composite materials with a given structure and set of performance properties depending on the field of practical application.*
Methods. *The composition of PEUs was studied by attenuated total reflection infrared (ATR-IR) spectroscopy using a program for correcting the spectra on an IR Fourier spectrophotometer, as well by differential scanning calorimetry (DSC) using a heat flow calorimeter. The viscosity of PEU solutions was determined on a rotational viscometer.*
Results. *The chemical composition of PEUs and the nature of the formation of hydrogen bonds were studied. An analysis of the spectra demonstrates the almost complete identity of the PEUs synthesized from the same 4,4'-diphenylmethane diisocyanate. In the studied PEUs of the Vitur and Desmopan® brands, as well as Sanpren, pronounced absorption bands characteristic of urethane groups involved in the formation of hydrogen bonds are visible in the region from 1702 to 1730 cm^{-1}. The temperature transitions and thermal stability of the investigated PEUs were determined by DSC. The influence of the ratio of rigid and flexible blocks, as well as the nature of hydrogen bonds on the melting temperatures of polymers, was shown. Analysis of the DSC curves demonstrated all the studied PEUs to have high melting points ranging from 159 to 215°C.*

From the studied temperature dependences of the structural viscosity of thermoplastic PEUs solutions, all solutions were established to have a minimum viscosity anomaly; the value of the logarithm of viscosity depends on the chemical composition and structure of the initial PEUs. It is shown that the viscosity anomaly of PEU solutions can be reduced with increasing temperature.
Conclusions. *A comparison of the chemical composition, structure, thermal and rheological characteristics of thermoplastic PEUs with PEU solutions widely used for the production of fibrous-porous materials and coatings of Sanpren LQ-E-6 and Vitur R 0112 grades demonstrates their practicability as production materials and coatings having a predetermined structure and a set of properties depending on the requirements and operating conditions of finished products.*

Keywords: *poly(ether urethane), polymer solutions, nonwoven substrates, electroforming, phase separation, polymer films*

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НАУЧНАЯ СТАТЬЯ

Физико-химические основы переработки растворов термопластичных полиэфируретанов для прогнозирования возможности их применения в производстве волокнисто-пористых композиционных материалов

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Аннотация

Цели. *Изучить структуру и свойства растворов термопластичных полиэфируретанов (ПЭУ) для прогнозирования возможности их применения в производстве волокнисто-пористых полимерных композиционных материалов и покрытий с заданной структурой и комплексом эксплуатационных свойств, зависящими от области практического применения.*
Методы. *Состав ПЭУ изучали методом инфракрасной (ИК) спектроскопии с преобразованием Фурье в сочетании с методом многократного нарушенного полного внутреннего отражения и методом дифференциально-сканирующей калориметрии (ДСК) с использованием калориметра теплового потока. Вязкость растворов ПЭУ определяли на ротационном вискозиметре.*
Результаты. *Изучен химический состав ПЭУ и характер образования водородных связей. Анализ ИК спектров демонстрирует практически полную идентичность ПЭУ, синтезированных на основе одного и того же 4.4'-дифенилметандиизоцианата. В исследуемых ПЭУ марок Витур и Desmopan®, а также Санпрен, можно увидеть, что в области от 1702 до 1730 см$^{-1}$ присутствуют явно выраженные полосы*

поглощения, характерные для уретановых группировок, задействованных в образовании водородных связей. Методом ДСК определены температурные переходы и термостойкость исследуемых ПЭУ. Показано влияние соотношения жестких и гибких блоков, а также характер водородных связей на температуры плавления полимеров. При анализе кривых ДСК, показано, что все исследуемые ПЭУ обладают высокими температурами плавления, находящимися в диапазоне от 159 до 215 °С. Также исследованы температурные зависимости структурной вязкости растворов термопластичных ПЭУ. Установлено, что все растворы имеют минимальную аномалию вязкости, при этом величина логарифма вязкости зависит от химического состава и структуры исходных ПЭУ. Установлено, что аномалия вязкости растворов ПЭУ может быть снижена при повышении температуры.

