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Composites Based on Polyurethane and Modified Petroleum Asphaltenes

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Abstract. In this work, polyurethane composites with petroleum asphaltenes and their modified derivatives have been obtained and studied. The changes in the mechanical and thermal characteristics of polyurethane composites depending on the content of asphaltene fillers in concentrations of 1 and 2.5 wt% are shown. The distribution of native and modified asphaltenes in the polymer matrix was assessed using the X-ray power diffraction method. Composites with native asphaltenes and asphaltenes bearing amino groups showed the best performance in terms of distribution homogeneity in the matrix of polyurethane obtained from 2,4-toluylene diisocyanate (TDI) and polyethylene glycol adipate. It has been shown that the use of carboxylated (CA) and sulfonated (SA) asphaltenes in polyurethane composites leads to incomplete curing of the polymer. A significant decrease in the strength and elongation at break, as well as an increase in material hardness, was recorded for a composite containing 2.5 wt% of sulfonated asphaltene. The use of aminated asphaltenes makes it possible to increase the elongation at break due to additional interaction with TDI at the production of polyurethane composites. Composites with native and sulfonated asphaltenes showed the best thermal stability.

Keywords: asphaltenes, chemical modification, composite, polyurethane, PEGA, TDI, properties.

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Композиты на основе полиуретана и модифицированных нефтяных асфальтенов

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Аннотация. В работе получены и исследованы полиуретановые композиты с нефтяными асфальтенами и их модифицированными производными. Показаны особенности изменения механических и термических характеристик полиуретановых композитов в зависимости от содержания асфальтеновых наполнителей при степени наполнения 1 и 2.5 мас.%. Распределение нативных и модифицированных асфальтенов в матрице полимера оценивалось с помощью метода порошковой рентгеновской дифракции. Композиты с нативными асфальтенами и асфальтенами, включающими аминогруппы, продемонстрировали лучшие показатели по однородности распределения в матрице полиуретана, полученного из 2,4-толуилендиизоцианата (ТДИ) и полиэтиленгликольадипината. Показано, что использование карбоксилированных СА и сульфированных SA асфальтенов в полиуретановых композитах приводит к неполному отверждению полимера. Значительное снижение показателей прочности и растяжения при разрыве, а также возрастание твердости материала зафиксировано для композита с 2.5 мас.% сульфированных SA асфальтенов. Использование аминированных асфальтенов позволяет увеличить показатель растяжения при разрыве за счет дополнительного взаимодействия с ТДИ при получении полиуретановых композитов. Композиты с нативными и сульфированными SA асфальтенами продемонстрировали наилучшую термостабильность.

Ключевые слова: асфальтены, химическая модификация, композиты, полиуретаны, ПЭГА, ТДИ, свойства.

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Introduction

Petroleum asphaltenes are perspective fillers in polymer industry due to their structural features and characteristics, as well as high resource potential [1]. Investigation of asphaltenes as fillers of various polymers revealed their ability to improve mechanical and rheological characteristics, protect the composites against UV radiation, and inhibit thermal oxidative destruction [2–6]. In this case, the compatibility of asphaltenes with the polymer matrix is a decisive factor, which determines the characteristics of polymer composites.

The dispersion of polymer-asphaltene composites for the asphaltenes with diverse polarity was studied at mixing with a wide range of polymer matrices (PP, PS, PC, and PMMA) [2]. The authors identified that more polar asphaltenes provide better dispersion in the polymers with a higher parameter of polar solubility, which is related to the higher affinity between the matrix and filler with identical polarity. The authors of the work [4] determined that asphaltenes acquire and, then, lose solubility in the polymer during high-temperature curing of epoxy resin and form fine reinforcing particles, which significantly increase the strength of the cured polymer. Han et al. [5] showed that homogeneous dispersion of fractal aggregates is firstly formed at the asphaltene content of 1 % in epoxy resin and that they are consolidated into the network microstructure with an increase in concentration, which leads to the nonuniform distribution in the matrix. Wu and Kessler [6] functionalized asphaltenes with silane derivatives and used them as a reinforcing filler in the epoxy resin. This led to a more remarkable increase in the Young's modulus associated with enhancement of phase interaction of functionalized asphaltenes and epoxy matrix. Diverse characteristics of polyurethanes (PU) affected nearly all fields of materials science, from shoes to aircraft coatings [7]. However, there are yet no data on the compatibility of polyurethanes with petroleum asphaltenes and no studies on the polyurethane–asphaltene composites.

