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Synthesis and properties of SWCNT- and MWCNT-reinforced PIR and PUR foam composites

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Using small amounts of single-walled (SWCNTs) and multi-walled (MWCNTs) carbon nanotubes (CNT) (0.005 to 0.1%), rigid closed-cell composite polyurethane (PUR) and polyurethane-polyisocyanurate (PIR) foams have been synthesized. The effect of these additives on the morphological, physical-mechanical and thermophysical characteristics of the obtained materials is studied. Based on the data obtained, the addition of small amounts (up to 0.05%) of nanotubes into the foam composition leads to an increased degree of order in the cellular structure of PUR and PIR foams, improving their main thermophysical and physical-mechanical properties. The addition of CNTs leads to a slight decrease in the foams apparent density. In particular, the significant decrease in the average size and increase in cell density are observed. Such a change in the cellular structure leads to an increase in the polymer compressive strength and a decrease in its thermal conductivity. In the case of composite PIR foams, a decrease in damage by mass of the polymer during combustion is noticed.

Keywords: Carbon nanotubes, Cell morphology, Compressive strength, Polyurethane, Polyurethane-polyisocyanurate foam, Thermal conductivity

Introduction

Polyurethanes are complex polymeric materials, usually obtained by chemical interaction of liquid isocyanate and polyol components. Currently, polyurethane is one of the most large-tonnage polymeric materials. Rigid polyurethane (PUR) and polyurethane-polyisocyanurate (PIR) foams, discussed in the present paper, are mainly used as heat-insulating materials in such areas as building construction, production of household appliances and refrigeration equipment, transportation of liquefied natural gas, and pipe insulation[1,2]. In particular, these materials have found application in the thermal insulation of cryogenic tanks of spacecraft[3,4].

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 properties and are less flammable than conventional polyurethane foams. It is important to note that in the framework of the synthesis of both polyurethane and, mainly, PIR foams, a number of secondary chemical processes occur, the consideration of which is beyond the scope of this work[5,6].

Nevertheless, in some cases it is advisable to resort to using not the original polymer material, but composites based on it, in order to obtain a material with better performance characteristics. This step can be taken to achieve both an economic factor, since the use of a number of readily available fillers leads to a significant reduction in the cost of the system, and functional one, since the introduction of fillers into the polymer matrix can significantly improve the physical-mechanical, thermophysical, morphological, and other important properties of polyurethane materials[7]. This approach to the improvement of polyurethane foams properties was found more than half a century ago[8].

Today, filled PUR 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 PUR industry are chalk[9], carbon black[10], sand[11], expandable graphite[12], titanium dioxide[13], and a wide range of other oxides and inorganic salts.

It is known that an increase in the degree of dispersion of the filler introduced into the composition significantly increases the increment of the improved characteristic due to a more uniform distribution of the solid phase over the polymer network. Within the framework of this approximation, nanosized fillers and nanocomposite materials obtained on their basis are of considerable interest[14,15]. The transition from micro- to nanosized fillers significantly changes both the physical and chemical properties of polymer matrices due to a significant increase in the specific surface area of the filler.

Among relatively new nanofillers, of significant interest are carbon nanotubes (CNTs), discovered by Iijima in 1991[16]. CNTs are extremely light and strong materials that can be used to impart a wide range of different properties to a composite polymer matrix, including additional reinforcement[17]. A significant disadvantage of these additives is a high tendency to aggregation under the action of van der Waals forces due to the large surface area of filler particles. Thus, the main issue that needs to be resolved in the framework of developing a technique for the synthesis of nanocomposite polymeric materials with the addition of CNTs is the problem of aggregation of these additives. One of the most effective ways to solve this problem is ultrasonic treatment of CNT suspensions[14,18]. However, sonication conditions must be carefully optimized in order to develop a highly efficient method for producing nanocomposite polyurethane materials with improved functional characteristics, and the selection of these conditions is likely to be somewhat different for each individual composition.

It should be noted that today the greatest attention of researchers is focused on the study of composite polyurethane elastomers, coatings, dispersions, and other non-foamed materials, the addition of CNTs to the compositions of which leads to a significant increase in tensile strength and elongation at break of the resulting materials[19,20,21]. There is also a significant improvement in thermal and electrical conductivity[20,22,23,24,25], thermal stability[26] and other properties[27,28,29,30]. Polyurethane composite foams obtained using CNTs have received far less attention. In particular, we have not been able to identify any scientific publications devoted to polyurethane-polyisocyanurate (PIR) composite foams of this type, whichdetermines the relevance of this work.

