The use of a mixer with built-in Parshall's venturi for modification of bentonite designed for the filling of polymer resins

Mariusz Oleksy[1), *)], Joanna Oliwa[1)], Grzegorz Budzik[2)], Rafał Oliwa[1)], Katarzyna Bulanda[1)], Maciej Nędza[3)]

DOI: dx.doi.org/10.14314/polimery.2019.6.6

Abstract: Research was carried out on modification of bentonite with the use of a mixer with built-in Parshall's venturi. Aqueous suspensions of bentonite with a concentration of 12 % by weight were used. The advantage of using such an innovative mixer is to achieve much better results of the moving apart layers after modification, which significantly facilities the penetration of polymer chains between them. It should also be noted that the size of the tiles calculated from Scherrer's formula did not decrease after modification with the use of a mixer with built-in Parshall's venturi. Unfortunately, this unfavorable effect was observed for modified bentonites using an anchor mixer. Bentonites modified in this way were used to obtain composites on the epoxy resin matrix Epidian 6 with 3 wt % of their content. Mechanical properties were evaluated and a clear improvement in tensile strength, Young's modulus and notch-free impact strength was found. It was found that the obtained mechanical test results for these composites with the addition of bentonites modified with the use of anchor stirrer are worse in comparison to composites with the addition of bentonite modified with the use of a stirrer with built-in Parshall's venturi.

Keywords: modified bentonite, anchor mixer, Parshall's venturi, epoxy resin.

Wykorzystanie mieszadła z wbudowanymi zwężkami Parshalla do modyfikacji bentonitu przeznaczonego do napełniania żywic polimerowych

Streszczenie: Bentonit w postaci 12 % mas. wodnej zawiesiny modyfikowano z wykorzystaniem innowacyjnego mieszadła z wbudowanymi zwężkami Parshalla. Zastosowanie tego mieszadła pozwala na lepsze rozsunięcie warstw w modyfikowanym bentonicie, co znacznie ułatwia wnikanie łańcuchów polimerów. W przeciwieństwie do modyfikacji bentonitu za pomocą mieszadła kotwicowego nie zaobserwowano niekorzystnego zjawiska zmniejszenia wielkości płytek, obliczonej ze wzoru Scherrera. Zmodyfikowane bentonity wykorzystano do otrzymania kompozytów z ich 3 % mas. udziałem na osnowie żywicy epoksydowej Epidian 6. Stwierdzono wyraźną poprawę właściwości mechanicznych wytworzonych kompozytów, m.in.: wytrzymałości na rozciąganie, modułu Younga oraz udarności bez karbu, w porównaniu z właściwościami osnowy, jak również właściwościami takich kompozytów z udziałem bentonitów modyfikowanych za pomocą mieszadła kotwicowego.

Słowa kluczowe: bentonit modyfikowany, mieszadło kotwicowe, zwężki Parshalla, żywica epoksydowa.

As it is known, modified layered aluminosilicates are obtained by the exchange of metal cations present between layers to organic cations. Hydrothermal techniques are commonly used to modify these aluminosilicates. Relevant parameters ensuring proper process efficiency are mixing time, temperature, modifier dosing speed, but most of all the mixing process itself [1–3]. In order to ensure proper mixing efficiency, especially when the viscosity of the reaction system increases, different mixing methods and elements are used during dropping a modifier. In the literature, especially patent literature, there are studies on the modification of alumino-

1) Rzeszów University of Technology, The Faculty of Chemistry, Department of Polymer Composites, al. Powstańców Warszawy 12, 35-959 Rzeszów, Poland.

2) Rzeszów University of Technology, The Faculty of Mechanical Engineering and Aeronautics, Department of Mechanical Engineering, al. Powstańców Warszawy 8, 35-959 Rzeszów, Poland.

3) Technical Office – Technique 5, 36-020 Borek Stary 423c, Poland.

*) Author for correspondence; email: molek@prz.edu.pl

silicates with the use of specially constructed elements of apparatus: auger mixer [4], centrifugal mixer [5], vane mixer [6] and with the use of high-pressure nozzles [7]. Unfortunately, these solutions have one major drawback, which is the size of bentonite tiles is significantly reduced after modification. Our previous experience with modification of bentonites [8–11] allowed us to optimize the method of modification of bentonite with the use of a mixer with built-in Parshall's venturi and to investigate the effect of the addition of such modified bentonites on the mechanical properties of composites on the epoxy resin matrix with their addition.