Выводы. *Исследование химического состава, структуры, термических и реологических характеристик термопластичных ПЭУ с позиции их сравнения и сопоставления с широко применяемыми для производства волокнисто-пористых материалов и покрытий растворов ПЭУ марок Санпрен LQ-E-6 и Витур Р 0112 позволяет прогнозировать возможность их использования для производства материалов и покрытий с заранее заданной структурой и комплексом свойств в зависимости от требований и условий эксплуатации готовых изделий.*

Ключевые слова: *термопластичные полиэфируретаны, растворы полимеров, полимерные пленки, реологические свойства*

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INTRODUCTION

According to classical concepts, poly(ether urethane) (PEU) products, including flexible polymeric materials and coatings based on them, can be obtained from solutions either by fixing the shape by removing the solvent during the drying process or by phase separation in a non-solvent medium. At the same time, the structure of the material and its properties are largely determined by the chemical composition of the initial PEUs, as well as the nature of the structure formation of the solution, depending on the type of solvent used, its thermodynamic compatibility with the polymer, etc. This constitutes the theoretical basis for obtaining fibrous-porous polymer composite materials having a predictable structure and a set of operational properties.

Approaches have been developed for the targeted modification of PEU solutions in order to create synthetic leather with improved performance properties[1,2] [1]. Results of a study into the production of nanofibrous medical materials by electrospinning from PEU solutions were presented in [2, 3]. Fibrous-porous composites based on polyurethanes have been obtained for the creation of cell scaffold-type matrices [4]. The structure, as

[1] Bokova E.S. *Physicochemical bases and technology of modification of polymer solutions in the production of fibrous-porous materials*. Dr. Sci. Thesis (Eng.). Moscow: MGUDT. 2007. 467 p. https://new-disser.ru/_avtoreferats/01003409553.pdf

[2] Grondkovski M. *Modifikatsiya poliuretanovykh sistem gidrolizatami kollagena dlya sozdaniya iskusstvennykh kozh s uluchshennymi gigienicheskimi svoistvami* (*Modification of polyurethane systems with collagen hydrolysates to create artificial leathers with improved hygienic properties*). Cand. Sci. Thesis (Eng.). Moscow: MTILP; 1990. 244 p. (in Russ.).

well as physicomechanical, optical and a number of other indicators of the performance properties of thermoplastic PEUs have been studied in order to create innovative materials by extrusion and 3D printing [3, 5–7]. The creation of protective coatings based on PEUs with a controlled hydrophilic-hydrophobic balance is thesubject of research in [8–10]. In this research, known approaches to the processing of PEU solutions and their directed modification are used in relation to thermoplastic PEUs of Russian and foreign production.

EXPERIMENTAL

The following PEU brands were used as objects of study in the work:

– Vitur TM-1413-85 (*NPF Vitur*, Vladimir, Russia)—product of the interaction of 4,4′-diphenylmethane diisocyanate and polyethylene butylene glycol adipate at a ratio of NCO:OH equal to 1:1 obtained by one-stage synthesis; weight average molecular weight (WAMW) is 40000;

– Vitur TM-0533-90 (*NPF Vitur*)—product of the interaction of 4,4′-diphenylmethane diisocyanate and polyoxytetramethylene glycol, at a ratio of NCO:OH groups equal to 1:1, obtained by a one-stage synthesis; WAMW is 40000;

– TPU-2 (*NPF Vitur*)—product obtained in a one-stage method based on polyethylene glycol adipate, diphenylmethane diisocyanate and 1,4-butanediol at a ratio of NCO:OH equal to 1:1; WAMW is 4800;

– Vitur TM-0333-95 (*NPF Vitur*)—product of the interaction of 4,4'-diphenylmethane diisocyanate and polyoxytetramethylene glycol, at a ratio of NCO:OH groups equal to 1:1, obtained by a one-stage synthesis; WAMW is 4400;

– Desmopan® 385 S (*Covestro AG*, Leverkusen, Germany)—product of the interaction of 4,4'-diphenylmethane diisocyanate and polyethylene butylene glycol adipate, obtained by a one-stage synthesis at a ratio of NCO:OH equal to 1:1; WAMW is 5700;

– Desmopan® 9873 (*Covestro AG*, Leverkusen, Germany)—product obtained by a one-stage synthesis based on 4,4'-diphenylmethane diisocyanate and polyoxytetramethylene glycol, at a ratio of NCO:OH groups equal to 1:1; WAMW is 4500.