In this work, investigations of polyurethane composites with petroleum asphaltenes and their modified derivatives including active functional groups were carried out. In the case of PU composites, mechanical and thermal characteristics, as well as distribution of native and modified asphaltenes in the polymer matrix were studied.

Experimental

Materials

The PU from poly(ethylene glycol adipate) (PEGA) with $M=1950$ g/mol of OMA-1950 brand produced by ООО “Kazanskii zavod malotonnazhnoi khimii” and toluene-2,4-diisocyanate (TDI) (Sigma Aldrich) were prepared. The NCO/OH ratios of 1.6/1 and 0.2 wt% of 2,4,6-tris(dimethylaminomethyl) phenol curing agent were employed. After mixing and degassing, the mixture was transferred to the mold and cured at 80°C for 72 h. The samples were maintained for 14 days before measurement of properties.

The PEGA and asphaltenes were physically blended at a mixing speed of 200 rpm at 80 °C for 60 min to facilitate homogenous melt-compounding. The PU composites with 1 and 2.5 wt% native and modified asphaltenes were prepared.

Methods and equipment

Native asphaltenes (A) were extracted from the heavy petroleum of Ashalchinskoye field by precipitation using 20-fold excess of hexane, followed by filtration and extraction by hexane from coprecipitated resins and oils in a Soxhlet apparatus.

Amine derivatives of asphaltenes (AA) were obtained as follows. To the mixture of concentrated sulfuric and nitric acid (20 mL/10 mL), 2 g of asphaltenes was gradually added at stirring. The temperature of the mixture (15–20°C) was maintained for 2 h. Then, excess distilled water was added, the product was filtered and washed until neutral pH and dried at room temperature for 72 h. The product of reaction, nitroasphaltenes (NA), was obtained with the yield of 2.43 g. Then, NA asphaltenes were reduced to AA asphaltenes. For this purpose, 2 g of asphaltenes NA was added at stirring to the mixture of 2.6 g of elemental sulfur to the solution of Na₂S·H₂O (19.5 g Na₂S in 20 mL H₂O) warmed to 70–75 °C. The reaction mixture was maintained for 30 min and cooled to room temperature. Solid AA product was filtered, washed with distilled water up to neutral pH, and dried at room temperature for 72 h (W= 86 wt% –1.71 g).

Sulfonated asphaltenes (SA) were obtained as follows. A portion of asphaltenes (1 g) was dissolved in 100 ml of benzene until complete dissolution and formation of a homogeneous solution. Then a 20-fold excess of sulfuric acid, concentrated by weight, was poured and sulfonation was carried out at a temperature of 80 °C for 4 hours. Afterwards, an excess of water was added and the product was filtered off and dried (W= 120 wt% – 1.2 g).

Carboxylated asphaltenes (CA) were obtained as follows. A total of 2 g of asphaltenes was dissolved in a three-necked flask in 100 mL of toluene (distilled over P₂O₅). Then, 1.5 g maleic anhydride (MA) was added at stirring on a magnetic stirrer under nitrogen flow, and the reaction mixture was refluxed for 8 h at 110 °C. After completion of reaction, toluene was distilled and the residue was washed with acetone on the filter to remove unreacted MA. The asphaltenes-maleic anhydride (AMA) product was dried (W=96 wt% – 1.93 g). After that, 1.5 g of AMA was hydrolyzed by refluxing with reflux condenser in aqueous NaOH (10 wt%) for 3 h until the suspension was dissolved. The reaction mixture was cooled and the CA product was precipitated by adding aqueous HCl (1M). The product was washed with diluted HCl and water and dried in furnace (W=98 wt% – 1.47 g).

Elemental composites of samples was determined using a CHNS-O Euro EA3028-HT-OM analyzer (EuroVector, Italy).

