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Hybrid polymer composites for rapid prototyping of gears

RAPID COMMUNICATION

Summary — Based on unsaturated polyester resin (UP) of type Polimal 109-32RPyk, there were obtained hybrid composites with addition of four different inorganic ingredients. There were assessed mechanical and processing properties of these composites, especially regarding their application to production of gears with rapid prototyping methods. There was determined an apparent improvement in mechanical properties of hybrid composite samples compared to the control sample of pure UP. Tensile strength increased by up to 85 %, unnotched impact strength — by 95 % and Brinell hardness of samples by as much as 110 %. With a coordinate measuring machine there was also examined geometric accuracy of models produced from the obtained composites. Using a scanning electron microscope (SEM) there was observed surface morphology of brittle fractures.
Key words: unsaturated polyester resin, hybrid composites, mechanical properties, morphology, gears.

ZASTOSOWANIE KOMPOZYTÓW HYBRYDOWYCH DO SZYBKIEGO PROTOTYPOWANIA KÓŁ ZĘBATYCH

Streszczenie — Na bazie nienasyconej żywicy poliestrowej (UP) typu Polimal 109-32RPyk otrzymano kompozyty hybrydowe z dodatkiem czterech różnych składników nieorganicznych (tabela 1). Oceniono właściwości mechaniczne oraz przetwórcze tych kompozytów, zwłaszcza z punktu widzenia ich zastosowań do otrzymywania kół zębatych w metodach szybkiego prototypowania. Stwierdzono wyraźną poprawę właściwości mechanicznych próbek kompozytów hybrydowych w porównaniu z kontrolną próbką czystej UP. Wytrzymałość na rozciąganie wzrosła maksymalnie o 85 %, udarność bez karbu o 95 %, a twardość próbek wg Brinella aż o 110 % (tabela 1). Na stanowisku współrzędnościowym zbadano także dokładność geometryczną modeli wytworzonych z otrzymanych kompozytów i porównano je z modelem wykonanym z czystej UP (rys. 2 i 3). Za pomocą skaningowego mikroskopu elektronowego (SEM) obserwowano morfologię na powierzchni kruchych przełomów (rys. 1).
Słowa kluczowe: nienasycona żywica poliestrowa, kompozyty hybrydowe, właściwości mechaniczne, morfologia, koła zębate.

According to the definition, a hybrid composite is a composite material in which two or more high-performance reinforcements are combined [1]. This contrasts with the term hybrid material or hybrid polymer which is understood as a polymer where an organic part is combined on the molecular level with an inorganic part [2].

The main reason for growing interest in the hybrid composites [3—14] is that they combine ease of shaping, typical of polymers, with much improved stiffness and impact strength. A well designed hybrid composite makes use of the advantages of components to eliminate or minimize the effects of failures that occur when unmodified polymers are used. Another purpose of using hybrid reinforcements is to reduce anisotropy and improve surface quality of parts, minimize the cost of products, *e.g.* by replacing, at least in part, expensive fillers, such as carbon or aramid fibers with more economical ones (glass or natural fibers) while preserving required toughness of the composite.

The aim of our studies was preparation of hybrid composites from unsaturated polyesters containing modified layered aluminosilicates and spherical fillers.

EXPERIMENTAL

Materials

Modified bentonite: Nanobent® ZR1 (ZR1), and halloysite (H) were kindly provided by ZGM Zębiec (Po-

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land). Unsaturated polyester resin Polimal® 109-32RPyk (UP) and curing agent Luperox K-1 were products of ZCh Organika-Sarzyna (Poland). Dolomite P20 (P20) was a product of "PIOTROWICE" Sp. z o.o. plant (Poland). Barquat CB80 which is quaternary ammonium salt (QAS) was purchased from Lonza, Switzerland. Silica HDK N-20 (HDK) was a product of Wacker Chemie company (Germany). Modified vermiculite (MV) was obtained from Vermiculite mineral (ZGM Zębiec, Poland) which was modified with QAS according to the procedure described previously [14, 15].

Preparation of composites

The filler containing compositions of UP used in this work are presented in Table 1. The composites were prepared in several stages. Initially, the resin was combined with selected components with a slowly-rotating laboratory mixer and then the mixture was further homogenized using:

— an ultrasonic cleaner U-501 (a product of "ULTRON", Olsztyn, Poland) for 30 min,

— high-speed blade homogenizers 302 and 309 (products of "Mechanika Precyzyjna", Poland).

