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The influence of nanoclays on the mechanical and thermal properties of rigid PIR and PUR foams

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Abstract: The effect of small amounts of chemically modified nanosized clays (from 0.05 to 1 %) on the morphological, physical-mechanical and thermophysical characteristics of rigid polyurethane-polyisocyanurate (PIR) and polyurethane (PUR) foams has been studied. The effect of these additives on the structure of the resulting material, the change in its compressive strength, Young's modulus, mass loss during combustion, and thermal conductivity are evaluated. Based on the results obtained, it is noted that the addition of small amounts (up to 0.2 %) of chemically modified Cloisite 30B nanoclay effectively reduces the average cell size of nanocomposite foams, which leads to an improvement in their performance.

Keywords: polyurethane; polyurethane-polyisocyanurate foam; nanosized fillers; compressive strength; cell morphology; thermal conductivity

INTRODUCTION

Currently, one of the largest tonnage polymers is polyurethane - a polymeric material, traditionally obtained by polycondensation (polyaddition) of aromatic or aliphatic di- and polyisocyanates with polyol resins.[1] Due to the distinctive features of the material, such as high heat and sound insulation characteristics in the case of polyurethane foams, and high physical and mechanical properties, polyurethanes have now become an integral part of everyday life. One of the main industrially significant types of polyurethane are rigid polyurethane (PUR) and polyurethane-polyisocyanurate (PIR) foam. PIR foams are obtained using isocyanate trimerization catalysts as a result of technological processes similar to those in the case of PUR foams. It should be noted that PIR foams have improved thermal insulation characteristics and are less flammable than conventional polyurethane foams. The formation reactions of urethane and isocyanurate groups

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are shown in Figure 1.[2] It is important to note that in the framework of the synthesis of both polyurethane and, mainly, polyurethane-polyisocyanurate foams, a number of secondary chemical processes occur, the consideration of which is beyond the scope of this publication.[3,4]

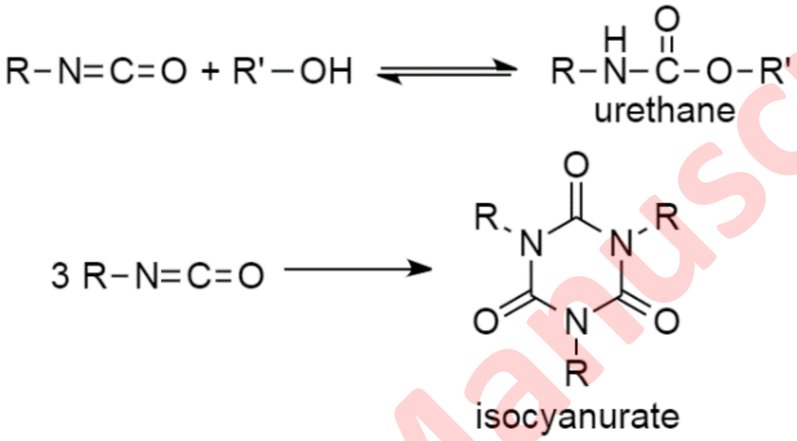

Figure 1. Reactions of urethane and isocyanurate formation

It is important to note that the annually growing demand for polymeric materials inevitably leads to the presentation of ever greater requirements in terms of functional (physical-mechanical, thermophysical, etc.) characteristics of the resulting polymers, which the latter, in the case of a very wide range of applications, no longer meet. One of the most promising ways to solve this problem is the synthesis of composite materials based on these polymers. Today, filled polyurethane systems are used everywhere, while the mass fraction of the filler in the formulation can traditionally vary from 1 to 50 % by weight of the composition. The most common fillers currently used in the polyurethane industry are chalk, carbon black,[5] sand,[6] expandable graphite,[7] titanium dioxide,[8] and a wide range of other oxides and inorganic salts.

It should be noted that the introduction of such inorganic additives in acceptable amounts into systems for producing foams contributes to a decrease in the average cell size of the formed foam,[9] since fillers act as a nucleating agent, creating many smaller cells.[10,11] In addition, these additives prevent the additional growth of bubbles due to an increase in the viscosity of the reaction medium.[12] Thus, the use of nanosized fillers to a large extent contributes to the improvement of the morphological characteristics of foams and, as a result, to an increase in a number of performance characteristics, increasing strength indicators,[13,14] to a significant extent, preventing a gradual increase in the thermal conductivity of foams during aging.[15,16]

The trend towards the addition of micro-sized clays (mainly montmorillonite and vermiculite) in polyurethane foam compositions arose about 20 years ago.[17-19] Nanoclays, on the other hand, are finely dispersed material that improves the mechanical and thermal insulation characteristics of polyurethane composite foams due to a significantly increased specific surface area.[20]

