Composites of phenol-formaldehyde resin used for impregnating fiberglass mesh
(Rapid Communication)

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Abstract: The study was carried out to obtain composites based on phenol-formaldehyde resin (PF) in combination with selected bentonites modified with quaternary ammonium salts (QAS). Mechanical and structural properties of the obtained composites were assessed, particularly in terms of their applicability for fiberglass mesh impregnation. It was stated that the composite based on PF and 3 wt % of bentonite modified with 2-hydroxypropyltrimethylammonium chloride had the best utility properties.

Keywords: phenol-formaldehyde resin, bentonite, impregnate for fiberglass mesh, mechanical properties, brittle fractures.

Kompozyty żywicy fenolowo-formaldehydowej stosowane jako impregnat siatek z włókna szklanego

Streszczenie: Otrzymano kompozyty na osnowie żywicy fenolowo-formaldehydowej (PF) z wybranymi bentonitami modyfikowanymi czwartorzędowymi solami amoniowymi (QAS). Oceniono właściwości mechaniczne i strukturalne tych kompozytów pod kątem ich zastosowań jako impregnaty siatek z włókna szklanego. Stwierdzono, że kompozyt PF z dodatkiem 3 % mas. bentonitu modyfikowanego chlorkiem 2-hydroksypropylotrimetyloamoniowym charakteryzuje się najlepszymi właściwościami użytkowymi.

Słowa kluczowe: żywica fenolowo-formaldehydowa, bentonit, impregnat siatek z włókna szklanego, właściwości mechaniczne, kruche przełomy.

Phenol-formaldehyde resins (PF) are used for instance in production of laminates, and as adhesives or binding agents. The large variety of applications inspired a number of studies exploring possible modifications of these resins with the use of nanofillers (layered aluminosilicates). Various methods are used to obtain nanocomposites with aluminosilicate as an additive, based on novola and resol phenolic resins, *via* melt intercalation, *in situ* polymerization, and prepolymer intercalation. Yet it is difficult to modify these polymers using layered aluminosilicates and to obtain exfoliated or even intercalated structure. This is linked with the rigid, three-dimensional molecular structure of phenolic resins, and in particular resols. Due to this, in the market we can observe constantly growing demand for polymer materials with enhanced mechanical properties, and as a result there is a need for developing novel compositions based on PF with better performance characteristics in comparison to traditional unmodified thermosetting resins. Recent years have brought a number of publications devoted to development of nanocomposites based on PF [1–6]. The present study continues research into the application of bentonites modified with quaternary ammonium salts (QAS) to produce composites, based on PF and showing far better mechanical and rheological properties.

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EXPERIMENTAL PART

Materials

The following raw materials were used in the experiments:

– bentonite modified with decyltrimethylammonium chloride (BQAS1) according to the procedure described in patent [7],

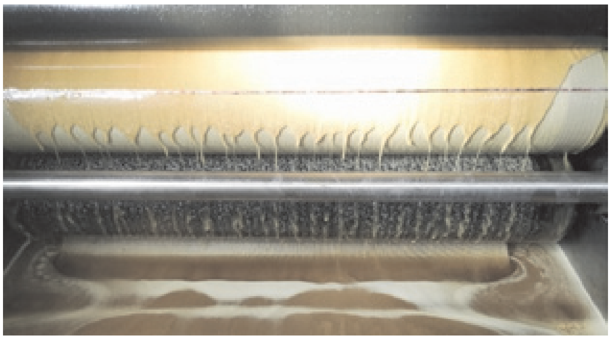

Fig. 1. View of supersaturating rollers along the line designed for coating fiberglass meshes with PF composition

– bentonite modified with 2-hydroxypropyltrimethylammonium chloride (BQAS2) according to the procedure described in patent [7],

– bentonite modified with decyl-2-hydroxypropyldimethylammonium chloride (BQAS3) according to the procedure described in patent [7],

– phenol formaldehyde resin (PF) type DS.-05, produced by Lerg Pustków,

– fiberglass meshes with the basis weights of: 195, 265, 464 g/m^2 manufactured by Rymatex Sp. z o.o.

Preparation of PF composites

The modified bentonites were introduced in amount of 1.0 to 3.0 wt % to liquid PF using multistage homogenization. This process involved initial blending with slow-rotating mechanical stirrer at room temperature, after which the mixture was heated to 50 °C and stirred in an ultrasonic homogenizer. The subsequent stage of homogenization was carried out under reduced pressure, at a temperature of 50 °C in a high shear mixer with a turbine stirrer rotating at the speed of 4000 min^{-1}. Final homogenization was performed in a cylinder-cylinder type triturator, with a small gap of ~0.5 mm, to enable high shear as a result of high speed rotation of the moving cylinder, at 6000 min^{-1}.