Experimental Section

Materials

For the synthesis of PUR and PIR foams, a mixture of polyether polyols (H6007 (HongBaoLi PU, China) and HF-310 (Zhejiang Hengfeng New Material, China)), tris(2-chloropropyl)phosphate (Shijiazhung Hejia Chemical Products, China) as a flame retardant, a mixture of 1,1,4,7,7-pentamethyldiethylenetriamine (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, was used as the isocyanate component.

Single-walled and multi-walled carbon nanotubes were used as nanosized fillers. Single-walled carbon nanotubes (SWCNTs) Tuball produced by OCSiAl (Russia) were used. The average length of the SWNTs used was less than 5 μm, the diameter was about 1.6 nm, the total amount of impurities was <20% (<15% of the impurities are metallic inclusions).Multi-walled carbon nanotubes (MWCNTs) used were obtained from representatives of the Ulyanovsk State Technical University. The average length of used MWCNTs was 1-20 μm, outer diameter 40-60 nm, inner diameter 10-30 nm, total amount of impurities <2%.Features of the synthesis and other characteristics of MWCNTs were described in detail elsewhere [31] and remain outside the scope of this study.

Carbon nanotube suspensions

The insertion of fillers into the isocyanate component to obtain PUR and PIR foams was carried out by ultrasonic dispersion for 20 min 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 in accordance with ISO 3219-2:2021 at 25°C. Further in the work, the average viscosity values determined by analyzing three samples are given.

PUR and PIR foams preparation

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 min. After adding the required weight of isocyanate, 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 min after mixing the components, fragments were cut out from the core of the formed foams, which were subsequently used as analyzed samples.

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.

Apparent density

The determination of the apparent density of the synthesized foams was carried out in accordance with ASTM D1622, for which cubic samples of 50 mm × 50 mm ×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 at 10% linear strain in accordance with the EN 826:2013 method. 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 number 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. 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 Laser Comp Fox600 HFM and Fox200 SN instruments in accordance with UNI EN 12667:2001. The size of each sample was 200 mm × 200 mm × 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 ($\overline{\Phi}$) 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 formula (1) and the anisotropy coefficient in accordance with formula (2). Further in the paper, the averaged values of these quantities determined by analyzing five samples are given.

$$\overline{\Phi} = \frac{\sum_{i,j=1}^{m,l} \Phi_{i,j}}{m+l} \quad \text{... (1)}$$

where $\overline{\Phi}$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.

$$A_{y/x} = \frac{\dfrac{\sum_{i=1}^{m} \Phi_i}{m}}{\dfrac{\sum_{j=1}^{l} \Phi_j}{l}} \quad \text{... (2)}$$

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[33,34,35]. 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 Eq. (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.

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

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. 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, the dynamic viscosity of the resulting SWNTs and MWCNTs suspensions in the polyisocyanate component used was determined. The trend in dynamic viscosity versus filler content is shown in Fig. 1. 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 carbon nanotubes on the physical-mechanical, thermophysical, and morphological properties, samples of rigid closed-cell PUR and PIR 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 nanotube concentration of 0.01 and 0.02% and 2–3 s 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 1 and 2.

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 [36]. 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 Fig. 2: the standard (non-filled) PUR and PIR foams are shown in Fig. 2(a) and (c), respectively, and microphotographs of nanocomposite foam samples (comprising 0.05% of MWCNTs) are shown in Fig. 2(b) and (d).

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

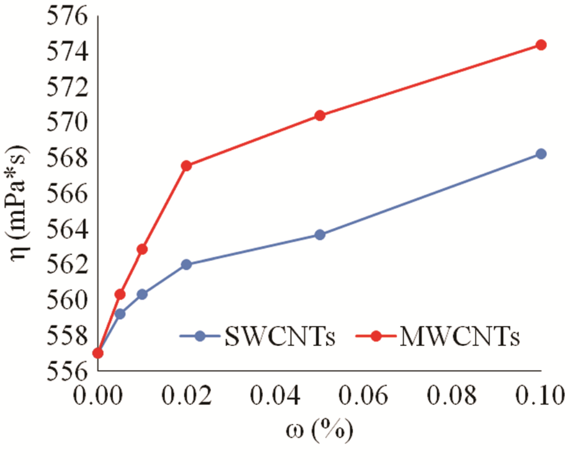

Fig. 1 — Dependence of the dynamic viscosity of the isocyanate component on filler content