It is extremely necessary to select the optimal amount of nanofiller, since at an excessively high content of these additives, a significant deterioration in the morphology of the material and degradation of performance characteristics are noted.[21,22] This deterioration in morphology can manifest itself both as an increase in the average cell size,[13] and a decrease in their density,[23] and an increase in the anisotropy coefficient of the foam.[24,25]

Thus, in the case of polyurethane and polyurethane-polyisocyanurate foams, nanoclays are of significant interest. In this regard, it is expedient to develop formulations of new nanocomposite materials based on polyurethane-polyisocyanurate and polyurethane foams using the additives described above, which have improved performance characteristics.

EXPERIMENTAL

Materials

For the synthesis of polyurethane and polyurethane-polyisocyanurate foams, a mixture of polyether polyols (H6007 (HongBaoLi PU, China) and HF-310 (Zhejiang Hengfeng New Material, China)), tris(2-chloropropyl)phosphate (TCPP, Shijiazhung Hejia Chemical Products, China) as a flame retardant, a mixture of 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA, Evonik, Germany) and dibenzylamine (Evonik, Germany) as catalysts for urethane and urea formation, a solution of potassium acetate in diethylene glycol in the assessment of 30:70 (Evonik, Germany) as trimerization catalyst, as well as water and n-pentane (for synthesis, Ekos-1, Russia) as blowing agents, were used. A highly functional polymeric MDI - Lupranat M50 (BASF, Germany) - with dynamic viscosity of 557 mPa s, determined at 25 °C in accordance with ISO 3219-2:2021,[26] and NCO content of 31.5 %, determined in accordance with ISO 148696:2009,[27] was used as the isocyanate component. The composition of the systems used is shown in Table 1.

Table 1. The composition of PIR/PUR foam systems.

Component	Amount, g	
	PUR foam	PIR foam
Polyether polyols blend	50.0	50.0
TCPP	7.0	7.0
PMDETA	0.8	0.8
Dibenzylamine	2.1	2.1
Potassium acetate in diethylene glycol (30:70)	-	2.5
water	2.4	2.4
n-pentane	2.7	2.7
Polymeric MDI (Lupranat M 50)	62.3	155.8

Commercially available chemically modified organoclays Cloisite 30B (surface layer modified with a quaternary salt of bis-2-hydroxyethylmethylammonium, modifier content <90 meq / 100 g) and Cloisite 25A (surface layer modified with a quaternary salt of diethylmethylammonium, content modifier <95 meq / 100 g) manufactured by BYK Additives (Germany).

Nanoclay suspensions

The insertion of fillers into the isocyanate component to obtain PUR and PIR foams was carried out by ultrasonic dispersion using an Inlab I100-6/4 unit equipped with an I10-2.0 ultrasonic generator at a frequency of 22.5 kHz with an output power of 2 kW.

Dynamic viscosity measurements

The dynamic viscosity of the suspensions obtained was measured using a Lamy RM200 CP4000 Plus rotary rheometer using R-6 disc (ϕ14.62 mm) at shear rate of 60 rpm in accordance with ISO 3219-2:2021[26] at 25 °C. Further in the work, the average viscosity values determined by analyzing three samples are given.

PUR and PIR foams preparation

The isocyanate and polyol components were thermostated at 20 °C. To obtain foam samples, the required weights of the blended polyether component were placed in plastic cylinders with a volume of 1000 cm^3, the required amount of n-pentane was added, after which it was actively mixed in the component for two minutes. After adding the required weight of isocyanate (or nanoclay suspensions), the system was mixed for five seconds using an automatic mixer at a speed of 3000 rpm. Foaming was carried out in the above-described plastic containers or wooden cubes with a volume of 15625 cm^3. 10 minutes after mixing the components, fragments were cut out from the core of the formed foams, which were subsequently used as analyzed samples.

Gel time

The so called "gel time" was tested as the time elapsed from the start of mixing polyol and isocyanate components to the point at which soft threads are formed when an ordinary wire yarn is touched to the surface of the foaming material and withdrawn.

Isocyanate group content measurements

The content of isocyanate groups in the polyisocyanate used was determined using the potentiometric titration method on an 848 Titrino plus Metrohm automatic titrator in accordance with ISO 148696:2009.[27]

Apparent density

The determination of the apparent density of the synthesized foams was carried out in accordance with ASTM D1622-20,[28] for which cubic samples of 50×50×mm in size were cut from the obtained materials. Further in the work, the average apparent density values determined by analyzing five samples are given.

