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SHAPING MECHANICAL AND THERMAL PROPERTIES OF POLYMER NANOCOMPOSITES

Key words

Nanocomposite, layered aluminosilicates, dispersion, mechanical properties, exfoliation.

Abstract

The paper presents the test results of the mechanical and thermal properties of nanocomposites based on chemically hardening epoxy resin. NanoBents ZS-1, ZR-1, ZW-1, and Closite 30B were used as nanofillers. Mechanical and ultrasound homogenisations were used to manufacture the nanocomposites. After crosslinking the nanocomposites with triethylenetetramine, their shock resistance, bending, modulus and deformation strength, as well as heat distortion temperature and linear thermal expansion coefficient were specified. Based on a two-factor experiment plan, the impact of manufacturing parameters (time and amplitude) on the mechanical properties of composites was determined. The structure of aluminosilicates dispersed in the polymer matrix was determined by examining x-rays diffraction (XRD), and the surface cracking morphology was determined by a scanning electron microscope (SEM). Based on the results, it was concluded that the best results could be obtained using a 1% m/m of layer aluminosilicates. Utilising a higher amplitude

of ultrasound homogenisation leads to creating nanocomposites with better mechanical properties.

Introduction

Polymer nanocomposites are modern engineering materials in which at least one dispersed nanofiller has at least one dimension smaller than 100 nm. Basing the criteria around the number of dimensions of the nanofiller, polymer nanocomposites can be divided into three categories: nanocomposites containing nanofillers with one dimension in the nano range (montmorillonite, saponite, and hectorite), two dimensions below 100nm (whiskers, nanotubes) and polymers that have all three dimensions in the nano scale (silver, iron particles). These advanced materials have a number of important characteristics: large value for elasticity modulus, high shock resistance, high deformability, low density, barrier attribute regarding gas permeability, optical transparency, and increased thermal stability and heat resistance [1–3].

Dispersion of nanoparticles and their homogeneous distribution is an important factor determining the properties of a polymer nanocomposite, apart from the type and properties of the nanofiller and polymer carcass types. These conditions are difficult to technically fulfil because, due to their small size, nanoparticles have a strong tendency to form agglomerates, bound mainly by Van der Waals forces. They also increase the adhesiveness of compositions with polymers. Nanocomposites containing aluminosilicates (mainly montmorillonite, MMT) are becoming increasingly important. Montmorillonite is a natural, layered loam-like material. Choosing the right polymer (epoxy) carcass and aluminosilicate, homogenisation conditions (shear stress temperature, chemical processes) can be utilised to achieve dispersion in the resin of nanoparticles created in the process of disintegration of the crystalline structure of aluminosilicates. This method of manufacturing nanocomposites is beneficial, because it allows avoiding energy-intensive processes of obtaining nanoparticles, agglomeration problems, and safety issues. The reason for this is that the components themselves are in the micro scale. By modifying the surface (MMT), we can facilitate the process of nano-dispersion and improve the adhesion of resin and nanofiller [4–7].

The goal of this paper is to evaluate the impact of the kind and percentage by weight of layered aluminosilicates along with manufacturing parameters on the mechanical and thermal properties of nanocomposites on an epoxy resin carcass.

1. Subject and research methods

The research was focused on Epidian 5 nanocomposites on an epoxy resin carcass manufactured by Organika – Sarzyna Chemical Plant and, as nanofillers, montmorillonite – Cloisite 30B made by Southern Clay Products Inc. and NanoBenty ZS-1, ZR-1 and ZW-1 (modified with quaternary ammonium salts manufactured by ZakładyGórniczo-MetaloweZębiec. Percentages by weight of montmorillonites in the epoxy carcass were 1, 2, 3, 4, and 5%, resulting nano-dispersions consisting of different amounts of fillers that were cross-linked using aliphatic polyamine (triethylenetetramine).

2. Preparing the filler in an organic dispersant.

The first phase consisted of preparing a 15% filler suspension in an organic dispersant – acetone. Dispersion was prepared at room temperature using an ultrasound homogeniser (80% amplitude, dispersion time 5 minutes.). The result of the dispersion was a stable and highly adhesive suspension that was then supplied to epoxy resin in various quantities, resulting in different percentages by weight of the filler in the composition.

Montmorillonite (MMT) dispersion in the epoxy resin was conducted using a HeidolphDiax 600 mechanical homogeniser equipped with a rotary knife (∅10mm) as well as a Hielscher UP200H ultrasound homogeniser with a S3 sonotrode (∅3mm, max amplitude: 210μm, operational frequency: 24kHz). Mechanical and ultrasound homogenisation was employed for manufacturing nanocomposites at a rotating speed of 9500 rpm and amplitude of 100%. Dispersion time was identical at (10 minutes.).