EXPERIMENTAL PART

Materials

The following substrates were used in the study: benzyldimethylenediethylenediethylammonium chloride (QAS) UNHCR, butyltriphenylphosphonium chloride (QPS) Dishman Group, India, epoxy resin Epidian 6 (EP) and hardener Z-1 ZCh Ciech-Sarzyna S.A., bentonite Special (BS) of ZGM Zębiec k/Starachowic.

Modification of bentonite QAS and QPS

The method of modification of bentonite IV with ammonium salt (QAS) or phosphonic salt (QPS) with the use of a mixer with Parshall's built in venturi, developed and applied for patent, was carried out in three stages [12]. In the first stage, to enrich the bentonite and remove impurities (*e.g.* SiO_2), a 12 % aqueous suspension of bentonite was mixed using the mixer described in the utility formula [13] and shown in Fig. 1a, for 1 hour at a rotational speed of 100 rpm. In the second stage the mixing speed was increased to 150 rpm and mixture was heated to 70 °C for QAS or 90 °C for QPS. Then, a 50 % solution of QAS or QPS in ethanol in the amount of 28 g of QAS/100 g of Special bentonite (BS) or 30 g of QPS/100 g of BS was dripped. After condensation of the modifier, the reaction mixture was mixed at a constant mixer speed of 150 rpm for 2 hours for QAS and 3 hours for QPS. After cooling the reaction mixture to room temperature, the modified bentonite was seeped on the Buchner funnel and dried in a chamber with forced air circulation at 100 °C to achieve humidity ≤ 0.4 wt %. The dried modified bentonite was ground and sieved through a sieve with a mesh size of less than 0.06 mm. For comparison BSQAS and BSQPS were modified according to the procedure described in our earlier patent [8] using an anchor mixer (Fig. 1b). The bentonites thus obtained were used to fill the epoxy resin Epidian 6.

Preparation of epoxy resin composition

The obtained modified bentonites were introduced in the amount of 3.0 % by weight into the Epidian 6 resin (EP) using multi-stage homogenization based on: preliminary stirring with a slow-running mechanical stirrer at room temperature, after which the mixture was heated to 50 °C and stirred with an ultrasonic homogenizer. The next stage of homogenization is carried out in a high-speed mixer with a turbine mixer in a vessel under reduced pressure, at a temp. of 50 °C and a rotational speed of the mixer of 4000 rpm. The final homogenization was carried out in a cylinder-cylinder type grinders with a small ~ 0.5 mm gap which ensures intensive shear thanks to the high rotational speed of the moving cylinder of 6000 rpm.

Preparation of composite fittings for strength tests

To the investigated EP compositions 13 wt % of hardener Z-1 (calculated as resin) was added and thoroughly mixed. The composition was then vented and cast at room temperature into silicone molds prepared according to ISO 527-1:1998 standards in the laboratory vacuum chamber VAKUUM UHG 400 (Schuechl, Germany). After 24 hours the molded parts were postcured at 100 °C for 5 hours in accordance with the resin manufacturer's recommendations.

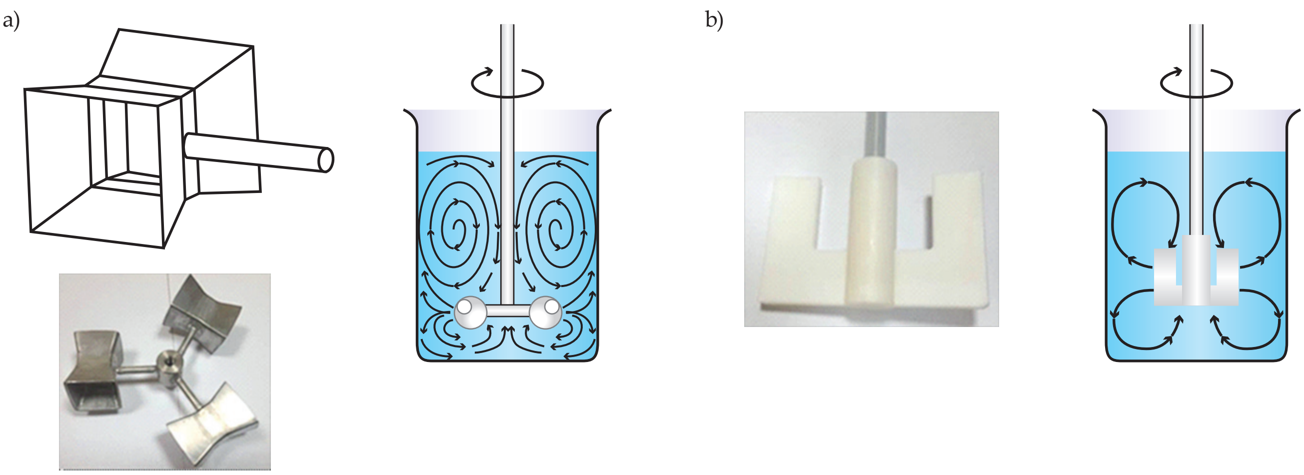

Fig. 1. Mixers used in the process of bentonite modification: a) mixer with built-in Parshall's venturi (M1), b) anchor mixer (M2)