Mechanical tests

The determination of compressive strength and Young's modulus was carried out in the direction of foaming on Roell/Zwick Z005 universal testing machine at a strain rate of 10 mm min^{-1} at 10 % linear strain in accordance with the EN 826:2013 method.[29] Within this work, only the relative compressive strength and Young's modulus are considered, numerically equal to the ratio of the compressive strength and Young's modulus to the square of the apparent density of the foam sample. The data shown in the work are averages calculated from analyzes of five samples of each of the investigated formulations of polyurethane-polyisocyanurate and polyurethane foams.

Open cell content

The content of open cells (OC / %) in the analyzed polyurethane and polyurethane-polyisocyanurate foams was analyzed using an AccuPyc II 1340 gas pycnometer in accordance with ASTM D6226-05.[30] Further, the paper presents the average value of the content of open cells in the studied samples, determined from the results of three independent measurements.

Thermal conductivity

The thermal conductivity of the analyzed polyurethane-polyisocyanurate and polyurethane foams was determined at 24 °C using LaserComp Fox600 HFM and Fox200 SN instruments in accordance with EN 12667:2001.[31] The size of each sample was 200×200×25 mm. Further, the paper presents the average values of thermal conductivity determined by analyzing three samples.

Morphological characteristics analysis

The morphological characteristics of the closed-cell structure of the foam samples were studied using the method of scanning electron microscopy (SEM). A Hitachi TM4000 Plus II instrument was used as a scanning electron microscope. Using a blade, 0.5 mm thick layers of the analyzed foam were cut out, which were subsequently placed in the sample compartment of the above-described photomicrograph instrument.

The average cell size (Φ) and the anisotropy coefficient ($A_{y/x}$) were estimated using the ImageJ software with the help of the intersection method, in accordance with the methods proposed by Brondi *et al*.[32] Each analyzed micrograph was overlaid with a grid composed of equidistant perpendicular lines (m vertical lines of length h and l horizontal lines of length w). For each of the lines, the number of crossed cells (n_i, n_j) was counted. Dividing the length of each individual line by a certain number of intersections, we found the lengths of the chords of the cells (Φ_i and Φ_j, *i.e.* one-dimensional values). This operation was carried out for each of the lines of the constructed grid, after which the average cell size was determined in accordance with equation (1) and the anisotropy coefficient in accordance with equation (2). Further in the paper, the averaged values of these quantities determined by analyzing five samples are given.

$$\overline{\Phi} = \frac{\sum_{i,j=1}^{m,l} \Phi_{i,j}}{m+l} \tag{1}$$

where Φ is average cell size, $\Phi_{i,j}$ are the lengths of cell chords, m is the number of vertical grid lines, l is the number of horizontal grid lines.

$$A_{y/x} = \frac{\sum_{i=1}^{m} \Phi_i}{m} \Bigg/ \frac{\sum_{j=1}^{l} \Phi_j}{l} \tag{2}$$

where $A_{y/x}$ is the anisotropy coefficient, $\Phi_{i,j}$ are the lengths of cell chords, m is the number of vertical grid lines, l is the number of horizontal grid lines.

Cell density was estimated using ImageJ software according to Kumar's theoretical approximation principle.[33,34] After opening the microphotograph in the ImageJ program, the area for analysis was selected. The number of cells and the square of the analyzed area of the micrograph were determined. The density of cells in the volume was estimated in accordance with the equation (3) proposed by Kumar, which can be expressed in terms of the number of cells located per cubic centimeter of the analyzed foam (cells cm^{-3}). Further in the work, the average values of cell density determined by analyzing five samples are given.

$$N_f = \left(\frac{n}{A}\right)^{\frac{3}{2}} \qquad (3)$$

where N_f is the density of cells in the foam, n is the number of cells in the analyzed area of the microphotograph, A is the square of the analyzed area, cm^2.

Combustibility

In order to assess the change in the combustibility of the analyzed polyurethane-polyisocyanurate foams, samples (30 mm*30 mm*15 mm) were vertically fixed in a tripod, after which the edge (30 mm*30 mm) was blown over for 30 seconds by the flame of a gas burner located at a distance of 5 cm from the sample, so that the entire surface of the facet was covered in flames. The gas flow rate was 0.36 ml s^{-1}. Further, the paper presents the average values of the degree of damage by mass (S_m) determined by analyzing five samples, calculated taking into account the change in the mass of the analyzed samples before and after the test.

RESULTS AND DISCUSSION

In accordance with the ISO 3219-2:2021 method,[26] the dynamic viscosity of the resulting organoclay suspensions in the polyisocyanate component used was determined. The trend in dynamic viscosity versus filler content is shown in Figure 2.

