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COMPOSITES THEORY AND PRACTICE

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THE APPLICATION OF NanoBent®ZR2 AS FILLER FOR MODIFICATION OF COMPOSITES CONTAINING GLASS REINFORCED POLYESTER WASTE

In this study, organically treated montmorillonite was used as a filler for composites containing glass reinforced polyester waste. The composites were prepared by in-situ polyester polymerization when the organoclay was added to the reaction medium simultaneously with the monomers. The influence of the amount of nanofiller on the selected properties of composites with waste has been tested. In this work, composites composed of polyester resin Polimal 109-32K (product of Organika--Sarzyna) and nanofiller NanoBent®ZR2 - organophilized montmorillonite (product of ZG-M "Zębiec" S.A.) have been obtained. The filler was introduced to the compositions in the amounts of 1, 2, 3 wt.% of all the components. The influence of the nanofiller on the density of the composites as well as on the compressive strengths and the flexural strengths of the polyester composites with a glass reinforced polyester recyclate was examined. There were presented the relationship between water absorption and soaking time for composites with different nanofiller contents. It was observed that an addition of 2 wt.% nanofiller NanoBent®ZR2 to composites with 10 or 12 wt.% of recyclate causes an increase in the density and the strength. Styrene diffuses into the galleries of the organoclay montmorillonite easily, resulting in a decrease in the amount of styrene available for crosslinking in the medium, which decreases the chain length between the crosslink sites leading to higher strength. It was found that the composites with NanoBent®ZR2 absorb less moisture than the unfilled ones.

Keywords: **material recycling, nanofiller, NanoBent®, glass reinforced polyester waste**

ZASTOSOWANIE NanoBentu®ZR2 JAKO NAPEŁNIACZA DO MODYFIKACJI KOMPOZYTÓW Z RECYKLATEM POLIESTROWO-SZKLANYM

W przedstawionej pracy zastosowano organofilizowany montmorylonit jako napełniacz do kompozytów z recyklatem poliestrowo-szklanym. Kompozyty były otrzymane metodą in situ na etapie syntezy poliestru. Zbadano wpływ nanonapełniacza na wybrane właściwości kompozytów z recyklatem poliestrowo-szklanym. W pracy do otrzymania kompozytów zastosowano żywicę poliestrową Polimal 109-32K (produkt Zakładów Chemicznych Organika - Sarzyna) oraz jako nanonapełniacz: NanoBent®ZR2 - organofilizowany montmorylonit (produkt Zakładów Górniczo-Metalowych „Zębiec" S.A.). Nanonapełniacz dodawany był w ilości 1, 2 i 3% wag. do całej kompozycji. W artykule omówiono podstawowe parametry, tj. gęstość, wytrzymałość na ściskanie i zginanie, kompozytów z recyklatem bez nanonapełniacza oraz z jego udziałem. Przeanalizowano także zależność chłonności wody od czasu nawilżania dla kompozytów z 10% wag. i 12% wag. ilością recyklatu z różną zawartością nanonapełniacza. Zaobserwowano, że dodatek 2% wag. nanonapełniacza NanoBentu®ZR2 do kompozytów zawierających 10% wag. lub 12% wag. recyklatu poliestrowo-szklanego powoduje wzrost gęstości oraz wytrzymałości. Styren dyfunduje bardzo łatwo do galerii organofilizowanego montmorylonitu, a w związku z tym znajduje się go mniej w mieszaninie, co powoduje powstawanie krótszych łańcuchów polimerowych o lepszych właściwościach wytrzymałościowych. Zaobserwowano, że kompozyty z nanoapełniaczem NanoBentem®ZR2 absorbują mniej wody niż kompozyty bez nanonapełniacza.

Słowa kluczowe: **recykling materiałowy, nanonapełniacz, NanoBent®, odpady poliestrowo-szklane**

INTRODUCTION

In the field of polymers, a wide variety of materials is used as fillers and much research is focused on the nano scale. The unique properties obtained by a nanocomposite may be attributed to a well-dispersed reinforcing phase creating a large interfacial surface area. Nanoclays, in addition to their primary function as high aspect ratio reinforcements, also have important functions such as thermal and barrier properties and synergistic flame retardancy. Many nanoclays are built of smectites clay 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 and its specific surface and large ion exchange capacity. However, the hydrophilic character of MMT is a barrier for the easy dispersion of clay platelets in most of the polymer. A modification of MMT is necessary in order to decrease the surface tension, and 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 [1-7].