After dispersion, the composition was vented at a temperature of 60°C in a vacuum drier under a negative pressure of -0.8 kg/cm^2 for 3 hours. After removing the solvent, the Z1 hardener was added and compositions were placed in casts in which they were left for hardening for 24 hours at room temperature and then additionally cross linked at a temperature of 80°C for 3 hours. The resulting nanocomposite samples were used for testing their mechanical properties (shock resistance and bending strength). After crosslinking, shock resistance of the nanocomposites was tested using the Charpy method with a notch using a Zwick 5012 apparatus according to PN-81/C-89 029 norm. Bending strength was tested using an Instron 5566 stress test apparatus according to ISO 178 norm. Five samples of nanocomposites were used for testing. Thermal properties of nanocomposites were determined through measurements of heat distortion temperature under HDT stress tested using a modified Vicata apparatus and a linear thermal expansion coefficient determined using a Cosfeld dilatometer.

The created nanocomposites were also tested using x-ray diffractometry (XRD), which is used to determine layer distances in layered aluminosilicates or nanocomposites containing them. Testing with wide-angle x-ray scattering was conducted using an URD – 6 Seifert diffractometer with CuK_{α} radiation and under the following conditions: accelerating current – 40 kV, anode current – 30mA. Monochromatization of the beam was achieved using a nickel filter and pulse height analyser. A scintilation counter was used as a detector.

X-ray diffractograms were done using a stepwise approach in the deflection angle band characteristic for layered aluminosilicates from 1.2^{o} to 8^{o} with a step of 0.05^{o}. The morphology of nanocomposites' surface was determined using images from (SEM) S2460 N Hitachi scanning microscope. The accelerating current was 15 kV, and the vacuum type was high. Images were taken after sputter coating the samples with a layer of gold (SE detector).

3. Results

Results of mechanical properties testing of created nanocomposites are presented in Figures 1–4. The obtained results indicate that the kind and percentage by weight of NanoBents clearly affects the mechanical properties of polymer nanocomposites.

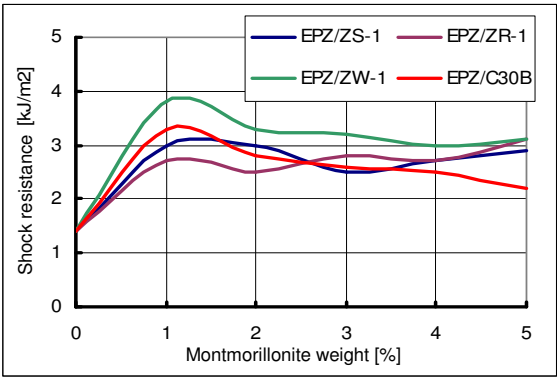

Fig. 1. Shock resistance of nanocomposites

Analysing the effect of the content of aluminosilicates on resistance to dynamic impact (shock resistance), bending stress rupture, and bending deformation, we can observe a large, almost two-fold increase of these values for nanocomposites with 1% of their weight being domestic NanoBents. Nanocomposites with ZR-1 NanoBents show the highest values of stress and bending deformation. A further increase of the nanofillers' content leads to a sharp decrease in tested properties. For example, bending deformation for

nanocomposites with a montmorillonite weight content at 2–5% is similar to that of a non-filled epoxy carcass. The lowest changes of bending stress and stress rupture were observed while using nanocomposites with Closite 30B montmorillonite. Analysing bending modulus presented in Figure 4 shows that increasing the weight percentage content of nanofillers in the epoxy carcass leads to the increase of this parameter. Following the curves presented in Fig. 4 shows, however, that an increase of the weight percentage of nanofillers above 1% does not lead to the increase of the nanocomposite's stiffness determined by bending modulus.