Table 1 — Physical-mechanical properties of PUR/PIR foams

	Foam sample	ω (%)	γ (kg/m^3)	σ (kPa)	$\sigma_{rel.}$ (kPa*m^6/kg^2)	E (kPa)	$E_{rel.}$ (kPa*m^6/kg^2)
PUR foam	Standard (no filler)	0.000	40.35	209.71	0.129	1974.10	1.21
	SWCNTs	0.005	40.31	213.00	0.131	1994.83	1.23
		0.010	40.24	216.76	0.134	1987.33	1.23
		0.020	40.27	218.37	0.135	1997.99	1.23
		0.050	40.16	220.43	0.137	1991.67	1.23
		0.100	40.08	219.19	0.136	1988.83	1.24
	MWCNTs	0.005	40.36	214.87	0.132	1994.04	1.22
		0.010	40.28	218.90	0.135	1979.63	1.22
		0.020	40.24	223.53	0.138	1982.59	1.22
		0.050	40.13	226.84	0.141	1981.40	1.23
		0.100	40.10	224.73	0.140	1992.66	1.24
PIR foam	Standard (no filler)	0.000	40.32	266.09	0.164	3319.21	2.04
	SWCNTs	0.005	40.28	271.28	0.167	3328.17	2.05
		0.010	40.23	277.19	0.171	3335.14	2.06
		0.020	40.24	279.95	0.173	3363.02	2.08
		0.050	40.13	282.96	0.176	3385.93	2.10
		0.100	40.05	281.02	0.175	3336.14	2.08
	MWCNTs	0.005	40.33	275.35	0.169	3349.75	2.06
		0.010	40.25	282.53	0.174	3365.68	2.08
		0.020	40.21	290.86	0.180	3354.06	2.07
		0.050	40.10	296.80	0.185	3325.52	2.07
		0.100	40.07	293.02	0.182	3344.10	2.08

Table 2 — Morphological and thermophysical properties of PUR/PIR foams

	Foam sample	ω (%)	$\bar{\Phi}$ (μm)	$A_{y/x}$ (a.u.)	N_f (cell/cm^3*10^3)	λ (mW/(m*K))	OC (%)	S_m (%)
PUR foam	Standard (no filler)	0.000	568.32	1.12	5.58	26.41	5,.62	
	SWCNTs	0.005	556.95	1.09	8.48	25.87	5.73	
		0.010	539.90	1.05	11.49	25.66	5.77	
		0.020	522.29	1.06	16.80	25.60	5.84	
		0.050	503.25	1.03	20.81	25.54	5.87	
		0.100	514.90	0.95	18.92	25.57	5.98	
	MWCNTs	0.005	551.27	1.07	9.10	25.81	5.74	
		0.010	534.22	1.06	11.38	25.59	5.77	
		0.020	517.17	1.08	17.19	25.51	5.84	
		0.050	500.12	1.04	20.37	25.42	5.88	
		0.100	511.49	0.94	18.58	25.48	5.95	
PIR foam	Standard (no filler)	0.000	681.07	1.07	3.27	24.17	6.24	57.03
	SWCNTs	0.005	665.68	1.04	5.07	23.67	6.36	56.81
		0.010	642.59	1.01	6.93	23.50	6.41	55.98
		0.020	618.73	1.02	10.22	23.43	6.49	55.24
		0.050	592.95	0.98	12.71	23.36	6.52	54.82
		0.100	608.73	0.91	11.53	23.41	6.64	55.07
	MWCNTs	0.005	657.98	1.03	5.45	23.62	6.38	56.77
		0.010	634.89	1.01	6.87	23.43	6.41	56.46
		0.020	611.81	1.03	10.46	23.35	6.49	53.04
		0.050	588.72	1.00	12.43	23.28	6.53	52.33
		0.100	604.11	0.90	11.32	23.31	6.60	52.94

results confirming the decrease in the foam density with the introduction of small amounts of carbon filler were obtained by Pikhurov[37]. 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 [38].

