Hybrid composites with epoxy resin matrix manufactured with vacuum casting technology (*Rapid Communication*)

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DOI: dx.doi.org/10.14314/polimery.2014.677

Abstract: The paper presents the methodology of the process of manufacturing of technical profile models on the example gear wheels made of epoxy composites cast in silicone molds using vacuum casting technology. Research on preparation of epoxy resin composites filled with hybrid modifiers has been carried out. Mechanical and processing properties of composites have been evaluated, particularly in terms of application in rapid prototyping of gear wheels. Considerable improvement of tensile strength (up to 44 %) and unnotched impact strength (up to 93 %) has been observed. Geometric accuracy of gear wheels prepared by casting of the analyzed hybrid composites has been determined using a coordinate measuring machine. Morphology of the brittle fracture of studied composites has been observed on brittle fractures using a scanning electron microscope (SEM).

Keywords: epoxy resin, polyhedral silsesquioxane, modified bentonite, modified silica, vacuum casting, hybrid composite, mechanical properties.

Kompozyty hybrydowe na osnowie żywicy epoksydowej wytwarzane metodą odlewania próżniowego

Streszczenie: W artykule przedstawiono metodykę procesu wytwarzania modeli profili technicznych na przykładzie kół zębatych wykonanych z kompozytów epoksydowych metodą odlewania próżniowego w formach silikonowych. Otrzymano kompozyty na osnowie żywicy epoksydowej napełnione modyfikatorami hybrydowymi. Oceniono właściwości użytkowe i przetwórcze kompozytów, zwłaszcza pod względem możliwości ich zastosowania w metodach szybkiego prototypowania do otrzymywania kół zębatych. Stwierdzono wyraźną poprawę wytrzymałości na rozciąganie (do 44 %) oraz udarności bez karbu (do 93 %). Na stanowisku współrzędnościowym określono także dokładność geometryczną odlanych modeli kół zębatych, a za pomocą skaningowego mikroskopu elektronowego (SEM) zbadano ich morfologię, obserwowaną na kruchych przełomach.

Słowa kluczowe: żywica epoksydowa, poliedryczny oligosilseskwioksan, modyfikowany bentonit, modyfikowana krzemionka, odlewanie próżniowe, kompozyt hybrydowy, właściwości mechaniczne.

Recently, rapid manufacturing (RM) technologies have gained importance in manufacturing of prototypes and small batches of technical cast profiles. One of the methods of rapid manufacturing is vacuum casting (VC) of parts made of unsaturated polyester, polyurethane or epoxy thermoset resins in silicone molds. These molds are produced by transposing a model prepared using the method of stereolithography or 3D printing to a thermoset silicone rubber. Resins used in VC technology should have the following properties: good dimensional stability, low shrinkage and high strength allowing conducting prototype fatigue tests at a test station. These are the major reasons for the growing demand for compositions with better functional properties. In the last years projects on hybrid composites with polyurethane or epoxy matrix in rapid manufacturing of prototypes were carried out, *e.g.* medical vascular implants [1—4].

Previous research on the application of hybrid composites in RM has indicated that such composites allow eliminating costly metal models at the stage of preparation of test gears [5—9].

The aim of this work was the development of new hybrid composites filled with two filler types of different geometric structure: silsesquioxanes (POSS) modified

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layered aluminosilicates (bentonites) and POSS modified silica. Our recent studies confirmed that these composites may have improved mechanical strength and dimensional stability of cast models. Prototypical models made of hybrid composites were used in testing of new transmission solutions built with parts made of polymer materials.

EXPRIMENTAL PART

Materials

The following products have been used in the research:

— epoxy resin Epidian 6 (EP) with Z-1 hardener (triethylenetetramine), „Organika-Sarzyna" Chemical Plant (Poland);

— bentonite modified with octakis(tetramethylammonium)octasilsesquioxane (BP1), according to the procedure described in the patent [10];

— bentonite modified with octakis{3-[*N*-(hydroxyethyl)dimethylamino]propyl} octasilsesquioxane (BP2), according to the procedure described in the patent [10];

— silica modified with 20 parts by weight of mono[3-(2-aminoethylamino)propyl]hepta-(isobutyl)octasilsesquioxane (K), according to the procedure described in the patent application [11].