FTIR spectra of samples were recorded in the range of 4000–400 cm⁻¹ on a Vector-22 IR-Fourier spectrometer (Bruker, Germany) with the optical resolution of 4 cm⁻¹. Samples were prepared in tablets with KBr (Acros Organics 206391000).

Tensile strength (TS) and Elongation at break (ε) of the composites were determined according to ISO 527–2:2012 on a Test tensile machine.

The hardness of the PU samples was determined using Shore-D durometer, model TBP-D, according to ISO 868:2003.

The thermal degradation of samples was investigated by TGA using a thermogravimetric instrument STA 449F3 (NETZSCH–Gerätebau GmbH, Germany). An amount of 10–20 mg of sample was heated from 30 up to 500 °C under an argon atmosphere (flow of 50 mL/min) with a heating rate of 10K/min. High purity argon was applied at a gas flow rate of 50 ml/min.

Powder X-ray diffraction measurements were performed on a Bruker D 8 Advance diffractometer equipped with Vario attachment and Vantec linear PSD, using Cu radiation (40 kV, 40 mA) monochromated by the curved Johansson monochromator (λ Cu $K_{\alpha 1}$ 1.5406 Å). Room-temperature data were collected in the reflection mode. Samples in the form of 2mm thick plate were placed on a poly(methyl methacrylate) plate and fixed in a standard sample holder, which was kept spinning (15 rpm) throughout the data collection. Patterns were recorded in the 2θ range between 3° and 80°, in 0.008° steps, with a step time of 0.1–1.0s. For each of the samples several diffraction patterns were obtained with different data acquisition times. Processing of the obtained data performed using EVA software packages [EVA v.11.0.0.3. User Manual. SOCABIM 2005].

Results and discussion

Modification of asphaltenes

Petroleum asphaltenes represent a mixture of polycyclic aromatic hydrocarbons with various O-, S-, and N-functional groups and side alkyl chains. The composition and content of functional groups in asphaltenes could vary significantly depending on their source. Modification of asphaltenes could increase the number of functional groups capable of covalent binding to the active isocyanate group TDI during the synthesis of PU.

AA asphaltenes were prepared according to the modified procedure described in [8]. As a result of modification, a notable increase in the nitrogen content was recorded in the products (Table 1). In IR spectrum of the NA product, the bands of nitro groups appeared at 1344, 1537, 1648 cm^{-1} (C-NO₂ aromatic), and 834 cm^{-1} (C-NO₂ aliphatic); those of nitroso groups appeared 1277 cm^{-1} and those of carbonyl groups appeared at 1719 cm^{-1} . After reduction, the AA product showed the appearance of the bands at 3359 (free), 3223 (associated), and 1596 cm^{-1} , which is intrinsic for stretching and bending vibrations of N-H group in amines.

SA asphaltenes were prepared by exposure of concentrated sulfuric acid on native asphaltenes dissolved in benzene. As a result, there is oxidation and sulfonation of molecules of asphaltenes and a notable increase in sulfur and oxygen contents (Table 1). In IR spectra of the SA product, the vibration

Table 1. Elemental composition of samples

Samples	Contents elements, wt%					H/C
	C	H	N	S	O*	
A (native)	80.85	8.29	1.41	7.30	2.15	1.23
NA	58.20	5.56	6.42	5.50	24.32	1.15
AA	62.14	6.63	4.87	6.27	20.09	1.28
SA	65.95	6.57	1.10	10.87	15.51	1.19
CA	79.34	8.20	1.30	6.81	4.35	1.24

*oxygen concentration was calculated as a difference between 100 % and the sum of the concentrations of the other elements

bands of sulfonic acid RSO_3H (1171 cm^{-1}), alcohol or phenol C-O (1225 cm^{-1}) and carboxylic groups C=O (1701 cm^{-1}) appeared, and the band intensity of sulfoxide groups S=O (1032 cm^{-1}) increases due to the oxidation of native sulfur in asphaltene molecules [9].

CA asphaltenes were synthesized according to the procedure from [10] by the reaction of asphaltenes with maleic anhydride (MA) and subsequent hydrolysis of the product. In IR spectrum of the CA product, the absorption bands of carboxylic groups appeared at $1782\text{--}1703\text{ cm}^{-1}$ (C=O) and 1222 cm^{-1} (C-O), which indicates the addition of MA to polyaromatic core of asphaltenes.