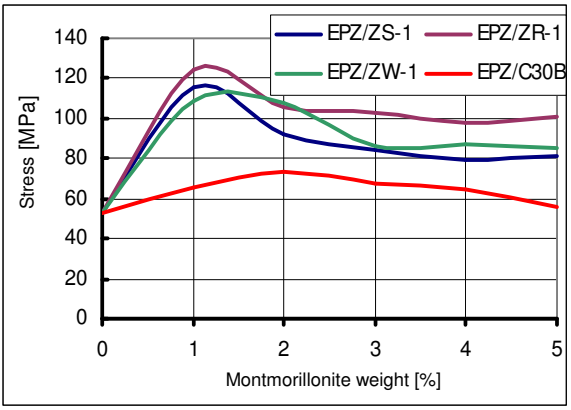

Fig. 2. Bending stress during nanocomposite rupture

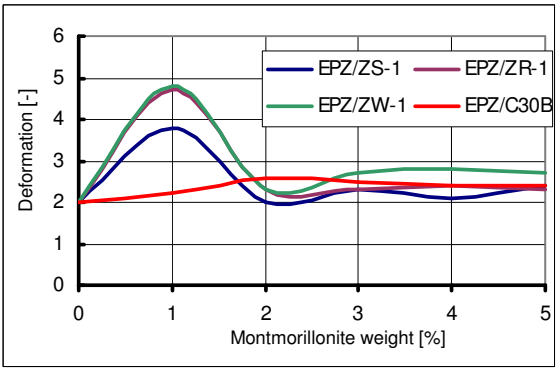

Fig. 3. Deformation during nanocomposite rupture

Fig. 5 presents the test results of heat distortion temperature under stress (HDT) and the linear thermal expansion coefficient of nanocomposites with 1% m/m of layered aluminosilicates.

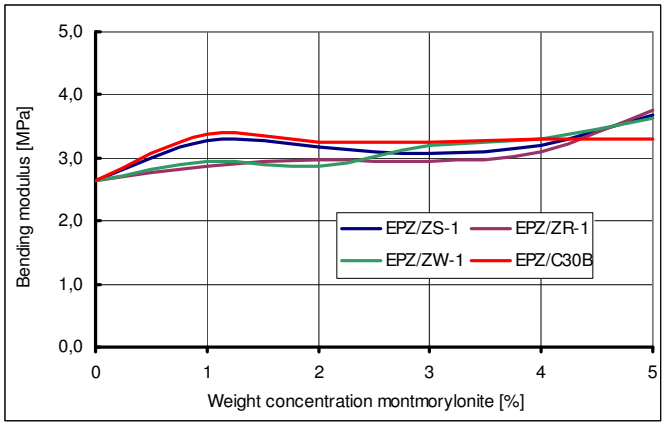

Fig. 4. Modulus during nanocomposite bending

a) b)

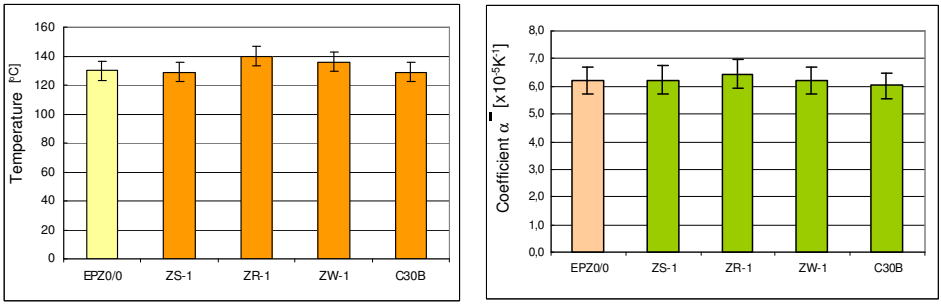

Fig. 5. HDT and linear thermal expansion coefficient of nanocomposites

Contrary to mechanical properties, the application of layered aluminosilicates has little effect of thermal properties of cross-linked polymer nanocomposites. The addition of nanofillers (ZR-1 and ZW-1) at 1% of weight increases slightly the heat distortion temperature under the stress of nanocomposites, compared with non-filled epoxy resin. The highest heat distortion temperature (about 10^{o} above the polymer carcass) was observed in nanocomposite with NanoBent ZR-1 content. Similar results were achieved during testing of the linear thermal expansion coefficient.

For the composite epoxy resin/NanoBent ZR-1 (1% m/m), the impact of sonotrode's amplitude and homogenisation time on its mechanical properties was tested. Testing was conducted according to a programme designed for two-factor experiment plan. The amplitude (%) and homogenisation time (min.) were assumed as variables. Example relations between mechanical properties of nanocomposites and their manufacturing conditions are presented in Figures 6–7.