T a b l e 1. Compositions based on unsaturated polyester resin Polimal® 109-32RPyk used for rapid prototyping

Symbol of composition	Type of filler and its concentration, wt. %				
	MV	ZR1	H	P20	HDK
K 1	1				
K 2		1			
K 3			2		
K 4				2	
K 5					1
K 6	1		2		
K 7	1			2	
K 8	1				1
K 9		1	2		
K 10		1		2	
K 11		1			1
K 12	1		2	2	
K 13	1		2		1
K 14	1			2	1
K 15	1		2	2	1
K 16		1	2	2	
K 17		1	2		1
K 18		1		2	1
K 19		1	2	2	1

The shear rates generated by the blades in the homogenizers was in both cases about 850 s^{-1} and the time of mixing was 20 min. Hence, the overall time of homogenization was *ca*. 70 min (30 min with ultrasonic waves, 20 min in homogenizer 302, and 20 min in homogenizer 309). The temperature of homogenization was 50 °C. In order to prevent aging, the compositions were stored in a fridge at 4 °C until they were used for casting.

Samples for testing mechanical properties

The compositions were thoroughly mixed with Luperox K-1 curing agent (in amount of 2 wt. %) degassed in laboratory vacuum chamber (VAKUUM UHG 400, Schuechl, Germany) and cast into silicone molds prepared according to ISO 527-1:1998 standard. After 24 hrs the samples were post-cured for 2 hrs at 80 °C.

Preparation of prototype specimens

The specimens of gear were prepared from the composite precursors with the vacuum casting method (VC). The models were cast in silicone molds (MM 240 TV A+B, company ACC Silicones, Germany) and cured in a vacuum chamber VAKUUM UHG 400 (Germany). Before the actual cast, the silicone molds were heated in an oven for 2 hrs at 60 °C. Each UP composition containing 2 wt. % of Luperox curing agent was placed in the chamber, where it was thoroughly mixed and degassed before casting into silicone molds. Then it was cured at room temperature (25 °C) for 24 hrs and post-cured at 80 °C for 2 hrs.

Methods of testing

Mechanical properties

The tensile strength measurements were carried out at 20 °C on an FP 100 testing machine at the rate of elongation of 2 mm/min, according to ISO 527-1:1998 standard. The Brinell hardness was measured according to ISO 2039-1:1987 standard. The impact strength was measured with a Charpy hammer of impact energy 0.5 J, according to PN-EN ISO 179-2:2001 standard.

Morphology testing

The impact fracture surfaces obtained after freezing the samples in a dry ice bath were examined in the scanning electron microscope (SEM) Jeol 234a (Japan).

Measurements of geometric precision of prototype specimens

The analyses of geometric precision of different models of gear wheels cast from different composite precursors were performed on a coordinate measuring machine WENZEL LH 87 equipped with Metrosoft CM3.8 special software, which records deviations during measurements. The software provides also geometric interpretation of deviations with respect to both the mold and the nominal model (3D-CAD). The measurements were performed using a measuring head equipped with a ball 2 mm in diameter. The scan rate was 4 mm/s with the scanning step of 0.5 mm. The measuring path consisted of 1601 points.

RESULTS AND DISCUSSION

Mechanical properties of the composites

Changes in mechanical properties of the composites relative to those of unfilled unsaturated polyester resin (UP) are collected in Table 2. Tensile strength (σ_r), Charpy impact strength (*U*), and Brinell hardness (*HB*) were measured. Introduction of a nanofiller to the resin along with fillers such as halloysite (H), colloidal silica (HDK) or dolomite powder (P20) clearly improves the tensile strength (by 85 %), impact strength (by 95 %) and Brinell hardness (by as much as 110 %). By applying different combinations of fillers, improvements in all mechanical properties are possible, which is not always the case when a single filler is used. And this is very important when gear prototypes are prepared for fatigue tests. Another advantage of using two or more fillers is cost reduction, since the amount of more expensive nanofiller can be reduced by applying a cheaper aluminosilicate, such as halloysite.

