The investigation of polyester composites filled by modified bentonite*)

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Abstract: In this study, organically treated montmorillonite, NanoBent®ZR2 (SN), was used as a nanofiller for polyester composites containing 10, 12 or 15 wt % of glass reinforced polyester waste (W). The nanofiller was introduced to the compositions in the amount of 2 wt % of all the components. The composite matrix was unsaturated orthophthalic polyester resin (P) and dolomite dust (D) and glass reinforced polyester waste were used as a filler. The morphology of polyester/nanofiller composites (P98/SN2) and polyester composites with dolomite dust, glass reinforced waste and nanofiller were tested by means of wide angle X-ray scattering (WAXS) and scanning electron microscopy (SEM). The influence of the nanofiller on the strengths of the polyester composites was also examined. SEM studies revealed incomplete montmorillonite dispersion in the polyester matrix. After adding nanofiller to a polyester composite with 15 wt % of glass polyester waste, an increase in the compressive strength was observed. The proposed method for improving the properties of composites with glass reinforced polyester waste as a nanofiller is a new solution and to our knowledge has not been suggested so far.

Keywords: polyester composites, nanofiller, glass reinforced polyester waste, modified montmorillonite.

Badania kompozytów poliestrowych napełnionych modyfikowanym bentonitem

Streszczenie: Do kompozytów na bazie ortoftalowej nienasyconej żywicy poliestrowej (P, 18 % mas.), napełnionych odpadami poliestrowo-szklanymi (W) w ilości 10, 12 lub 15 % mas. oraz mączką dolomitową (D, odpowiednio, 65—72 % mas.), dodawano 2 % mas. nanonapełniacza — organicznie modyfikowanego montmorylonitu (SN, rys. 1). Otrzymane kompozyty badano metodami szerokokątowej dyfrakcji promieniowania rentgenowskiego (WAXS) (rys. 2) i skaningowej mikroskopii elektronowej (SEM) (rys. 3—5). Określono wpływ dodatku montmorylonitu na wytrzymałość na ściskanie i zginanie. Stwierdzono niecałkowite rozproszenie montmorylonitu w napełnionej osnowie poliestrowej. Wyniki badań wskazują, że dodatek 2 % mas. modyfikowanego montmorylonitu do kompozytów poliestrowych z udziałem 15 % mas. odpadów poliestrowo-szklanych pozwala na uzyskanie materiału wykazującego korzystne właściwości wytrzymałościowe. Proponowany sposób modyfikacji kompozytów zawierających odpady poliestrowo-szklane jest rozwiązaniem nowym i dotychczas niestosowanym.

Słowa kluczowe: kompozyty poliestrowe, nanonapełniacz, odpady poliestrowo-szklane, modyfikowany montmorylonit.

Unsaturated polyester resins compounded with fillers find a wide range of applications [1, 2]. The use of a nanofiller provides an opportunity for obtaining new polymer materials with unique properties. The unique properties obtained by a nanocomposite may be attributed to a well-dispersed reinforcing phase creating a large interfacial surface area. Many nanoclays are built of smectite clays known as montmorillonite (MMT), a hydrated sodium calcium aluminum magnesium silicate hydroxide, $(Na,Ca)(Al,Mg)_6(Si_4O_{10})_3 \cdot nH_2O$. Montmorillonite is most often applied because of its high availability, low price, its' specific surface and large ion exchange capacity. However, the hydrophilic character of MMT is a barrier for the even dispersion of clay platelets throughout the polymer. A modification of MMT is necessary in order to decrease the surface tension, decrease the wettability and give MMT an organophilic character. Quaternary ammonium salts containing at least an organophilic *n*-alkyl chain are most often used to replace the cations in the galleries [3—9].

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Oleksy et al. [7] studied the effect of quaternary ammonium salts as modifiers of bentonites on selected properties of polyester composites. The presence of modified smectite clays (NanoBent®ZR2) in a cured commercial polyester resin (2 wt %) improved their tensile strength by 22.5 %, Brinell hardness by 22 % and unnotched impact strength by 25 %. Modified montmorillonite significantly improved the polyester resin stability, with practically no influence on the gelation time. Another paper showed positive effects of montmorillonite on the properties of the composition of polyester resins with excellent thixotropy [8]. This was explained with respect to the chemical structure of the modifier as the presence of large aliphatic substituents resulting in the widening of the distance between the layers of montmorillonite, thus facilitating penetration of the polyester chain.

