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Composites of unsaturated polyester resins applied in vacuum casting technology

RAPID COMMUNICATION

Summary — The paper deals with hydrophobization of bentonites (layered aluminosilicates) with quaternary ammonium salts (QAS) and potential application of the products obtained as fillers for preaccelerated unsaturated polyester resins (UPs) to be applied in vacuum casting. Natural purified bentonites of "Special" and "SN" type, enriched with montmorillonite and modified with QAS according to the earlier patented method were used. An addition of modified bentonites (1.5 or 3.0 phr) to commercial preaccelerated UPs, caused a considerable improvement in mechanical properties (tensile strength, Brinell hardness and Charpy impact strength). Also, a clear effect of nanofiller concentration in resin on the quality of cast products was observed.

Key words: preaccelerated unsaturated polyester resin, bentonites, organic aluminum compounds, nanoparticles, nanocomposites, mechanical properties, vacuum casting.

KOMPOZYTY NIENASYCONYCH ŻYWIC POLIESTROWYCH STOSOWANE W TECHNOLOGII VACUUM CASTING

Streszczenie — Przedmiotem pracy były hydrofobizacja bentonitów (glin o budowie warstwowo-pakietowej) czwartorzędowymi solami amoniowymi (QAS) i możliwości zastosowania otrzymanego produktu jako napełniacze preakcelerowanych nienasyconych żywic poliestrowych (UP) do zastosowania w odlewaniu próżniowym Vaccum Casting. W pracy zastosowano naturalne oczyszczone i wzbogacone w montmoryllonit bentonity "Specjal" i "SN", a metoda ich modyfikacji QAS była zgodna z opatentowanym sposobem. Stwierdzono, że dodatek modyfikowanych bentonitów (1.5 i 3.0 %) do handlowych preakcelerowanych UP, spowodował znaczną poprawę właściwości mechanicznych (wytrzymałości na rozciąganie, twardości próbek wg Brinella oraz udarności bez karbu Charpy'ego). Zaobserwowano także wyraźny wpływ stężenia nanonapełniacza w żywicy na jakość odlewanych wyrobów.

Słowa kluczowe: preakcelerowana nienasycona żywica poliestrowa, bentonity, organogliny, nanocząstki, nanokompozyty, właściwości mechaniczne, odlewanie próżniowe.

Current investigations lead to considerable progress in the composite material engineering. This development concentrates on possibility obtaining of nanomaterials with the properties much exceeding those of traditional materials. Quite soon the nanotechnology shall contribute to raised precision in manufacture of equipment, as well as to its higher reliability and operation efficiency at lower production costs. Therefore we observe a steadily raising interest in polymers nanocomposites, including those on the basis of thermosetting polymers.

Research studies on the use of modified bentonites as fillers of multi-directional action for commercial synthetic resins were described in our earlier publications [1—9]. This paper constitutes a broadening of that research by filling of preaccelerated unsaturated polyester resins intended for vacuum casting.

EXPERIMENTAL

Materials

Two unsaturated poliester resins (UPs) produced by Z. Ch. "Organika-Sarzyna" i.e. Polimal® 109-32 RPyK (preaccelerated with cobalt) and Polimal® 101-36B (preaccelerated with tertiary amine) were used in the research tests.

To prepare UP composites the following bentonites were applied:

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— "Wyoming" bentonite (BW) — technical product delivered by CETKO-Poland Sp. z o.o.

— Bentonite, "SN" (BSN) and "Special" (BS) — technical products delivered by "ZĘBIEC" S. A. Mining & Metal Plant in Zębiec near Starachowice.

Bentonites were modified with quaternary ammonium salts (QAS) of the general formula $R_1R_2R_3R_4N^+Cl^-$, where R_1 and R_2 were $-CH_3$, R_3 was $-C_{12}H_{25}$ and R_4 was $-C_{12}H_{25}$ (QAS1) or $-CPhH_2$ (QAS2).

As curing agents Luperox® K-1 and Luperox® ANS-50 produced by Arkema Inc. were used.

Modification of bentonites with quaternary ammonium salts (QAS)

The previously developed and described [10, 11] procedure of bentonite modification with quaternary ammonium salts (QAS) was applied in this study.