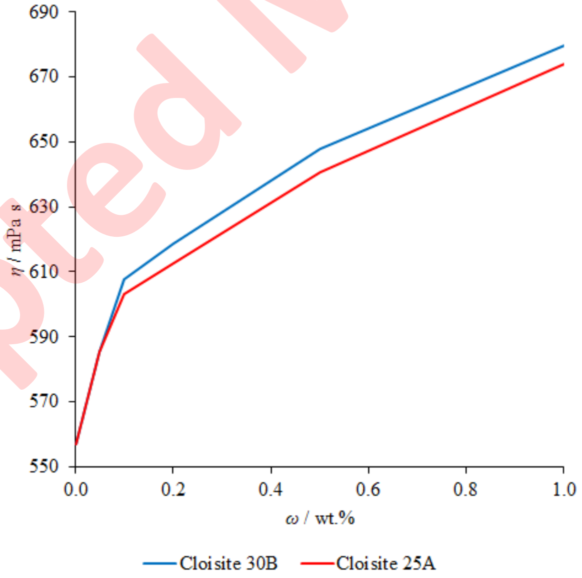

Figure 2. Dependence of the dynamic viscosity of the isocyanate component on filler content

Thus, there is a gradual increase in the dynamic viscosity of the isocyanate component as the content of the filler in it increases.

In order to study the effect of small additions of organoclays on the physical-mechanical, thermophysical, and morphological properties, samples of rigid closed-cell polyurethane and polyurethane-polyisocyanurate foams were obtained using the suspensions of the filler in polyisocyanate. It is noted that the addition of the considered fillers into the composition slightly shifted the parameters of the system, slowing down the so called “gel time” by 1–2 seconds in the case of organoclay concentration of 0.05 and 0.1 % and 2–3 seconds in the case of using these additives in higher concentrations. These minor changes in the technological parameters of the system are the result of a clear effect exerted by the additives on the physics of the foaming process.

The values of the physical-mechanical, morphological and thermophysical characteristics of the obtained composite foams determined using the methods described above are presented in Tables 2 and 3.

Table 2. Physical and mechanical characteristics of PUR and PIR foams

Foam sample		ω / wt.%	γ / kg m^{-3}	σ / kPa	$\sigma_{rel.}$ / kPa m^6 kg^{-2}	E / kPa	$E_{\text{rel.}}$ / kPa m^6 kg^{-2}
PUR foam	Standard	0.00	40.35	209.71	0.129	1974.10	1.21
	Cloisite 30B	0.05	40.15	229.51	0.142	1981.01	1.23
		0.10	39.95	238.80	0.150	1990.68	1.25
		0.20	39.81	246.51	0.156	1993.45	1.26
		0.50	39.72	245.13	0.155	1979.59	1.25
		1.00	39.49	242.05	0.155	1976.67	1.27
	Cloisite 25A	0.05	40.17	224.79	0.139	1983.54	1.23
		0.10	40.02	231.46	0.145	1981.21	1.24
		0.20	39.79	235.02	0.148	1981.60	1.25
		0.50	39.71	234.58	0.149	1977.65	1.25
		1.00	39.54	232.07	0.148	1992.46	1.27
PIR foam	Standard	0.00	40.32	266.09	0.164	3319.21	2.04
	Cloisite 30B	0.05	40.12	295.49	0.184	3328.50	2.07
		0.10	39.92	309.30	0.194	3333.48	2.09
		0.20	39.78	320.13	0.202	3331.49	2.11
		0.50	39.69	318.70	0.202	3350.41	2.13
		1.00	39.51	316.05	0.202	3325.85	2.13
	Cloisite 25A	0.05	40.14	288.41	0.179	3374.97	2.09
		0.10	39.99	298.31	0.187	3360.37	2.10
		0.20	39.76	303.58	0.192	3328.50	2.11
		0.50	39.68	302.11	0.192	3339.46	2.12
		1.00	39.61	301.00	0.192	3334.81	2.13

