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Poly(ethylene terephthalate) composite material with modified fly ash filler

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Abstract. The effect of the fly ash (FA) filler modified by sulphuric acid on the mechanical and physical properties of poly(ethylene terephthalate) composite material (PCM) has been investigated. The results of the presented study can be formulated as follow. The element and oxide composition of original (as received) fly ash is affected by the modification of sulphuric acid of 5 % concentration. At the same time, the variations in the particle size distribution of filler can be observed. In particular, the modified FA filler has an increased content of fine particles. The XRD pattern of as received fly ash indicates the presence of both crystalline (25 %) and amorphous phases (75 %) while XRD pattern of FA after chemical modification points to the fact that the content of crystalline phase has been increased up to 40 % but the content of amorphous phase has been decreased up to 60 %. The results of mechanical and physical properties of PCM with various content of unmodified fly ash filler (55, 60, 65, 70, and 75 %) indicate that compressive and flexural strength tends to rise with increasing concentration from 55 to 65 percent. In the certain case when the fly ash filler is modified by sulphuric acid of 5 % concentration, the values of compressive and flexural strength of PCM at 65 % FA loading is higher than compared with PCM on the base of unmodified filler. The strength gain may be attributed to the increasing crystallinity in the recycled poly(ethylene terephthalate) (rPET) matrix of the composite material as the fly ash content is increased. The XRD, DTA/TGA data of pure rPET and PCM are in conformity with the results of mechanical and physical properties of PCM.

1. Introduction

Plastics have outgrown most manufactured materials and have long been under environmental scrutiny. However, robust global information, particularly about their end-of-life fate, is lacking. By identifying and synthesizing dispersed data on production, use, and end-of-life management of polymer resins, synthetic fibers, and additives, the authors [1] estimate that 8300 million metric tons (Mt) as of virgin plastics have been produced until 2017. As of 2015, approximately 6300 Mt of plastic waste had been generated, around 9 % of which had been recycled, 12 % had been incinerated, and 79 % had been accumulated in landfills or the natural environment. If current production and waste management trends continue, roughly 12,000 Mt of plastic waste will be in landfills or in the natural environment by 2050 [1]. For instance, waste PET plastic is neither environmentally biodegradable nor compostable, which creates disposal problems. Recycling has emerged as the most practical method to deal with this problem, especially with products such as PET beverage bottles [2]. PET recycling is one of the most successful and common examples of polymer recycle processing. In Russian Federation of the total volume of recycled PET, about 63 % falls on fibers and non-woven materials, the second largest consumer (about 17 %) is the manufacture of preforms for PET bottles; the third is the production of strapping and packaging materials – about 16 %, and the production of polymer composites and other materials – less than 1 % [3].

The negative environmental impact of the steadily increasing use of plastic and composite materials requires the development of new combinations of materials, possibly with improved properties, but with reduced environmental harm [4]. Thus, the questions of application of polymer composite materials, made with the use of technological and operational waste, in building structures are topical today [5]. There is growing trend towards the development of composites with low environmental impact and good commercial

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viability. To achieve this goal, researchers implemented cost-effective processing methods and developed novel material systems involving low-cost fillers. One such material system is the so-called polymer concrete, which is often prepared by loading polyester resin with high levels of fillers such as fine sand, limestone or micro-marble particles [6, 7].

The use of fly ash of thermal power plants as a filler in polymer composite materials has recently attracted increased attention, especially in terms of cost / large stock ratio. It provides a number of advantages: it is the best way to recycle FA and, since it is cheap and abundantly available, it reduces the total cost of composites [8–11]. Fly ash has been used in polymer matrix composites, saving the other commonly used mineral fillers in polymers, thereby reducing the greenhouse emissions. Its applicability is widely studied in various building materials, but the scope of application is limited. As a result, FA is accumulated over the years in surrounding areas of thermal power plants and creates a huge environmental burden. In the Donbas region of Ukraine, more than 5 million m³ of ash and slag wastes are stored in ash dumps of thermal power plants.