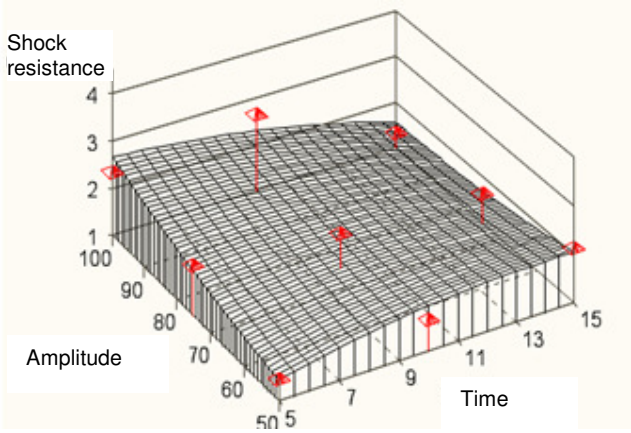

Fig. 6. Visualization of response surface as regression function graph calculated for shock resistance

Based on the results, it was concluded that both the amplitude and homogenisation time affect the composites' mechanical properties. The location of the apexes of the pyramids indicate the values of the tested characteristic (shock resistance) obtained in the analysis. Figure 6 shows that the best shock resistance values can be achieved with high amplitude and short homogenisation time.

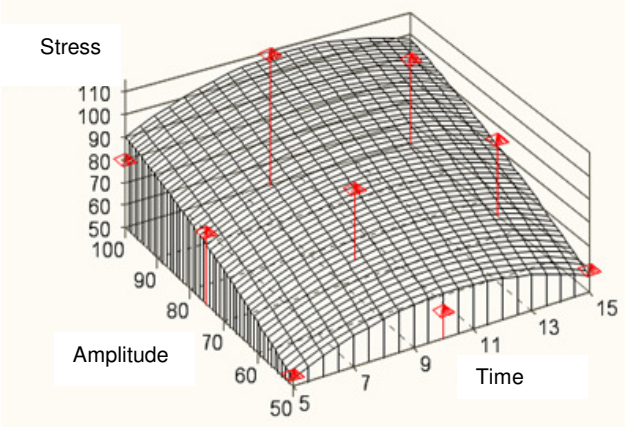

Fig. 7. Visualization of response surface as regression function graph calculated for stress

In case of stress (Fig. 7), we can observe a larger impact of amplitude than time. Higher sonotrode amplitude values induce higher stress. Independently from amplitude values, time close to the assumed central value of 10 minutes leads to higher stress.

In order to determine the structure of aluminosilicates based on epoxy resin, the analysis of created nanocomposites has been conducted by means of x-ray diffractometry (XRD) in the deflection angle band of 1.2 – 8°), which present peaks usual for layered aluminosilicates. Figure 8 presents the resulting diffractograms.

The resulting XRD diffractogram show no peaks usual for layered aluminosilicates, which indicates unstructured exfoliation of montmorillonite in the epoxy carcass. The presence of exfoliated plate nanofiller structures in the polymer carcass leads to a great improvement of mechanical properties in comparison to a non-filled epoxy carcass (Figs. 1–4).

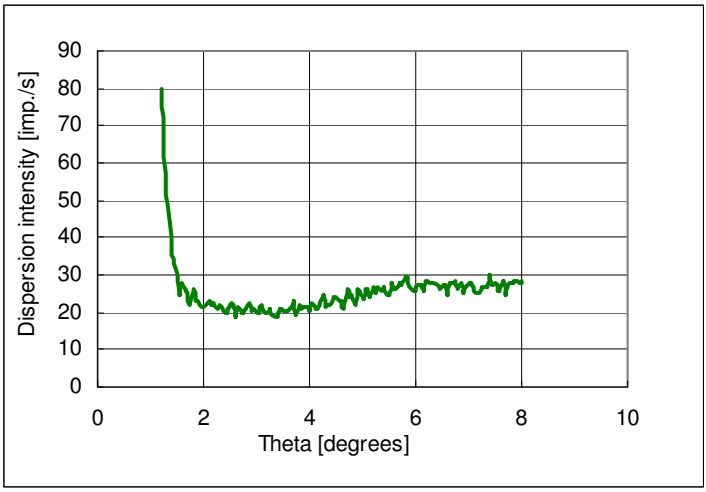

Fig. 8. XRD diffractogram of manufactured nanocomposite

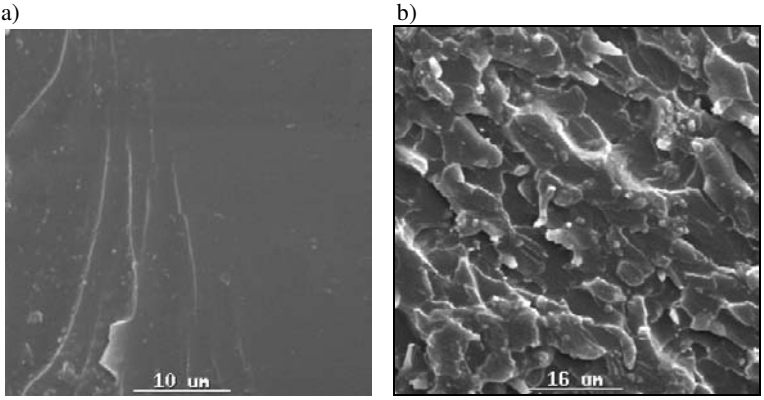

Fig. 9. SEM microscope images of cracking surface of a non-filled carcass, epoxy a) and nanocomposite b)