In 2012, the production volume of glass reinforced composites was more than 1 Mt in Europe and there is expected to be more than 300 kt of their waste. Several studies have reported how to solve the problem of glass reinforced polyester waste [10—12]. With a ban on the disposal of glass reinforced polyester waste into landfill sites and the ever increasing costs of waste disposal, the stabilizing of waste into a composite system has an increased attraction. Earlier research [13, 14] in the Department of Chemistry and Industrial Commodity Science in Gdynia Maritime University concentrated on the material recycling technology of glass reinforced polyester waste. They were shredded into smaller fragments and used as a filler in polyester resin. Our research showed that it is possible to add 10 wt % or 12 wt % of glass reinforced polyester waste to polyester composites (having 20 wt % of resin) with dolomite dust. The most expensive component of polyester composites is resin, thus it is reasonable to diminish that amount as much as possible. Therefore, composites with less than 20 wt % resin were the subject of this paper.

This paper complements the existing knowledge on the problem of material recycling of glass reinforced polyester waste by modification of composites with waste using nanofillers. The purpose of the present work is to obtain composites having 18 wt % of polyester resin, 10, 12 or 15 wt % of glass reinforced polyester waste and NanoBent®ZR2 as a nanofiller. In this way we will obtain a new composite system for the recycling technology of glass reinforced polyester waste, which from the ecological point of view is still attractive. A basic experimental study to analyze the possibilities of recycling more waste of polyester composites was done by adding 2 wt % of nanofiller. Earlier studies with polyester composites having 20 wt % of resin and different amounts of glass reinforced polyester waste showed that the optimum properties were found to be for composites containing 2 wt % of nanofiller (NanoBent®ZR2) [14]. The morphology of polyester/nanofiller composites and polyester composites with dolomite dust, glass reinforced polyester waste and NanoBent®ZR2 have been tested. The influence of NanoBent®ZR2 on the mechanical properties of composites with waste was also determined. To better understand the studied systems, the polyester resin with only added nanofiller was examined.

EXPERIMENTAL PART

Materials

Modified bentonite, NanoBent®ZR2 [15], was used as a filler for polyester composites containing glass reinforced polyester waste. The bentonite was developed at Rzeszow University of Technology and was obtained from ZGM Zębiec (Poland). This is a bentonite (SN) with quaternary ammonium salts of the general formulate $R_1R_2R_3R_4$, where R_1 and R_2 are $-CH_3$, R_3 and R_4 are $-C_{10}H_{21}$. Oleksy et al. [9] reported that modification of bentonite with *N*,*N*-didecyl-*N*,*N*-dimetylammonium-chloride changes its structure, causing an increase in the distance between the layers of clays from 12.5 Å to 18.4 Å as determined by X-ray studies. The cation exchange capacity (CEC) of the nanofiller is a minimum of 80 meq/100 g and with an average particle size of 20—60 μm. In this paper, a polyester composite with 2 wt % of modified bentonite used as nanofiller was tested.

The composite matrix (P) was an orthophthalic polyester resin, Polimal 109-32K (product of Organika-Sarzyna), at an amount of 18 wt %. According to the producer data sheet, this resin contains about 35 wt % of styrene and it is a liquid with viscosity of ~0.3 Pa · s [16].

The fillers were dolomite dust (D) (< 3 mm) in the amount of 65—72 wt % and glass reinforced polyester waste (W) in the amount of 10—15 wt %. The waste of glass fiber reinforced cold-cured polyester laminates (coming directly from a company operating in the polyester composites industry, as an industrial by-product), was ground in a shredder manufactured by Kubala Sp. z o.o. The recyclate was a mixture of glass fiber and cured polyester resin particles. The grains of the recyclate were of different sizes: smaller than 0.3 mm (14.6 %), size 0.3—3.15 mm (47.9 %) and larger than 3.15 mm (37.5 %).

Preparation of samples

The following samples with nanofiller were studied:

— polyester composites with dolomite dust, glass reinforced polyester waste,

— polyester composites with dolomite dust, glass reinforced polyester waste and nanofiller,

— polyester resin/nanofiller composite.