Modification of asphaltenes always results in a significant increase in oxygen content due to oxidation processes that run in parallel to main processes. The functional groups formed at the polyaromatic core of asphaltene molecules could form chemical bonds with TDI during the synthesis of PU, which can enhance phase adhesion of components and alter characteristics of the produced materials.

Mechanical and physical properties

Polyurethane condensation polymers do not have repeating identical monomer units and consist of different segments linked by various chemical bonds. Most important unit of these polymers is urethane bond ($-\text{NH}-\text{COO}-$), which is formed during the reaction of isocyanate group ($-\text{N}=\text{C}=\text{O}$) with alcohol group of polyols. In addition to two principal raw materials (polyols and isocyanates), the fillers, which increase hardness, tensile strength, and thermal stability and make the composite material cheaper, are often used [11, 12].

The effect of fillers on composite characteristics depends on their concentration, particle size and shape, as well as interactions with matrix. Inert fillers are not involved in curing of polyurethane and do not alter the NCO-to-OH ratio. When there are functional groups on the filler surface (hydroxyl, carboxylic, amino groups, and others), which are reactive towards isocyanate groups, there is additional covalent binding and crosslink. However, active filler can have a different impact on the composite characteristics in reactive systems depending on its effect on the curing process. If particles react with matrix, they can form strong bonds and increase strength, as well as affect stoichiometry and lead to incomplete curing. When the filler inhibits curing, the matrix around particles would possess a lower degree of curing and, consequently, lower mechanical characteristics.

As follows from Table 2, addition of fillers to PU decreases mechanical characteristics (TS and ϵ) to a different extent and slightly alters hardness values of the polymer. A notable decrease in tensile strength and tensile failure values was recorded in the case of the specimen filled with 2.5 wt% of SA asphaltenes, while the Shore D hardness increases almost by the factor of three. Addition of 1 wt% of SA asphaltenes increases the hardness of PU composite by the factor of 1.6; however, tensile strength and elongation at break values change to a lower extent relative to pure PU.

Abrupt changes in the properties of PU can be caused by a change in the degree of crosslinking. To evaluate the degree of curing, we carried out swelling tests in toluene over 72-h period (Fig. 1).

The degree of swelling was calculated using equation $\frac{\omega_1 - \omega_0}{\omega_0} * 100\%$ as the mass ratio of swollen

polymer ω_1 and the specimen before swelling ω_0 in the case of PU and its composites with 2.5 wt%

Table 2. Mechanical properties of samples

Samples	Shore D Hardness	TS, MPa	$\epsilon, \%$
PU	17.8	35.5	892
PU + 1 wt% A	18.3	23.9	757
PU + 2.5 wt% A	19.8	24.0	795
PU + 1 wt% AA	17.5	26.0	879
PU + 2.5 wt% AA	16.5	22.0	940
PU + 1 wt% SA	27.7	24.8	723
PU + 2.5 wt% SA	52.7	8.9	10
PU + 1 wt% CA	17.8	22.6	775
PU + 2.5 wt% CA	18.1	22.7	787

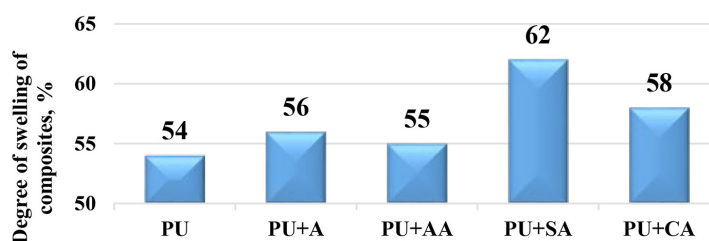


Fig. 1. Degree of swelling of PU and PU composites with 2.5 wt% fillers

of modified asphaltenes. Due to the fact that a lower degree of swelling indicates better curing, it is evident that the specimens filled with 2.5 wt% SA and CA asphaltenes are isolated in the less cured form, while the results vary within the measurement error in the case of other specimens.

