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SYNTHESIS AND PROCESSING OF POLYMERS AND POLYMERIC COMPOSITES

СИНТЕЗ И ПЕРЕРАБОТКА ПОЛИМЕРОВ И КОМПОЗИТОВ НА ИХ ОСНОВЕ

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RESEARCH ARTICLE

Development of a polyurea-based composition with an extended life span

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Abstract

Objectives. *Improvement of the technology for obtaining polymer-sprayed coatings based on polycarbodiimides (polyureas) with high chemical, hydrolytic, and abrasive resistance and improved physical and mechanical properties, as well as obtainment of polyurea compositions with a lifetime of at least 5 min without loss performance characteristics (i.e., "hand-applied" polyureas) suitable for repair of coatings already in use.*

Methods. *The reaction rate between isocyanate and amino groups is almost a hundred times higher than that between isocyanate and hydroxyl groups, necessitating the use of special high-performance and high-pressure installations equipped with self-cleaning mixing chambers and heating of components. The following are determined from the obtained materials: strength, elongation at break according to the standard method, Taber abrasion, and Shore hardness.*

Results. *Three methods of slowing down the reaction are investigated: 1) the synthesis of prepolymers with the content of NCO groups from 10.5% to 18%; 2) the addition of a plasticizer into the prepolymer in the amount of 1–10 mass parts; and 3) the introduction of polyesters into the composition and radiation of the so-called "hybrid" systems. When using 14% polyesters with a molecular weight of 2000 Da, only "hybrid" systems make it possible to obtain compositions with a lifetime of more than 5 min. At the same time, the tensile strength decreases by 20%, and the abrasion increases by 40%; however, such "hybrid" systems have a higher adhesion force and are cheaper than pure polyureas, allowing them to be used as "repair" systems.*

Conclusions. *The developed composition and technology of applying "hybrid" systems allow for the repair of existing coatings without using specialized devices. "Manual" polyurea is easy to use and does not require special training.*

Keywords: *polyurea, lifetime, polymer coatings, physical and mechanical properties*

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НАУЧНАЯ СТАТЬЯ

Разработка композиции на основе полимочевины с увеличенным сроком жизни

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Аннотация

Цели. *Совершенствование технологии получения полимерных напыляемых покрытий на основе поликарбодиимидов (полимочевин), с высокой химической, гидролитической и абразивной стойкостью и улучшенными физико-механическими показателями, а также, получение полимочевинных композиций с временем жизни не менее 5 мин без потери эксплуатационных характеристик (полимочевин «ручного» нанесения), пригодных для ремонта уже эксплуатирующихся покрытий.*
Методы. *Скорость реакции между изоцианатными и аминогруппами практически в сто раз превышает скорость реакции между изоцианатными и гидроксильными группами, что вызывает необходимость использовать специальные высокопроизводительные установки высокого давления, оснащенные самоочищающимися смесительными камерами и обогревом компонентов. У полученных материалов определяли прочность, удлинение на разрыв по стандартной методике, истираемость по Таберу и твердость по Шору.*
Результаты. *Исследованы три способа замедления реакции: во-первых, синтез предполимеров с содержанием NCO-групп от 10.5% до 18%; во-вторых, введение в предполимер пластификатора в количестве 1–10 масс.ч.; в-третьих, введение в композицию полиэфиров и получения «гибридных» систем. Показано, что только «гибридные» системы при использовании полиэфиров с молекулярной массой 2000 Да, в количестве 14% позволяют получить композиции с временем жизни более 5 мин. При этом прочность на разрыв снижается на 20%, истираемость увеличивается на 40%, но такие «гибридные» системы имеют более высокую силу адгезии и дешевле по сравнению с чистыми полимочевинами, что позволяет использовать их в качестве «ремонтных» систем.*
Выводы. *Разработанный состав и технология нанесения «гибридных» систем позволяют производить ремонтные работы существующих покрытий без применения специализированных устройств. Полимочевина «ручного» нанесения удобна в эксплуатации и не требует специальной подготовки.*

Ключевые слова: *полимочевина, время жизни, полимерные покрытия, физико-механические свойства*

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INTRODUCTION

The technology of obtaining polymer-sprayed coatings based on polycarbodiimides (polyureas) has been developing at an outstripping pace in the recent years. This is associated with the high chemical, hydrolytic, and abrasive resistance of these coatings and their excellent physical and mechanical properties[1,2].