In the case of composite polyester resin/nanofiller (P98/SN2), first NanoBent®ZR2 in the amount of 2 wt % was mechanically mixed with the polyester resin at a „frame" rate of approximately 2000 rpm/min. Then, the initiator (methyl ethyl ketone peroxide, Metox-50 from Oxytop Sp. z o.o.) in the amount of 0.01 wt % and the accelerator (cobalt naphthenate 10 %, from ILT) in the

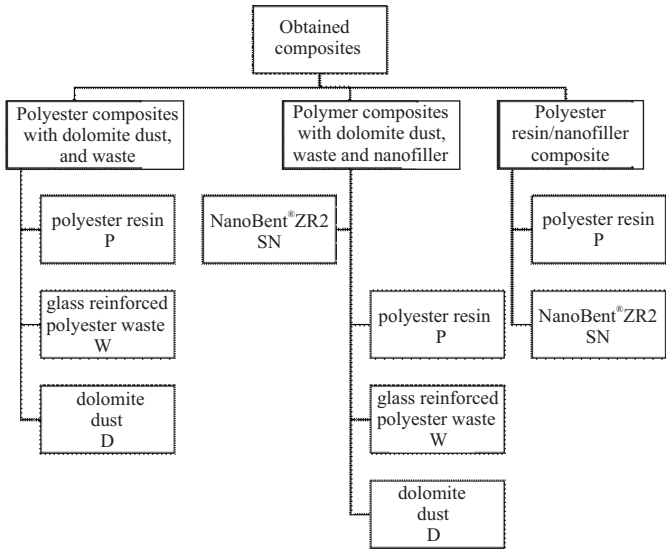


Fig. 1. Composition of composites studied in this paper

amount of 1 wt % were added and all components were mixed for a second time at room temperature.

Polyester composites with dolomite dust (72, 70 and 65 wt %), glass reinforced polyester waste (10, 12 and 15 wt %) with nanofiller (2 wt %) were obtained in a similar way as above. The fillers were mixed with the resin before the addition of the initiator and accelerator.

T a b l e 1. Sample compositions

Symbol of sample	Polyester resin, %	Dolomite dust, %	Glass reinforced polyester waste, %	Nano-filler, %
P18/W10/D72/SN0	18	72	10	0
P18/W10/D70/SN2	18	70	10	2
P18/W12/D70/SN0	18	70	12	0
P18/W12/D68/SN2	18	68	12	2
P18/W15/D67/SN0	18	67	15	0
P18/W15/D65/SN2	18	65	15	2

For comparison, polyester composites with dolomite dust and glass reinforced polyester waste without nanofiller were also prepared. Fig. 1 and Table 1 show the composition of all of the studied composites.

Methods of testing

The morphology of the composites was determined by means of wide angle X-ray scattering (WAXS) and scanning electron microscopy (SEM). The WAXS examinations were performed with CuK_α radiation at a wavelength of 1.5418 Å and nickel filtering. Measurements at standard parameters (voltage 30 kV, anodic current 25 mA) were performed within the 2θ angle range 1—10°. The X-ray diffractograms were recorded by a computer-controlled horizontal diffractometer, TUR M-62, equipped with a HZG-3 type goniometer.

For SEM studies, cryo-fractured surfaces of the samples (20 × 5 × 10 mm in size) coated with gold were used for observation under a SEM ZEISS EVO-40 operated at 10 kV.

The compressive strength and flexural strength of the composites of the samples (40 × 40 × 160 mm) were determined with a Universal Testing Machine EDB-60, under a rate of 2.64 kN/min according to the PN-EN 12372:2010P and PN-EN 1926:2007E standards. In the three-point-flexural test, the gauge length was 100 mm.

RESULTS AND DISCUSSION

Polyester resin/nanofiller composite

In Fig. 2, the results of WAXS studies for polyester resin/nanofiller composite (P98/SN2) and nanofiller (NanoBent®ZR2) are shown. WAXS pattern of the NanoBent®ZR2 has a peak at a 2θ value of 4.34° and that corresponds to an intergallery spacing of 20.33 Å. There is no such a peak observed in the WAXS pattern for P98/SN2 composite. The absence of a peak in Fig. 2 for the composite samples shows that they do not have an intercalated structure. However, this result does not preclude the creation of an exfoliated structure. The WAXS results are consistent with the works of other authors [3, 17—19] for composites with 1—5 wt % of nanofiller. According to these results, the disappearance of the above-mentioned peak may indicate the separation of the nanofiller layers and the formation of an exfoliated morphology. Such a suggestion, however, must be confirmed using other methods.