Fig. 3 shows the dependence of the change in relative compressive strength on the content of carbon nanotubes in the composition. There is a gradual increase in the compressive strength index of the obtained composite foams is observed This takes place until the mass concentration of the additive is equal to 0.05%, 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

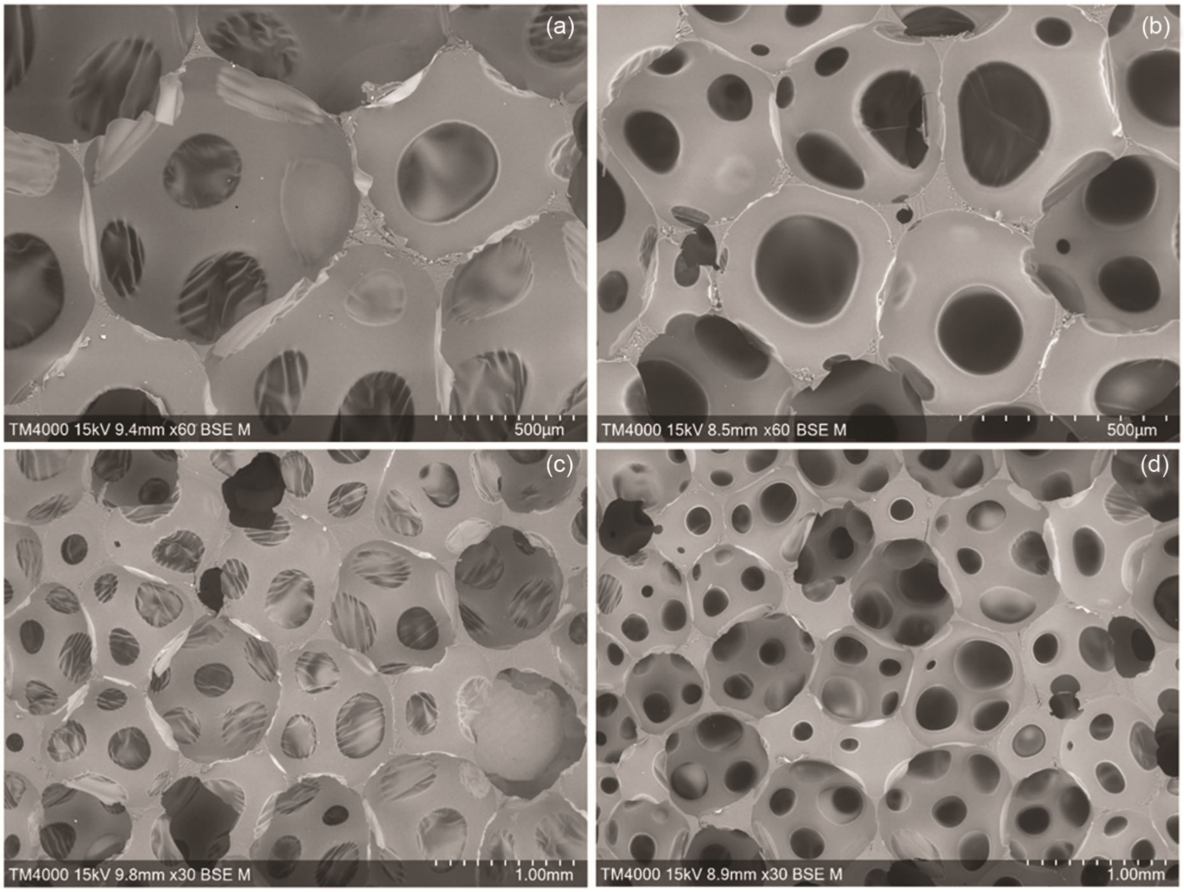

Fig. 2 — Microphotographs of the obtained non-composite and composite PUR (A, B) and PIR (C, D) foams

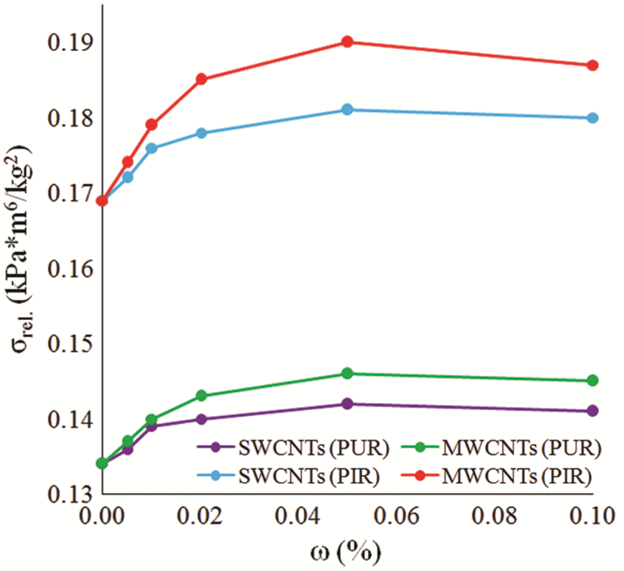

Fig. 3 — Dependence of relative compressive strength on filler content

pattern was previously revealed by Gibson and Ashby[39], 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.

