

Received July 19, 2019; reviewed; accepted October 18, 2019

The use of waste materials as fillers in polymer composites - synthesis and thermal properties

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Abstract: This paper presents the synthesis and characterization of new polymeric materials in form of composites. As a fillers, waste materials of inorganic origin (ash and silica gel), were used. In the synthesis of composites, two derivatives of bisphenol A (glycerolate diacrylate, and epoxy resin, Epidian® 5), were applied. The compositions were prepared with an increasing amount of fillers 0-40% w/w in both tested systems. Composites were analyzed using the thermogravimetric analysis (TG/DTG), which showed the influence of different fillers on their thermal properties. Moreover, the proper course of the polymerization reaction was confirmed by spectroscopic analysis (ATR/FT-IR). It has been shown that new resistant materials can be obtained, using cheap and waste materials, by simple synthesis which does not require monitoring of the reaction course or expensive polymerization initiators.

Keywords: waste materials, composites, thermal properties, UV-polymerization

1. Introduction

Industrial development and urbanization contribute to generation of many different wastes. For this reason, effective recycling of these contaminants has become a national interest. Nowadays implementing rules of green chemistry and the idea of global sustainability in the economy become more and more popular in developed countries (Kuity et al., 2014). Thus, the focus of the sustainable development is to manage the wastes in an environmentally friendly way, using different wastes to design novel materials and preserving the primary energy resources (Sienkiewicz et al., 2017).

The waste materials, which can be used as fillers, should have low maintenance requirements and sufficient resistance, which is essential for example in construction industry. Besides, the type of waste materials (natural or synthetic) plays a pivotal role in applicability of these substances as fillers (Dewil et al., 2006; Khalid et al., 2016; Klapiszewski et al., 2016).

One of the most commonly selected wastes is fly ash. This is a mineral by-product produced due to the combustion. About 750 million tons of fly ash is produced annually. Its major components are metallic oxides: SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO, K₂O. Fly ash also contains many elements such as Cr, Pb, Ba, Sr, S and Zn occurring in significant quantities. This material is useless and harmful to the environment and human health, but its compatibility with other materials (e.g. polymeric ones) is of specific importance. Thus, recovery of fly ash is an efficient way to prevent such danger and its effective management (Khalid et al., 2016; Ranjbar and Kuenzel, 2017). Fly ash reutilization is significant in the construction or road industry. It has potential application in the treatment of wastewater and flue gas. Actualizing the latent applications can assist in achieving additional utilization of these materials, e.g. agriculture, geopolymers, catalysis and zeolite synthesis (Yao et al., 2015). Coal fly ash is rich in alumina, making it a potential substitute for bauxite. With the diminishing reserves of bauxite resources as well as the increasing demand for Al₂O₃, recovering this oxide from fly ash has attracted great attention (Yao et al., 2014).

Silica is another common filler which production does not affect the natural environment due to lower CO₂ emission. This material increases hardness and decreases extension of rubber composites (e.g. tyres) (Ren and Sancaktar, 2019; Martin et al., 2015). In the study by Raja and Tapas (Raja and Tapas, 2016), utilization of fly ash in asphalt blends, as replacement of standard fillers, was made. Therefore, fly ash was compared with hydrated lime, which is the commercial additive. Another paper (Shafi et al., 2019) describes the experiments on silica gel containing composites. This filler was used for modification of mechanical properties and thermal stability of silica aerogel/glass fiber composite. The results proved that silica gel can level brittleness of silica aerogel in the composite. There are many reports in the literature about the use of ash, silica and other materials as fillers for rubber and polymer matrices. Sarkwi et al. tried to fill natural rubber with silica (Sarkawi et al., 2014). They investigated the interactions between the filler and the natural rubber, as well as between the filler and the rubber coupled using the silane agent. Cazan and coworkers (Cazan et al., 2019) described new multifunctional composites based on rubber from tyres and polyethylene terephthalate as reinforcement components. They modified the structure of composites by adding CaO, ZnO, ash and other different ceramic powders as fillers, to improve mechanical properties. Some fillers increased the plasticity of composites, which may then have an interesting application (Gargol et al., 2019).