Table 3. Morphological and thermophysical characteristics of PUR and PIR foams

Foam sample		ω / wt.%	Φ / μm	$A_{y/x}$ / a.u.	N_f / cell cm^{-3} 10^3	λ / mW m^{-1} K^{-1}	OC / %	S_m / %
PUR foam	Standard	0.00	568.32	1.12	5.58	26.41	5.62	
	Cloisite 30B	0.05	528.54	1.04	16.13	25.58	5.97	
		0.10	500.12	1.00	20.26	25.34	6.01	
		0.20	454.66	0.97	33.87	25.13	6.13	
		0.50	471.71	0.92	30.79	25.13	6.24	
		1.00	511.49	0.88	29.46	25.19	6.41	
	Cloisite 25A	0.05	539.90	1.06	15.23	25.61	6.01	
		0.10	505.80	0.99	18.47	25.40	6.13	
		0.20	471.71	0.98	32.48	25.22	6.18	
		0.50	488.76	0.91	29.46	25.23	6.29	
		1.00	522.85	0.86	27.44	25.27	6.52	
PIR foam	Standard	0.00	681.07	1.07	3.27	24.17	6.24	57.03
	Cloisite 30B	0.05	627.20	1.02	9.78	23.40	6.63	48.35
		0.10	588.72	0.95	12.36	23.17	6.68	46.22
		0.20	527.15	0.93	20.79	22.96	6.81	42.03
		0.50	550.24	0.88	18.89	22.97	6.93	42.05
		1.00	604.11	0.85	18.06	23.03	7.12	44.78
	Cloisite 25A	0.05	642.59	1.03	9.25	23.41	6.68	49.35
		0.10	596.41	0.94	11.23	23.23	6.81	47.01
		0.20	550.24	0.93	19.93	23.07	6.87	44.27
		0.50	573.32	0.88	18.06	23.06	6.99	44.61
		1.00	619.50	0.82	16.82	23.11	7.24	47.04

As a result of the introduction of the considered additives into the composition for the synthesis of PIR and PUR foams, there is a slight decrease in the apparent density of the resulting materials. Similar results confirming the decrease in the foam density with the introduction of small amounts of carbon filler were obtained by Pikhurov *et al.*[35] It is noted that the proven decrease in the apparent density of the materials under consideration can be explained by the increasing degree of stabilization of the three-dimensional polymer network.[36]

Figure 3 shows the dependence of the change in relative compressive strength on the content of organoclays in the composition.

Thus, a gradual increase in the compressive strength index of the obtained composite foams, which takes place until the mass concentration of the additive is equal to 0.2 %, subsequently this index only slightly decreases. In the case of Young's modulus, no such trend is observed: this value remains almost unchanged when the fillers considered in this work are introduced, regardless of their concentration. This pattern was previously revealed by Gibson *et al.*[37], who proved that Young's modulus does not change significantly even with a significant decrease or increase in the average size of the foam cells (the trends of parameter is described below). On the contrary, the compressive strength index is closely related to the morphology of the cellular structure, increasing with an increase of homogeneity of the spatially cross-linked polymer network.

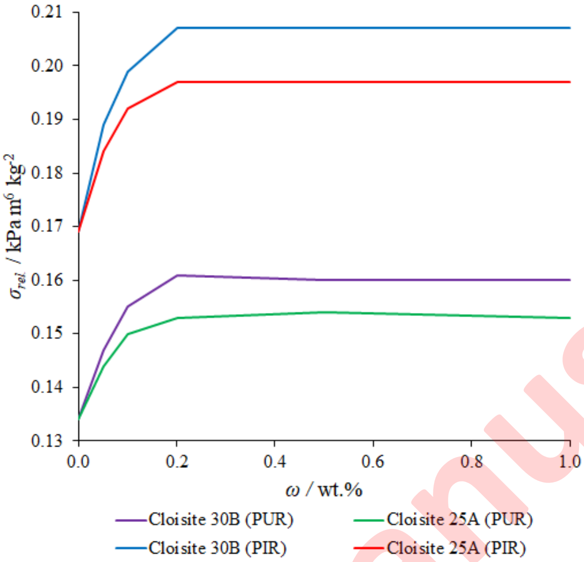

Figure 3. Dependence of relative compressive strength on filler content

The observed difference between the relative strengths of composite foams obtained using Cloisite 30B and Cloisite 25A can be explained by the presence of hydroxyl groups on the surface of Cloisite 30B particles, which contribute to a better distribution of nanosized filler particles over the emerging polymer matrix.

It is known that the strength characteristics of both PIR and PUR foams largely depend on the morphology of the cellular structure of the material.[38] Within the framework of this work, the change in the morphological characteristics of the obtained foams was analyzed using the method of scanning electron microscopy. SEM microphotographs examples are presented in Figure 4: the standard (non-filled) polyurethane and polyurethane-polyisocyanurate foams are shown in Figures A and C, respectively, microphotographs of nanocomposite foam samples (comprising 0.2 % Cloisite 30B) are shown in Figures B and D.