For the purposes of comparison, we used Sanpren LQ-E-6 PEU (*Sanyo Chemical*, Japan), synthesized in the form of a 30% solution in dimethylformamide and traditionally used to obtain highly porous materials and coatings. PEU was obtained by a two-stage synthesis based on polyethylene glycol adipate and diphenylmethane diisocyanate at a ratio of NCO:OH equal to 4:1; WAMW is 25000.

Based on the recipe features of the synthesis of polyurethanes, the composition and properties of finished products primarily depend on the nature and type of polyesters, diisocyanates and chain extenders used. According to the data given in [11], in the synthesis of polyurethanes, possible variations for obtaining products with different ratios of flexible and rigid blocks (index NCO/OH) include regulating the length of the rigid segment, as well as changing the flexibility of the linear part macromolecules through the use of highly flexible polyethers or polyesters with medium or low flexibility.

In the present work, the PEU composition was studied using the Fourier-transform infrared spectroscopy (FTIR) method in combination with the multiple frustrated total internal reflection on an IFS-113V IR-Fourier spectrophotometer (*Bruker*, Germany), as well as by differential scanning calorimetry (DSC) using a TA 3000 heat flux calorimeter (*Metler*, Switzerland). The viscosity of PEU solutions was determined on a rotational viscometer RN4.1 SE (*Rheotest*, Germany).

RESULTS AND DISCUSSION

The spectral analysis (Fig. 1), which demonstrates the almost complete identity of the PEUs synthesized from the same 4,4'-diphenylmethane diisocyanate, can be used to identify the main absorption bands characteristic of the functional groups that make up the PEUs. Thus, the interval 3328–3331 cm^{-1} corresponds to stretching vibrations of NH groups, while the absorption band in the range 1800–1728 cm^{-1} is characteristic of stretching vibrations of the C=O group. The absorption interval characteristic of the stretching vibrations of the ether group lies in the range from 1300 to 1500 cm^{-1}. The presence of an absorption band in the region of 2800–3200 cm^{-1} is characteristic of stretching vibrations of C–H bonds, while a narrow absorption range of 1450–1460 cm^{-1} is responsible for the phenyl radical in 4,4'-diphenylmethane diisocyanate.

According to [12], the absorption band in the region of 1740 cm^{-1} is characteristic of the urethane group, which is free from the formation of hydrogen bonds (both in the NH and CO groups), while the absorption bands in the range from 1702 to 1730 cm^{-1} correlate with the vibrations of urethane groups included in hydrogen bonds differing in energy. In the studied PEUs of the Vitur and Desmopan® brands, as well as Sanpren, clearly pronounced absorption bands characteristic of urethane groups involved in the formation of hydrogen bonds are clearly visible in the region