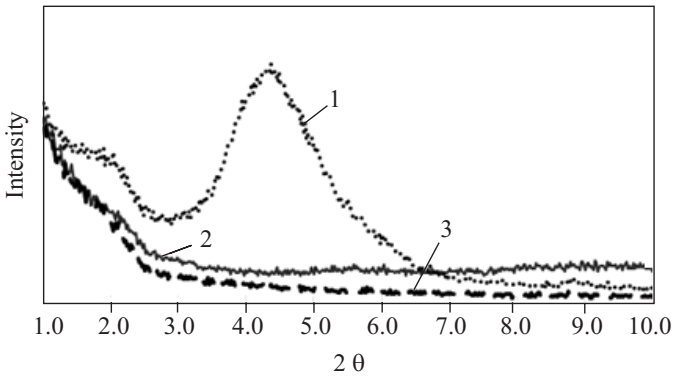
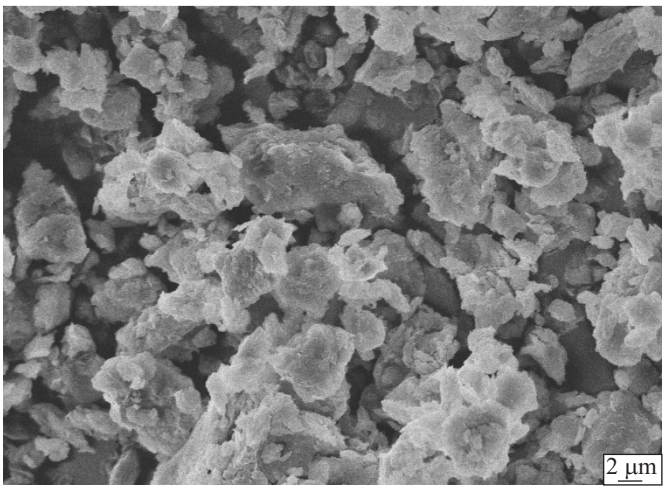


Fig. 2. 1 — WAXS pattern of SN, 2 — P98/SN2 and 3 — P18/W15/D65/SN2

SEM micrographs (Fig. 3: SN and P98/SN2) indicate a more complicated morphology for the studied composites. There are areas in the images of composite where separate particles of nanofiller (area indicated with continuous lines in Fig. 3b), where a good adhesion to the resin is present

a)



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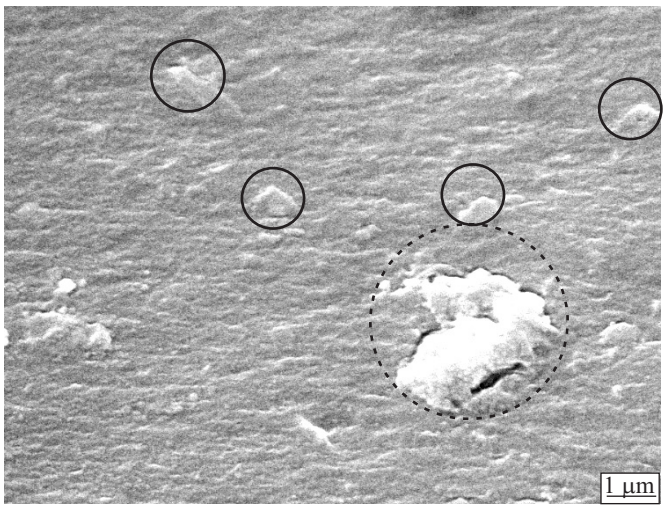
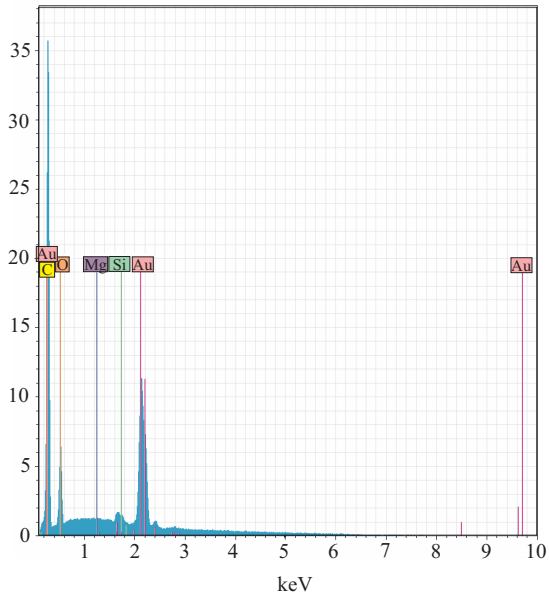