Preparation of epoxy resin composition

Modified bentonite (BP1 or BP2) and modified silica (K), in equal proportions, were added in the total amount of 1.5; 3.0 and 4.5 wt % to liquid EP and the obtained mixture was homogenized in a multistage process. First, modified bentonite was added to epoxy resin and dispersed to get a homogeneous suspension, next, modified silica was added and dispersed analogously. Three-stage homogenization was carried out as follows:

— preliminary mixing at the room temperature for 20 min using a low-speed stirrer;

— mixing for 15 min using an ultrasonic homogenizer, mixture preheated to 50 °C;

— mixing using a high-speed turbine mixer, in a container preheated to 50 °C, at stirrer speed of 10 000 rpm (homogenizing in the mixer for 30 min);

— final homogenizing for 15 min in a cylindrical grinder (cylinder with a small gap of 0.75 mm and moving cylinder speed of 6000 rpm, which guaranteed high shearing).

Compositions prepared this way were stored at the temperature of approx. 4 °C, in order to prevent filler sedimentation.

Samples of the compositions are denoted by symbols containing symbols of components and value of filler content, which illustrates an example: EPBP1K-1.5.

Preparation of cast test specimens and gear wheel prototypes made of EP composites

Prepared EP compositions were cured with Z-1 hardener (13 wt %), as recommended its manufacturer. Compositions were degassed in a laboratory vacuum chamber VAKUUM UHG 400 (Schuechl, Germany) and cast at the temperature of 40 °C into silicone molds for cast profiles for strength testing according to ISO 527-1:1998 standard. In the case of gear wheels casting, silicone molds were preheated to 40 °C for 2 h before the operation started. Cast profiles and prototypes were cured at the room temperature for 24 h and then post-cured at the temperature of 100 °C for 6 h. After two days, strength tests of cast profiles were carried out according to appropriate standards.

Methods of testing

Thixotropic properties of hybrid compositions before curing

Thixotropic properties of the analyzed compositions were determined at 25 °C with use of a RheoStress RS6000 rotational viscometer. The analyses were carried out using the method of flow hysteresis loop test, mentioned in the reference materials [12], with increasing and decreasing shear rate. Measurements were made using the cone-plate system with diameter of 20 mm. The obtained results were used in calculating the area of flow hysteresis loop, which evaluates the energy of break down thixotropic structure of the studied compositions.

Mechanical properties of cured composition

Stress tension at break (σ_r) was determined according to ISO 527-1:1998 standard, with use of the INSTRON 5967 tensile testing machine. Tension speed was 2 mm/min and measurement temperature was controlled and kept at 23 °C.

Hardness (Rockwell scale — *HR*) was determined using a ZWICK 3106 hardness tester, according to EN 10109-1 standard. Applied indenter load was 358 N. The arithmetic mean of at least 10 measurements has been taken as the final result.

Charpy impact strength (*U*) was determined according to PN-EN ISO 179-1 standard, with use of a Gerhard Zorn PSW4J (Germany) instrument, equipped with 1 J impact energy hammer and a digital result display.

Analyzing geometric accuracy of produced gear wheel models

Geometric accuracy of gear wheel models cast from the prepared composites in a silicone mold was analyzed using a WENZEL LH 87 coordinate measuring machine with standard Metrosoft CM3.8 software installed, which enables controlling deviations in the course of the measurement. Evaluations were made with a measurement head with a 2 mm probe, with scanning speed of 4 mm/s and scanning step of 0.5 mm. The measuring path contained 1601 points.

Morphology of composites

The morphology of composites was observed by scanning electron microscopy (SEM) using instrument type Jeol 234a. The samples were frozen in dry ice and then fractured by impact-breaking. Before SEM observations the samples were coated with a thin layer of gold.

RESULTS AND DISCUSSION

Analysis of rheological properties of the tested compositions

The value of the viscosity hysteresis loop area (the area contained between curve 1 determined at increasing shear rate and curve 2 determined at decreasing shear rate, shown for exemplary sample in Fig. 1) reflects the energy required to break down the thixotropic structure.

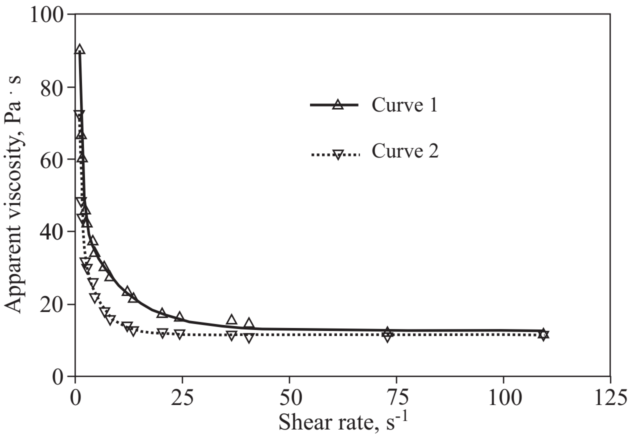

Fig. 1. Changes in apparent viscosity of EPBP1K-3.0 composite at increasing (curve 1) and decreasing (curve 2) shear rate