Study on the use of waste materials as cheap fillers for polymer composites is the most reasonable and compatible with the green chemistry. The aim of this paper was synthesis and improvement of thermal resistance, and rigidity of polymeric composites by adding two types of wastes (ash and silica gel).

2. Materials and methods

2.1. Materials

Epidian® 5 (Fluka) was used as a monomer, whereas triethylenetetramine (TETA) (Merck) acted as a cross-linking agent. *N*-vinyl-2-pyrrolidone (Fluka) and bisphenol A glycerol diacrylate (Bis.GDA) (Sigma Aldrich) were used as monomers in the polymerization reaction. As a photoinitiator of polymerization, 2,2-dimethoxy-2-phenylaceto-phenone (Irgacure® 651) was applied (Sigma Aldrich), while the benzoyl peroxide (BPO) (Fluka) was a thermal polymerization initiator. In both systems, silicon dioxide (waste silica gel obtained after emptying the chromatography column) or ash (obtained after burning hard coal) were employed as fillers. Structures of listed reagents are presented in Fig. 1.

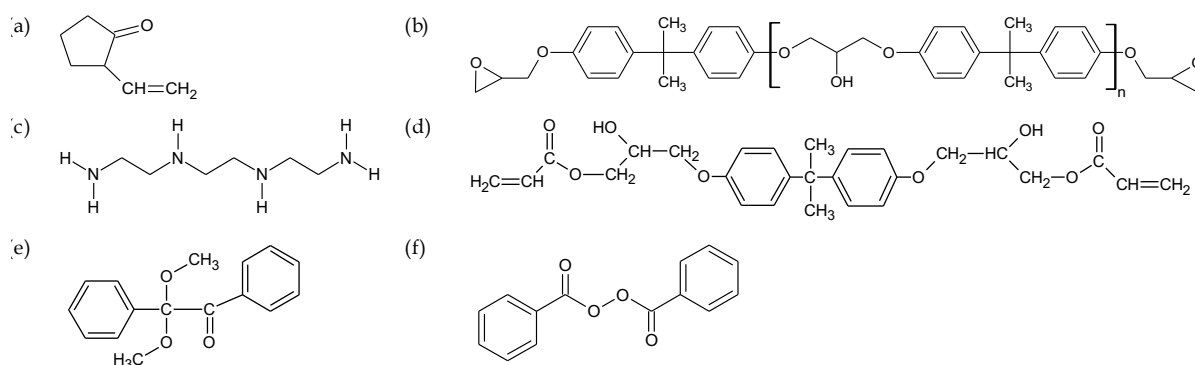


Fig. 1. Chemical structures of the reactants: a) *N*-vinyl-2-pyrrolidone; b) Epidian® 5; c) triethylenetetramine; d) bisphenol A glycerol diacrylate; e) 2,2-dimethoxy-2-phenylaceto-phenone; f) benzoyl peroxide

2.2. Preparation of composites based on epoxy resin

The weighted amount of Epidian® 5 and triethylenetetramine as cross-linking agents were put into the glass vessel. Next, the content was thoroughly mixed and the filler material was added in small portions. The content of vessel was poured into a glass mold to obtain a sample in the disc form. The cross-linking process took place at room temperature within 5 hours. The same procedure was repeated for all samples. In addition, polymerization of the epoxy resin was carried out, resulting in a reference sample without a filler (sample III). The ratio of the epoxy resin to the crosslinking agent in each case was 10:1

(w/w). The total weight of the blends containing the above-mentioned components was 15 g. The detailed information about reagents and their amount is presented in Table 1.