T a b l e 2. Results of mechanical tests of the composites prepared in this work expressed as percentage change of the property relative to that of the neat unsaturated polyester resin

Composite	$\Delta\sigma_r$, %	ΔU, %	ΔHB, %
K 1	38.4	20.8	45.1
K 2	30.5	18.3	39.6
K 3	10.4	40.3	5.2
K 4	5.4	35.3	5.2
K 5	10.3	5.5	10.6
K 6	55.3	70.2	75.3
K 7	45.3	55.2	60.4
K 8	45.2	45.7	55.2
K 9	50.7	60.3	65.4
K 10	48.4	55.3	50.7
K 11	50.5	45.3	60.4
K 12	70.5	90.6	95.3
K 13	85.6	85.2	110.5
K 14	80.3	75.4	95.2
K 15	85.2	95.5	95.3
K 16	65.6	80.4	85.4
K 17	75.3	80.4	100.2
K 18	70.3	70.5	85.1
K 19	80.2	90.4	90.3

Structure and morphology

Fig. 1 showing the SEM microphotographs of the brittle fracture surfaces of the samples revealed significant differences in morphology of UP composites containing different fillers. On the fracture surface of the neat UP resin (Fig. 1a) one observes only small wrinkles caused by the crack. The presence of vermiculite modified with QAS (MV), H or HDK changes the fracture surface dramatically (Fig. 1b). In this microphotograph one can see fragments resembling shattered plates with the phases (resin or fillers) hardly distinguishable. This morphology may reflect the layered structure of aluminosilicate (MV) and its organophilic character facilitating compatibility with the resin.

Geometric precision

The coordinate measuring technique provides an assessment of the dimension and shape precision of the gear cast from the composites studied in this work. Measurements were made by a measuring head having the probe about 2 mm in diameter at the scanning speed of 4 mm/s, with the scanning step 0.5 mm. The measure path contained 1601 points. It is possible to analyze the results of measurements (in protocol — Figs. 2 and 3) along the whole measure path and in interesting points (in the tables within figures). The tables include the following information: the point number, nominal value,

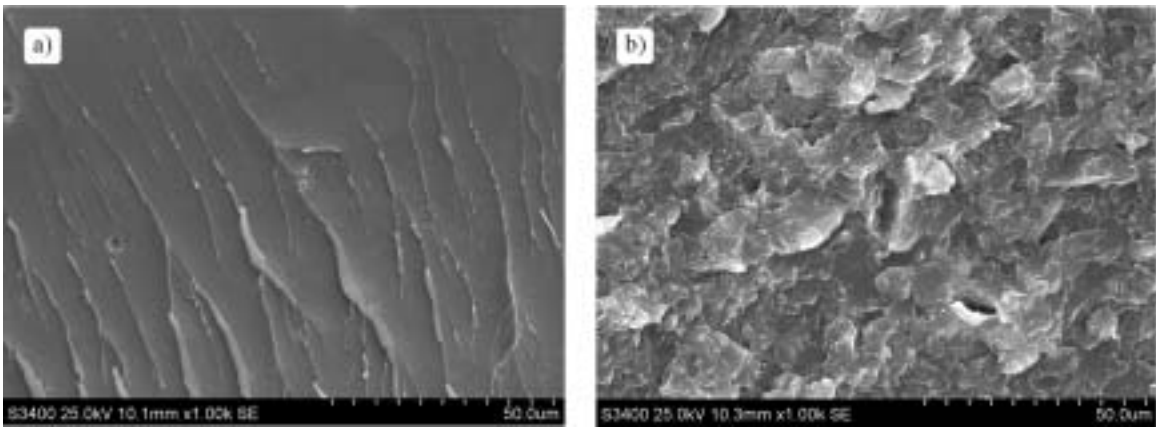

Fig. 1. SEM micrographs of brittle fracture surfaces of cured UP samples: a) neat UP resin, b) UP resin containing 1 wt. % of QAS modified vermiculite, 2 wt. % of halloysite and 1 wt. % of colloidal silica (sample K13)