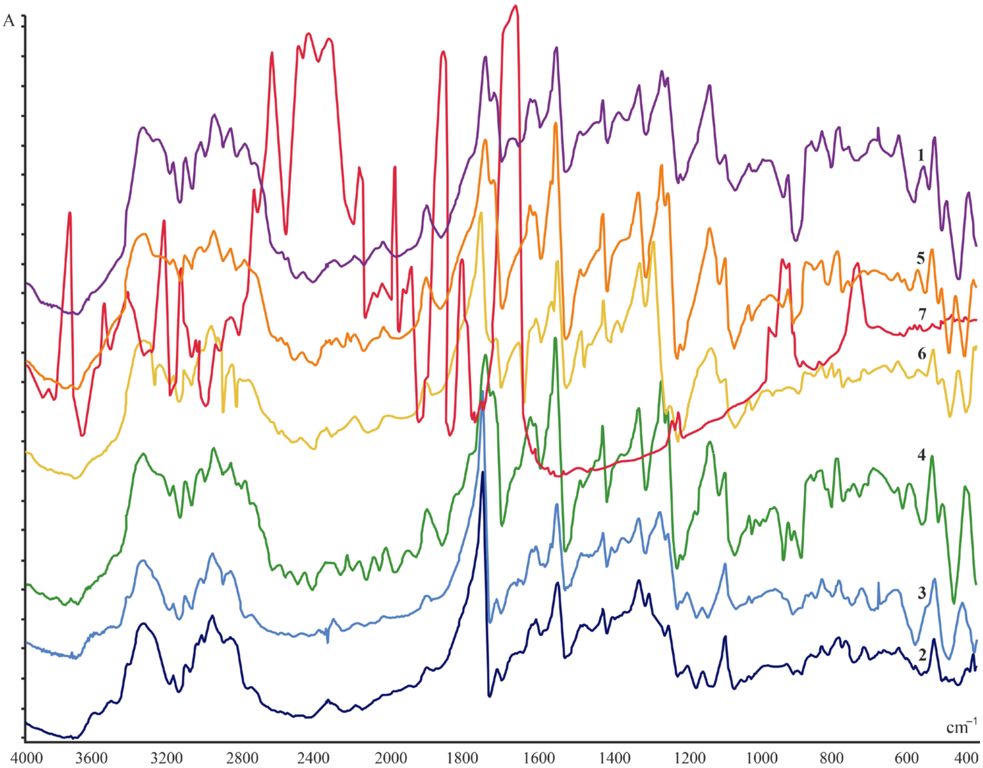

Fig. 1. Infrared spectra of films based on solutions of polyesterurethane brands:
(1) Vitur TM-0333-95; (2) Vitur TM-1413-85; (3) Desmopan® 385 S; (4) Desmopan® 9873; (5) TPU-2;
(6) Vitur TM-0533-90; (7) Sanpren LQ-E-6.

from 1702 to 1730 cm^{-1} as consistent with the data of [11], in which the object of study was a PEU based on 4,4'-diphenylmethane diisocyanate.

The presence of hydrogen bonds in PEUs predetermines the energy density of cohesion, i.e., the strength of intermolecular interaction, which in turn affects the melting point of PEUs. Thus, it was demonstrated in [11] that the intramolecular approach of the NH group, which is a proton donor, and the CO group, which is an acceptor, occurs more easily if the number of carbon atoms in two neighboring diisocyanate residues is even. On this basis, if n and m are odd, the convergence of the NH and CO groups is insufficient, the PEU has an irregular structure, the intermolecular interaction will be weaker, and, consequently, the melting point will be lower.

In the studied PEUs, the diisocyanate has an even number of carbon atoms, which creates more favorable conditions for the formation of hydrogen bonds and should lead to an increase in the melting point.

Figure 2 shows the temperature transitions of the studied PEUs, determined by the DSC method.

From the analysis of DSC curves, all PEUs under study can be seen to have high melting points ranging from 159 to 215°C. At the same time, as obtained on the basis of simple oligoesters, there is a single *endo* peak characterizing the melting of the crystalline part polymer on the thermograms of PEU brands Desmopan® 9873, Vitur TM-0333-95, Vitur TM-0533-90 (Fig. 3, curves 1, 4, 6).

In PEUs obtained on the basis of polyesters of the Desmopan® 385 S, TPU-2, Vitur TM-1413-85, and Sanpren LQ-E-6 brands, crystallization is poorer due to the greater rigidity of macromolecules and greater intermolecular interaction; here, since crystallites with different degrees of defectiveness are formed, whose melting occurs in a different temperature range, two endo peaks are present on the DSC curves melting (Fig. 2, curves 2, 3, 5, 7).

Such PEU behavior corresponds to the data [13], where, by studying the temperature transitions in PEUs of the Perlon U brand, the authors demonstrated that less perfect (more defective) crystalline formations melt at a lower temperature than less defective ones. Additionally, the presence of two melting ranges in PEUs based on polyesters can be explained by more favorable conditions for the formation of hydrogen bonds, which results in the initial destruction of the associates stabilized by H-bonds followed by the melting of the crystalline part of the polymer.

