DOI: 10.6060/ivkkt.20236606.6719

УДК: 666-405.8

ТЕПЛОВЫЕ ХАРАКТЕРИСТИКИ ПОЛИМЕРНЫХ КОМПОЗИЦИОННЫХ МАТЕРИАЛОВ ПЕНОПОЛИУРЕТАН-ХИТИН

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Проблема замены упаковки для пищевых продуктов, получаемой из синтетических полимеров, на биоразлагаемые пленочные материалы, производимые на основе природного сырья, является чрезвычайно актуальной, что связано с общим ухудшением экологии. Поэтому тенденция использования природных полимеров для частичной или полной замены материалов на нефтяной основе вызывает интерес и внимание многих ученых. В данной работе использовали хитин (Ct) размерами 1-3 мм (CtS) и 5-10 мм (CtL) для наполнения пенополиуретана (ПУ) для получения полимерных композиционных материалов (ПКМ) ПУ-хитин (ПУ-Ct). Оценивались тепловые свойства (высокотемпературная стойкость, теплоизоляционная способность, горючесть) полученных ПКМ. Результаты показали, что наполнение ПУ хитином и размер наполнителя существенно не повлияли на высокотемпературную стойкость ПУ-Ct. Термостойкость ПУ-Ct аналогична ПУ без наполнителя, но значительно выше, чем у хитина. В случае полужестких материалов чем выше степень наполнения, тем выше коэффициент теплопроводности. Полужесткие материалы, содержащие 10% масс. хитина, имели теплопроводность, соизмеримую с исходным ПУ. Размер наполнителя не повлиял на теплоизоляцию получаемого материала. В то же время добавление хитина в эластичный ПУ (эПУ) снижало теплопроводность разработанного ПКМ. Увеличение содержания хитинового наполнителя в ПУ повышало скорость горения ПКМ по сравнению с исходным ПУ, но снижало по сравнению с хитином. Существенного влияния размера хитина на воспламеняемость ПУ-Ct не наблюдалось. Таким образом, материалы полужесткие ПУ, содержащие 10 % по массе хитина, были рекомендованы для замены исходных полужестких ПУ в качестве изоляционных материалов. эПУ-Ct был рекомендован для использования в областях, где требуется низкая или средняя изоляция.

Ключевые слова: пенополиуретан, хитин, полимерный композиционный материал, тепловая характеритика, горючесть, высокая термостойкость

Для цитирования:
Чан И.Д.Ч., Зенитова Л.А., Хоанг Т.Д., До Т.Х., Ву Т.К. Тепловые характеристики полимерных композиционных материалов пенополиуретан-хитин. *Изв. вузов. Химия и хим. технология*. 2023. Т. 66. Вып. 6. С. 111–122. DOI: 10.6060/ivkkt.20236606.6719.

For citation:
Tran Y.D.T., Zenitova L.A., Hoang T.D., Do T.H., Cuong V.T. Thermal characterizations of polymer composite materials polyurethane foam-chitin. *ChemChemTech* [*Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol*.]. 2023. V. 66. N 6. P. 111–122. DOI: 10.6060/ivkkt.20236606.6719.

THERMAL CHARACTERIZATIONS OF POLYMER COMPOSITE MATERIALS POLYURETHANE FOAM-CHITIN

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The problem of replacing food packaging made from synthetic polymers with biodegradable films based on natural materials is highly relevant and associated with general environmental degradation. Therefore, the trend of using natural polymers to partially or entirely replace petroleum-based materials is exciting and attended by many scientists. In this work, chitin (Ct) with sizes of 1–3 mm (CtS) and 5–10 mm (CtL) was filled into polyurethane foam (PU) to obtain polymer composite materials (PCM) PU-chitin (PU-Ct). The thermal properties (high-temperature resistance, heat-insulating ability, flammability) of the obtained PCMs were evaluated. The results showed that the chitin filling to the PU and the size of the filler did not significantly affect the high-temperature resistance of PU-Ct. The heat resistance of PU-St was similar to the PU without filler but significantly higher than that of chitin. In the case of semi-rigid materials, the higher the filling ratio, the higher the coefficient of thermal conductivity. Semi-rigid materials containing 10% mass chitin had a thermal conductivity commensurate with the original PU. The size of the filler had not affected the thermal insulation of the obtained material. Meanwhile, the filling of chitin to the elastic PU (FPU) reduced the thermal conductivity of the developed PCM. Increasing the degree of chitin filler in PU increased the flammability of PCM compared with the original PU but decreased compared with chitin. There was no significant effect of chitin size on the flammability of PU-Ct. Thus, semi-rigid PU materials containing 10% by mass of chitin were recommended to replace the original semi-rigid PU as insulating materials. The FPU-Ct was recommended for use in fields that require low or medium insulation.

Key words: polyurethane foam, chitin, polymer composite material, thermal properties, flammability, high-temperature resistance

INTRODUCTION

In recent years, polyurethane foam (PU) has been one of the most commonly used synthetic polymer materials in the material market [1]. Because of the outstanding properties of this material, such as high strength [2], relatively low density [3-4], good mechanical properties, high wear resistance, shock absorption function, excellent flexibility and elasticity [2-3], high reusability [5], excellent thermal stability and fire resistance [6-7], short production lead times [8]. With the wonderful properties of PU, this material can be flexibly applied in many different fields such as packaging, cushioning in bedding, furniture [1,9-10], automotive interiors, carpet underlay, auto technology, textiles, adhesives, coatings, building materials (used in roof and wall insulation, insulated windows, and doors), biological materials [1,7,11-12], refrigerators, freezers [7].