It should be noted that the introduction of the additives under consideration significantly affects the uniformity of the structure of the final polymer. Trends in the average cell size and cell density in the synthesized PIR and PUR foams from the content of a small amount of organoclays are shown in Figures 5 and 6.

It is important to note that the introduction of a filler significantly affects both the average cell size and their density, contributing to the formation of the cells closest in size. It is assumed that such a modification of the cellular structure of the emerging foam makes a significant contribution to the identified increase in the functional characteristics of the foam.

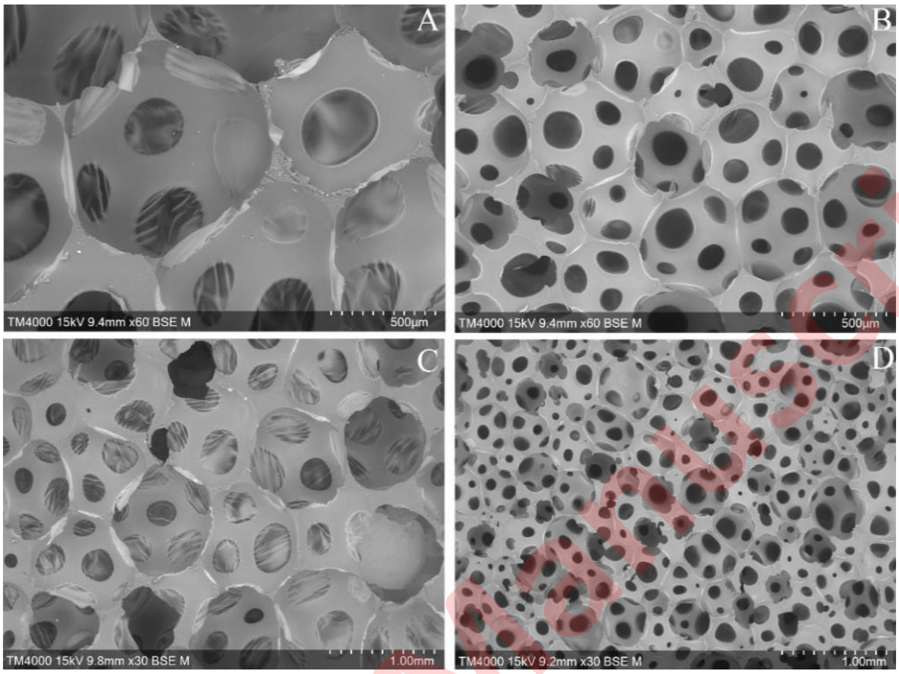

Figure 4. Microphotographs of the obtained non-composite and composite PUR (A,B) and PIR (C,D) foams

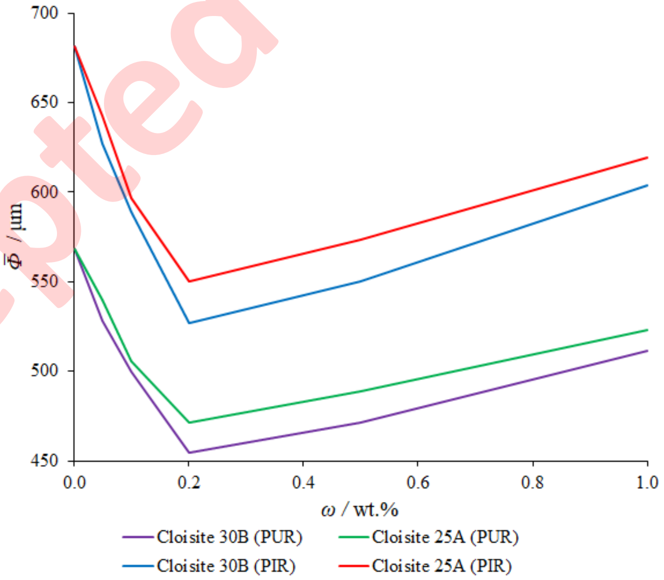

Figure 5. Dependence of the change in the average cell size of the composite foam on the content of the filler