A wide range of properties, which can be obtained due to a change in the structure of the polyurea composition, makes it suitable for use in many areas: in construction [1, 2], in the field of protection of mining and processing equipment [3, 4]. Unlike polyurethane and rubber, which are also actively used in the mining and processing, polyurea can be applied as a lining composition not only in the factory; there are no restrictions on the geometry of the protected surface.

This study aimed to develop repair compounds that can be manually applied to any of the most difficult surfaces. Moreover, the properties of such compositions should be comparable to those of the original polyurea coating. This goal was achieved by using hybrid polyurethane–polyurea coatings. When developing this system, the authors proceeded from the theoretical premises described in the study of S.V. Romanov (see Footnote 1).

Polyureas are an ideal material for covering large surfaces with high strength and low abrasion, which can only be applied to the surface using high-pressure (more than 100 atm) installations. After the warranty period, cracks and chips appear on the coating, which must be eliminated. For such cases, a hand-applied composition is used, which is mainly in contact with the original polyurea. The adhesion to which is a priori very high.

To obtain polyurea in the coating technology, only high-pressure installations equipped with a self-cleaning mixing chamber and heating of components are used because of the very short lifetime of the composition [5, 6]. This factor determines another indisputable advantage of polyureas, which consists in their almost complete insensitivity to the surrounding moisture.

Figure 1 schematically shows the reaction of the polyurea formation.

The disubstituted urea reacts with the isocyanate group to form biuret (Fig. 2).

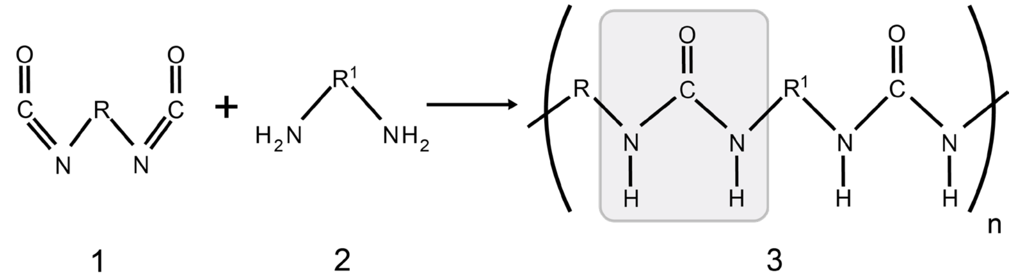

Fig. 1. Process of the polyurea formation: (1) diisocyanate, (2) polyester amine, and (3) polyurea.

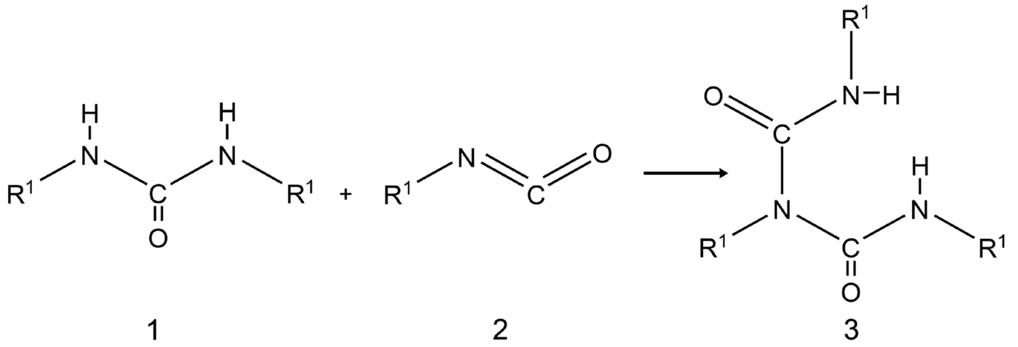

Fig. 2. Biuret production process: (1) disubstituted urea, (2) isocyanate, and (3) biuret.