As mentioned above, one of the excellent properties of PU is its thermal properties. Due to their low thermal conductivity, PU foams are considered one of the materials today that offer the best thermal insulation with minimal thickness [4]. Therefore, polyurethane foams are now an optimal choice for the thermal insulation of buildings. In addition to low thermal conductivity, they are also known as a material with high thermal properties in recent years [6]. A material with good fire resistance or low flammability is required for application in construction works or other thermal industrial fields. Therefore, PU is also considered a material that meets the fire resistance standards for building materials. With such good thermal properties, the use of PU is increasing rapidly and widely worldwide.

According to statistics, the PU market will have reached over 70.5 billion USD by 2021; it is expected that the global scale of this material will increase sharply soon. It is estimated that by 2030 the global PU market will reach 105.45 billion USD [13].

The consumption of PU is on a rapid growth track. Therefore, it is necessary to further promote the synthesis and production of PU, aiming to meet the growing consumer market of this potential material. Traditionally, PU foam is mainly produced by polyol and isocyanate derived from petroleum [14]. The exploitation of these two components in large quantities leads to significant negative impacts on the gradually depleted and non-renewable petroleum resources [15]. It is recognized that this mining not only causes resource depletion and pollution to the surrounding environment but also significantly affects the health of humans and living creatures [14]. With such obstacles, in recent years, the substitution of petroleum-based materials with natural, environmentally friendly fillers in the production of PU has been attracting much attention [1, 14].

Chitin is a natural polysaccharide and is relatively abundant in nature; its yield is second only to cellulose. Chitin is mainly used in wastewater treatment, medicine, agriculture, and cosmetics [16]. The formulation of this natural polymer consists of N-acetyl-D-glucosamine repeat units joined by β-1,4 bonds [17]. The formula of chitin contains functional groups, such as hydroxyl, amine, methylol groups; therefore, this natural polymer has attracted considerable attention in resource extraction based on these functional groups. Besides, beneficial properties such as nontoxicity, biodegradability, biocompatibility, antimicrobial activity [18], etc. have led to application in many different industries also researching the use of chitin as a filler to replace petroleum-based raw materials partially or entirely. Scientists Fajardo and Kawano have conducted several studies on using chitin as a filler to add to rubber. Developed composite materials have been shown to have good strength in terms of mechanical properties [17,19]. The combination of chitin into polyurethane for biomedical materials has been investigated. This composite is evaluated to have high stability with low mass loss in simulated living tissue. It has also been proven that non-toxic products are produced when using this material; at the same time, the in vitro biocompatibility of this material has also been noted. However, the research on grafting chitin into PU is mainly limited to biomedical materials. In recent times, the addition of chitin to the polymer matrix PU has also been studied in a few of our previous works. However, the obtained materials are only evaluated and investigated in wastewater treatment, such as oil spill removal [3, 8, 20] and heavy metal ion adsorption [21]. There are hardly any studies that discuss the thermal properties of PU-Ct composites.

Thus, this study investigated polyurethane-grafted-chitin materials (PU-Ct) thermal properties. The mechanism of polymer matrix formation is also proposed in this research. In addition, the properties of high-temperature resistance, thermal conductivity, and flammability of the material have also been studied. From the survey results, there are recommendations for the application of these developed composites.

MATERIALS AND METHODS

Materials. In this study, chitin from shrimp shells of two sizes: 1-3 mm (CtS) and 5-10 mm (CtL), was obtained from Ho Chi Minh, Vietnam. The elastic (E) and rigid (R) polyol-containing component (component A) with hydroxyl content of 38 mg KOH/g, moisture content of 3.5-4.1%, and the elastic isocyanate-containing (component B) with NCO content - 29.4-30.8 wt% were purchased from Vladimir, Russia.

Preparation of polyurethane-grafted chitin (PU-Ct). PU-Ct polymer composites were synthesized in two steps:

(1) Step 1: preparation of the mixture of component A-Ct;

(2) Step 2: copolymerization through grafting polymers.

The synthesis process details were given in Fig.1 in an NCO/OH ratio of 1:0.6 and were performed at room temperature for predetermined times.