Preparation of UPs composites with bentonites

Composites of Polimal® 109-32 RPyK or Polimal® 101-36 B, containing one of modified or unmodified bentonites (BSN, BS or BN) in amounts 0, 1.5 or 3.0 phr (by weight) were prepared. The composites were premixed using slow-speed mechanical stirrer, and then, for good dispersion of the filler in the resin, a homogenization was carried out in an U-501 ultrasonic washer (produced by "ULTRON" ZUE, Olsztyn) at 50 °C for 60 min and high-speed homogenizer of type 309 (produced by the "Mechanika Precyzyjna" Production Cooperative). The shear rate of the stirrer in the chamber of the rubbing unit was approximately 1050 s^{-1}. In order to prevent the mixture ageing, it was kept at temp. approximately 4 °C.

Preparation of samples

Composites of UPs with selected bentonites were cured using the proper curing agent (Luperox® K-1 for Polimal® 109-32 RPyK UP and Luperox® ANS-50 for Polimal® 101-36B UP) in amounts 2 phr (by weight).

Then the whole was mixed thoroughly and samples for strength tests were cast in silicone molds prepared according to standard ISO 527-1:1998. The crosslinking was carried out at 20 °C for 24 hours, and then these sample shapes underwent a postcuring at 80 °C for 2 hours, according to the producer's recommendations.

Methods of testing

Tensile strength testing was carried out by using the testing machine Fp 100 type, at the rate of 2 mm/min, at temp. 20 °C according to ISO 527-1:1998 standard. The measurements results were recorded and calculated with the use of the test machine program. The tests were carried out for dumbbell samples.

The Brinell hardness measurements were carried out using HPK hardness tester (produced by Feinmechanik Rolf Heckert in former East Germany) according to ISO 2039-1:1987 standard. The arithmetic mean from at least 10 measurements was accepted as a final result.

The impact strength of the samples was determined with Charpy pendulum machine of impact energy 1.0 J according to PN-EN ISO 179-2:2001 standard.

Casting of models of composites in silicon mold matrices

The process of making models of tested composites with the use of vacuum casting method consisted of four basic stages:

— generation of solid (3D) model with the use of CAD (CATIA) software,

— making of stereolithographic model,

— making of silicon mold matrix,

— casting of composite model.

Silicon molds were obtained by casting of stereolithographic model with polysiloxane rubber. After rubber crosslinking, the molds were split or cut so as to enable subsequent removal of composite model without damage (see Fig. 1) [12].

Casting of composite model was performed using vacuum casting apparatus of VAKUUM UHG 400 type, at temp. 20 °C, pressure 2 hPa and the rotational speed of the stirrer of 30 r.p.m. being kept.

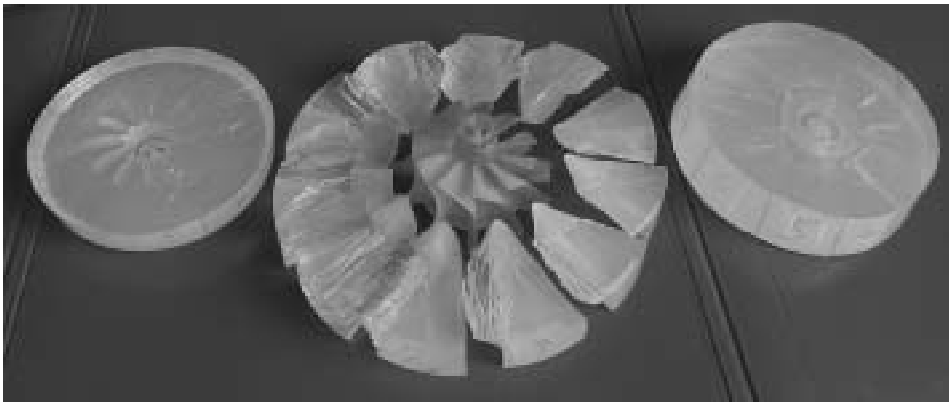

Fig. 1. Appearance of silicon mold matrix used for casting of models made of composites tested

The process of composite model casting proceeded as follows: once the assumed vacuum was reached, the composite ingredients were mixed with crosslinking system and then poured into previously prepared silicon mold. Low pressure facilitated mold filling and degassing of the compositions. The preliminary crosslinking of casting in mold lasted 12 hours, and then they underwent a final curing at temp. 80 °C for 2 hours.