The results of the hysteresis area determination for prepared composites are collected in Table 1.

a) b)

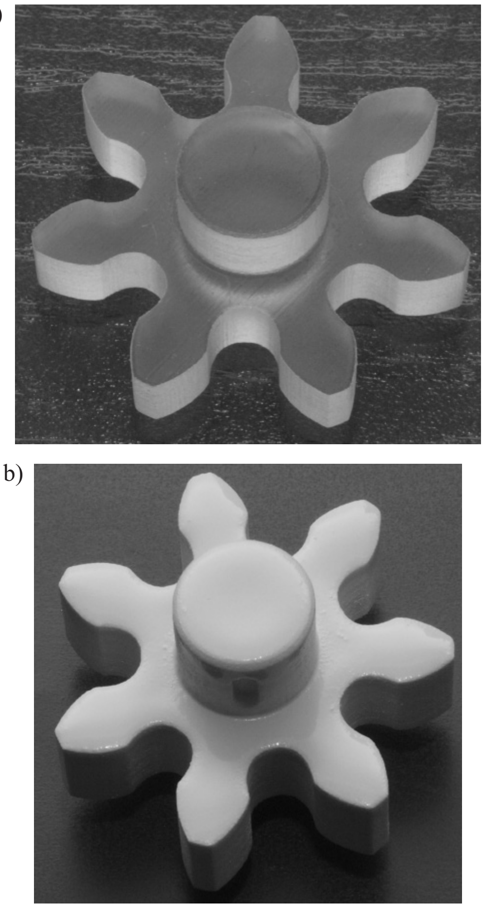

Fig. 2. View of gear wheel prototypes made of: a) unfilled EP, b) EPBP1K-3.0

It has been found that EP compositions containing combinations of BP1 or BP2 filler and K were characterized by good thixotropic properties. Additionally, an increase in the area of the viscosity hysteresis loop with increase of the amount of fillers used in the composition has been observed. Unfortunately, in the course of casting of gear wheel prototypes, significant increase of viscosity has been found in compositions containing 4.5 wt % of fillers, which considerably hindered filling and degassing of the mold cavity. In the case of casting gear wheel models using compositions with 1.5 wt % and 3.0 wt % of filler addition, no such difficulties have been found. Gear wheel prototypes made of unfilled EP and EPBP1K-3.0 composition are presented in Fig. 2.

T a b l e 1. Results of determination of the hysteresis area and mechanical properties of epoxy composites

Determined property	Sample symbol						
	EP	EPBP1K-1.5	EPBP1K-3.0	EPBP1K-4.5	EPBP2K-1.5	EPBP2K-3.0	EPBP2K-4.5
Area of viscosity hysteresis loop, J/m^3	—	7.1	9.2	12.8	7.1	8.9	11.2
Break tension (σ_r), MPa	46.2 ± 1.3	53.87 ± 0.9	65.88 ± 0.8	66.57 ± 1.1	51.42 ± 0.8	63,43 ± 1.1	64.13 ± 0.9
Charpy impact strength (*U*), kJ/m^2	4.2 ± 1.3	6.09 ± 0.43	8.1 ± 0.57	7.65 ± 0.61	5.90 ± 0.32	7.32 ± 0.41	7.44 ± 0.52
Hardness (Rockwell scale) (*HR*), N/mm^2	144.9 ± 2.3	143.88 ± 2.1	153.74 ± 1.6	156.35 ± 1.1	144.32 ± 1.2	154.03 ± 1.4	156.64 ± 0.9
Radial shrinkage (S_p), %	2.0	1.2	0.9	0.8	1.2	1.0	0.8
Axial shrinkage (S_o), %	1.9	1.1	0.7	0.6	1.1	0.8	0.7

Analysis of mechanical properties of obtained composites

In Table 1 are shown the mechanical properties of prepared composites and unfilled EP: stress tension at break (σ_r), Charpy impact strength (U) and hardness (Rockwell scale, HR). Adding a combination of nanofillers (POSS-modified bentonite and POSS-modified silica) to EP has a considerable impact on tensile strength, increasing it by up to 44 %. Unnotched impact strength can rise as a result of such modification by as much as 93 % (Table 1). Slight improvement of Rockwell hardness by 6—8 % has been observed for composites with 3 and 4.5 wt % content of fillers.