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[1] Romanov S.V. Sprayablepolyureas with extended service life in extreme conditions: Cand. Sci. Thesis. Kazan: KNR TU; 2019. 127 p. (in Russ.).

[2] Timakova K.A. Development of the composition and production technology of one-pack non-foaming polyurethane sealant based on domestic polyesters: Cand. Sci. Thesis. Vladimir: VGU; 2018. 136 p. (in Russ.).

The isocyanate component is called component B. It is a prepolymer containing isocyanate groups at the ends of the macromolecule, allowing the classification of polyurea as a class of polyurethane coatings [5, 6].

The market share of polyurea products is growing annually. Along with this, the number of problems associated with this product is also increasing. One of the urgent tasks is to solve the need for the local repair of polyurea coatings. It is not economically feasible to use polyurea with a short lifetime for every repair because it is a substance that cannot be applied without the help of special equipment. Therefore, studies are underway to slow down the reaction of obtaining polyurea [7].

MATERIALS AND METHODS

The following materials were used to obtain a polyurea coating: mixture used as the amine component (component A) was Jeffamine D-2000 (a mixture of polyoxypropylene amines with ~2000 Da molecular weight); Jeffamine T-5000 (a mixture of polyoxypropylene amines with ~5000 Da molecular weight) (*Houfa*, China), Deadta 80 (*Dow Chemical Company*, Midland, Michigan, USA), and Polilink 4200 (*ACETO GmbH*, Germany) were used as crosslinking agents, as well as the adhesion promoter was Silquest A187 (*Momentive*, Russia).

Isocyanate component (component B): a prepolymer synthesized from propylene glycol and polyisocyanate was used (Millionate MR200 (*Khimtrast*, Russia)) with a mass fraction of NCO groups of 10.5–18% [7–10]. We also used a plasticizer (i.e., dioctyl phthalate) from *Vitakhim* (Russia) and a modifier (i.e., polyester) Coradol 56-200 with 2000 Da molecular weight from *Himseil* (Russia).

The prepolymer preparation technique was similar to that described in the above study of Romanov.

The sample's tensile strength and elongation were determined using standard methods on a GP2DLC-0.5 universal tensile testing machine (*Tochpribor*, Russia). The tensile strength and the elongation at break were determined according to GOST 21751-76[3] on blades of Type 1 with a 3.0 ± 0.2 mm thickness at 100 mm/min clamping speed of the tensile testing machine.

Taber abrasion was determined on a Taber rotary platform abrasion tester model 5135/5155 (*TABER® Industries*, USA), disk H18, 1000 cycles. Meanwhile, hardness was determined according to GOST 263-75[4] on a device for measuring the material hardness according to Shore A on 6 mm-thick samples on a TVR-D installation (*Metrotest*, Russia).

RESULTS AND DISCUSSION

Polyurea has become an excellent solution for waterproofing large areas. The lifetime of this two-component system in its classical design does not exceed 10–15 s [11–13].

Several advantages and disadvantages are associated with such a short lifetime. First is the need for expensive and difficult-to-maintain equipment, which largely hinders the use of polyurea systems.

Polyurea systems are currently classified as follows according to their lifetime:

– "classic" polyurea: lifetime of up to 20 s;
– "slow" polyurea: lifetime from 3 to 4 min; and
– "manual" polyurea: lifetime of more than 5 min.

The lifetime is taken to be the gelation time, that is, the time after which the composition stops flowing from the glass rod.