RESULTS AND DISCUSSION

Selection of the suitable methods for thorough dispersion of the filler in a resin is very important for obtaining of composites and/or nanocomposites. In our study a combined ultrasonic and rubbing methods were applied by using ultrasonic washer and high-speed homogenizer.

Application of such combination of methods improved significantly the homogenization of the filler in a resin and as a result the composites with modified bentonites became more clear after rubbing through screens. This effect was also augmented by the applied optimum temperature of homogenization, which was 50 °C and caused a reduction in mixture viscosity, what in turn additionally improved an exfoliation of studied bentonites in the resins [6, 9]. The composites with unmodified bentonites showed much higher sedimentation of the filler and lower transparency of the mixtures.

Results of mechanical properties tests of studied composites are listed in Table 1.

The addition of bentonites BSN, BS or BW, both unmodified and modified with QAS, to Polimal® 109-32 RPyK and Polimal® 101-36B UPs was found to cause a raise in tensile stress at break (σ_r) of tested composites. In case of composites of UPs with unmodified bentonites BSN, BS or BW, the rise in rupture stress value was from 17.6 to 28 %, compared to unfilled, Polimal® 109-32 RPyK, and 12.1 to 25 % compared to unfilled, Polimal® 101-36B. The best results of tests were obtained for the composites of UPs with addition of 3 phr of unmodified BS. A strong effect of σ_r rise occurred only in case of composites with bentonites BSN, BS or BW modified with QAS and it was in the range from 50.2 to 88 % for composites based on Polimal® 109-32 RPyK UP and was in the range from 49.8 to 85.8 % for composites based on Polimal® 101-36B UP. The best results of tests were achieved for 5 phr of bentonite content in the composite. The chemical structure of QAS used for bentonite modification, type of modified bentonite and UP used were observed to have also clear effects on the obtained results of tests (Table 1). The highest improvement in discussed properties was obtained for composites UP-bentonites modified with QAS2, which had one benzyl substituent and three aliphatic substituents, including one with long carbon chain (n = 12). The best results of tests were obtained for composites of Polimal® 109-32 RPyK and 3 phr of BS modified with QAS2 because tensile strength grew as much as 88 %.

Further analysis led to finding that Brinell hardness (H_k) of tested composites was affected by such factors as: the type of bentonite used for modification and chemical structure of the modifying agent, *i.e.* QAS, concentration of the filler in a composite as well as the type of preaccelerated UP used for filling. As could be expected the growth in hardness of composites with the addition of unmodified bentonites is not so significant in case of composites containing modified bentonites (Table 1). An

Table 1. Results of mechanical properties of composites: σ_r — tensile stress at break, H_k — Brinell hardness, U_k — Charpy unnotched impact strength

Content and type of bentonite in the composite	Polimal® 109-32 RPyK			Polimal® 101-36B		
	σ_r, MPa	U_k, kJ/m^2	H_k, N/mm^2	σ_r, MPa	U_k, kJ/m^2	H_k, N/mm^2
0.0 phr	50.0	8.0	86.5	48.0	7.5	81.2
1.5 phr of BSN	59.0	8.5	91.2	54.0	8.0	85.2
3.0 phr of BSN	64.0	9.0	96.8	60.0	8.5	90.4
1.5 phr of BSN$_{\text{QASA1}}$	76.0	13.6	113.2	70.0	12.9	107.4
1.5 phr of BSN$_{\text{QASA2}}$	87.3	15.2	124.5	82.5	14.4	118.3
3.0 phr of BSN$_{\text{QASA1}}$	84.7	14.4	123.6	80.0	13.5	119.2
3.0 phr of BSN$_{\text{QASA2}}$	92.4	16.2	134.5	86.4	15.3	130.2
1.5 phr of BS	60.1	8.7	92.4	55.2	8.1	88.1
3.0 phr of BS	64.8	9.2	97.3	60.0	8.7	91.9
1.5 phr of BS$_{\text{QASA1}}$	77.4	14.1	114.2	71.9	13.4	110.0
1.5 phr of BS$_{\text{QASA2}}$	88.5	16.0	125.2	83.0	15.2	120.1
3.0 phr of BS$_{\text{QASA1}}$	85.6	15.0	124.1	80.0	14.3	120.0
3.0 phr of BS$_{\text{QASA2}}$	94.0	16.9	135.3	89.2	15.9	130.6
1.5 phr of BW	58.8	8.4	90.8	53.8	8.1	84.9
3.0 phr of BW	63.6	8.9	96.0	56.9	8.4	90.0
1.5 phr of BW$_{\text{QASA1}}$	75.1	13.0	112.5	70.0	12.4	106.9
1.5 phr of BW$_{\text{QASA2}}$	86.4	14.8	123.7	81.0	14.1	117.8
3.0 phr of BW$_{\text{QASA1}}$	83.4	14.0	123.0	79.0	13.3	117.4
3.0 phr of BW$_{\text{QASA2}}$	91.2	15.6	133.7	86.2	15.0	127.2