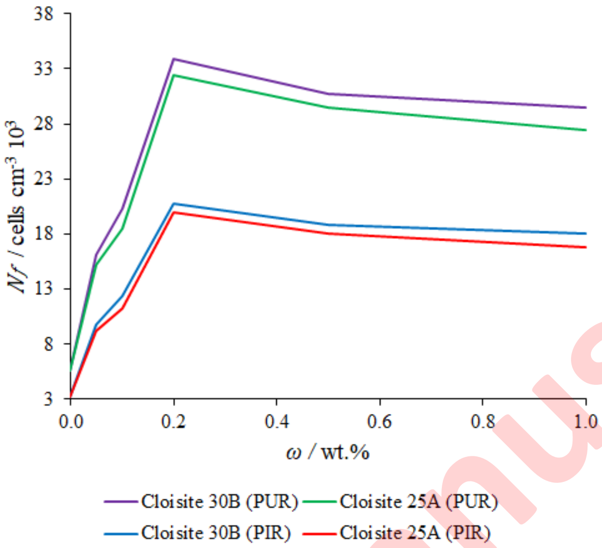

Figure 6. Dependence of cell density change in composite foams on filler content

Based on the information presented in Table 3, we failed to identify a clear dependence of the anisotropy coefficient of PIR and PUR foams on the type and concentration of the introduced fillers. Nevertheless, it is known that the introduction of such additives can lead to an increase in the anisotropy coefficient of composite foams,[39] however, an increase or decrease in this index has only a small effect on the performance characteristics of composite foams, which was proved in literature.[35]

It is important to note that in a number of studies, for example,[13,35] as a consequence of the introduction of a filler into the system, an increase in the average cell size is noted. Apparently, this trend is associated with an insufficient degree of dispersion of the solid phase during the preparation of the initial suspensions.

The dependence of the thermal conductivity of the obtained PIR and PUR foams on the content of the filler is shown in Figure 7.

Thus, when small amounts of the considered additives are introduced into the composition, a noticeable decrease in their thermal conductivity index is noted. The most noticeable decrease in this characteristic was observed in the case of PIR foams, which may be due to the better distribution of the filler in the polymer matrix. Such an effect is quite natural, since in the framework of this work, the filler was dispersed directly in the isocyanate component, the excess of which occurs during the synthesis of PIR foams.

Espadas-Escalante *et* al.[40] noted an increase in the thermal conductivity of composite foams, probably associated with an insufficient degree of homogeneity of the final suspension used for the synthesis of foams.

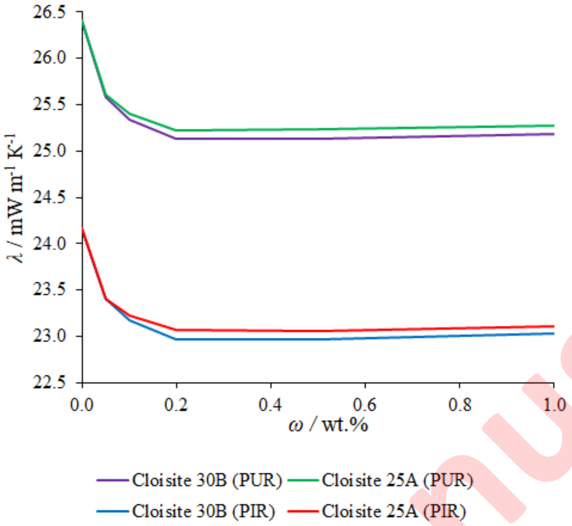

Figure 7. The dependence of thermal conductivity of composite foams from filler content

Since one of the most important characteristics of PIR foams is combustibility, the effect of fillers introduced into the composition on the stability of the final foams was evaluated by assessing the degree of damage by mass during combustion. The results obtained are shown in Figure 8.

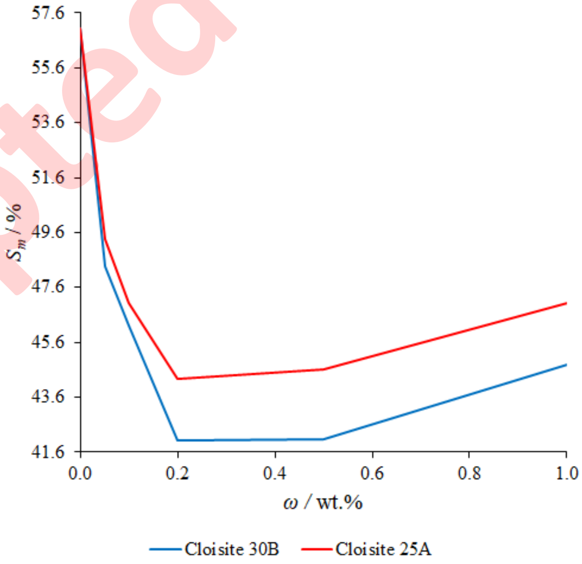

Figure 8. The dependence of damage by mass of composite foams from filler content

Based on the data presented in Figure 8, the combustibility of the analyzed PIR foams significantly decreases when small additives of the considered fillers are introduced into the composition.

The dependence of the content of open cells in PIR and PUR foams on the content of the filler is shown in Figure 9.