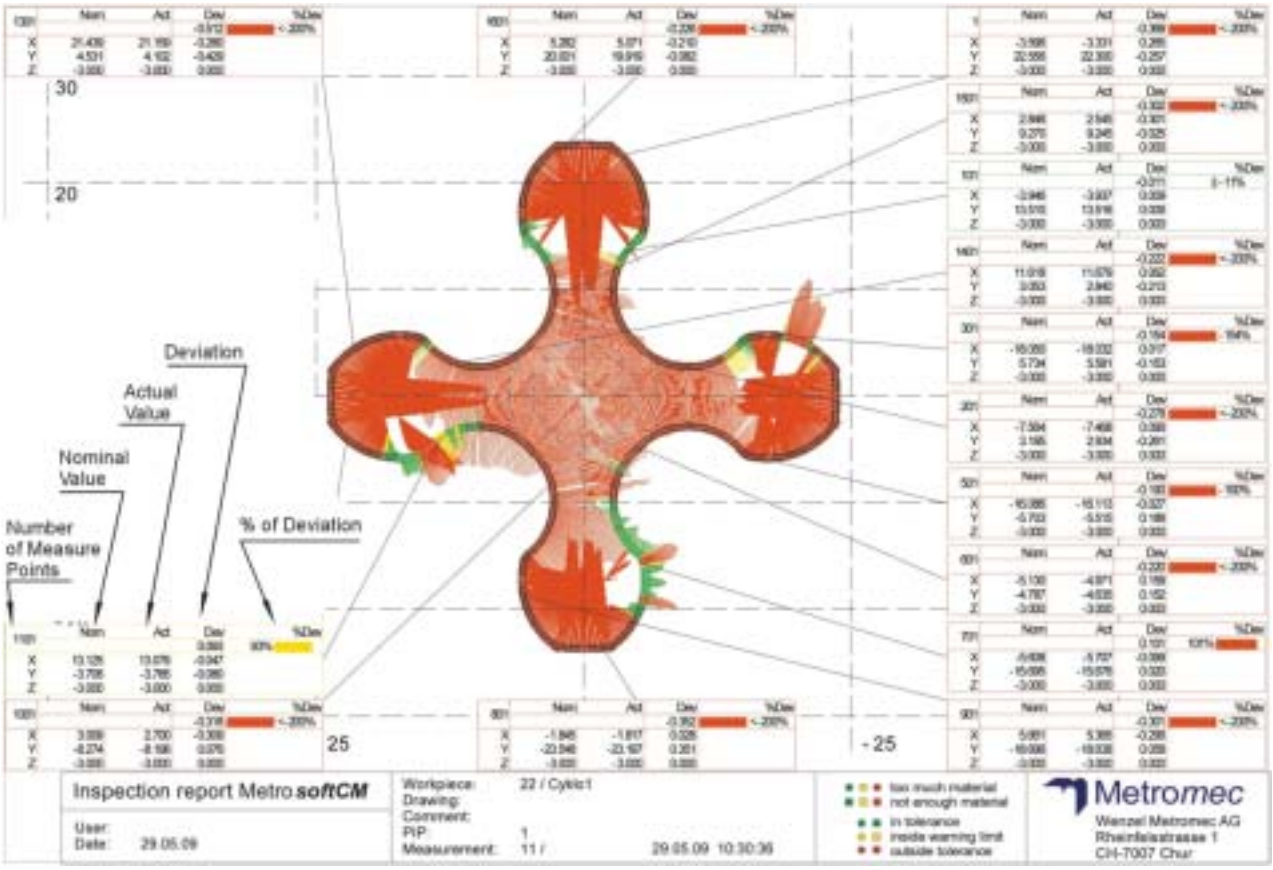

Fig. 2. Measuring protocol of the toothed wheel cast from unfilled unsaturated polyester resin