Fig. 2. Appearance of an impeller obtained from composite based on Polimal® 109-32 RPyK with 3 phr of BS modified with QAS2

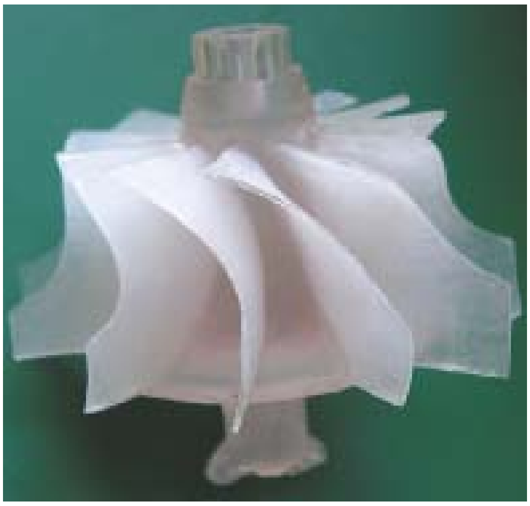

Fig. 3. Appearance of an impeller obtained from composite based on Polimal® 109-32 RPyK with 1.5 phr of BS modified with QAS2

improvement of H_k as in a case previously discussed is noticeable here. A clear improvement of hardness was observed for composites of UPs with 3 phr addition of BS modified with QAS2. It grew by 50.6 % for composites based on Polimal® 109-32 RPyK UP and by 60.8 % for composites based on Polimal® 101-36B UP.

The results of unnotched impact strength U_k in Charpy pendulum tester of samples of UP composites with modified bentonites confirmed the previously described observations (Table 1). It was found that addition of bentonites modified with QAS to UP had a very favorable effect on improvement their U_k. In case of composites of both applied UPs and 3 phr of modified QAS2 BS addition U_k value increased as much as approximately 112 % (Table 1).

Suitability of above described composites for vacuum casting of technical cast profiles was also tested. These tests have shown that composites used and tested by us were very suitable for obtaining the models of complex samples by using low-pressure casting method. The only problem which was observed in making these castings was a worse mold filling for composites with 3 phr of modified bentonites (Figure 1). This effect was not observed for composites with 1.5 phr of modified bentonite (Figure 2). It is probably because of thixotropic properties bestowed on UPs by modified bentonites. At lower concentration of modified bentonite (1.5 phr) in the composite, the apparent viscosity of the system is low enough, so that it does not hamper the flow of cast composition in a mold. A clear rise in viscosity was observed at 3 phr addition of the above bentonite, with adverse effect on good aeration of cast composite, and thus on the product obtained. Therefore an addition of 1.5 phr of modified bentonite to UPs seems to be an optimum, because the obtained composites are characterized by good strength properties and a potential for their application to vacuum casting of models of complex structure.

CONCLUSION

— An addition of 1—3 phr modified bentonites to UPs improved strongly the strength properties of obtained composites: tensile stress at break, Brinell hardness and Charpy unnotched impact strength.

— The type of bentonite, its content in the composite, as well as homogenization temperature and method, were all found to have significant effect on mechanical properties of composites obtained.

— Smaller content of modified bentonite (1.5 phr) affected better mold filling during vacuum casting.

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