Methods of testing

Mechanical properties test

The tensile strength was determined in accordance with ISO 527-1:1998 using an Instron 5967 type testing machine equipped with a video extensometer. The tensile velocity was 2 mm/min and the temperature was 23 °C.

Charpy impact strength was determined in accordance with PN-EN ISO 179-1 with a PSW4J type machines, manufactured by Gerhard Zorn (Germany) using a 1 J impact energy hammer with digital reading of the result.

Testing the effectiveness of bentonite modification

In order to obtain the efficiency of bentonite modification, differential scanning calorimetry (DSC) analysis of unmodified bentonite and modified bentonites BSQAS and BSQPS was performed. The measurement was carried out with Mettler Toledo DSC 822e type apparatus with the following parameters: measurement time 45 min, temperature range 0–450 °C, heating speed 10 °C/min.

Tile spacing in modified bentonites was evaluated by wide angle X-ray scattering (WAXS) using SAXS Bruker Nanostar-U diffractometer. The determination was performed for powdered fillers in the direction perpendicular to the packet surface, *i.e.*, between the network planes 001. The distance between the bentonite plates (d_{hkl}) was calculated from the Bragg's formula:

$$n \cdot \lambda = 2 \cdot d_{hkl} \cdot \sin\theta \tag{1}$$

where: n – degree of diffraction (n = 1, 2...), d_{hkl} – distance between consecutive crystallographic planes [nm], λ – radiation wavelength X [nm], 2θ – the angle at which the diffractive peak occurs, as read from the WAXS chart.

The size of the tiles in Scherrer's pattern was also determined:

$$B = \frac{K\lambda}{D_{hkl}\cos\theta_{hkl}} \tag{2}$$

where: B – reflex width dependent on the size of crystallites [rad], K – Scherrer's constant, $K \approx 1$, λ – wavelength of monochromatic radiation used [nm], D_{hkl} – mean dimension of crystallites in the direction perpendicular to the plane (hkl) [nm].

RESULTS AND DISCUSSION

Evaluation of the effectiveness of bentonite modifications

Based on the obtained DSC thermogram (Fig. 2) for unmodified BS, one sharp peak in the temperature range 70–140 °C associated with the removal of moisture absorbed by the sample and crystalline water is visible. However, in the case of modified bentonites similar effects were obtained only in the temperature range 40–100 °C for both BSQAS and BSQPS. In addition, on the BSQAS curve in the temperature range 220–280 °C and 410–430 °C there are two distinct endothermic peaks associated with the decomposition of the modifier. In the case of BSQPS there was a mild decomposition of this salt and an immediate decomposition of phosphine, resulting in an endothermal peak beginning at a much higher temperature of 310 °C (Fig. 2). Thus, the presence of QAS or QPS in samples of modified bentonites can be confirmed from the DSC curves.

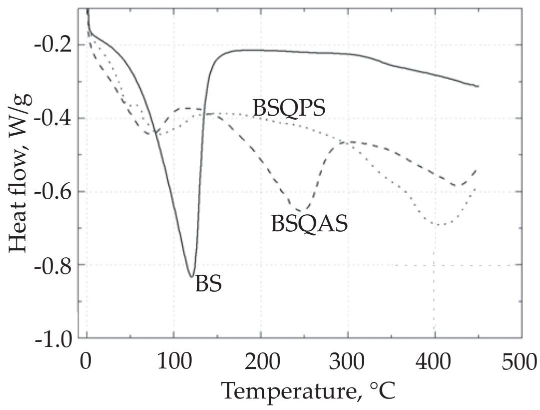

Fig. 2. DSC curves of bentonites BS, BSQAS and BSQPS

However, it is not possible to determine whether these modifiers have been adsorbed on the surface of bentonite or whether they have been built into the interlayer space. It should also be mentioned that no differences were observed between thermograms of modified bentonites obtained with the use of the M1 mixer and thermograms of bentonites modified with the use of the M2 mixer according to the procedure described in [8].