Based on scanning electron microscope images (SEM) shown in Fig. 9a, we can observe that cracking surface of the unmodified polymer carcass is smooth, glassy, and typical for brittle material, with low resistance to dynamic interactions. The cracking surface of a nanocomposite (Fig. 9b), however, shows multiple cracks connected with the presence of a nanofiller as well as plastic deformation areas. The visible microcracks absorb the energy required to destroy the sample, which causes a great improvement in the mechanical properties of polymer carcass. A conclusion can be drawn from the presented image about the homogeneous composition of the nanocomposite and good dispersion of nanofiller.

Conclusions

The obtained test results of mechanical properties indicate that the best results are achieved using 1% by weight of nanofillers. The result is a nanocomposite structure with high mechanical resistance. A fivefold increase in percentage by weight of NanoBents does not give the expected results. It gives a minuscule increase or drop in the selected resistance properties compared with non-filled epoxy resin. The nanofillers used have little effect on the thermal properties of polymer carcass. The relationship between the mechanical properties of nanocomposites and methods of manufacturing allows for setting such homogenisation parameters (amplitude and time) for which the best resistance values can be expected.

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References

1. Kacperski M.: Nanokompozyty polimerowe cz. 1. Charakterystyka ogólna, napełniacze oraz nanokompozyty na podstawie polimerów utwardzalnych. Polimery, 2002, s. 11–12, 47, 801–807.
2. Gołębiewski J.: Nanokompozyty polimerowe. Struktura, metody wytwarzania i właściwości. Przemysł Chemiczny, 2004, 1, 83, s. 15–20.
3. Królikowski W., Rosłaniec Z.: Nanokompozyty polimerowe. Kompozyty, 2004, 4, 9, s. 3–15.
4. Yasmin A., Luo J., J., Abot J., L., Daniel I., M.: Mechanical and thermal behavior of clay/epoxy nanocomposites. Composites Science and technology 66 (2006), pp. 2415–2422.

5. Mohamed Ali Nour.: Polymer/clay nanocomposites. Polimery 2002, 47, nr 5, pp. 326–331.
6. Pielichowski K., Leszczyńska A.: Polyoxymethylene-based nanocomposites with montmorylonite: oan introductory study Polimery 2006, 51, nr 2, pp. 143–148.
7. Malesa M.: Nanonapełniacze kompozytów polimerowych. Elastomery 2004 nr 3, pp. 12–17.

Kształtowanie właściwości mechanicznych i cieplnych nanokompozytów polimerowych

Słowa kluczowe

Nanokompozyt, glinokrzemiany warstwowe, dyspersja, właściwości mechaniczne, eksfoliacja.

Streszczenie

W pracy przedstawiono wyniki badań właściwości mechanicznych i cieplnych nanokompozytów na osnowie chemoutwardzalnej żywicy epoksydowej. Jako nanonapełniacze zastosowano NanoBenty ZS-1, ZR-1, ZW-1 oraz Closite 30B. Do wytwarzania nanokompozytów wykorzystano połączoną homogenizację mechaniczną i ultradźwiękową. Po usieciowaniu nanokompozytów za pomocą trietylenotetraaminy zbadano ich udarność, wytrzymałość na zginanie, moduł i odkształcenie przy zginaniu oraz temperaturę ugięcia pod obciążeniem i współczynnik liniowej rozszerzalności cieplnej. Na podstawie programu dla dwuczynnikowego planu eksperymentu określono wpływ parametrów wytwarzania (amplitudy i czasu) na właściwości mechaniczne kompozytów. Strukturę glinokrzemianów zdyspergowanych w matrycy polimerowej określono na podstawie wyników badań dyfrakcji promieni rentgenowskich (XRD), a morfologię powierzchni pękania nanokompozytów określono przy użyciu skaningowej mikroskopii elektronowej (SEM). Na podstawie uzyskanych wyników stwierdzono, że najlepsze rezultaty daje zastosowanie glinokrzemianów warstwowych w ilości 1% m/m. Zastosowanie wyższych wartości amplitudy homogenizacji ultradźwiękowej sprzyja wytworzeniu nanokompozytu o lepszych właściwościach mechanicznych.