Preparation of fiberglass mesh reinforced with composites based on PF

The obtained composition of PE with 1 or 3 wt % addition of bentonites was applied to impregnate fiberglass meshes with varied basis weights: 195, 265 or 464 g/m^2. The impregnation was performed using a coating line, presented in Fig. 1, with supersaturation speed of 5 m/min and the drying duct length of 12 m. The temperature of drying was 140 °C. From the obtained meshes the disks with outer and inner diameters of 229 and 23 mm, respectively, were cut. These disks, shown in Fig. 2, were applied during dynamic strength testing. The squares with a side of 250 mm were also cut and were subjected to additional crosslinking process at 160 °C for the period of 4 h.

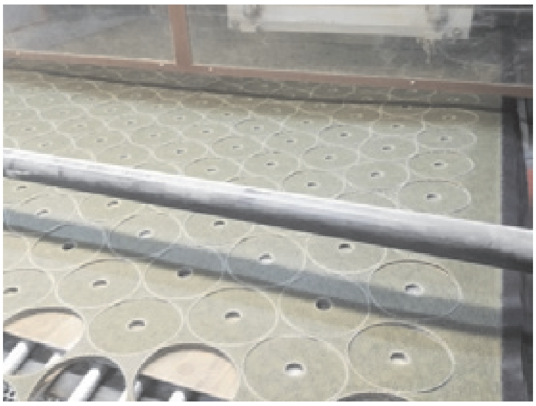

Fig. 2. View of the location designed for cutting disks out from glass meshes saturated with PF composition

Testing methods

Measurements of dynamic breaking strength of the abrasive disks were performed in accordance with PN--EN 12413:2007 standard. The tests were carried out in a grinding wheel with a diameter of 230 mm and thickness of 2 mm, at the temperature of 25 °C.

Shear strength was determined using shear frame test shown in Fig. 3. The tests were performed using Zwick/Roell testing machine with extension speed of 2 mm/min, for crosslinked squares. Shear stress was determined according the formula:

$$\tau = \frac{P}{\sqrt{2} \cdot a \cdot b} \quad (1)$$

where: τ – shear stress, P – maximum force, a – sample thickness, b – sample side length.

Brittle fracture morphology in the hardened fibrous composites was examined with a scanning electron microscope (SEM), type JEOL JSM-5500 LV. Fractures were obtained after composite profiles were chilled in dry ice and subjected to impact breaking. Before the measurement the samples were coated with gold.

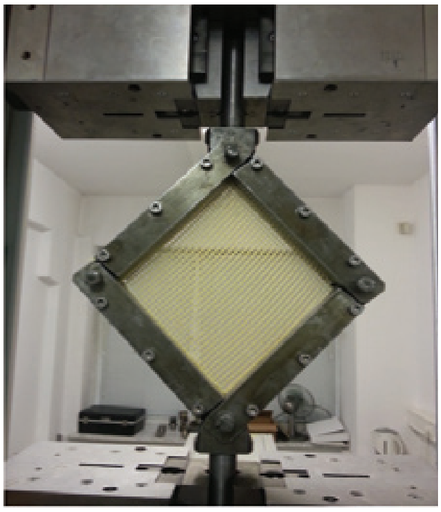

Fig. 3. View of sample fixed in a holding frame before shear test

T a b l e 1. The mechanical properties of the examined composites

Examined property	Symbol of the composite						
	PF	PF + 1 wt % BQAS1	PF + 3 wt % BQAS1	PF + 1 wt % BQAS2	PF + 3 wt % BQAS2	PF + 1 wt % BQAS3	PF + 3 wt % BQAS3
Mesh with basis weight of 195 g/m^2							
Shear stress, MPa	0.52 ± 0.5	0.57 ± 0.3	0.62 ± 0.4	0.78 ± 0.2	0.86 ± 0.4	0.67 ± 0.4	0.75 ± 0.5
Dynamic breaking strength of the abrasive disk, rpm	10 430	10 640	10 920	11 270	11 970	10 990	11 550
Mesh with basis weight of 265 g/m^2							
Shear stress, MPa	0.74 ± 0.6	0.81 ± 0.4	0.89 ± 0.3	1.11 ± 0.2	1.23 ± 0.3	0.96 ± 0.3	1.07 ± 0.3
Dynamic breaking strength of the abrasive disk, rpm	14 900	15 200	15 600	16 100	17 100	15 700	16 500
Mesh with basis weight of 464 g/m^2							
Shear stress, MPa	1.036 ± 0.4	1.134 ± 0.6	1.246 ± 0.5	1.554 ± 0.4	1.722 ± 0.7	1.344 ± 0.6	1.498 ± 0.4
Dynamic breaking strength of the abrasive disk, rpm	20 860	21 280	21 840	22 540	23 940	21 980	23 100

RESULTS AND DISCUSSION

Mechanical properties

In order to identify the effect of the type and amount of the modified bentonites, used for preparation of the hybrid fibrous composites, on their mechanical properties the measurements of dynamic breaking strength of the abrasive disk and shear stress were carried out. The relevant results are listed in Table 1.