Table 1. Amounts of all components used in the synthesis of epoxy resin-based composites

| Sample number | Ia | Ib | Ic | IIa | IIb | IIc | III |
|--------------------------|------------------|------------------|------------------|-------|------|------|-------|
| Type of filler | SiO ₂ | SiO ₂ | SiO ₂ | ash | ash | ash | - |
| Mass of filler (g) | 3.0 | 4.5 | 6.0 | 3.0 | 4.5 | 6.0 | 0 |
| Epidian® 5 (g) | 10.91 | 9.54 | 8.18 | 10.91 | 9.54 | 8.18 | 13.64 |
| TETA (g) | 1.09 | 0.95 | 0.82 | 1.09 | 0.95 | 0.82 | 1.36 |
| Quantity of filler (w/w) | 20 | 30 | 40 | 20 | 30 | 40 | 0 |

2.3. Preparation of composites based on bisphenol A glycerol diacrylate

The process of sample preparation consisted of several stages. Bisphenol A glycerol diacrylate (Bis.GDA) and *N*-vinyl-2-pyrrolidone were added to the glass vessel. Next the 1 wt.% of UV-initiator (2,2-dimethoxy-2-phenylacetophenone) and 1 wt.% of thermal polymerization initiator (benzoyl peroxide) were added and mixed to dissolve the ingredients. The whole content was moved into a glass circle container, placed under a UV lamp and polymerized within 30 minutes. Subsequently the polymerization process was continued at 70 °C for two hours in the heating chamber. The amounts of reactants used are presented in Table 2.

Table 2. Amounts of all components used in the synthesis of Bisphenol A glycerol diacrylate based composites

| Sample number | IVa | IVb | IVc | Va | Vb | Vc | VI |
|--------------------------|------------------|------------------|------------------|------|------|------|-------|
| Type of filler | SiO ₂ | SiO ₂ | SiO ₂ | ash | ash | ash | - |
| Mass of filler (g) | 3.0 | 4.5 | 6.0 | 3.0 | 4.5 | 6.0 | 0 |
| Bis.GDA (g) | 8.19 | 7.14 | 6.09 | 8.19 | 7.14 | 6.09 | 10.29 |
| NVP (g) | 3.51 | 3.06 | 2.61 | 3.51 | 3.06 | 2.61 | 4.41 |
| Irgacure 651 (g) | | | | 0.15 | | | |
| BPO (g) | | | | 0.15 | | | |
| Quantity of filler (w/w) | 20 | 30 | 40 | 20 | 30 | 40 | 0 |

2.4. Characterization of the products

Attenuated total reflection-Fourier transform infrared (ATR/FT-IR) spectra were obtained using a FTIR spectrophotometer TENSOR 27 (Bruker, Germany). Spectra were recorded in the frequency range of 400–400 cm⁻¹ with a resolution of 4 cm⁻¹ and 32 scans. The dynamic thermogravimetric analysis (TG) was performed using thermal analyzer STA 449 F1 Jupiter (Netzsch, Selb, Germany). The thermal analysis of all samples was done in the Al₂O₃ crucible with the sample mass about 5 mg. As a reference the empty Al₂O₃ crucible was used. Dynamic scans were performed at the heating rate of 10 °C/min in the temperature range of 0–1000 °C, in inert atmosphere: in helium (with the flow 25 cm³/min). Mechanical properties of samples were also compared by means of the Shore apparatus. 10 measurements were made for each sample and the average hardness was calculated in D scale.

3. Results and discussion

Figure 2 illustrates the images of 12 obtained composites and 2 reference samples. The discs differ in color, which is a consequence of the presence of various fillers in their composition. All tested materials were subjected to a spectroscopic analysis. Characteristic bands related to the functional groups are visible on the curves. The courses of spectra presented in Fig. 3ab are quite similar because the main components of these compositions are Epidian® 5 and a curing agent. The same similarity was observed in the case of spectra presented in Fig. 3c and d, which concern the NVP and Bis.GDA containing samples. However, after the addition of silica the spectra show clear bands in the range of 1084–1088 cm⁻¹ which correspond to the stretching vibrations of Si-O groups (Fig. 3a and c). The presence of ash in

the composites is confirmed by the peak at 1035-1039 cm^{-1} derived from the S=O stretching vibrations (Fig. 3b and 3d).