Fig. 3. SEM micrographs of the samples studied: a) SN, b) P98/SN2



Element	AN	Series	Net	Wt %	Norm. wt %	Norm. at %	Error in %
Carbon	6	K-series	58382	27.50	38.03	79.93	3.23
Oxygen	8	K-series	11422	5.66	7.81	12.32	0.80
Magnesium	12	K-series	250	0.08	0.10	0.11	0.03
Silicon	14	K-series	1519	0.67	0.93	0.83	0.06
Gold	79	M-series	53409	38.41	53.13	6.81	1.47
			Sum:	72.29	100	100	

Fig. 4. EDS result of SN microparticles in polyester resin

but there are also areas where agglomerates of the nanofiller (3 μm in size) with poor adhesion to polyester resin are visible (area indicated by dashed lines in Fig. 3b). Thus SEM analysis shows that only partial exfoliation of the nanofillers in polyester resin takes place. The nanofiller microparticles in the polyester resin in Fig. 3b were identified by EDS analyses from their peak values of carbon, oxygen, magnesium and silicon; a representative EDS result of a nanofiller microparticle is showed in Fig. 4.

Mechanical testing revealed that the addition of 2 wt % of NanoBent®ZR2 to the resin resulted in an increase in the compressive strengths to 24.1 ± 2.2 MPa from 15.5 ± 1.7 MPa for neat polyester resin. This can be explained by partial exfoliation of nanofiler particles. Unsaturated polyester can be dissolved in a polymerizable monomer such as styrene monomer, which diffuses through the galleries of the organoclay more easily than uncured polyester owing to its smaller molecular structure [4]. This reduces the styrene amount available for crosslinking in the medium, which is the reason of lower molecular weight between the crosslinking sites leading to restrictions in chain mobility and increasing the compressive strength. This mechanism for unsaturated polyester–layered silicate nanocomposite was described by Shu and co-workers [4].

Polyester composite with dolomite dust, glass reinforced polyester waste and nanofiller

In the WAXS pattern of the polyester composites with 10 wt %, 12 wt % or 15 wt % of glass reinforced polyester waste, dolomite dust, and NanoBent®ZR2 there was also no such WAXS peak, corresponding to (001) basal reflection of nanofiller preserving its stack-like organization (Fig. 2). Thus, the WAXS results indicate the absence of basal reflections that would be a suggestion of exfoliated structure.

The SEM microstructure of P18/W15/D65/SN2 is presented in Fig. 5a and we can see that it is complex. The polyester matrix in some places exhibits breaks through a