The data show visible influence of the applied fillers (BQAS1, BQAS2 and BQAS3) on the examined strength related characteristics. The improvement in these characteristics was correlated with the content of the filler in the resin (over content range which was tested). The best results were observed in the case of glass meshes supersaturated with PF with 3 wt % addition of BQAS2. For this sample it was stated a significant improvement in the relevant properties: dynamic breaking strength by approx. 15 %, and shear stress by approx. 66 %, in comparison to composites based on unmodified PF.

In the remaining layered composites containing 3 wt % of BQAS3 there was an increase in dynamic breaking strength by approx. 11 %, and in shear stress by approx. 45 %. The lowest increase in the examined strength related characteristics was observed in the composites with 3 wt % addition of BQAS1.

SEM analysis of brittle fractures of the composites

Brittle fractures occurring in samples of fibrous composites were examined in parallel to the arrangement of fibers. The analysis was designed to assess the effects of modified aluminosilicates in the composite microstructure.

As it is shown in Fig. 4 the morphology of brittle fractures from glass laminates based on PF composition with 3 wt % of BQAS2 significantly differs from the morphology of the composites based on unmodified PF. In the case of unmodified matrix the surface of the fracture is smooth which confirms easy crack propagation (Fig. 4a).

a)

b)

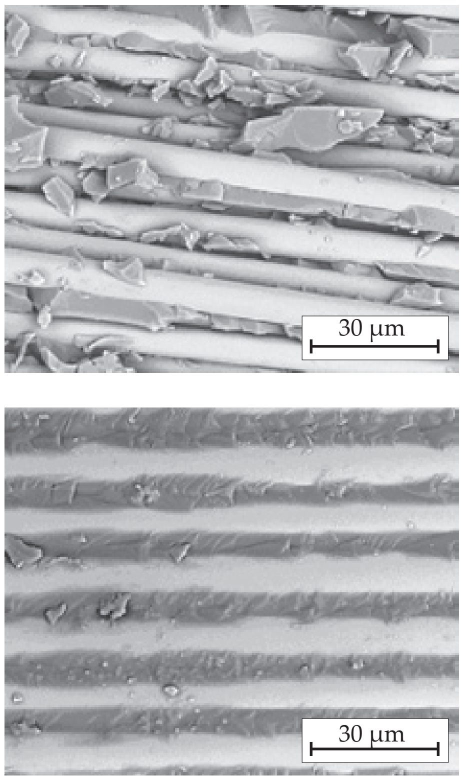

Fig. 4. SEM microphotographs of brittle fractures of the composites based on: a) unmodified PF, b) PF with 3 wt % of BQAS2

When bentonite is added, the surface becomes irregular and coarse, and contains numerous fissures, which prevent crack propagation. Moreover, in composites based on PF there are visible single fibers and empty spaces left by them, unlike in composites based on PF + 3 wt % BQAS2 matrix, in which composite surrounds the fibers and visibly clings to them, because of its better adhesive properties (Fig. 4b).

REFERENCES

[1] Kaushik A., Singh P., Verma G.: *Journal of Thermoplastic Composite Materials* **2010**, *23*, 79.
http://dx.doi.org/10.1177/0892705709098155

[2] Rivero G., Vazquez A., Manfredi L.B.: *Journal of Applied Polymer Science* **2009**, *114*, 32.
http://dx.doi.org/10.1002/app.30574

[3] Lopez M., Blanco M., Ramos J.A. *et al.*: *Journal of Applied Polymer Science* **2007**, *106*, 2800.
http://dx.doi.org/10.1002/app.26928

[4] Kaynak C., Tasan C.C.: *European Polymer Journal* **2006**, *42*, 1908.
http://dx.doi.org/10.1016/j.eurpolymj.2006.03.008

[5] Wang H., Zhao T., Yana Y., Yu Y.: *Macromolecular Rapid Communications* **2002**, *23*, 44.

[6] Wang H., Zhao T., Yan Y., Yu Y.: *Journal of Applied Polymer Science* **2004**, *92*, 791.
http://dx.doi.org/10.1002/app.13662

[7] *PL Pat. Appl.* 1 4461 559.8 (2014).

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