Significant differences in the modification process efficiency between bentonites modified with the use of a mixer with built-in Parshall's valves and bentonites modified in accordance with the previous method [8] were observed on WAXS thermograms. WAXS results are presented in Table 1 and on their basis it was found that the distance between BS modified QAS and QPS bentonite plates significantly increased from 12.7 Å for unmodified BS to about 20.8 Å for BSQPS modified with M2 mixer and 23.6 Å for BSQPS modified with M1 mixer. For bentonite modified with M2 QAS, 31.2 Å was obtained. On the other hand, a much better effect was obtained when the process of modification of bentonite with this salt was carried out with the use of M1 mixer, the layers stretched to 34.6 Å (Table 1). It should also be mentioned that the size of the tiles calculated from the Scherrer's formula did not decrease significantly after modification with the use of the M1 mixer. Unfortunately, this unfavorable effect was observed in the case of modified bentonites with the use of M2 mixer. The tiles size decreased from 143.0 Å for BS to 138.8 Å for BSQAS and 137.2 Å for BSQPS.

T a b l e 1. Results of WAXS BS, BS modified QAS and QPS tests with mixers M1 and M2

Symbol of bentonite	Slide the tiles in the direction d_{001}, Å		Size of tiles, Å	
	Type of mixer			
	M1	M2	M1	M2
BSQAS	34.6	31.2	142.6	138.8
BSQPS	23.6	20.8	141.7	137.2

For BS, the tile spacing in the direction d_{001} = 12.7 Å and the calculated tile size 143.0 Å.

T a b l e 2. Results of mechanical properties of the composites tested calculated as a relative change in relation to unfilled EP: breaking stress ($\Delta\sigma_r$), Young's modulus (ΔE) and Charpy impact strength (ΔU)

Symbol of bentonite	Relative change in breaking stress ($\Delta\sigma_r$), %		Relative Young's modulus change (ΔE), %		Charpy relative change in impact strength (ΔU), %	
	Type of mixer					
	M1	M2	M1	M2	M1	M2
BSQAS	36	27	23	17	84	62
BSQPS	28	21	20	13	69	54

Mechanical properties of the obtained composites

Relative changes of mechanical properties of the tested composites related to unfilled resin EP are presented in Table 2: breaking stress ($\Delta\sigma_r$), Young's modulus (ΔE) and Charpy impact strength (ΔU). The introduction of modified BSQAS or BSQPS bentonites of 3 % by weight into the resin clearly improves tensile strength, Young's modulus, and notch-free impact strength (Table 2).

It was found that the obtained results of mechanical tests for these composites with the addition of bentonites modified with the use of M2 mixer were lower in comparison to the composites with the addition of bentonite modified with the use of M1 mixer. This is probably due to the greater dispersion of the bentonite layers, which significantly facilitates the penetration of epoxy resin between the layers. This effect is also supported by the fact that the modified bentonite plates did not decrease as in the case of composites containing modified bentonite with the use of M2 mixer.

CONCLUSIONS

The developed and new patent pending method of modification of bentonites with the use of the M1 mixer allows to obtain much better results of bentonite modification (greater expansion of layers and not reduction the size of tiles).

The use of a mixer with built-in Parshall's venturi allows to reduce the speed of the mixer, thus avoiding strong airing of bentonite suspensions, which facilitates the filtration process.

A clear influence of the size of expansion of layers and the size of bentonite tiles after modification on the mechanical properties of composites with their addition was observed.

REFERENCES

[1] Delaplace G., Gu Y.Y., Liu M. *et al.*: *Chemical Engineering Science* **2018**, *192*, 1071. https://doi.org/10.1016/j.ces.2018.08.023
[2] Grenville R.K., Giacomelli J.J., Van Ommeren G.J. *et al.*: *Chemical Engineering Research and Design* **2018**, *137*, 395. https://doi.org/10.1016/j.cherd.2018.07.017
[3] http://Mieszadło/EFC%20Parshall%20Flume%20Brochure.pdf
[4] *CN Pat*. 101 774 596 (B) (2012)
[5] *CN Pat*. 204 211 495 (U) (2015)
[6] *CN Pat*. 103 896 291 (A) (2014)
[7] *CN Pat*. 203 741 052 (U) (2014)
[8] *EN Pat*. 178 900 (2000)
[9] *EN Pat*. 178 866 (2000)
[10] *EN Pat*. 226 833 (2017)
[11] *EU Pat*. 2 910 526 (2019)
[12] *Pat. appl. P*. 486 721 (2019)
[13] Utility model W.126 351

Received 16 I 2019.