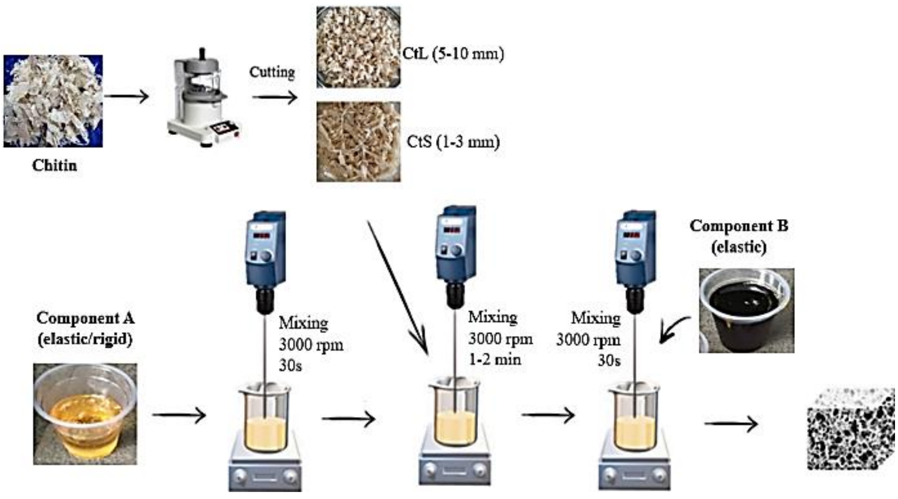

Fig. 1. Schema of preparation PU-Ct
Рис. 1. Схема приготовления ПУ-Ст

The formula of components A and B, the chitin-filling ratio, and the symbols of the samples are presented in Table 1. First, the high-speed agitator uniformly dispersed chitin into pre-mixed component A. Next, component B was added to the mixture of component A-Ct and kept stirring for a predetermined time. After entirely raising the foam, the obtained materials were left to stand for one day for curing. The final products were cut into the appropriate size to study the thermal characterizations.

Table 1

The formula of preparation of PU-Ct

***Таблица 1*. Формула приготовления ПУ-Ст**

Symbol	The formula of preparation of PU-Ct
Semi-rigid materials	
SPU	100 A (R): 60 B (E)
SPU-10CtS*	100 A (R): 60 B (E): 16 CtS
SPU-20CtS	100 A (R): 60 B (E): 32 CtS
SPU-50CtS	100 A (R): 60 B (E): 80 CtS
SPU-10CtL	100 A (R): 60 B (E): 16 CtL
SPU-20CtL	100 A (R): 60 B (E): 32 CtL
SPU-50CtL	100 A (R): 60 B (E): 80 CtL
Elastic materials	
FPU	100 A (E): 60 B (E)
FPU-10CtS	100 A (E): 60 B (E): 16 CtS
FPU-20CtS	100 A (E): 60 B (E): 32 CtS
FPU-50CtS	100 A (E): 60 B (E): 80 CtS
FPU-10CtL**	100 A (E): 60 B (E): 16 CtL
FPU-20CtL	100 A (E): 60 B (E): 32 CtL
FPU-50CtL	100 A (E): 60 B (E): 80 CtL

Notes: *SPU-10CtS – Semi PU filling 10% mass. chitin with size 1-3 mm, **FPU-10CtL – flexible PU filling 10% of mass chitin with size 5-10 mm

Примечания: *СПУ-10КтС – Полуполиуретановый наполнитель 10% масс. хитина размером 1-3 мм, **FPU-10CtL – гибкий полиуретановый наполнитель 10% от массы хитина размером 5-10 мм

Characterization of obtaining PCM PU-C. The thermal stability of materials PU-Ct was evaluated according to GOST R 57931-2017 [22] using a thermogravimetric analyzer TGA (STA6000, PerkinElmer, USA) with a heating rate of 3 °C/min; the temperature range was set at 30-300 °C.

The moisture determination of PU-Ct was carried out using a moisture analyzer thermogravimetric (MS-70 AND, Japan).

The method for determining thermal conductivity under stationary thermal conditions was according to GOST 7076-99 [23]. Materials were crushed to size 100×100 mm, 10-20 mm thick.

The method of determining flammability according to GOST 28157-2018 [24]. Use the method to determine the flame propagation speed along a horizontal fixed specimen. Five samples in the form of rods with sizes (150±5) mm long, 10-15 mm wide, and 10-13 mm thick were tested in this test. The samples shall be marked perpendicular to the axis at 25 mm and 100 mm from the part where the sample was exposed to the flame. To do this, place the sample holder and burner in a laboratory fume hood. The test piece was clamped at the farthest end, 25 mm from the mark, and positioned, so its longitudinal axis was horizontal. Then, the samples were burned and recorded the time, so the remaining length of the test samples at a time (t) was between the 25 mm and 100 mm marks. The flame speed was calculated according to the formula:

$$V = \frac{60.L}{t}$$

where, L – the length of the flamed sample, mm; t – the flame time, s.

RESULTS AND DISCUSSIONS

Mechanism of synthesizing PU-Ct. The formation of polyurethane foam was based on the following reactions [25]:

(1) between the isocyanate group of the isocyanate-containing component B and the hydroxyl group of the polyol-containing component A with the formation of a urethane bond according to reaction (1);

$$\text{R-NCO} + \text{R-OH} \rightarrow \text{R-NH-COO-R} + \Delta H \qquad (1)$$

(2) when the isocyanate group of component B interacts with water, carbamic acid was formed according to reaction (2), which decomposed into amine and carbon dioxide - reaction (3);

$$\text{R-NCO} + H_2O \rightarrow \text{R-NH-CO-OH} \qquad (2)$$

$$\text{R-NH-CO-OH} \rightarrow \text{R-NH}_2 + CO_2 \qquad (3)$$

(3) between the isocyanate group of component B and the amino group of the amine, with the formation of a substituted urea bond - reaction (4).

$$\text{R-NCO} + \text{R-NH}_2 \rightarrow \text{R-NH-CO-NH-R} \qquad (4)$$

Fig. 2 shows the formula of chitin, which contains hydroxyl and methylol groups. Therefore, it could be assumed that, in addition to the main reaction between the isocyanate group of component B and the hydroxyl group of component A, during the preparation of PU, the interaction between the hydroxyl and methylol groups of chitin with the isocyanate group of component B could occur with the formation of a urethane bond according to reaction (1).