Fly ash, being generated as a waste material, needs to be benefitted before its use as a filler in plastic materials. The main drawbacks of fly ash in comparison with commercial mineral fillers are its larger particle size and smooth spherical inert surface. The surface modification of fly ash can be achieved through two methods; the first is a chemical activation and the second is a mechanical activation. It is well known that FA has a surface polarity due to the presence of silanol, aluminol and other types of –OH groups attached to the metal/non-metal atoms of the constituents of FA. On the other hand, many of the commercial polymers do not have substantial polarity that can match with that of the FA particles [6, 7]. Therefore, building up interfaces based on electrostatic attraction is highly unlikely. It has been determined that fly ash with the surface activated by alkali treatment of sodium hydroxide solution proved to develop uniform interfaces in polymer composite material, with significant effect on the compression resistance and on impact [12]. According to [13] treatment of fly ash by sulphuric acid can obviously change the surface area, microstructure and phase composition. Besides, it has been reported that the surface silanol groups responsible for generating Brönsted acidity are enhanced [14]. The results of our recent investigation pointed out that treatment of fly ash filler by 5 % concentration solution of sulphuric acid to improve adhesion to the rPET polymeric matrix increases the overall properties of PCM, especially compressive strength and apparent density. The highest value of compressive strength of samples with unmodified fly ash filler had PCM with 65 % filler concentration. On the other hand, PCM samples with modified fly ash filler had the compressive strength value that is higher on 11.2 % [15].

It is a matter of common knowledge, that PET is a crystallisable thermoplastic polymer because of its regularity in chemical and geometric structures. It is either in the semi-crystalline or in the amorphous state [16, 17]. The degree of PET crystallinity is about 65–85 % [13]. Nucleating agents affect the crystallization of PET. Some studies have investigated the effect of the additives on crystallization behaviour. Talc, kaolin, silicon oxide, and titanium oxide have been used as fillers; they act as effective nucleating agents for PET. The overall rate of crystallization depends on the volume concentration, the size distribution, and the nucleating ability of the additives [18]. In turn, the levels of crystallinity and morphology significantly affect the properties of the polymers [19].

In a presence of inorganic filler, the crystallization conditions of polymers and, consequently, the general degree of crystallinity and the nature of supramolecular formations are changed. The factors which affecting the properties of crystalline polymers in the absence of filler also determine the mechanical behaviour of filled crystalline polymers. It should be borne in mind that the filler is often incorporated into the polymer precisely with the aim of influencing the nature of crystallization and structure formation and, thus, its mechanical properties [20]. For instance, the crystalline morphology and the crystallization behaviour of PET in the PET/SiO₂ composites were affected significantly by the SiO₂ inorganic nanoparticles [21]. According to [12] the incorporation of fly ash (0.25 % by mass) into PET polymer matrix increases the crystallinity of the composite by 24 % compared to the original polymer sample. The results of the investigation [22] indicate that both nano-CaCO₃ and ultra-fine talc exhibited heterogeneous nucleation effect on the crystallization of poly(trimethylene terephthalate) (PTT) composite, and more significant nucleation effect was observed in PTT/nano-CaCO₃ composite due to the smaller size and better dispersion of nano-CaCO₃ in PTT matrix. Mechanical properties study suggested that the incorporation of nano-CaCO₃ and ultra-fine talc greatly improved the tensile and flexural properties of PTT composite.

In another study [21] the authors have reported that attributed to the formation of Si–O–Ti bonds in the PET matrix, the crystalline morphology and the crystallization behaviour of the PET in PET/SiO₂/TiO₂ composites were affected significantly by the SiO₂ and TiO₂ inorganic nanoparticles (content of filler 5.49, 10.07, and 13.05 wt. %). At the same time, no quantitative data regarding PCM with high level (more than 50 wt. %) of mineral filler, in particular fly ash chemically modified by sulphuric acid, have previously been reported. Therefore the aim of this study is to investigate the mechanical (compressive and flexural strength) and physical (apparent density, water absorption) properties of poly(ethylene terephthalate) composite material filled with high level content of fly ash (55–75 wt. %) in original (as received) and chemically modified state. Besides, it is necessary to take into account and to investigate the influence of fly ash filler on the polymer crystallization characteristics in accordance with XRD and DTA/TGA data of pure rPET and PCM.