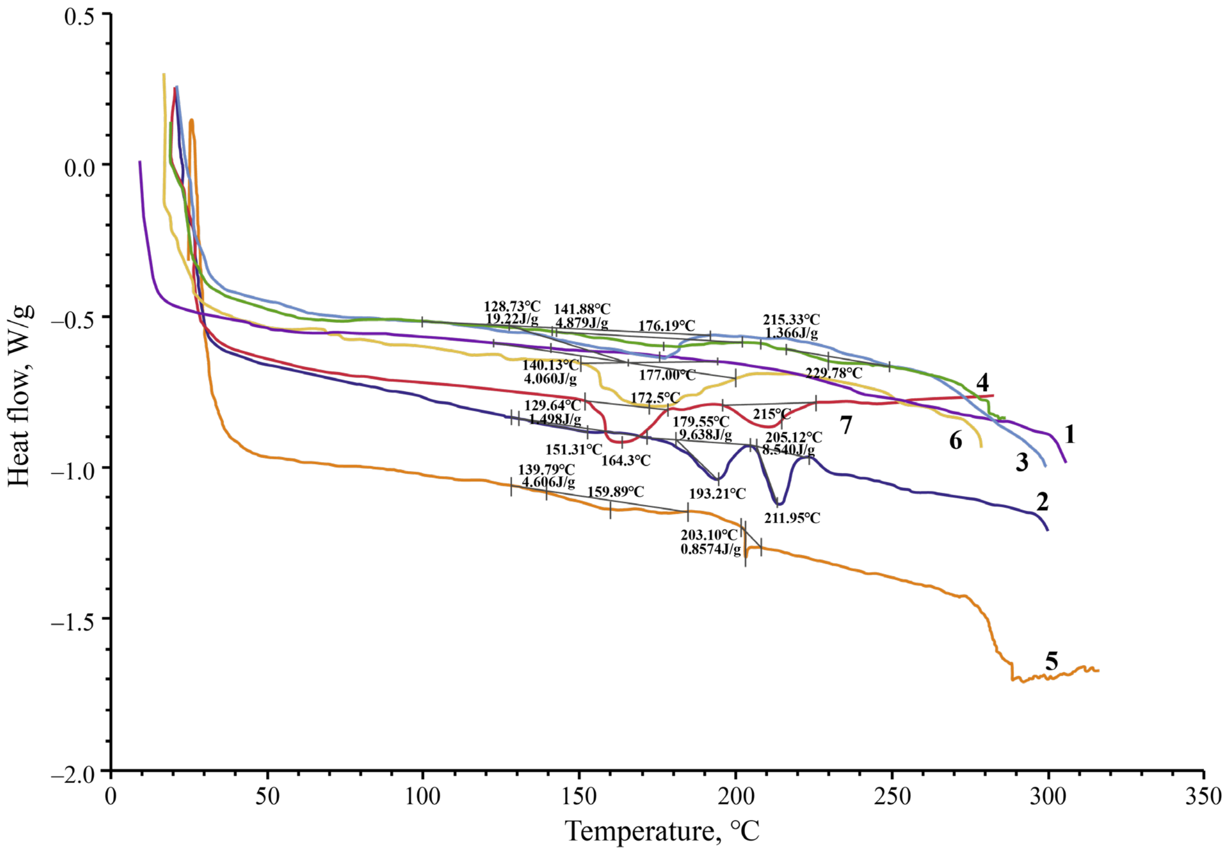

Fig. 2. Differential scanning calorimetry curves of films made of polyesterurethane: (1) Desmopan® 9873; (2) Desmopan® 385 S; (3) TPU-2; (4) Vitur TM-0333-95; (5) Vitur TM-1413-85; (6) Vitur TM-0533-90; (7) Sanpren LQ-E-6.

Based on the classical concepts of the chemical composition of PEUs, as well as numerous experimental studies of the reactions occurring during its synthesis[3], linear and spatially cross-linked PEUs include urethane, urea, ether, and ester groups [11], which affect the processes of its processing (dissolution, melting), as well as the structure of the properties of finished products.

PEUs synthesized in the form of concentrated polymer solutions in dimethylformamide (DMF) are traditionally used for the production of fibrous-porous polymer composite materials and coatings. Thermoplastic PEUs used in the present work to solve similar problems related to the possibility of fiber and film formation were converted into a fluid state by dissolving in DMF.