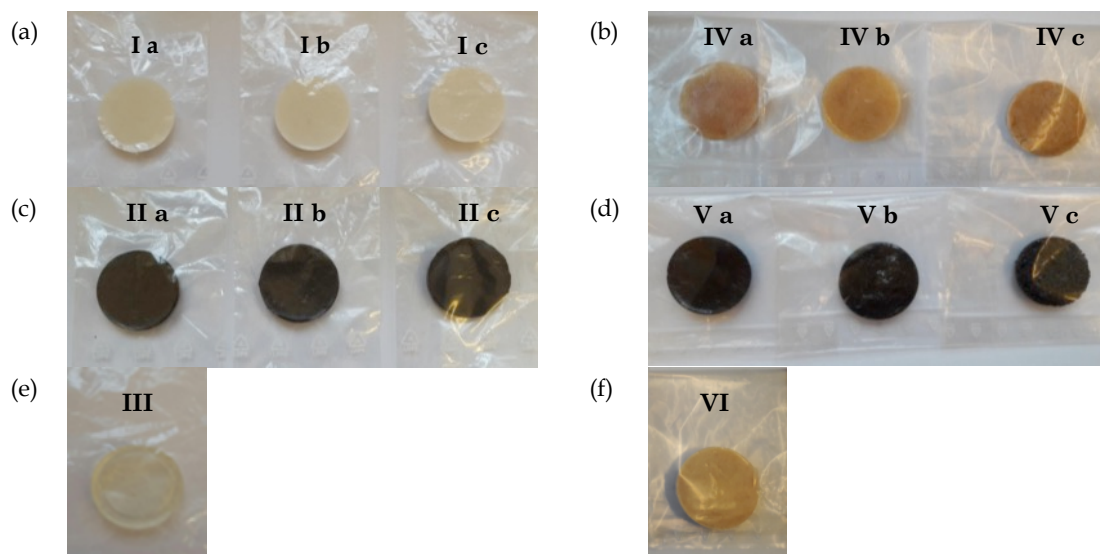


Fig. 2. Photos of composites containing: a) Epidian® 5 and SiO_2 ; b) Epidian® 5 and ash; c) reference sample containing only Epidian® 5; d) Bis.GDA and SiO_2 ; e) Bis.GDA and ash; f) reference sample containing only Bis.GDA