Analysis of geometric accuracy

The obtained composite gear wheels were analyzed with coordinate measuring technique in terms of shape and dimensional accuracy. Measuring results indicate that actual dimensions of produced gear wheels differ in relation to the dimensions of the silicone mold cavity, that should result from radial shrinkage (S_P) and axial shrinkage (S_o) (Table 1). By introducing the combination of fillers, shrinkage of analyzed composites was reduced, which resulted in improvement of dimensional accuracy of the models, *e.g.* gear wheels.

Significant effect of the used hybrid fillers and their content in the composite on this undesirable phenomenon was observed. Best results of radial and axial shrinkage reduction have been reached for EPBP1K-4.5 composite, where S_P was reduced from 2.0 % (unfilled EP) to 0.8 %, while S_o from 1.9 % (EP) to 0.6 % (Table 1). It guarantees proper functioning of the gear wheels used in fatigue tests carried out at measuring stations.

Characteristics of composites morphology

SEM microphotographs of brittle fractures of tested cast profiles, shown in Fig. 3, indicated significant differences in morphology of EP composites with the addition of hybrid fillers. On the surface of the fracture of unfilled hardened EP resin (Fig. 3a), only small furrows caused by the fracture are visible. The addition of BP1 and K causes a radical change in composite morphology (Fig. 3b). Fragments resembling shattered platelets become visible on the fracture surface, and phases (resin or fillers) can hardly be distinguished. This morphology may reflect the layered structure of modified layered aluminosilicate (bentonite) and its organophilic character, which facilitates penetration of polymer chains between filler platelets and gives the composite layered structure. With a larger amount of these fillers in the composite (Fig. 3c), filler agglomerates with size of 1 μm have also been observed. It indicates that a micro-composite structure was formed in certain areas, which reduces the strengthening effect in the case of composites containing EPBP1K-4.5 (Table 1).

CONCLUSIONS

— The presence of hybrid fillers in EP compositions significantly improves the thixotropic properties. The optimal amount of fillers, which enables good filling of the mold during low-pressure casting composite was found between 1.5 and 3.0 wt %.

— Developed multi-stage homogenized hybrid filled EP composites had regular layered morphology, visible in SEM micrographs, and considerably improved mechanical properties. In comparison to unfilled EP, tensile strength increased by up to 44 % and unnotched impact strength by even 93 %.

— Using of hybrid filler combinations to EP influenced reduction of radial and axial shrinkage. It has been reflected also in the improvement of dimensional accuracy of the cast gear wheels which has guaranteed proper intermating of gears. The lowest dimensional molding shrinkage has been observed for gear wheel prototypes made of EPBP1K-4.5 composite.

ACKNOWLEDGMENT

Financial support of Structural Funds in the Operational Program — Innovative Economy (IE OP) financed from the European Regional Development Fund — Project „Modern

a) b) c)

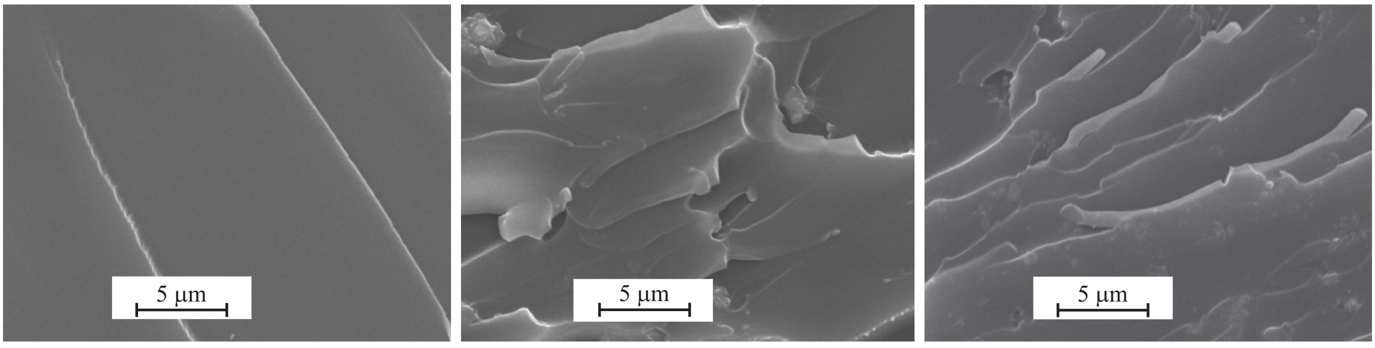

Fig. 3. SEM microphotographs of brittle fracture surfaces of: a) unfilled EP, b) EPBP1K-3.0, c) EPBP1K-4.5

material technologies in aerospace industry", No. POIG.01.01.02-00-015/08-00 is gratefully acknowledged.

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Received 1 IV 2014.

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