Fig. 2 presents TGA and derivative thermogravimetry (DTG) curves of the pure PU and PUs composites with 2.5 wt% fillers. Thermal stability study of PU and its composites using TGA technique in inert argon atmosphere showed that addition of native and modified asphaltenes affect marginally the thermal stability of the specimens, except for the composites with AA asphaltenes. PU composites

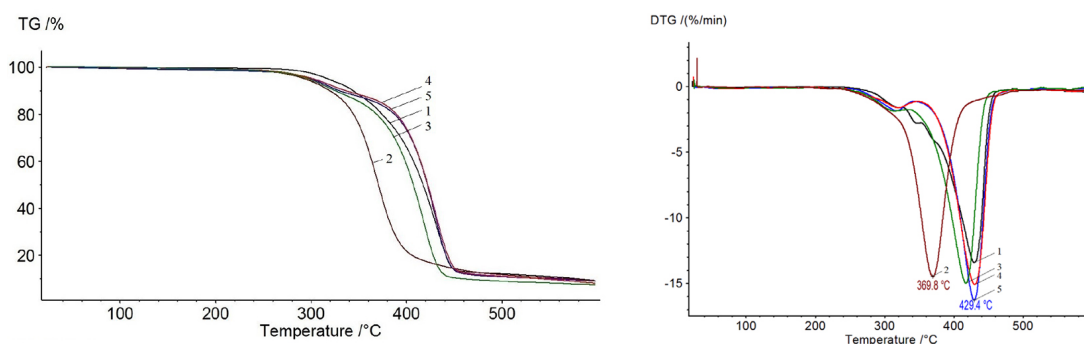


Fig. 2. TG and DTG curves of the PU (black (1)) and composites with 2.5 wt% AA (brown (2)), CA (green (3)), SA (red (4)), A (blue (5)) asphaltenes

Table 3. The temperature of 5, 10 and 50 % weight loss of samples according TGA

Samples	T _{5%} [°C]	T _{10%} [°C]	T _{50%} [°C]
PU	318.1	344.0	417.3
PU + 1 wt% A	307.3	337.8	419.9
PU + 2.5 wt% A	300.3	329.7	421.8
PU+1 wt%AA	301.9	327.0	381.5
PU+2.5 % AA	294.1	319.6	370.5
PU + 1 wt% SA	300.8	329.9	423.9
PU + 2.5 wt% SA	303.0	336.3	422.2
PU + 1 wt% CA	307.3	325.0	408.7
PU + 2.5 wt% CA	297.7	325.5	407.1

show a lower thermal stability at the earlier stage (T_{5%} and T_{10%}) as compared to pure PU; however, the composites with native A and modified SA asphaltenes demonstrated opposite trend at higher temperature (T_{50%}) (Table 3). The good thermal stability of composites with SA asphaltenes seems to be related to the post-curing of the composite under conditions of increasing temperature during TGA. A significant decrease in thermal stability was recorded for the PU composites filled with AA asphaltenes, which is related to the presence of a larger number of biuret bonds possessing lower temperature of destruction as compared to urea and polyurethane bonds [13].

X-ray powder diffraction studies

A series of polyurethane composites with native and modified asphaltenes A, AA, SA and CA were studied by powder X-ray diffraction; the obtained experimental diffraction patterns of the samples are shown in the Fig. 3–7. For comparison, an analysis of the phase state of the original polyether urethane PU and individual asphaltenes A, AA, SA, and AC was preliminarily carried out. As can be seen from the diffraction pattern of original polyurethane (blue curve in Fig. 3) broadened peaks are observed in the range of 2θ angles of 20.5° and 43°, which indicates an amorphous structure of the sample under study.

For asphaltene samples, typical diffraction patterns are observed with two adjacent diffuse peaks in the region of diffraction angles 2θ 16–19° and 25–27°, which are usually correlated with the contributions to the diffraction of more or less ordered aliphatic and aromatic components of asphaltene, respectively [14, 15]. A qualitative analysis of the diffraction patterns presented in Figure 3 indicates that the content and nature of the distribution of the components are somewhat different for pairs of asphaltenes – asphaltenes SA, AA and asphaltenes A, AC.