One of the indicators that depends on the chemical composition of the polymer, characterizes its thermodynamic affinity for the solvent, predetermines the processes of structure formation in solutions and the technological features of their processing into finished products, is structural viscosity.

In this work, the structural viscosity of PEU solutions was determined on a rotational viscometer. The concentration of the studied solutions (*C*, %) was 15%; the temperatures (*T*, °C) of the experiment were 20 ± 2°C and 50 ± 2°C (Figs. 3 and 4).

From the analysis of the viscosity curves in the range of shear rates under study, most solutions exhibit the behavior of Newtonian fluids without the effect of the viscosity anomaly characteristic of structured polymer systems. At the same time, for PEU grades TPU-2 and Desmopan® 9873 (Fig. 3, curves 4, 5), more hydrogen bonds break at higher shear in the shear rate range from 2 to 3 s^{-1}.

The viscosity values of PEU grades Vitur TM-0533-90, TPU-2, and Sanpren LQ-E-6 (Fig. 3, curves 1, 3, 4) lie in the region of higher values than those of other grades of PEUs. According to the literature data [13], the flexibility of the chain of PEU macromolecules is determined by the properties of the oligoester block. Based on the data on internal rotation in organic molecules [13], it can be argued that internal rotation around the C–O bond is facilitated compared to the C–C bond.

[3] Grondkovski M. *Modifikatsiya poliuretanovykh sistem gidrolizatami kollagena dlya sozdaniya iskusstvennykh kozh s uluchshennymi gigienicheskimi svoistvami* (*Modification of polyurethane systems with collagen hydrolysates to create artificial leathers with improved hygienic properties*). Cand. Sci. Thesis (Eng.). Moscow: MTILP; 1990. 244 p. (in Russ.).

Thus, it can be assumed that PEUs having heterobonds in the form of an ether group in macromolecules will have greater chain flexibility. Therefore, in PEU solutions based on oligoesters (Desmopan® 9873, Vitur TM-0333-95, Vitur TM-0533-90), the hydrodynamic radius of macromolecular coils will be smaller, and, consequently, the structural viscosity will be lower, as confirmed by the data in Figs. 3 and 4.

However, PEU brand Vitur TM-0533-90, synthesized on the basis of a simple oligoester, has viscosity values almost an order of magnitude higher than those of other brands of PEUs, which also contain blocks based on polyethers (Vitur TM-0333-95, Desmopan® 9873).

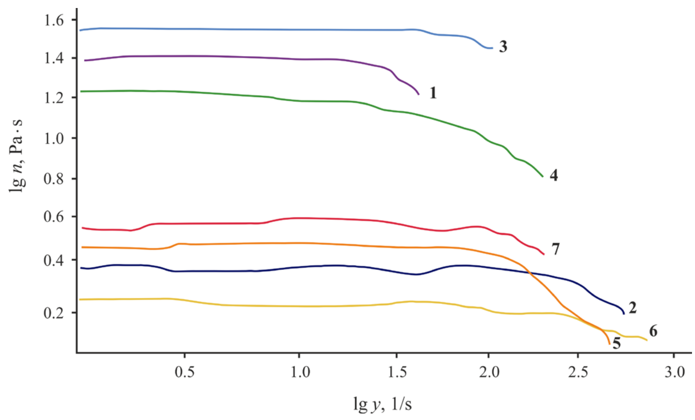

Fig. 3. Viscosity of shear rate dependence for polyesterurethane solutions of the brand: (1) Vitur TM-0533-90; (2) Vitur TM-1413-85; (3) Sanpren LQ-E-6; (4) TPU-2; (5) Desmopan® 9873; (6) Desmopan® 385 S; (7) Vitur TM-0333-95. $C_{solution} = 15\%$; $T = 20 \pm 2°C$.