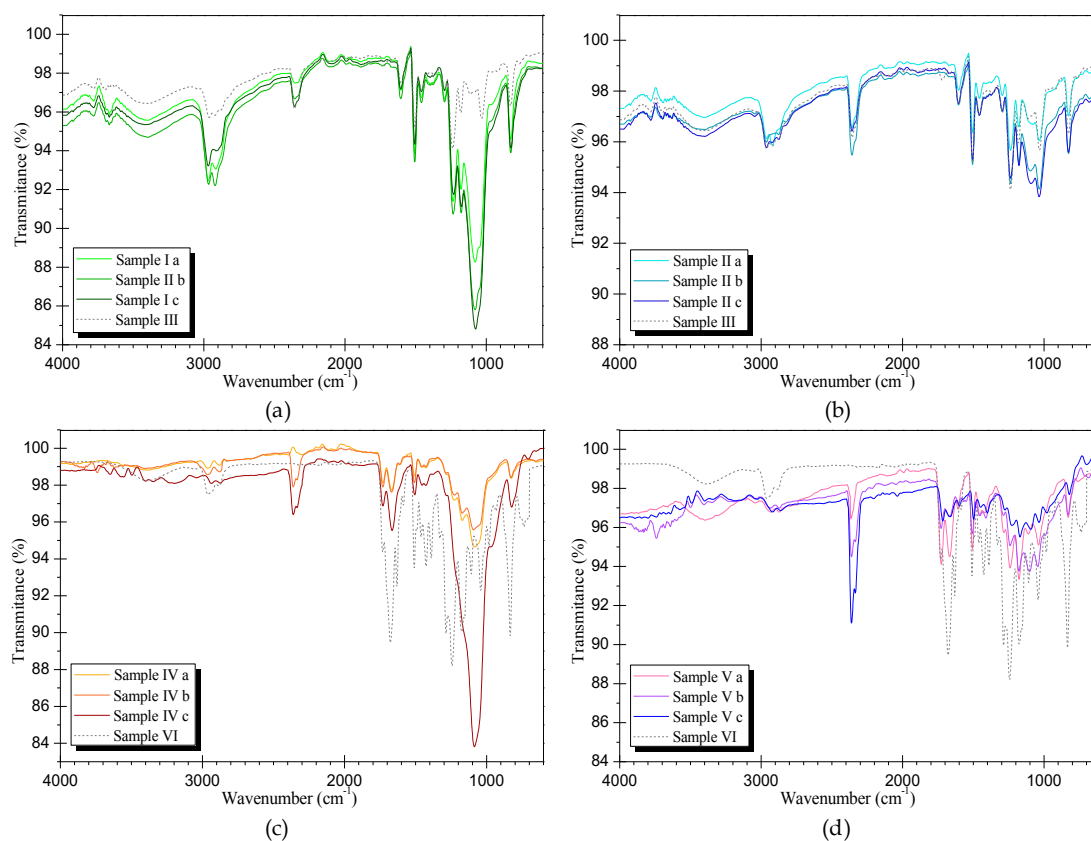


Fig. 3. The ATR/FT-IR spectra of composites: a) samples based on Epidian® 5 and SiO_2 ; b) samples based on Epidian® 5 and ash; c) samples based on Bis.GDA, NVP and SiO_2 ; d) samples based on Bis.GDA, NVP and ash.

The few differences in the shape and shifting of the characteristic bands of the functional groups were observed. Both components: Epidian® 5 and Bis.GDA have aromatic rings in their structures. For this reason, the vibrations of these groups are visible in all spectra. In the range of: 823-860 cm^{-1}

deformation vibrations of Ar and Ar-H are visible. The peaks from 1510 to 1615 cm^{-1} can be attributed to the symmetric and asymmetric stretching vibrations aromatic of ring. Additionally, the Ar-O-Ar group vibrations at 1243-1260 cm^{-1} are visible. The signals from 1425 to 1470 cm^{-1} correspond to the deformation vibrations of methyl and methylene groups. These structure fragments are also confirmed by the stretching vibrations bands in the range of 2895-2966 cm^{-1} . Moreover, a signal at 1726 cm^{-1} , found in all spectra, originates from the carbonyl groups.

3.2. TG/DTG analysis of the obtained composites

The curves obtained from the TG and DTG analyses of all samples are presented in Figs. 4 and 5. The measurements data are additionally summarized in Table 3. The system is considered to be stable until 5% of its mass is lost. For each material the mass loss factors: initial temperature decomposition (ITD), $T_{20\%}$ (temp. at 20% weight loss), $T_{50\%}$ (temp. at 50% weight loss), maximum decomposition temperature (T_{max}) and the final mass of sample (m_{final}), were determined.