Fig. 4a shows experimental diffraction patterns for samples of pure polyurethane, and polyurethanes modified with native asphaltenes at its content of 1 wt% and 2.5 wt%. As a comparison of the diffraction patterns shows, the introduction of the native asphaltenes did not lead to noticeable structural changes in the modified polyurethane in both cases. Samples with 1 wt% and 2.5 wt% asphaltenes are also amorphous, and the invariance of the shape of the amorphous halo testifies in favor of the assumption of a homogeneous distribution of asphaltenes molecules in the polymer matrix. This is also evidenced by the uniform black color of the obtained samples of the modified polyurethane (Fig. 4b).

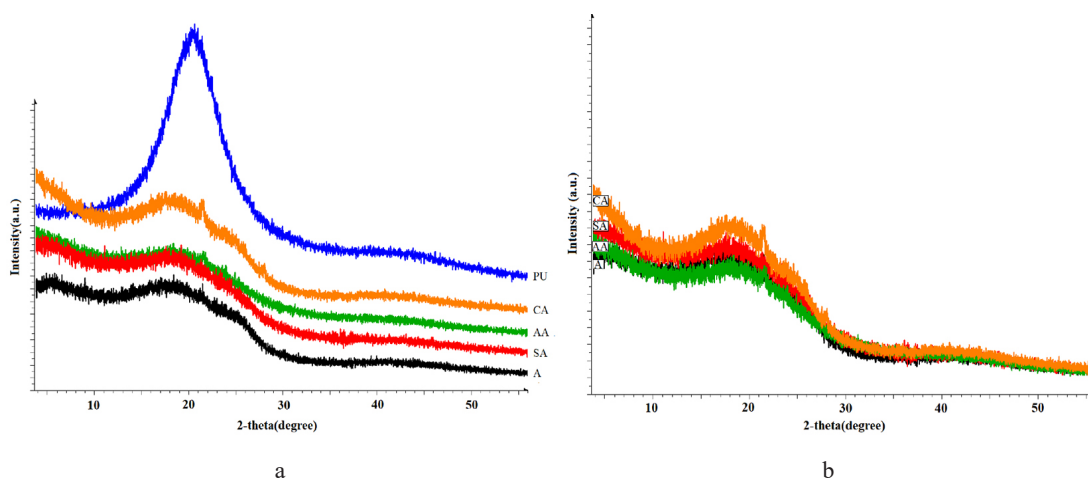


Fig. 3. Experimental powder diffraction patterns for samples: initial PU (blue curve) and asphaltenes A (black curve), SA (red curve), AA (green curve) and CA (orange curve): (a) for clarity, the curves are shifted relative to each other along intensity axes; (b) X-ray diffraction patterns of four asphaltene samples are conditionally superimposed on each other