The original method of bentonite modification developed in the Rzeszow University of Technology [8, 9] was used by ZGM Zębiec (Poland) to obtain Nanobent®ZR2 which is bentonite (SN) modified with quaternary ammonium salts of the general formulate $R_1R_2R_3R_4$, where R_1 and R_2 were $-CH_3$, R_3 was $–C_{10}H_{21}$ and R_4 was $–C_{10}H_{21}$. Oleksy et al. [7] reported that the modification of bentonite with N,N-didecyl-N,N-dimetylammoniumchloride changes its structures causing an increase in the distance between the layers of clays from 12.5 Å to 18.4 Å, which was proved by X-ray studies.

Oleksy et al. [5] studied the effect of quaternary ammonium salts as modifiers of bentonites on selected properties of polyester composites. The presence of smectic clays modified by N,N-didecyl-N,N-dimetylammoniumchloride 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, practically not influencing the gelation time. The compositions of polyester resins containing 2 wt.% of modified smectites had excellent thixotropy [6].

Several studies have reported how to solve the problem of glass reinforced polyester waste [10-12]. The material recycling of polyester-glass waste was carried out in this study. The purpose of the presented work has been the application of NanoBent®ZR2 as a filler in composites with glass reinforced polyester waste. The research examined the change in the composites characteristics such as: density, flexural strength, compressive strength and water uptake.

EXPERIMENTAL PROCEDURE

Materials

The wastes of glass fibre reinforced cold-cured polyester laminates were ground in a shredder manufactured by Kubala Sp. z o.o. The recyclate was a mixture of cured polyester resin particles and glass fibre.

The materials used for the composites with glass reinforced polyester waste were:

1. nanofiller NanoBent®ZR2 delivered by ZGM Zębiec S.A. (Poland), organophilized montmorillonite (cation exchange capacity CEC minimum 80 meq/100g, d_{001} = 1.84 nm)
2. unsaturated ortophthalic polyester resin Polimal 109-32 K - manufactured by "Organika-Sarzyna" S.A. (Poland)
3. initiator (methyl ethyl ketone peroxide)
4. accelerator (cobalt naphthenate)
5. dolomite dust manufactured by Kambud Sp. z o.o.

The components in the composites used in this research are presented in Table 1.

The compositions were mixed with the initiator (in the amount of 0.01 wt.%) and accelerator (in the amount of 1 wt.%) at 22°C in our laboratory. Specimens of 40x40x160 mm were made.

TABLE 1. **Contents of components in composites**
TABELA 1. **Udział składników w kompozytach**

Formulation*	Recyclate [%]	Nanobent [%]	Resin [%]	Dolomite dust [%]
10 0	10	0	20	70
10 1	10	1	20	69
10 2	10	2	20	68
10 3	10	3	20	67
12 0	12	0	20	68
12 1	12	1	20	67
12 2	12	2	20	66
12 3	12	3	20	65
15 0	15	0	20	65
15 1	15	1	20	64
15 2	15	2	20	63
15 3	15	3	20	62

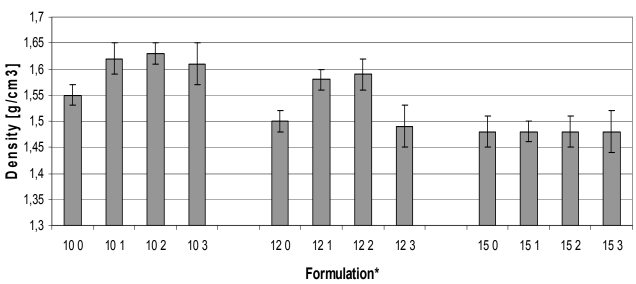
*Formulation: where the first two figures stand for the amount of recyclate and the third one for the amount of nanofiller

Methods

The physicochemical (density, water uptake) and mechanical (compressive strength and flexural strength) properties were measured. The mechanical properties of the composites were determined by using a Universal Testing Machine EDB-60 according to the PN-EN 12372:2007 and PN-EN 1926:2007 standards. In the flexural test, the gauge length was 100 mm.

Results

In Figure 1 the density of the polyester composites with glass reinforced polyester waste with and without the nanofiller is presented.