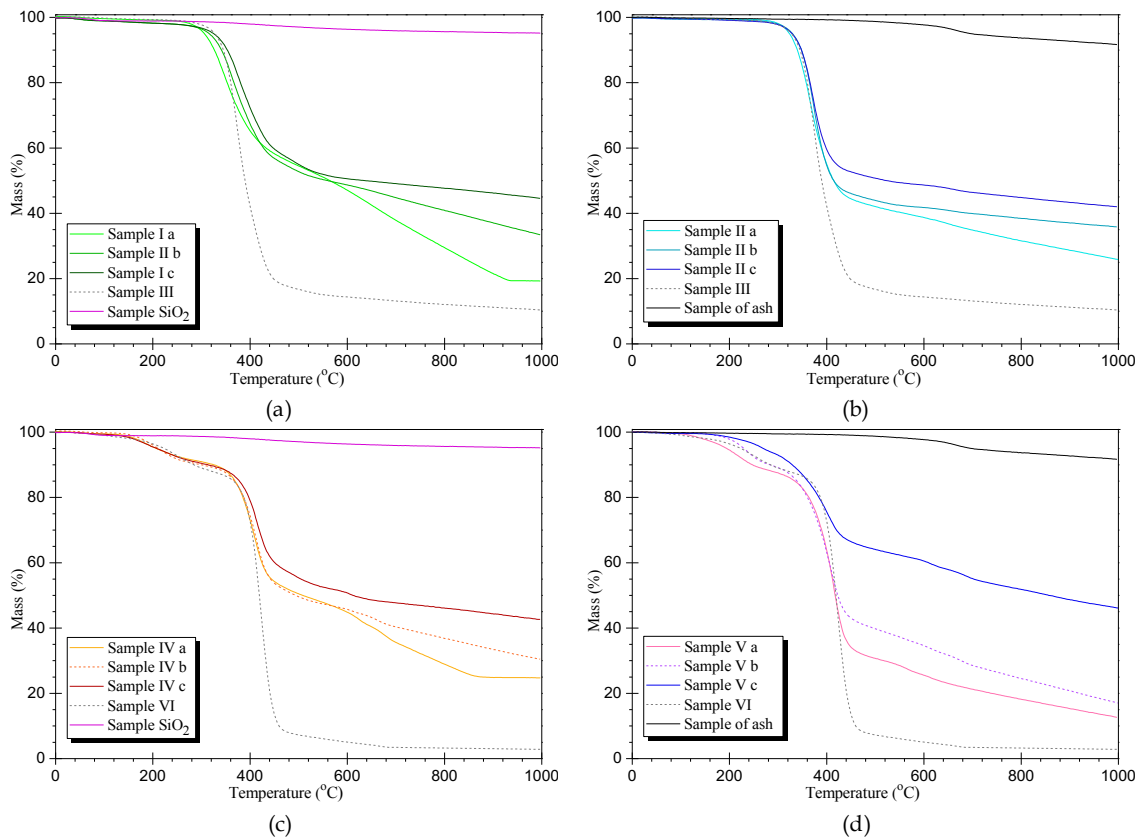


Fig. 4. The TG curves of the composites: a) samples based on Epidian® 5 and SiO_2 ; b) samples based on Epidian® 5 and ash; c) samples based on Bis.GDA, NVP and SiO_2 ; d) samples based on Bis.GDA, NVP and ash

By comparison of the obtained data, it can be stated that at the beginning of the analysis, higher thermal resistance was found for Epidian® 5 based composites as compared to the composites based on Bis.GDA. The initial decomposition temperatures of the materials based on the epoxy resin ranges from 305 to 329 $^{\circ}\text{C}$ while for the materials containing Bis.GDA they are in the range 206–267 $^{\circ}\text{C}$. This phenomenon is caused by the strong cross-linking effect of the epoxy resin in the initial polymerization stage.

Analysis of the DTG curves proved that in case of the materials based on Bis.GDA two separate signals related to the degradation stages (T_1 and T_{max}), were noted. The first peak of the decomposition (T_1), that ranges from 190 to 260 $^{\circ}\text{C}$, concerns the decomposition of ester fragments derived from aliphatic acrylates. The second decomposition stage (T_{max}) takes place between 394 – 425 $^{\circ}\text{C}$ and is related to total degradation of samples (destruction of aromatic fragments in their structure). The DTG curves derived from Epidian® 5 based composites have different character. Epoxy resins undergo strong

cross-linking reaction with amines, thus, their aliphatic chain is shorter as compared to Bis.GDA, and on the DTG curve only one decomposition peak is visible. The maximum decomposition peak (T_{max}) for the above-mentioned materials is observed in the temperature range of 353–377 °C.