It is important to note 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 carbon nanotubes are shown in Figs 4 and 5.

The introduction of the filler significantly affects both the average cell size and cell density, contributing to the formation of the cells closest in size. In particular, the addition of 0.05% of MWCNTs into the PIR foam composition has led to a decrease

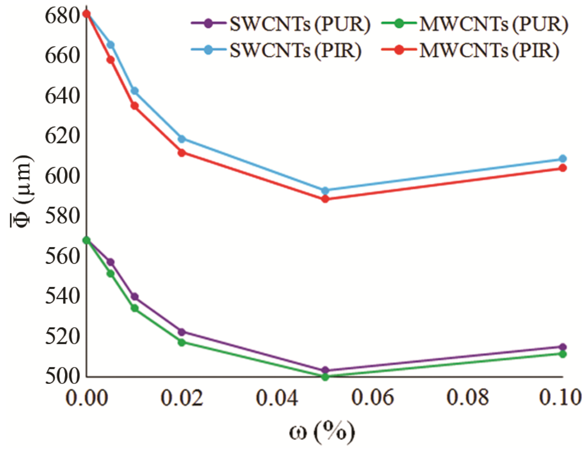

Fig. 4 — Dependence of the change in the average cell size of the composite foam on the content of the filler

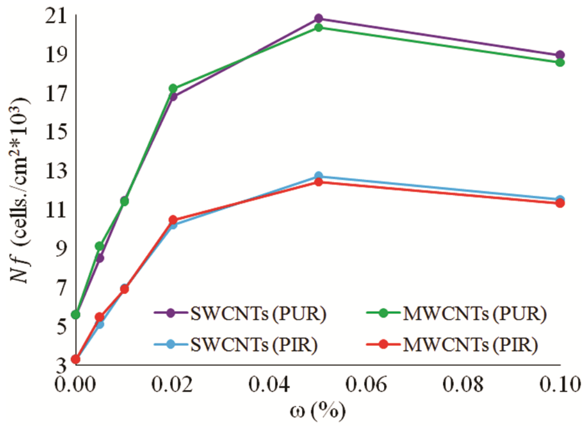

Fig. 5 — Dependence of cell density change in composite foams on filler content

in the average cell size by 13.6%. It is assumed that such a modification, which makes it possible to obtain a more uniform and fine-cell stable structure during the foam formation, makes a significant contribution to the identified increase in the functional characteristics of the foam.

It is important to note that in a number of studies, for example[37,40], 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 and a high degree of agglomeration of the filler particles.

Based on the information presented in Table 2, 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[41], however, an increase or decrease in this index has only a small effect on the performance characteristics of composite foams, which was proved by Pikhurov[37].

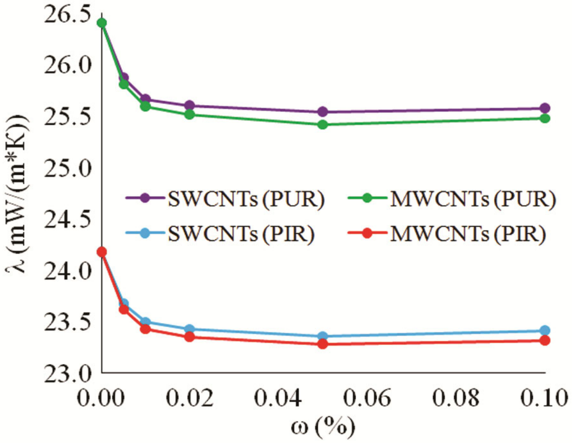

Fig. 6 — The dependence of thermal conductivity of composite foams from filler content