The application of the "classic" and "slow" polyureas is impossible without pressure washers; hence, they cannot be used for most local repairs. "Manual" polyureas do not require special equipment. The composition lifetime allows them to be applied through manual stirring.

Unlike "classical" polyureas, "manual" systems have not been sufficiently studied.

In studies on the retardation of polyurea compositions, prepolymers have been synthesized with the content of NCO groups from 10.5% to 18%.

The reaction rate decreases with the decrease in the content of the NCO groups in the system, albeit this decrease being very small, as shown by the table below.

A decrease in the content of the NCO groups in component B leads to a decrease in the coating hardness, which is unacceptable. To avoid this, further studies are advised to rely on a formulation with an NCO-group content of at least 12.5%.

The first step in solving this problem is to use the strategy of introducing a small amount of plasticizer into component A of the system.

Figures 3 and 4 illustrate graphs of the lifetime dependence and performance characteristics of polyureas on the plasticizer percentage in the system.

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[3] GOST 21751-76 Sealants. Determination method of tensile strength, ultimate elongation at break and deformation set after break. Moscow: Izd. Standartov; 1983.

[4] GOST 263-75. Rubber. Method for determination of Shore A hardness. Moscow: Izd. Standartov; 1983.

Performance characteristics of coatings with different contents of the NCO-groups in component B

Content of NCO groups in component B, %	System lifetime, s	Shore hardness, units
10.5	14	60A
12.5	11	75A
14.0	9	80A
15.5	7	92A
18.0	5	70D

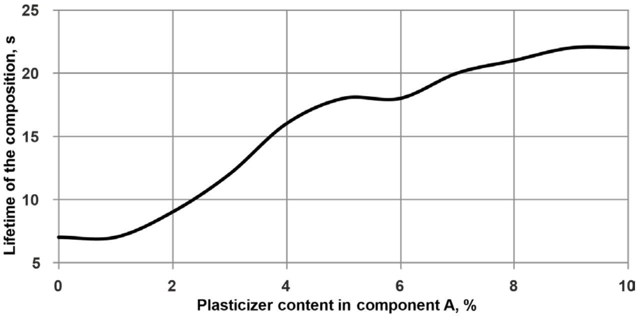
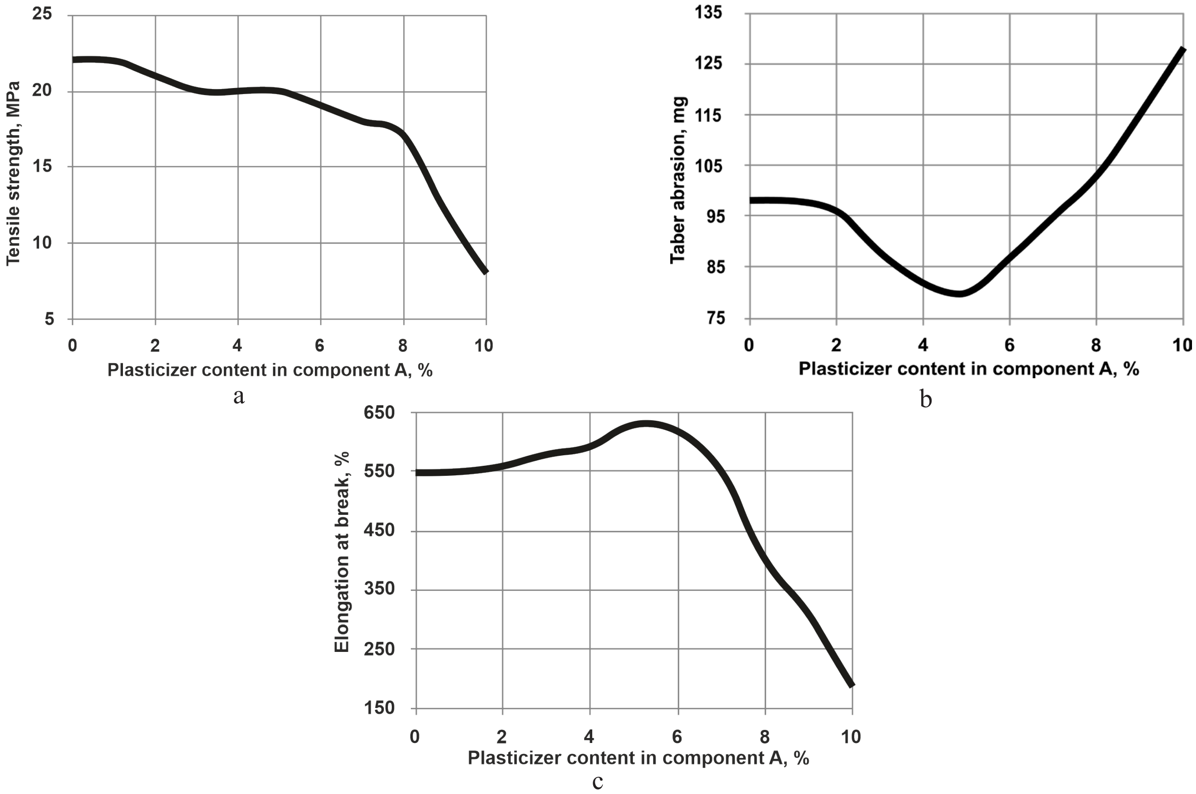