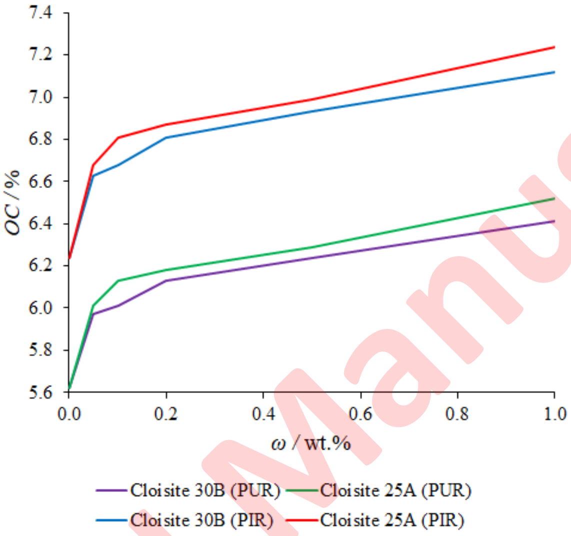

Figure 9. The dependence of the content of open cells in composite foams on the content of the filler

Thus, the content of open cells in the analyzed composite foam plastics naturally increases with an increase in the content of filler particles. However, there is an extremely low influence of this parameter on the other properties of PIR and PUR foams considered and described above. It is expected that such an increase in the content of open cells will primarily negatively affect the thermal conductivity of the synthesized foams, however, based on the above information (see Table 3, Fig. 7), the thermal insulation characteristics of the obtained foams only increase, which allows us to conclude that the degree of influence of such a small content of opened cells on other properties of the analyzed materials.

Figure 10 shows the dependence of the relative compressive strength on the average cell size of the obtained composite foams.

Thus, the relative compressive strength directly depends on the average cell size of the foams, increasing with a decrease in average cell size of the resulting foamed material. We conclude that in order to improve the strength characteristics of foam plastics, it is extremely advisable to obtain foam plastics with the best morphology of the cellular structure, including the lowest average cell size.

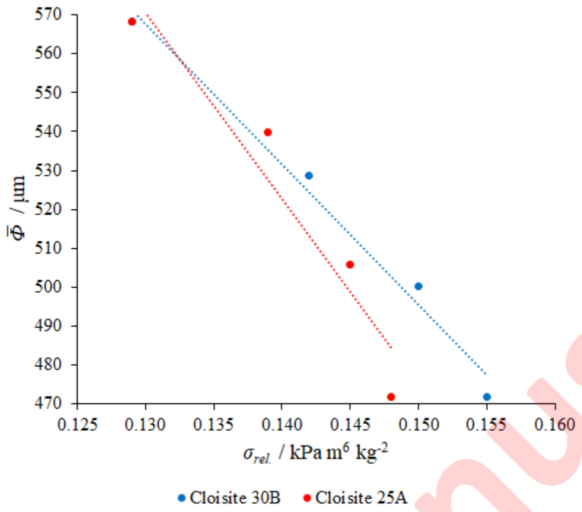

Figure 10. Dependence of relative compressive strength from the average cell size of composite foams

CONCLUSION

Thus, when using small amounts of chemically modified nanoclays (Cloisite 30B, Cloisite 25A), two series of composite polyurethane and polyurethane-polyisocyanurate foams were obtained. The main physical-mechanical, thermophysical and morphological characteristics of the synthesized materials have been studied. It is shown that the introduction of small additives of the considered fillers leads to an improvement in the main performance characteristics of PIR and PUR foams: an increase in relative compressive strength, a decrease in thermal conductivity and damage by mass during combustion. Based on the data obtained, it is expected that the use of the nanosized fillers described in the work will be appropriate in the development of new industrially used heat-insulating foams.

ИЗВОД

УТИЦАЈ НАНОГЛИНЕ НА МЕХАНИЧКА И ТОПЛОТНА СВОЈСТВА КРУТИХ ПИР И ПУР ПЕНА

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Проучн је ефекат малих током деведесетих глина нано сноге (од 0,05 до 1 %) на морфологију, максо-механичке и термофизичке стазе крутих полиуретан-полиизоцијанурата (PIR) и полиуретанске (PUR) пена. Процењени су ефекти ових адитива на структуру добијеног материјала, промену његове компресивне чврстоће, Јангов модул, губитак масе током сагоревања и топлотну проводљивост. На основу добијених резултата, констатује се да додавање малих количина (до 0,2 %) хемијски модификоване Cloisite 30B

наноглине ефикасно смањује просечну величину ћелија нанокомпозитних пена, што доводи до побољшања њихових перформанси.

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Supplementary material

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