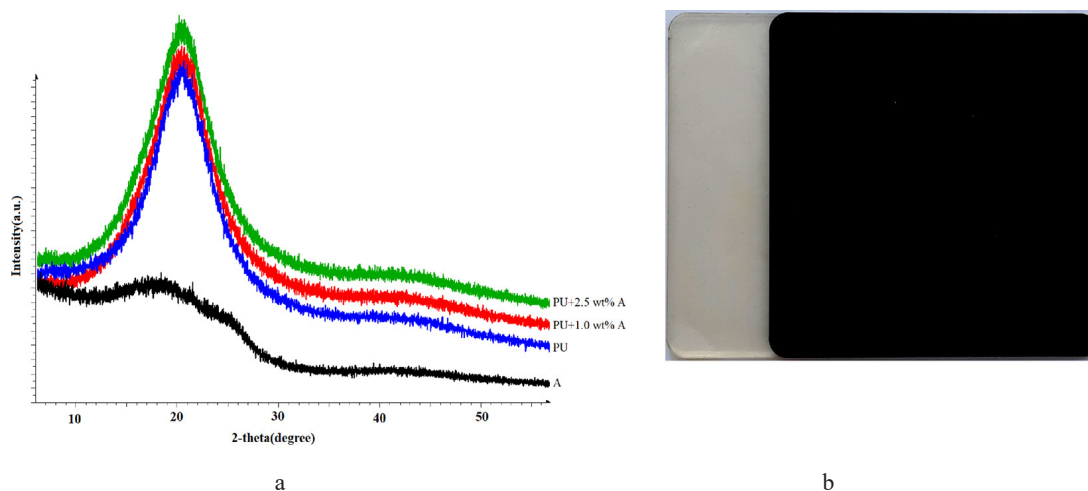


Fig. 4. Experimental powder diffraction patterns for samples (from bottom to top): native asphaltene A (black curve), original PU (blue curve) and samples of polyurethanes modified with native asphaltene at its content of 1 % (red curve) and 2.5 % (green curve): (a) for clarity, the curves are shifted relative to each other along the intensity axis; (b) photo of clarity PU and PU composite with 2.5 % wt. native asphaltene A

A similar picture is observed for polyurethane samples modified with different amounts of asphaltene AA (Fig. 5). The curves for both modified samples have two broadened peaks, which indicates their amorphous structure.

For polyurethane samples modified with asphaltene CA, the powder diffraction patterns (Fig. 6) show a number of weak interference peaks corresponding to the crystalline phase. Comparison of the obtained diffraction patterns with the experimental diffraction pattern for pure crystallized polyester indicates that the crystalline component in both modified polyether urethanes is the crystalline

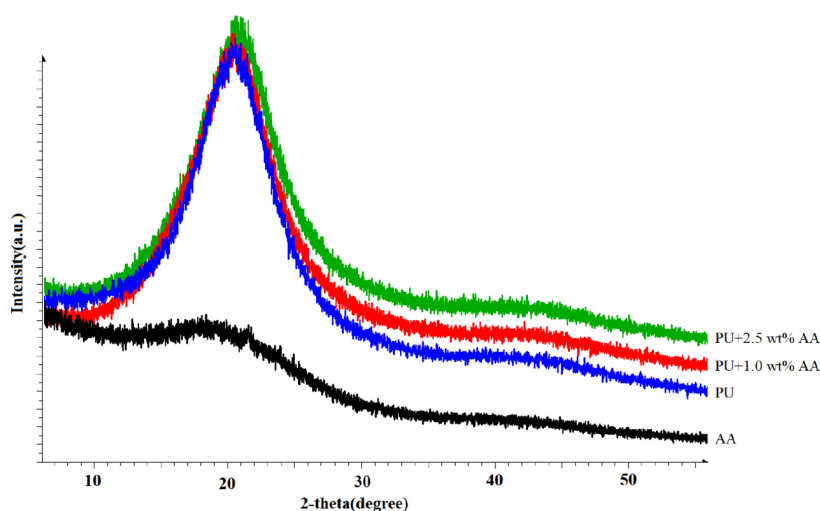


Fig. 5. Experimental powder diffraction patterns for samples (from bottom to top): modified asphaltenes AA (black curve), initial polyurethane (blue curve) and samples of polyurethanes modified with asphaltenes AA at its content of 1 % (red curve) and 2.5 % (green curve). For clarity, the curves are shifted relative to each other along the intensity axis

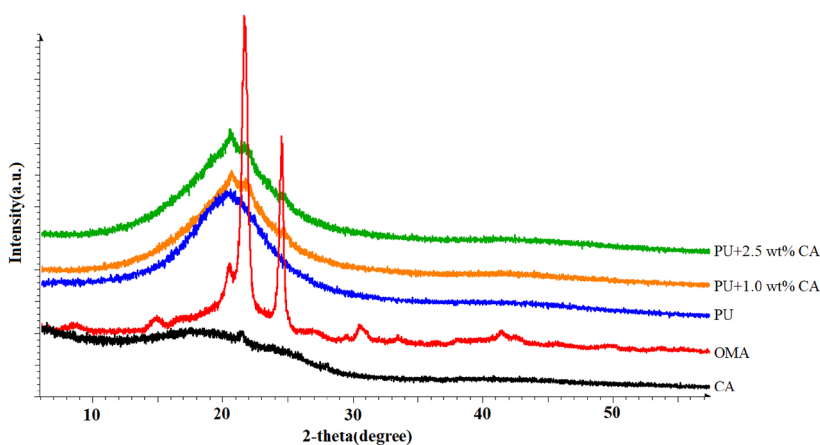


Fig. 6. Experimental powder diffraction patterns for samples (from bottom to top): modified asphaltenes CA (black curve), original polyester (OMA) (red curve), original PU (blue curve) and samples of polyurethanes modified with asphaltenes CA at its content of 1 % (orange curve) and 2.5 % (green curve). For clarity, the curves are shifted relative to each other along the intensity axis

phase of polyester. For these samples, the degree of crystallinity was calculated, which turned out to be 3.5 % and 2.9 %, respectively.