Fig. 3. Dependence of the composition lifetime on the plasticizer percentage in component A of the system.

The graphs show that the maximum possible amount of plasticizer that can be introduced into component A of the system does not exceed 5%. With the addition of a larger amount of plasticizer, the system lifetime significantly increases, but the physicomechanical parameters dramatically decrease. When 5% is added, these indicators practically do not deteriorate. Such indicators as abrasion and elongation at break even slightly increase.

However, the system lifetime can be increased only slightly. This indicator has a positive effect on the spreading of the polyurea system and, consequently, on the adhesion of the composition



a

b

c

Fig. 4. Dependence of the tensile strength of the composition (a), abrasion (b), and elongation at break (c) on the plasticizer percentage in component A of the system.

to the substrate. The resulting time is not allow working with this system without the help of additional equipment.

In our opinion, the main solution for slowing down the polyurea formation is to transfer the system to the "hybrid" system category, in which, along with polyester amines, polyesters (i.e., Coradol 56-200) are introduced into component A. As a consequence, both polyurea and polyurethane groups are formed during the reaction.

Hybrid systems have a number of advantages. The lifetime of such systems is somewhat longer; thus, they spread better, have high adhesion, and take the complex geometry of the protected surface well. They are somewhat cheaper compared to pure polyureas and are not inferior in terms of performance characteristics. However, due to their chemical composition, their sensitivity to moisture significantly increases, making it impossible to work with them in humid climates or bad weather conditions.

Polyesters with high-molecular weights were selected for this research, and we expected that additional spatial hindrances would give an additional increase in the system lifetime.

Figures 5 and 6 present graphs of the system lifetime and the main physical and mechanical parameters depending on the polyester percentage (molecular weight: 2000 Da) in component A of the system.