2. Materials and methods

2.1. Materials and methods

Class F (according to ASTM C-618) fly ash used in this study was collected from the thermal power plant of Donetsk region (Ukraine). The particle size distribution of fly ash was determined by the ANALYSETTE 22 Compact laser diffraction particle size analyser. The particle size of as received fly ash lies mainly in the range of 5–10, 10–20, 20–30, and 30–40 μm . The material has the specific surface area of 320 m^2/kg and bulk density of 1156 kg/m^3 . The composition of elements and oxides was determined by wavelength dispersive X-ray fluorescence method (ARL OPTIM'X 200W spectrometer). The main constituents are silica, alumina and ferric oxides of 57.19, 25.05, and 8.94 %, respectively, while traces of other oxides (K_2O 3.09 %, CaO 1.79 %, MgO 1.45 %, TiO_2 1.05 %, Na_2O 0.68 %, P_2O_5 0.27 %, and SO_3 0.18 %) were also detected.

PET bottles were as the raw material for manufacturing the rPCM matrix. PET bottles were prepared for processing by washing in warm water, removing caps and shredding into approximately 3–5 mm-size flakes using a knife crusher.

Diffraction studies of fly ash samples were conducted with the help of 26 ARL X'TRA X-ray diffractometer (ARL, Switzerland) using $\text{CuK}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$) at a voltage of 40 kV and a current of 20 mA. The scanning was carried in 4 to 70 degrees 2-theta range with a step of 0.02 degrees. X-ray phase studies of the rPET and PCM samples were performed on the X-ray diffractometer DRON-4-07 installation. The diffraction pattern was recorded at a wavelength of $\lambda = 1.54178 \text{ \AA}$ in a step-by-step mode ($2\theta = 10\text{--}80^\circ$ with a step of 0.1° and exposure time of 5 s) at 27 kV, 15 mA. PCM samples were prepared with different content of fly ash filler (55–75 wt. %).

Thermal analysis of the pure rPET and PCM samples using methods of thermogravimetric (TGA) and differential thermal analysis (DTA) (SETARAM Labsys DTA/TGA/DSC) in the temperature range 50–500 $^\circ\text{C}$ was carried out. Based on the analysis of the TGA-DTA curves, the temperatures of glass transition, melting and destruction of the rPET and PCM samples were determined and the influence of the filler addition on the thermal properties was analysed.

Compressive strength of the PCM samples was tested according to ASTM D 695 "Standard Test Method for Compressive Properties of Rigid Plastics" using servo-hydraulic system ADVANTEST 9. Compressive properties were checked at speed of 1.5 mm/min. Load cell of 5 kN was used to sense the load. Five specimens (12.7×12.7×25.4 mm prism) of each formulation were tested and their average value was calculated. Flexural strength of the PCM samples was tested according to ASTM D 790 "Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials" (procedure A, a strain rate of 0.01 mm/min, 127×12.7×3.2 mm molding bars of rectangular cross section). Apparent density and water absorption of the PCM samples were tested according to ASTM D 792 "Standard Test Methods for Density and Specific Gravity (Relative Density) of Plastics by Displacement" and D 570 "Standard Test Method for Water Absorption of Plastics", respectively.

2.2. Processing

Modifying the fly ash filler was achieved by acid-leaching method. Sulphuric acid (H_2SO_4) solution of 5, 10, and 15 % concentration was used for modification. A sample of fly ash filler was placed into the acid solution for about 1 hour then was dried to constant weight at a temperature of 105–110 $^\circ\text{C}$.

Melted recycled PET material and fly ash filler were mixed in a vessel to disperse fly ash particles in the polymer matrix. Samples of PCM were made by compression molding at a temperature of 255–285 $^\circ\text{C}$. After the molding process, the samples were cooled to solidify the melted rPET material to form a composite material having a matrix comprising rPET and dispersoids distributed in the matrix and comprising fly ash particles [2]. The PCM samples were prepared on the base of formulations with different content (55–75 wt. %) of unmodified (as received) and modified fly ash filler (Table 1).