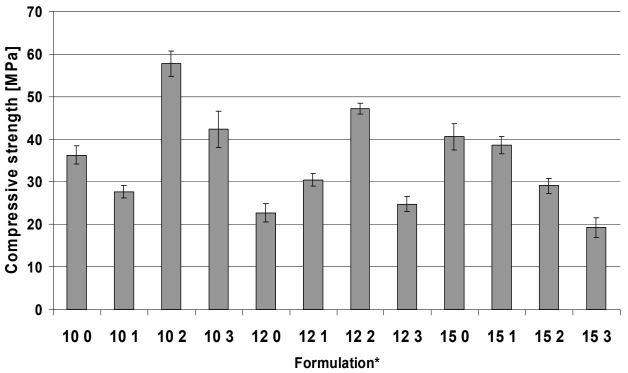


*Formulation: where the first two figures stand for the amount of recyclate and the third one for the amount of nanofiller

Fig. 1. Density of composites with recyclate with and without nanofiller
Rys. 1. Gęstość kompozytów z recyklatem bez i z nanonapełniacza

The addition of 1 or 2 wt.% of nanofiller to the composites with 10 or 12 wt.% of recyclate resulted in an increase in the density in comparison to the samples without nanofiller. Probably the addition of NanoBent®ZR2 allows one to reduce the amount of air bubbles being trapped in the resin matrix, which results in a higher weight of materials. The addition of nanofiller to composites with 15 wt.% of recylate did not change the density of the composites. The decrease in the density of the composite with 12 wt.% of recyclate and 3 wt.% of nanofiller was observed.

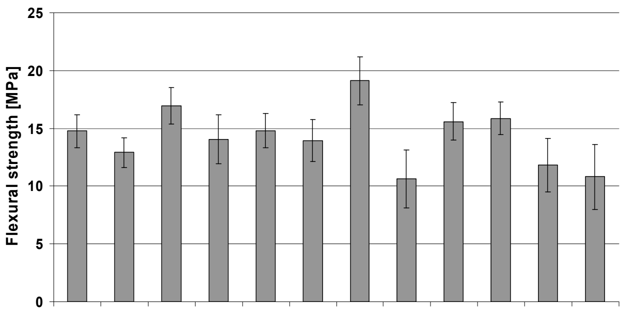
The flexural strengths and the compressive strengths of the composites with different amounts (10, 12, 15 wt.%) of recyclate with and without nanofiller are given in Figures 2 and 3.



*Formulation: where the first two figures stand for the amount of recyclate and the third one for the amount of nanofiller

Fig. 2. Results of compressive strengths of composites with recyclate with and without nanofiller

Rys. 2. Wyniki badań wytrzymałości na ściskanie kompozytów z recyklatem bez i z nanonapełniaczem



*Formulation: where the first two figures stand for the amount of recyclate and the third one for the amount of nanofiller

Fig. 3. Results of flexural strengths of composites with recyclate with and without nonofiller

Rys. 3. Wyniki badań wytrzymałości na zginanie kompozytów z recyklatem bez i z nanonapełniaczem

The addition of 1 wt.% of nanofiller to the composites with 10 and 12 wt.% of glass reinforced polyester recylate resulted in a reduction in compressive and flexural strengths. When the amount of nanofiller was increased to 2 wt.%, the compressive strength of composites with 10 wt.% of recyclate increased by up to 60% and the flexural strength - by up to 40% compared to the properties of the sample without the nanofiller. The addition of 2 wt.% of nanofiller to composites with a 12 wt.% of recyclate increases the compressive strength (by 50%) and the flexural strength (by 40%) compared to the properties of the sample without the filler. This is a result of the large surface area attained by adding nanofiller to the polyester with recyclates. The polyester interacts with the filler surface forming an interphase of absorbed polymer and the overall polymer-filler adhesion increases due to the high surface area and thereby improves the strength. Styrene diffuses through the galleries of the organoclay more easily owing to its smaller molecular structure than the polymer. This reduces the styrene amount available for crosslinking in the medium which is probably the reason for the lower molecular weight between the crosslinking sites leading to restrictions for chain mobility and increasing the flexural strength.

However, the addition of 3 wt.% of nanofiller to the composites with 10 wt.% of recyclate only slightly improves the compressive strength. The decrease in strength when the filler amount was 3 wt.% can be attributed to both the agglomeration of filler at higher contents and a decrease in the surface area available for polymer-filler interaction.

The addition of nanofiller to composites with 15 wt.% of recyclates does not improve the mechanical properties of the composites. At a higher recyclate amount, the positive effects of the nanofiller are not observed because a high amount of recyclate can create a restriction to obtaining high crosslinking density, thus leading to lower strength.