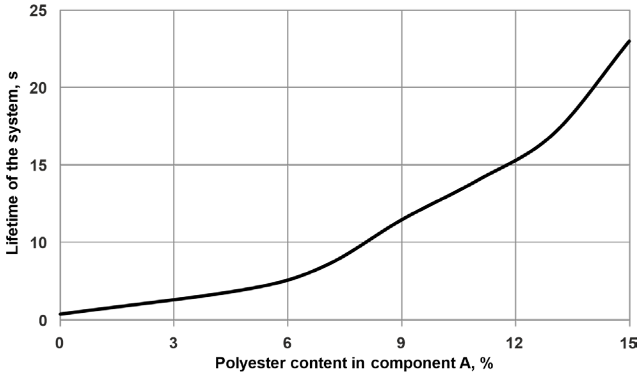
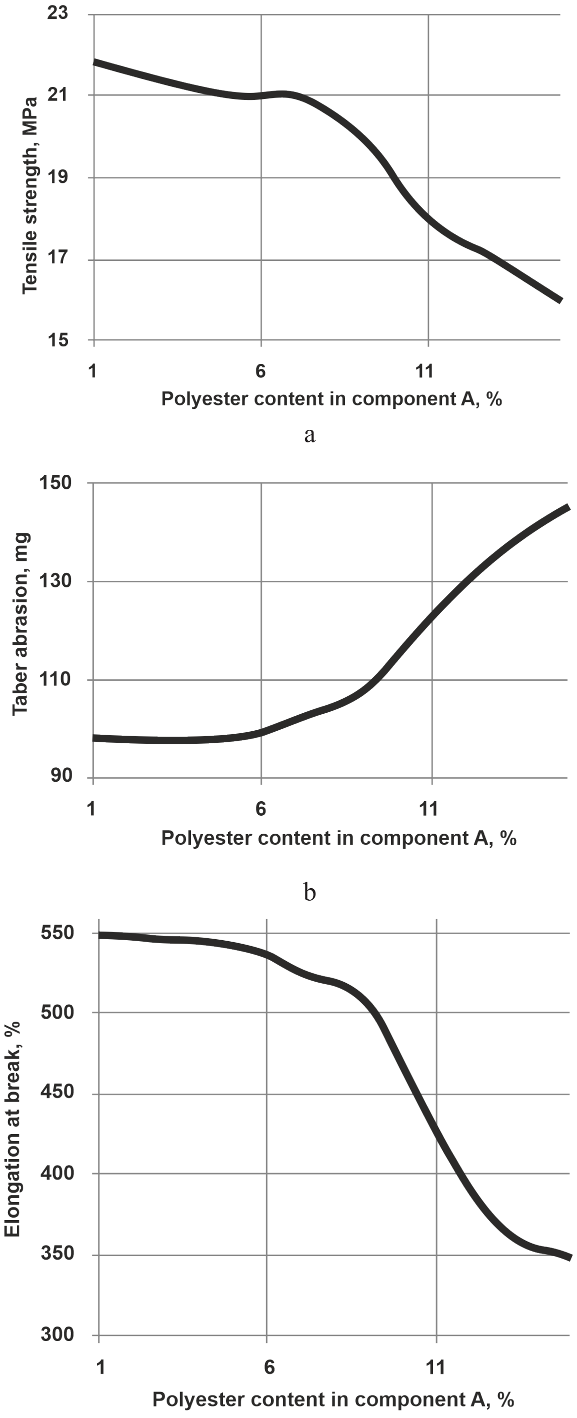


Fig. 5. Dependence of the composition lifetime on the polyester content in component A of the system.

Introducing high-molecular weight polyester increases the lifetime of the polyurea composition to the required values (5 min) and increases its abrasion while the tensile strength and elongation are reduced to an acceptable level. This allows this system to be used as a "manual" one.



a

b

c

Fig. 6. Dependence of the tensile strength (a), composition abrasion (b), and elongation at break (c) on the polyester content in component A of the system.

CONCLUSIONS

In this study, a polyurea composition with a lifetime of more than 5 min can be obtained with a curing rate of approximately 30 times slower than the original composition because of the partial replacement of amine groups with less active hydroxyl groups and because of the introduction of 10–15%

polyester with ~2000 Da molecular weight into the system. The resulting systems have the required strength characteristics and higher adhesive properties. This composition of "manual" application can be used for the repair of polyurea coatings without needing high-pressure installations.

Authors' contribution

All authors equally contributed to the study.

The authors declare no conflicts of interest.

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