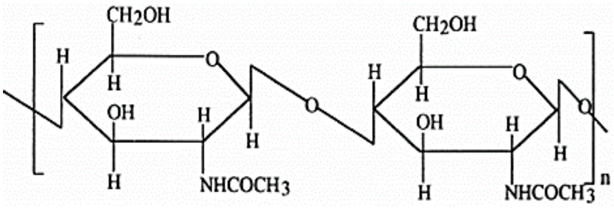

Fig. 2. The formula of chitin

Рис. 2. Формула хитина

Thus, the PU-Ct was obtained through a condensation reaction between the -NCO isocyanate group in component B and the hydroxyl group present in the polyol (component A), as well as in chitin, according to reaction (1). And the reaction of the -NCO group with the methylol group in chitin according to the reaction in Fig. 3 [26].

At the same time, the water in component A interacted with the NCO group of component B with the formation of carbamide acid according to reaction (2), which decomposes, forming an amine and carbonic dioxide - reaction (3). The isocyanate group, interacting with the amine, formed urea bonds according to the reaction (4). The participation of chitin in obtaining polyurethane foam affected the formation of the chemical network of the polymer.

The high-temperature resistant properties of the obtained PU-Ct. Studying the high-temperature resistant properties of materials helped to evaluate their thermal stability and presented the relationship between the structure and high-temperature resistant properties of the material.

Both for chitin and unfilled PU and PU-Ct, the mass losses curves occurred in two stages:

(1) First stage: The initial mass loss temperature at this stage occurred at 58 °C and continued up to 100 °C, related to the loss of the absorbed moisture and the low molecular weight components. It could be seen that chitin began to lose mass at 58 °C. This occurred due to the evaporation of a very significant amount of the moisture contents (Fig. 4). There was significantly less moisture in unfilled PU foam: 1.84% for SPU and 1.49% for FPU. The moisture content in these materials was mainly the moisture, which adsorbed from the outside. Meanwhile, the moisture content of chitin was up to 6.9%; therefore, as the chitin ratio increased, the moisture content of the material PU-Ct increased. At the same time, the size of the filler also affected the moisture content of the obtained material, which will be higher in the case of using CtL. This trend was consistent for both types SPU-Ct and FPU-Ct.

(2) Second stage: occurred in the range of 220-300 °C. For chitin, this stage corresponded to the onset temperature of thermal decomposition of acetyl and diacetyl groups [27]. As a rule, the onset temperature of thermal decomposition of the same type PU-Ct was not significantly different, ranging from 257-259 °C for SPU and 262-272 °C for FPU (Table 2), which was mainly related to the degradation of allophanate, biuret, and urethane groups [28]. These functional groups were lower thermal stability than the acetyl and diacetyl groups in chitin [29]. It was found that the filling ratio practically affected the onset temperature of degradation not significantly. However, the onset of degradation of samples SPU in the case of filling chitin with 5-10 mm (CtL) occurred earlier: 257 °C for SPU-10CtS and 246 °C for SPU-10CtL. Meanwhile, the decomposition onset temperature in the samples FPU-Ct increased compared to the blank FPU; at the same time, there was no significant difference in decomposition onset temperature between samples containing large and small chitin particles. In addition, it was noted that