The effect of soaking time on the percentage mass change of composites with 10 and 12 wt.% of glass reinforced polyester recyclate and with or without nanofiller is shown in Figures 4 and 5.

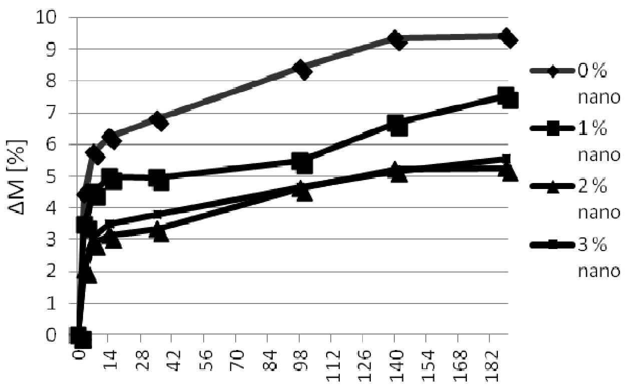


Fig. 4. Relationship of water absorption ΔM to soaking time for composites with 10% wt. of recyclate with different nanofiller content

Rys. 4. Zależność chłonności wody ΔM od czasu nawilżania dla kompozytów z 10% wag. ilością recyklatu z różną zawartością nanonapełniacza

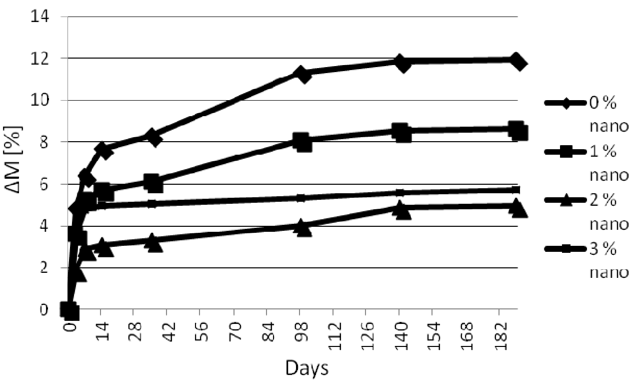


Fig. 5. Relationship of water absorption ΔM to soaking time for composites with 12% wt. of recyclate with different nanofiller content

Rys. 5. Zależność chłonności wody ΔM od czasu nawilżania dla kompozytów z 12% wag. ilością recyklatu z różną zawartością nanonapełniacza

The moisture content curves increased rapidly when the composites were first immersed in water. Both composites with 10 and 12 wt.% of glass reinforced polyester recyclate without nanofiller have high water absorption (after 190 days values are 9.4 and 12%). This may be due to the high amount of moisture absorption at the recyclate (glass and polyester) and polyester interphase region. This suggests that voids may be the reason for the high mass gain as a result of air entrapment in the composites with waste during the manufacturing stage, either due to air bubbles being trapped in the resin formulations during their preparation or to poor wetting of the glass reinforced polyester recyclate. The presence of voids and other defects leads to higher water absorption in the composites with waste.

When the mass change curves for the composites with and without nanofiller show the same profile with increasing soaking time, the mass gain is lower for the composites with the nanofiller. It is seen that the composites with the nanofiller gained less mass than the composites without the nanofiller. The results suggest probably lower void contents in the composites with the recyclate and NanoBent®ZR2. The lowest water absorption was observed after adding 2 wt.% of nanofiller to the composites with 10 and 12 wt.% of recyclate.

CONCLUSIONS

This study has compared some properties of polyester composites with glass reinforced polyester recyclate before and after the addition of nanofiller. The nanofiller NanoBent®ZR2 can increase both the compressive strength and the flexural strength compared to unfilled composites with 10 or 12 wt.% of glass reinforced polyester waste. This is probably because styrene diffuses through the galleries of the organoclay more easily owing to its smaller molecular structure than the polymer. This reduces the amount of styrene available for crosslinking in the medium, which is the reason for the lower molecular weight between the crosslinking site, leading to restrictions for chain mobility and increasing the strength. The nanofiller influences the density and the water absorption of the composites with glass reinforced polyester recyclate. It was found that the composites with NanoBent®ZR2 absorb less moisture than the unfilled composites and this may be due to the high void contents in the composites with recyclate and without the nanofiller. By adding 2 wt.% of nanofiller to the composites with 10 or 12 wt.% of recyclate, improvements in all the mechanical properties are possible and the composites can be applied in building materials like window sills.

The addition of nanofiller to the composites with 15 wt.% of recyclate does not increase the mechanical properties.

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