Table 1. Formulations of PCM.

Formulation, %	FA		Concentration of sulphuric acid, %
	as received	modified	
1 – rPET : FA = 45 : 55	+	–	–
2 – rPET : FA = 40 : 60	+	–	–
3 – rPET : FA = 35 : 65	+	–	–
4 – rPET : FA = 30 : 70	+	–	–
5 – rPET : FA = 25 : 75	+	–	–
6 – rPET : FA = 35 : 65	–	+	5
7 – rPET : FA = 35 : 65	–	+	10
8 – rPET : FA = 35 : 65	–	+	15

3. Results and Discussion

3.1. Physical properties and oxide composition of modified fly ash

The characteristics (element and oxide composition) of original (as received) and modified FA samples are displayed in Table 2 that indicates decreasing content of the major oxides (silica, alumina, and ferric) after the treatment of fly ash by sulphuric acid of 5 % concentration. At the same time, one can see the presence of significant increment in SO₃ concentration. The authors of the investigation [14] had reported that chemical activation of fly ash by 5M concentration of various acids (HCl, HNO₃, H₂SO₄, and HClO₄) resulted in changing element and oxide composition as well as in increasing specific surface area of material. The highest effect had been reached when sulphuric acid was used as a modifying agent.

Related investigations of the effect of activation and modification on the microstructure and element composition of fly ash and related results have been performed by Qiu, M., Wang, Y., Niu, M. et al. [13]. They believed that a corresponding chemical reaction of free inorganic composition of FA with acid was occurred; consequently, fly ash particles acted out the inherent surface hole. Besides, acid damaged aluminosilicate vitreous structure of particles surface and led to the Si–O and Al–O bond tetrahedron structure flabby and fractured with soluble SiO₂ and Al₂O₃ increasing and forming new cavities, thereby the specific surface area of fly ash was increased [13].

In this investigation, we established that chemical modification of FA by sulphuric acid brought the variations in the particle size distribution of filler. It was determined with the help of laser diffraction particle size analyser (Fig. 1). It can be seen that modified FA has an increased content of fine particles. The fineness of tested FA samples is represented by the particles with maximum (d₉₈%) and median (d₅₀%) size of 139.15 and 27.66 μm (unmodified FA), 84.79 and 18.55 μm (modified FA), respectively. Besides, the content of the particles less than 2 μm is 8.71 % (modified FA) as compared with 5.86 % (as received FA).

Table 2. Element and oxide composition of the fly ash used.

Element	Content, %		Oxide	Content, %	
	as received FA	modified FA		as received FA	modified FA
Si	26.74	23.73	SiO ₂	57.19	50.76
Al	13.26	11.03	Al ₂ O ₃	25.05	20.85
Fe	6.25	5.88	Fe ₂ O ₃	8.94	8.41
K	2.57	2.47	K ₂ O	3.09	2.97
Ca	1.28	1.16	CaO	1.79	1.62
Mg	0.876	0.670	MgO	1.45	1.11
Ti	0.632	0.604	TiO ₂	1.05	1.01
Na	0.501	0.357	Na ₂ O	0.676	0.482
P	0.118	0.123	P ₂ O ₅	0.270	0.282
S	0.072	4.890	SO ₃	0.180	12.22