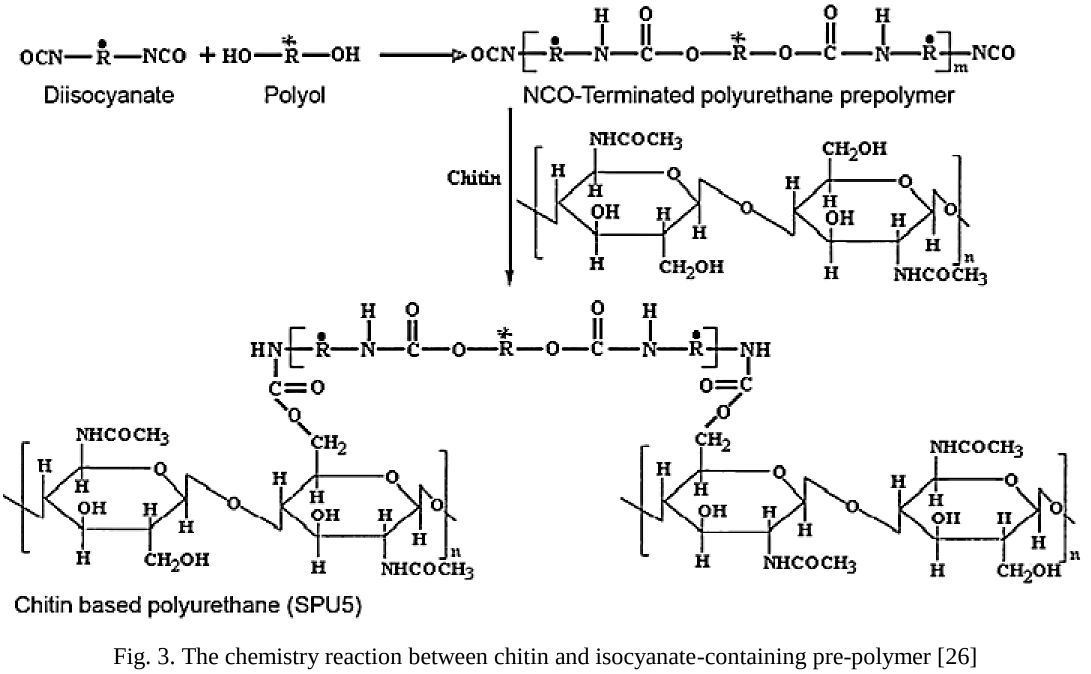

Fig. 3. The chemistry reaction between chitin and isocyanate-containing pre-polymer [26]
Рис. 3. Химическая реакция между хитином и изоцианатсодержащим преполимером [26]

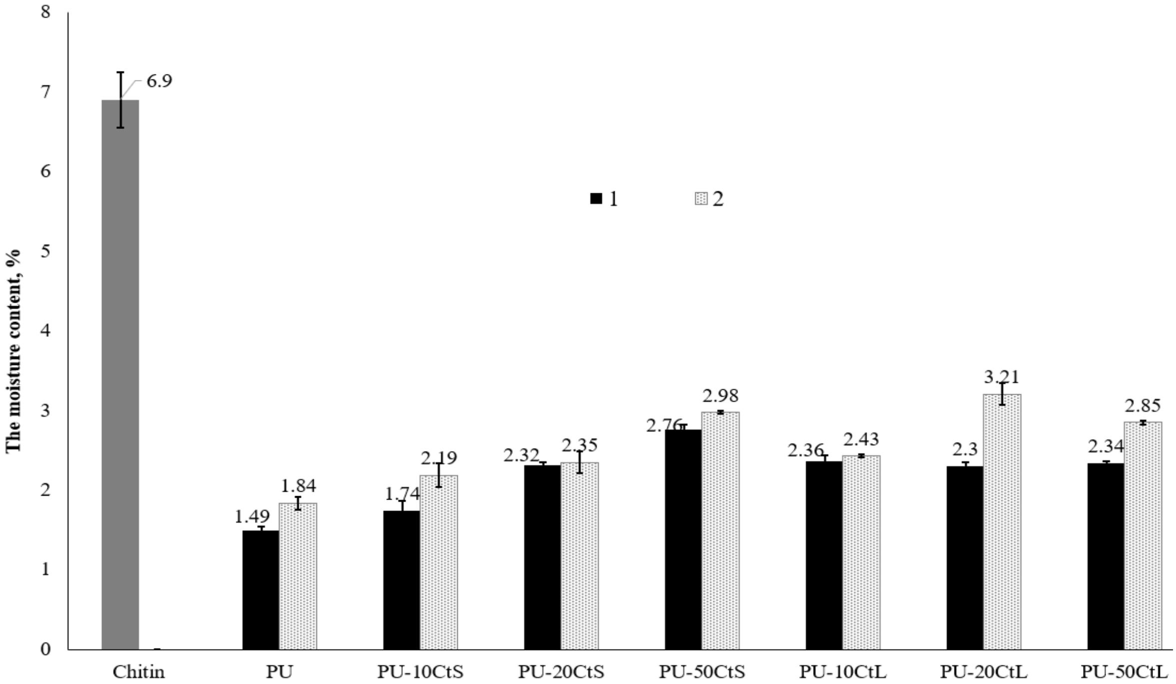

Fig. 4. The moisture content of materials (1 – Elastic materials, 2 – Semi-rigid materials)
Рис.4. Влажность материалов (1 – Эластичные материалы, 2 – Полужесткие материалы)

Table 2

TGA results of materials

***Таблица 2.* Результаты ТГА материалов**

Sample	CLMWC,%	IMLT, °C	OTTD, °C	T5, °C	T10, °C	T15, °C	ML300, %
Chitin	5.82	58.01	260.11	73	279	-	12.57
SPU	0.48	114.56	257.38	237	262	277	25.62
SPU-10CtS	1.08	105.56	257.38	233	263	279	21.72
SPU-20CtS	1.56	102.08	259.10	224	259	277	23.15
SPU-50CtS	1.79	84.63	257.68	232	270	289	17.24
SPU-10CtL	1.18	107.52	246.29	223	254	273	24.77
SPU-20CtL	1.08	106.39	248.00	213	246	267	25.07
SPU-50CtL	2.33	88.36	257.72	216	263	288	18.12
FPU	0.58	102.18	258.00	290	-	-	4.19
FPU-10CtS	0.71	107.57	264.51	289	-	-	5.65
FPU-20CtS	1.06	101.01	261.97	290	-	-	5.57
FPU-50CtS	1.50	100.61	263.13	291	-	-	5.42
FPU-10CtL	1.18	109.94	261.53	289	-	-	5.66
FPU-20CtL	0.99	102.04	262.63	288	-	-	5.80
FPU-50CtL	2.11	95.21	271.88	290	-	-	5.57

Note: CLMWC - Content of low molecular weight components, IMLT - The initial mass loss temperature, OTTD -The onset temperature of thermal decomposition, T5, T10, T15 - The temperature when weight loss 5%, 10%, 15%, ML300 - Total mass loss at 300 °C
Примечание: CLMWC - Содержание низкомолекулярных компонентов, IMLT - Температура начала потери массы, OTTD - Температура начала термического разложения, T5, T10, T15 - Температура при потере массы 5%, 10%, 15%, ML300 - Полная потеря массы при 300 °C

the more dense preparations with chitin content of 50% by mass in the FPU also had a higher onset temperature of thermal decomposition: FPU - 258ºC and FPU-50CtL -272 °C. Meanwhile, for SPU-Cts with 50% mass content, the onset temperature of thermal decomposition was almost not different between the filler-containing composite and the blank SPU.