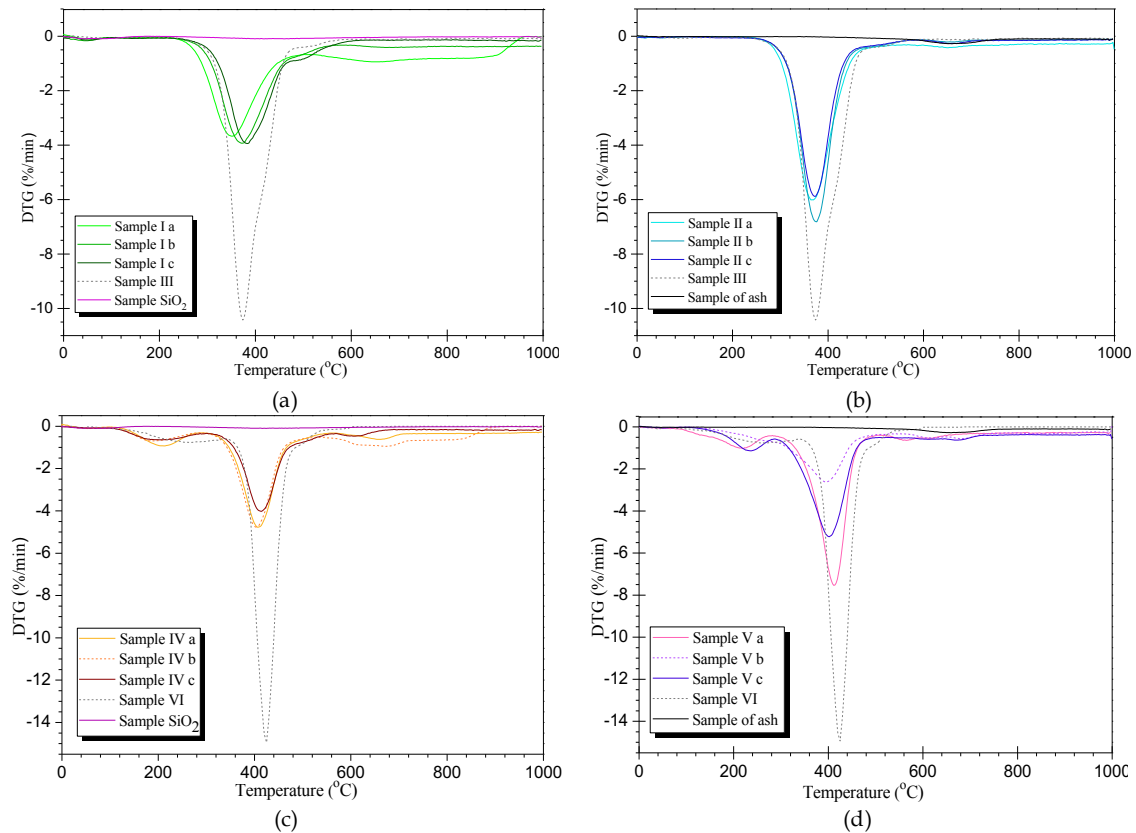


Fig. 5. DTG curves of the polymeric mixtures: a) samples based on Epidian® 5 and SiO₂; b) samples based on Epidian® 5 and ash; c) samples based on Bis.GDA, NVP and SiO₂; d) samples based on Bis.GDA NVP and ash

Table 3. Results of the TG/DTG analysis of prepared samples.