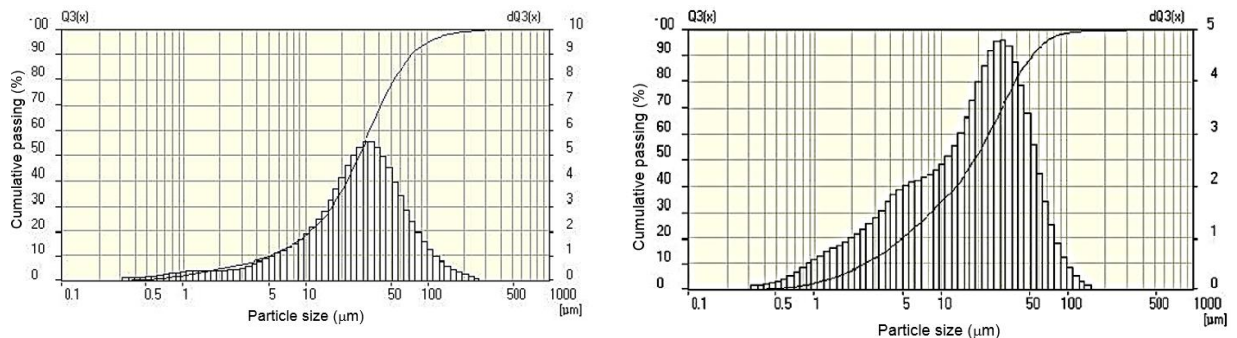
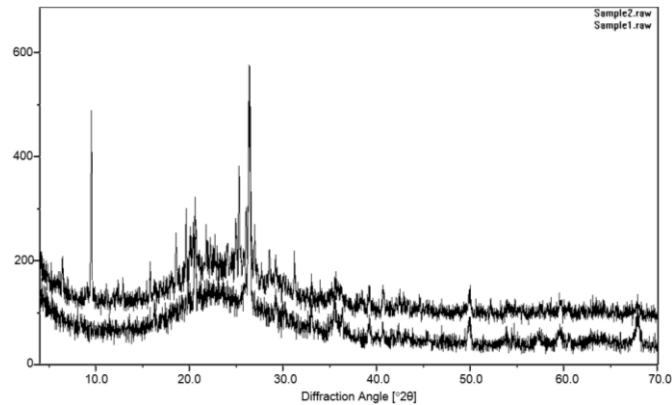


Figure 1. Integral and differential particle size distribution of as received fly ash (left) and modified fly ash (right).

The XRD patterns of as received fly ash shown in Fig. 2 indicate the presence of both crystalline (25 %) and amorphous phases (75 %). The main phases are quartz SiO₂ (19.6 %), hematite α-Fe₂O₃ (5.4 %), and amorphous substance (75.0 %). The diffraction peaks of 2θ°: 20.94° (*d*-spacing 0.424 nm), 26.67° (*d* = 0.334 nm), 36.65° (*d* = 0.245 nm), 50.29° (*d* = 0.181 nm), and 68.31° (*d* = 0.137 nm) all belong to the main characteristic peaks of quartz. Hematite is represented by diffraction reflections of 2θ°: 33.23°

($d = 0.269$ nm), 35.70° ($d = 0.251$ nm), 40.93° ($d = 0.220$ nm), and 54.16° ($d = 0.169$ nm). The broad halo over the range $15\text{--}35^\circ$ implies the presence of amorphous phase with crystalline inclusions of quartz.



**Figure 2. XRD patterns of fly ash filler:
sample 1 – FA as received; sample 2 – FA modified by sulphuric acid.**

XRD pattern of FA after chemical modification (Fig. 2) points to the fact that the content of crystalline phase has been increased up to 40 % while the content of amorphous phase has been decreased up to 60 %. In comparison with the unmodified sample the main crystalline phases are represented by the weaker diffraction peaks of quartz SiO_2 (11.8 % content) and hematite $\alpha\text{-Fe}_2\text{O}_3$ (3.3 %). On the other hand, some new substances in the crystalline state have been detected. They are: magnetite Fe_3O_4 (8.7 %) – diffraction peaks of 2θ : 18.24° ($d = 0.486$ nm), 30.06° ($d = 0.297$ nm), gypsum (calcium sulphate) $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (8.1 %) – 2θ : 9.9° ($d = 0.756$ nm), 29.17° ($d = 0.306$ nm), 31.9° ($d = 0.280$ nm), and alunogen $\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$ (8.1 %) – 2θ : 6.1° ($d = 0.145$ nm), 19.6° ($d = 0.453$ nm), 24.7° ($d = 0.360$ nm).