However, almost no negative effect of chitin when added to polyurethane foam on the heat resistance of the filled foam was noted. This was because the interaction of chitin with the isocyanate component during the synthesis of PU-Ct led to a denser spatial network. It was this denser spatial network that affected the high-temperature resistance of PU-Ct.

Table 3

DTG results of materials

***Таблица 3.* Результат ДТГ материалов**

Material	T_1^*, °C	T_2^{**}, °C
Chitin	58.23	-
SPU	104.03	198.89
SPU-10CtS	112.22	196.70
SPU-20CtS	97.92	198.45
SPU-50CtS	110.0	191.41
SPU-10CtL	110.42	198.96
SPU-20CtL	101.59	193.04
SPU-50CtL	71.06	201.75
FPU	108.33	197.92
FPU-10CtS	102.76	195.50
FPU-20CtS	108.31	196.94
FPU-50CtS	104.17	197.40
FPU-10CtL	108.18	195.28
FPU-20CtL	107.81	192.81
FPU-50CtL	97.78	197.22

Notes: * The temperature of degradation 1st peak,
** - The temperature of degradation 2nd peak
Примечания: * Температура разложения 1-го пика,
** - Температура разложения 2-го пика

Total mass loss at 300 °C of SPU was more than chitin. Filling chitin into PU reduced the total mass loss of the obtained PU-Ct; PU-Cts with large chitin particles had a higher degree of total mass loss than samples containing small chitin particles. In contrast, FPU lost mass to a lesser extent than chitin. Using chitin resulted in a higher total mass loss of the filled FPU; however, their total mass loss was insignificant. At the same time, the size of chitin in the materials PU-Ct did not significantly affect the total mass loss of the material at 300 °C.

The results of DTG (Table 3) also confirmed that chitin decomposition occurred at lower temperatures than other materials. Meanwhile, for both FPU-Ct and SPU-Ct, the DTG results showed that chitin filling in PU foam's composition did not significantly change the temperature of degradation peaks. The first peak appeared at about 100 °C, corresponding to the evaporation of moisture and low molecular weight components present in the material, as shown in Table 2 and Fig. 4. The second peak was observed between 191-201 °C, corresponding to the beginning of decomposition of the materials' acetyl, allophanate, biuret, and urethane groups.

Thus, the addition of chitin in the composition of PU foam hardly affected the heat-resistant properties of the obtained material. As a result, the SPU-Ct and FPU-Ct were both similar in heat resistance to the unfilled SPU and FPU; meanwhile, their heat resistance was significantly higher than that of chitin. Thus, it was shown that the composite materials PU-Ct could be used at sufficiently high temperatures.

The thermal conductivity or the thermal insulation of PU-Ct. Thermal conductivity was a physical property of any material, including polymer composites, that characterized its capability to conduct heat, or heat transfer, through a material. The better the thermal insulation, the less heat loss to the surrounding environment; this has been one of the causes of global warming. On the other hand, saving fuel in the heating process was also realized by using materials with good thermal insulation for buildings or wrapping heat pipes in construction and industry. Currently, polyurethane foam is known as one of the best thermal insulation materials on the market. In this regard, the thermal insulating capability of the developed composites PU-Ct was investigated in this study (Fig. 5).

The lower the material's thermal conductivity, the higher the capacity to insulate thermal. Fig. 5 showed that the composite materials SPU-Ct had a lower thermal conductivity coefficient than the foams FPU-Ct. It was explained because the material's thermal conductivity was mainly related to the number of closed cells and the size of the pores in the structure. The more closed cells a material contained, the more effective its thermal insulating properties were [30]. In our case, semi-rigid materials SPU-Ct had a significant number of closed cells; therefore, it was obvious that their thermal insulating properties were better. Meanwhile, elastic materials mainly contained tiny interconnected pores, so their thermal insulation capacity was lower than that of materials with closed pores (coefficient of thermal conductivity of SPU reached 0.025 W/mK, of FPU reached 0.048 W/mK).

In the case of semi-rigid materials, it was found that materials containing 10% by mass of chitin had a thermal conductivity commensurate with materials without filler. At the same time, the higher the ratio of filler addition, the higher the coefficient of thermal conductivity. For closed-cell-containing materials, chitin flakes in the composition had the effect of increasing the connection of the closed cells or had the effect of increasing the size of the pores. When filled with a low chitin ratio, the number of chitin flakes was not enough to increase the connectivity of the closed cells and their size. Therefore, the thermal insulation properties of materials containing 10% by mass of chitin were not different from that of the original SPU. However, when continuing to increase the higher filler rate at this time, the number of closed cells was greatly reduced, and the size of the cells also increased significantly, thus leading to a reduction in the thermal insulation properties of materials containing high chitin ratios. Besides, the size of the filler (CtS or CtL) slightly affected the thermal conductivity of the obtained material. Specifically, CtL-containing materials had a lower thermal conductivity than materials containing chitin of smaller size. Large chitin flakes easily disrupted the closed-cell structure and increased the pore size more easily than the small flakes. Therefore, it was obvious that the SPU-CtL had a lower coefficient of thermal conductivity than the SPU-CtS.