| Sample number | ITD (°C) | T _{20%} (°C) | T _{50%} (°C) | T ₁ (°C) | T _{max} (°C) | m _{final} (%) |
|---------------|----------|-----------------------|-----------------------|---------------------|-----------------------|------------------------|
| Ia | 305 | 352 | 564 | - | 353 | 19.3 |
| Ib | 315 | 367 | 560 | - | 371 | 33.4 |
| Ic | 325 | 380 | 637 | - | 377 | 44.5 |
| IIa | 323 | 357 | 414 | - | 364 | 25.9 |
| IIb | 329 | 364 | 414 | - | 376 | 35.8 |
| IIc | 329 | 365 | 524 | - | 372 | 42.0 |
| III | 327 | 360 | 390 | - | 374 | 10.5 |
| IVa | 206 | 385 | 507 | 209 | 404 | 24.7 |
| IVb | 210 | 387 | 492 | 190 | 406 | 30.4 |
| IVc | 206 | 397 | 611 | 208 | 414 | 42.6 |
| Va | 194 | 362 | 417 | 221 | 411 | 18.6 |
| Vb | 229 | 359 | 422 | 252 | 401 | 22.2 |
| Vc | 267 | 384 | 856 | 235 | 394 | 46.1 |
| VI | 222 | 386 | 417 | 260 | 425 | 2.84 |

The samples without fillers showed worse parameters of thermal stability. The addition of both filling materials to the samples caused an increase in their thermal stability in similar way. When comparing the individual numerical data, it can be seen that these values depend on the type of inorganic material. As expected the thermal stability of the obtained composites becomes higher with increasing inorganic filler content. The highest thermal resistance was found in the case of the

composites where 40 wt.% of filler was used. The latter conclusion about the thermal analysis refer to the final mass of the obtained materials. These numerical data are approximately equal to the percentage content of the filler in the samples.

3.3. Hardness measurements

The hardness values of the obtained materials are presented in Table 4. Numerical values of these parameters are expressed in the D scale.

Table 4. Numerical values of obtained composites hardness.

| Sample number | Hardness (D scale) | Sample number | Hardness (D scale) |
|---------------|--------------------|---------------|--------------------|
| Ia | 35 | IVa | 49 |
| Ib | 49 | IVb | 60 |
| Ic | 54 | IVc | 68 |
| IIa | 49 | Va | 51 |
| IIb | 55 | Vb | 59 |
| IIc | 61 | Vc | 66 |
| III | 30 | VI | 45 |

Hardness of the composites is in the range of 30 to 68 units. Both fillers addition, resulted in an increase of the hardness. The higher values of hardness were recorded for the Bis.GDA based composites. Moreover, the composites with ash as a filler are harder than those containing silica.

4. Conclusions

In this paper, synthesis of new polymeric inorganic-organic composites was discussed. Waste silica and ash were used as fillers. Several samples with different amount of a filler and reference material were synthesized in two different ways. Firstly, samples were prepared based on the derivative of Bisphenol A and epoxide. Polymerization was conducted in the UV light. The second series of samples contained the commercial epoxy resin. These composites were cross-linked at room temperature using TETA. Determination of a proper polymerization time, amount of ingredients and fillers (20, 30 and 40 w/w), and the synthesis processes, were optimized. The spectroscopy analysis (ATR/FT-IR) confirmed the presence of characteristic groups in composite structures such as ether group, methyl and methylene groups, aromatic rings as well as SiO₂ and sulfur containing fragments. The data obtained during the thermal analysis confirmed, that the amount of filler affect the thermal properties of the samples. Samples without fillers were characterized with worse thermal stability. This parameter became higher with increasing content of an inorganic filler. Samples containing silica had higher stability as compared to those filled with ash. Based on the hardness tests it can be assumed that filler type contributes to the increasing hardness of the obtained materials. Summing up, the addition of waste, inorganic fillers to the polymer composites is one of the possibilities of their application. The use of silica or ash reduces the amount of monomers which affects the cost of such materials. Thus, they can be used as cheap composites with good durability.

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