The dependence of the thermal conductivity of the obtained PIR and PUR foams on the content of the filler is shown in Fig. 6. 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. It is known that the introduction of CNTs into compositions for the production of polymeric materials contributes to an increase in their thermal conductivity, however, in this case, the opposite effect was observed, probably achieved due to a significant decrease in the average cell size of the resulting foams. When small amounts of nanotubes are introduced into the formulation, a sharp decrease in the thermal conductivity of the foam occurs due to significant changes in the polymer cellular structure morphology. Within the considered concentration range, with a further increase in the CNTs content in the composition, the thermal conductivity parameter of the resulting material reaches a plateau and does not undergo significant changes. It is important to note that with a

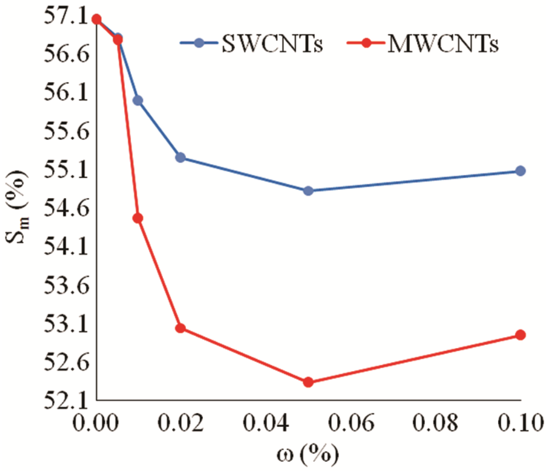

Fig. 7 — The dependence of damage on the mass of composite foams from filler content

further increase in the content of CNTs, a corresponding increase in the thermal conductivity index should be expected.

Espadas-Escalante *et al.*[42] 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 foam materials.

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 Fig. 7. Based on the data presented in Fig. 7, 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 Fig. 8. Thus, the number 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 2, Fig. 6), the thermal insulation characteristics of the obtained foams only increase, which allows us to conclude that the degree of influence of such a small number of opened cells on other properties of the analyzed materials.

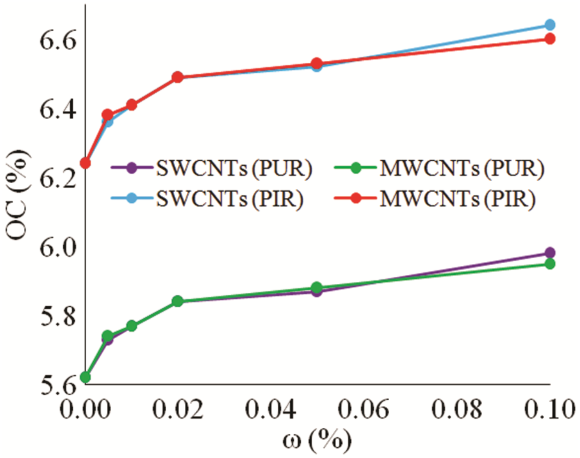

Fig. 8 — The dependence of the content of open cells in composite foams on the content of the filler

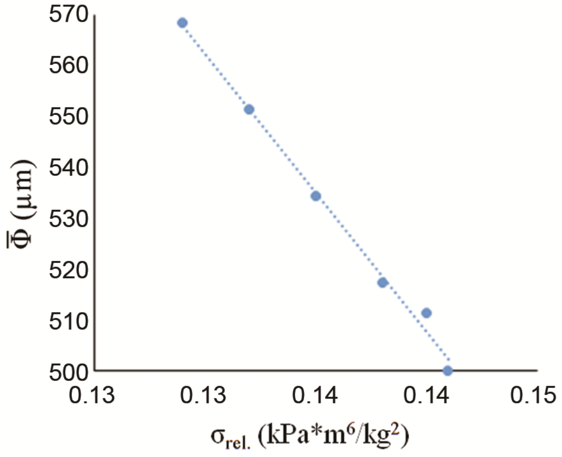

Fig. 9 — Dependence of relative compressive strength of MWCNT-PUR from the average cell size of composite foams

Fig. 9 shows the dependence of the relative compressive strength on the average cell size of the obtained composite foams. Here we note that the relative compressive strength directly depends on the average cell size of the foams. The strength increases significantly with a decrease in the average cell size. Similar results for non-filled compositions were obtained by Brondi *et al.*[32]. 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.

Conclusion

Two series of composite polyurethane and polyurethane-polyisocyanurate foams were obtained by using small amounts of single- and multi-walled carbon nanotubes,. 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. It is expected that the usage of chemically modified nanotubes will make it possible to obtain foams with better performance characteristics achieved due to a better distribution of nanosized filler particles over the emerging polymer matrix of the resulting foam. This issue is planned for further study.

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