The experimental curves for a series of samples of polyurethane modified with asphaltenes SA are shown in Fig. 7. For this series of samples, it was unexpected that with an asphaltene SA content of 2.5 wt% in the modified polyurethane, a high degree of crystallization of the polyester component is observed, while at asphaltenes content of SA of 1 %, no signs of crystallinity are observed at all. For a sample of modified polyurethane with asphaltenes SA content of 2.5 wt%, using the TOPAS program, the degree of crystallinity was calculated, which turned out to be 65.3 %. The asphaltenes phase itself

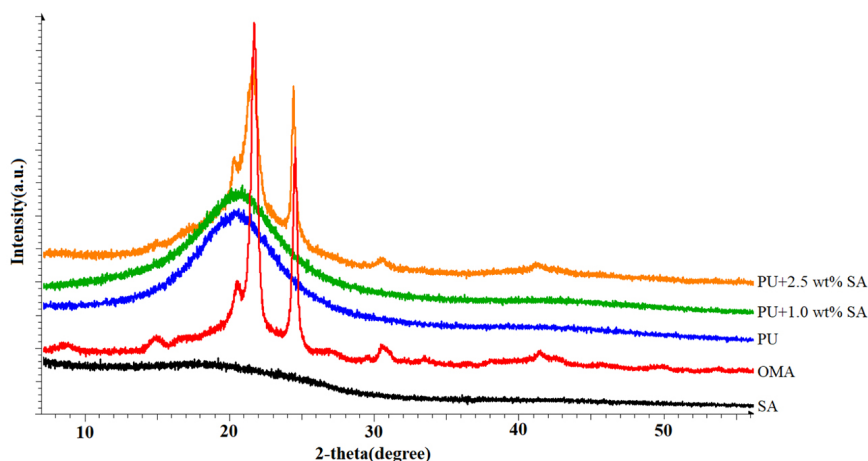


Fig. 7. Experimental powder diffraction patterns for samples (from bottom to top): asphaltenes SA (black curve), original polyester (OMA) (red curve), original PU (blue curve) and samples of polyurethanes modified with asphaltenes SA at its content of 1 % (green curve) and 2.5 % (orange curve). For clarity, the curves are shifted relative to each other along the intensity axis

does not manifest itself in any way on the diffractograms due to its nanostructured nature even in the initial state.

Conclusion

Thus, the introduction of native or modified asphaltenes in concentrations of 1 and 2.5 wt% into the polyurethane matrix does not lead to the separation of these components into individual phases, but most likely leads to their homogeneous distribution in the polymer matrix, which is reflected in the absence of visible manifestations of their contribution into the overall diffraction pattern. At the same time, in several cases of modification, namely, in the modification of polyurethanes with carboxylated or sulfonated asphaltenes, this process is accompanied by crystallization of the oligoether component of polyurethane, which indicates the degree of crosslinking of the material. The low degree of crosslinking for polyurethanes containing 2.5 wt% of sulfonated asphaltenes leads to a significant reduction in mechanical properties and an increase in the hardness of the composite. An interesting fact is the improvement in the thermal stability of the composite with sulfonated asphaltenes relative to pure polyurethane, which can be explained by post-curing of the composite at high temperatures in TGA experiment. On the contrary, the decrease in the thermal stability of the composite with asphaltenes containing amino groups is associated with the formation of biuret bonds, which have a low temperature of destruction compared to urea and urethane bonds. Nevertheless, the active binding of the amino groups of asphaltenes with isocyanate moieties during polyurethane polymerization leads to an improvement in the elongation at break compared to pure polyurethane. Composites containing 1 and 2.5 wt% of native asphaltenes showed good results in terms of hardness, thermal stability, and homogeneity of asphaltene distribution in the polymer matrix.

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