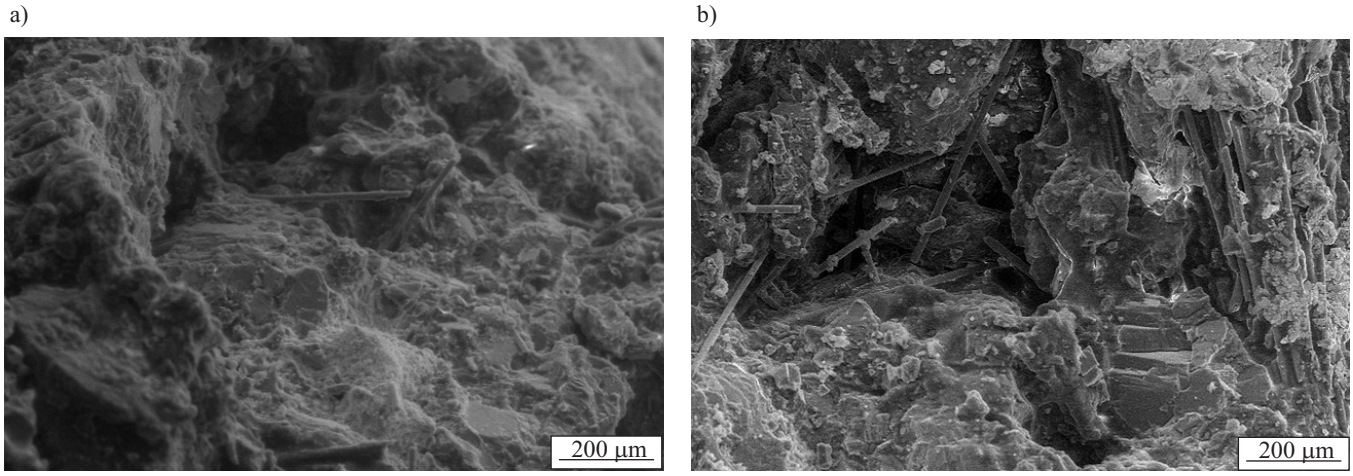


Fig. 5. SEM micrographs of the polyester composites: a) P18/W15/D65/SN2 and b) P18/W10/D70/SN2

ductile way. It shows filler particles evenly distributed in the continuous polyester matrix of the composite. The presence of glass fibers from the waste appears as rod shaped particles.

The SEM microstructure of P18/W10/D70/SN2 is presented in Fig. 5b. The composite constituents are not compact, good adhesion is not observed between them and more pores are visible than in P18/W15/D65/SN2 (with a small amount of dolomite dust). The explanation for this result can be discussed around the hydrophilic/hydrophobic character of the components. Organophilic nanofiller dispersed in hydrophobic polyester more easily interacts with hydrophobic glass reinforced polyester waste than with hydrophilic dolomite dust.

T a b l e 2. Mechanical properties of polyester composites with fillers (dolomite dust and glass reinforced polyester waste) with and without NanoBent®ZR2

Samples	Compressive strength, MPa	Flexural strength MPa
P18/W10/D72/SN0	45 ± 5.2	30.7 ± 4.8
P18/W10/D70/SN2	29.1 ± 4.8	25.3 ± 4.2
P18/W12/D70/SN0	25 ± 4.3	29.1 ± 5.3
P18/W12/D68/SN2	16.4 ± 3.8	24.8 ± 3.1
P18/W15/D67/SN0	12.2 ± 3.9	16.9 ± 4.5
P18/W15/D65/SN2	15.7 ± 4.5	24.1 ± 5.7

The results of mechanical property measurements are presented in Table 2 after adding nanofiller to the polyester composites with glass polyester waste. The addition of 2 wt % of the nanofiller to the composites with 10 wt % or 12 wt % of waste does not improve the mechanical properties (P18/W10/D70/SN2, P18/W12/D68/SN2). In contrast, application of 2 wt % of SN to the composite with 15 wt % of waste (P18/W15/D65/SN2) improves the mechanical properties. The waste particles are sufficiently close to one another and a more compact structure is received. Thus it is possible to add more waste into composites, which can be applied in building materials.

CONCLUSIONS

The morphology of polyester composites with dolomite dust, glass reinforced polyester and NanoBent®ZR2 and polyester/NanoBent®ZR2 composite have been studied with WAXS and SEM methods. The results for polyester/NanoBent®ZR2 samples obtained by the two methods are inconsistent. WAXS results show no intercalation structure but does not preclude of exfoliated morphology while SEM studies suggest that only partial exfoliation could take place. The addition of nanofiller to the composites does not result in a diffraction peak originating from the diffraction of the particles from montmorillonite. This indicates that the results for morphological studies of nanocomposites in which only WAXS results are presented should be more carefully scrutinized. By applying 2 wt % of NanoBent®ZR2 to polyester composite with 15 wt % of glass reinforced polyester waste, it is possible to improve their mechanical properties and recycle a larger amount of waste. In this way part, from the ecological point of view, glass polyester waste can be recycled and used in building materials.

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