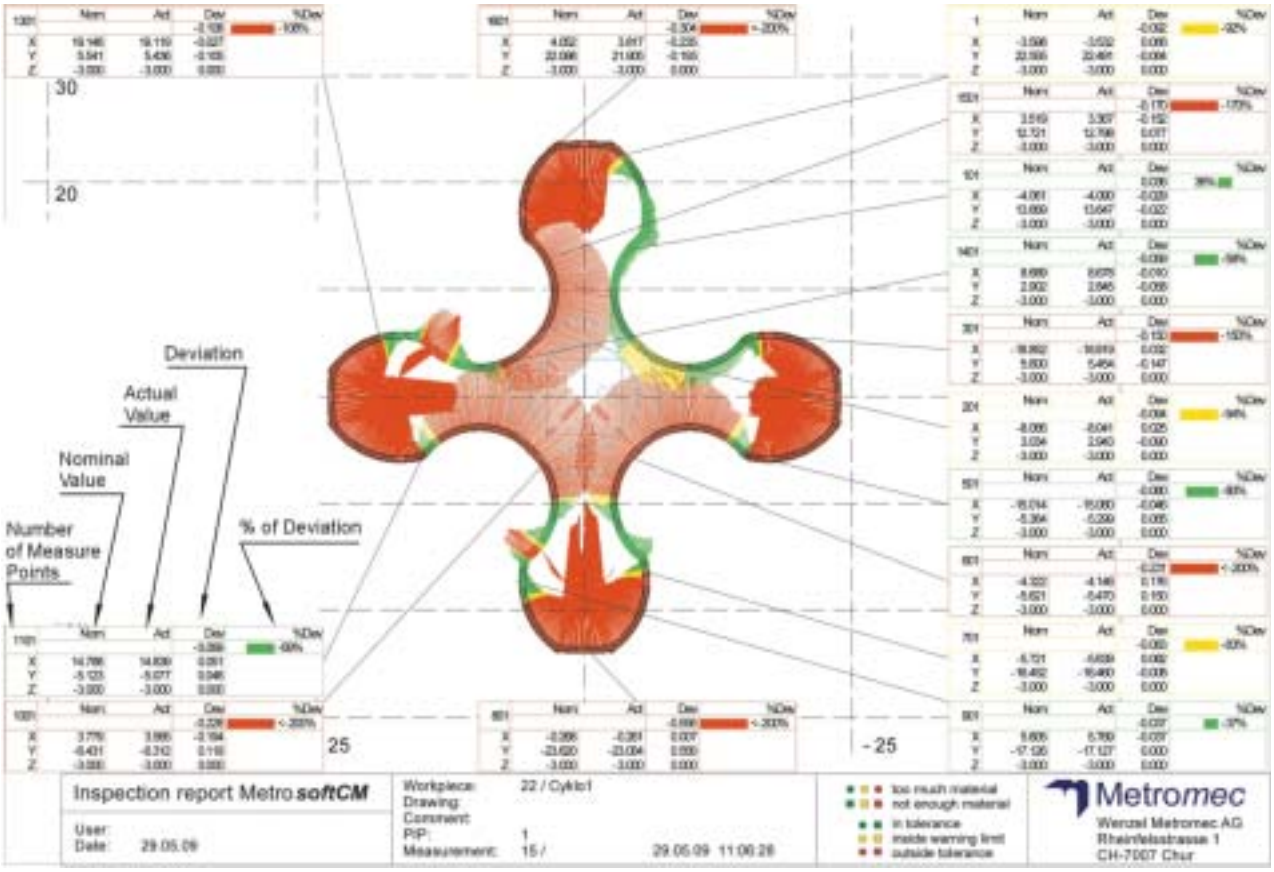

Fig. 3. Measuring protocol of the toothed wheel cast from unsaturated polyester resin filled with 1 wt. % of vermiculite modified with QAS, 2 wt. % of halloysite and 1 wt. % of colloidal silica

actual value, deviation and percent of deviation. The measurements indicate real dimensions of wheels to be considerably different from dimensions of the nest in the silicone mold, corrected for resin shrinkage. This means that the effect of shrinkage of the resin was substantially reduced by the presence of the fillers.

The measuring protocol for a model of tooth wheel cast from neat unfilled UP is presented in Fig. 2. In Fig. 3, on the other hand, there is presented a measuring protocol of that cast from UP resin filled with 1 wt. % of MV, 2 wt. % of H and 1 wt. % of HDK (sample K13). Both protocols contain plots of dimension deviations along measuring paths as well as the values of deviations at selected points.

CONCLUSIONS

The results of this work brought about the following conclusions:

— The fillers used for modification of commercial unsaturated polyester resin Polimal® 109-32RPyk substantially improved mechanical properties of composites as compared with the neat resin. For the best compositions, the tensile strength increased by 85 %, the unnotched impact strength by 95 % and Brinell hardness by 110 %.

— Another advantage of using a combination of fillers to modify the unsaturated polyester resin was reduction of cure shrinkage and hence improvement in dimensions accuracy of the elements cast from the composite precursors. The best dimensional accuracy was obtained for the testing wheels cast from UP filled with 1 wt. % of vermiculite modified with QAS, 2 wt. % of halloysite and 1 wt. % of colloidal silica.

— By applying multistage homogenization of the cast compositions, hybrid composites were obtained with a regular platelet structure of the brittle fracture surface well seen in the SEM micrographs. This structure provided improved mechanical properties of the composites.

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