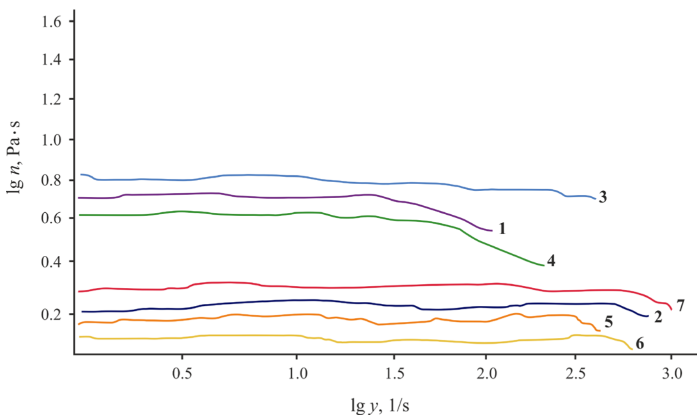

Fig. 4. Viscosity of shear rate dependence for polyesterurethane solutions of the brand: (1) Vitur TM-0533-90; (2) Vitur TM-1413-85; (3) Sanpren LQ-E-6; (4) TPU-2; (5) Desmopan® 9873; (6) Desmopan® 385 S; (7) Vitur TM-0333-95. $C_{solution} = 15\%$; $T = 50 \pm 2°C$.

Apparently, this is due to the WAMW of Vitur TM-0533-90 (40000), while the WAMW of Vitur TM-0333-95 and Desmopan® 9873 is equal to 4400 and 4500, respectively. Despite the fact that NCO/OH index is 1:1 for all studied grades of PEUs, the higher molecular weight of Vitur TM-0333-90 leads to an increase in viscosity due to the presence of closely spaced polar groups in the polymer chain as compared to low molecular weight grades of PEU Vitur TM-0333-95 and Desmopan® 9873.

Viscosity values for PEU grades Vitur TM-1413-85 and Desmopan® 385 S, synthesized on the basis of oligoesters, are almost an order of magnitude lower than those for PEU grades TPU-2 and Sanpren LQ-E-6, which are also obtained on the basis of adipic acid polyesters. According to [11], polyurethanes with more methyl groups in the oligoester block comprise a more flexible chain, since strongly interacting polar groups will be separated by methyl units, whose rotation is not hindered. Therefore, PEU grades Vitur TM-1413-85 and Desmopan® 385 S, which are synthesized from polyethylene butylene glycol adipate oligoester, have a greater chain flexibility than PEU grades TPU-2 and Sanpren LQ-E-6, which have a more rigid-chain polyethylene glycol adipate. As a result, PEU solutions of the Vitur TM-1413-85 and Desmopan® 385 S brands have a lower viscosity, even though the molecular weight, for example, of TPU-2 PEU is significantly lower than that of Vitur TM-1413-85.

The structural viscosity values can be expected to be inversely related to the temperature of the PEU solution: an increase in temperature leads to a twofold decrease in viscosity, as well as eliminating the effect of its anomaly.

CONCLUSIONS

In this research, Russian and foreign various brands of thermoplastic PEUs in the form of solutions in DMF are studied to investigate the possibility of their use in the production of fibrous-porous composite materials and coatings.

The chemical composition of PEUs and the nature of the formation of hydrogen bonds were studied using FTIR with multiple frustrated total internal reflection. The temperature transitions and thermal stability of the PEUs under study were determined by DSC. The influence of the ratio of rigid and flexible blocks on the melting temperatures of polymers, as well that due to the nature of hydrogen bonds, is demonstrated.

The rheological characteristics of thermoplastic PEU solutions have been studied. It has been established that all solutions have a minimum anomaly in viscosity, while the value of the logarithm of viscosity depends on the chemical composition and structure of the initial PEUs.

The possibility of using thermoplastic PEUs in the production of materials and coatings with a predetermined structure and a set of properties depending on the requirements and operating conditions of finished products has been confirmed by comparing their chemical composition, structure, thermal and rheological characteristics with PEU solutions of Sanpren LQ-E-6 and Vitur R 0112 grades widely used in the production of fibrous-porous materials and coatings.

Authors' contributions

G.M. Kovalenko – setting goals and objectives of the study, conducting experimental research, analyzing the results of the study, and writing the text of the article;

E.S. Bokova – literature analysis, summarizing the results of the study, writing conclusions on the study;

N.V. Evsyukova – literature analysis, experimental data processing, writing the abstract of the study.

The authors declare no conflicts of interest.

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