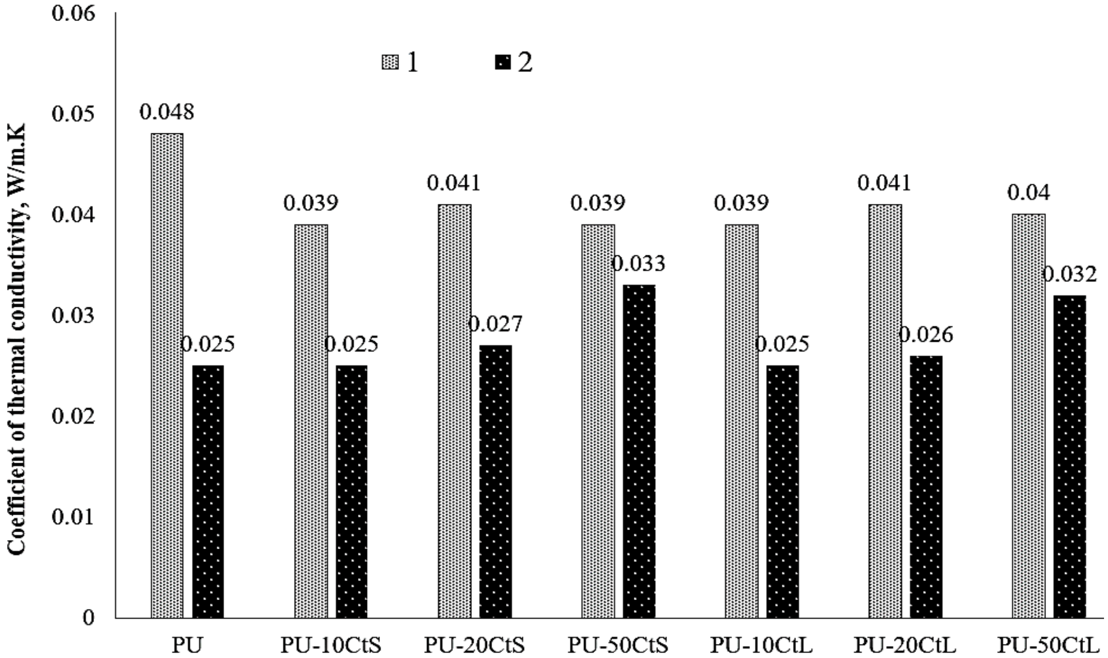

Fig. 5. The thermal conductivity of materials (1- Elastic materials, 2- Semi-rigid materials)
Рис. 5. Теплопроводность материалов (1 -Эластичные материалы, 2- Полужесткие материалы)

In contrast, for materials FPU-Ct, when chitin was added to composite materials, the heat transfer coefficient decreased; that was, the thermal insulation capacity of FPU-Ct increased. In this case, the chitin flakes acted as a barrier preventing the association between the open cells in the FPU. This meant an increase in the number of closed holes compared to the original FPU. As a result, the thermal insulating capacity of chitin-containing materials increased. The results also showed that increasing the chitin ratio and the size of chitin particles had almost no significant effect on the thermal conductivity of the materials, except for materials containing 50% mass of chitin.

Thus, it could be confirmed that polymer composite materials PU-Ct had good thermal insulation properties. Semi-rigid materials with the filling of 10% chitin (SPU-10Ct) could be used to replace the original material in civil construction or industrial heating equipment. Comparison with the thermal insulation properties of other materials (Table 4) presented those semi-rigid materials with 20% and 50% by mass of chitin could be used as an alternative to polystyrene foams in thermal insulation applications.

Meanwhile, the FPU-Ct with thermal conductivity in the range of 0.039-0.041 W/m.K could replace mineral wool because of their similar thermal insulating properties. Besides, comparing the thermal insulation properties of the developed composites with other materials showed that the results in this study of composites PU-Ct were comparable to the blank PU in other studies. At the same time, it was found that the thermal insulation property of CPU-10Ct was better than polystyrene foam 1.4 times, mineral wool – 1.24-1.8 times, brick – 19.6-34.8 times, concrete block – 14-31.6 times, expanded perlite – 1.6-2.4 times, wood chips – 1.52-4.28 times. Therefore, proposals for thermal insulation applications of the material PU-Ct were feasible. Because in addition to thermal insulation properties, evaluation of the lifetime of these materials has shown that it was more economical to use PU-based materials. In addition, our previous report also demonstrated that chitin filler was significantly economical compared to the original PU foams. Therefore, it was clear that the use of materials PU-Ct ensured the material's thermal insulation properties and the cost's reasonableness.

The flammability of developed materials PU-Ct. When using thermal insulations, their flammability was an essential factor. The flammability of the material was estimated by its burning speed.

Fig.6 showed that when filling chitin to both SPU and FPU, the flame speed of the obtained material increased. However, the burning speed of PU-Cts was improved compared to the original chitin. This was related to the presence of chitin in the foam matrix; because the burning speed of chitin was significantly higher than the blank PU; it reached 13.85 mm/min.

For SUP-Ct and FPU-Ct, the higher the chitin ratio, the higher the flame speed of the obtained material. However, this parameter of the SPU-Ct was slightly increased compared to the SPU, while the flammability of the FPU-Ct increased quite clearly compared to the pure material. Besides, it has also been noted that there was no effect significant of chitin size on the burning rate of the material. It should also be noted that the burning speed of semi-rigid materials was less than that of the elastic materials, which relates to the type and size of pores in the material's structure. The greater the number of interconnected pores and the larger the pore size, the less resistant the material is to flame propagation. Therefore, the FPU and the composites FPU-Ct were more flammable than the SPU and SPU-Cts.

However, the burning speed of the developed materials was less than 100 mm/min; therefore, materials PU-Ct were still classified as non-combustible materials [24]. Thus, it has been recommended that these materials can be used as thermal insulation without fear of fire, especially for semi-rigid composites.

Table 4

Thermal insulation properties of some materials

***Таблица 4.* Теплопроводность некоторых материалов**

Materials	Coefficient of thermal conductivity, W/m.K	References
SPU	0.025	In this study, [31]
SPU-10CtS/SPU-10CtL	0.025	In this study
SPU-20Ct/SPU-50Ct	0.027-0.033	In this study
FPU-Ct	0.039-0.041	In this study
PU in the other study	0.022-0.035	[32]
Polystyrene foam	0.035	[33]
Mineral wool	0.031-0.045	[33]
Brick	0.49-0.87	[33]
Concrete block	0.35-0.79	[33]
Expanded Perlite	0.040-0.060	[33]
Wood chips	0.038-0.107	[33]

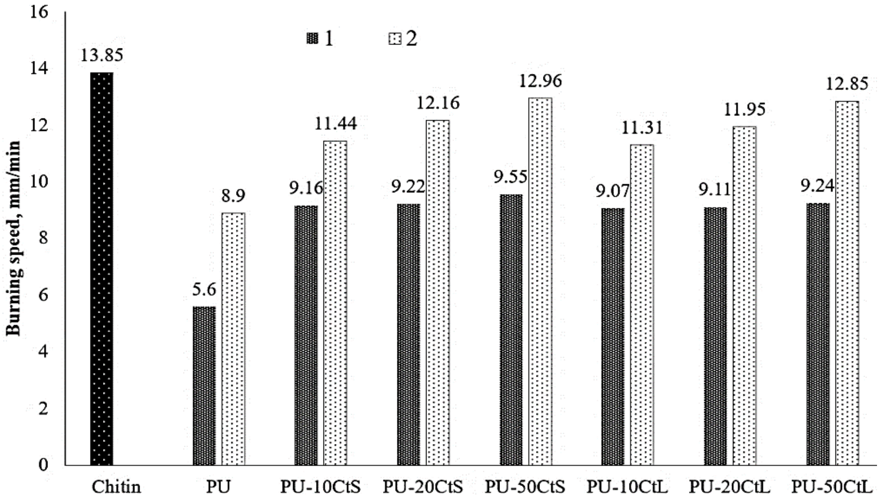

Fig. 6. The flammability of materials (1- Semi-rigid materials, 2- Elastic materials)

Рис. 6. Воспламеняемость материалов (1- Полужесткие материалы, 2- Эластичные материалы)

The higher the flame speed, the more combustible the material was; therefore, materials with low flame speed were preferred. Through the thermal properties of developed composites PU-Ct on two types of elastic and semi-rigid, it has been found that semi-rigid materials SPU-Ct have better applicability for thermal insulation or fields, which need high thermal stability. In particular, materials with a filling rate of 10% by mass were recommended to replace the original SPU as thermal insulation. For elastic composites FPU-Ct, it was recommended to use in fields that require low or medium thermal insulation.

CONCLUSION

This study investigated the thermal properties of PU-grafted-chitin materials (PU-Ct). Besides, the method of PU-Ct composite fabrication has also been proposed. The hydroxyl and methylol functional groups in chitin can participate in a chemical reaction with the isocyanate group to form a urethane bond similar to the reaction between the polyol and isocyanate group. Thereby creating a three-dimensional network that has specific effects on the heat properties of the obtained material. Thermogravimetric analysis (TGA) and differential thermal analysis (TDA) investigated the high-temperature resistance of materials. The results showed that the filling of chitin to the PU polymer matrix did not significantly affect the high-temperature resistance properties of the obtained material. Still, it improved more than that of chitin. The materials PU-Ct also had the same thermal insulation performance as the material without in the case of semi-rigid. Meanwhile, FPU-Cts have improved thermal insulation properties over the blank FPU. Furthermore, the flammability of filler-containing materials was significantly improved compared to the original chitin and slightly increased compared to the pure materials. Generally, the developed composites PU-Ct could be used as construction or industrial insulation materials. Therefore, material SPU-10Ct was more recommended for these applications.

The authors declare the absence a conflict of interest warranting disclosure in this article.

Авторы заявляют об отсутствии конфликта интересов, требующего раскрытия в данной статье.

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Поступила в редакцию 31.08.2022
Принята к опубликованию 13.03.2023

Received 31.08.2022
Accepted 13.03.2023