3.2. Mechanical and physical properties of PCM

The polymeric composite materials based on recycled PET and fly ash filler are low-cost materials that can be used in various building products, for indoor and outdoor applications like pavement slabs, roof tile, insulating wall, etc. Their particular application depends mainly on the physical and mechanical properties [12]. The compressive strength results are shown in Fig. 3. It can be seen that compressive strength tends to increase from 57.7 to 73.3 MPa with increasing concentration of unmodified fly ash from 55 to 65 percent. For comparison, the compressive strength value of virgin rPET sample is 55.8 MPa. The strength gain may be attributed to the increasing crystallinity in the rPET matrix of the composite material as the fly ash content is increased. During molding the fly ash filler is believed to act as a thermal insulator. This reduces the cooling rate and increases the crystallinity of the rPET material by allowing the rPET molecules to arrange themselves in an ordered pattern. Besides, the fly ash particle causes the crack to propagate around the particle, which increases the stress (energy) required to produce an equivalent crack length in contrast to the stress (energy) required with no fly ash particles present in the matrix [2]. However, when the fly ash filler content is beyond 65 % (from 70 to 75 %) compressive strength is decreased. Probably, the reason has to do with poor dispersion and homogenization of filler in the polymeric matrix at higher concentration, as well as decreased interfacial bonding. Thereby an effective total surface area for responding the applied stress is reduced. Besides, it is necessary to take into account the fact that in case of sufficiently thin layers of polymer between filler particles, the crystallization process is inhibited, and crystallization may not occur [20].

In the certain case when the fly ash filler is modified by sulphuric acid of 5 % concentration, the value of compressive strength of PCM sample at 65 % FA loading is higher on 18.9 percent (87.2 MPa) as compared with PCM sample on the base of unmodified filler. This result may come from the fact that modifying the surface of FA filler by sulphuric acid tends to strengthen acid-basic adhesion interactions between PCM components. In support of this interpretation, one can argue determined in our previous study [15] that the thermodynamic work of adhesion between rPET polymer and fly ash surface modified by 5 and 10 % concentration H_2SO_4 was increased on 1.29 and 2.14 %, respectively. However, the values of compressive strength of PCM samples containing 65 % of fly ash filler treated by sulphuric acid of 10 and 15 % concentration are well below the values of compressive strength of PCM samples containing 65 % of fly ash filler treated by sulphuric acid of 5 % concentration despite the higher thermodynamic work of adhesion. It is presumably because of the increased weak sulphuric formations (SO_3) on the FA surface after acid treatment that impedes the adhesion contact of components.

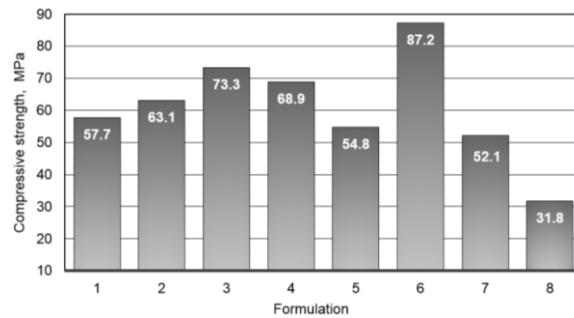


Figure 3. Compressive strength of PCM samples.

Flexural strength as well as compressive strength of PCM can be found to increase as the percent loading of fly ash is increased from 55 to 65 % (Fig. 4). For comparison, the flexural strength value of virgin rPET sample is 51.7 MPa. Thus, a relatively low content of FA 55–60 % does not provide the values of flexural strength compared to the virgin rPET sample. The optimal FA loading is 65 %, probably it is due to good dispersion of filler into polymer matrix and hence due to increasing the total area for deformation stress. However, beyond this value, the flexural strength decreases.

In the certain case when the fly ash filler is modified by sulphuric acid of 5 % concentration, the value of flexural strength of PCM sample at 65 % FA loading is higher on 5.1 percent (66.3 MPa) in comparison with PCM sample on the base of unmodified filler. It is also noteworthy, that flexural strength of PCM samples with FA modified by sulphuric acid of 10 and 15 % concentration is dramatically decreased.

It has been determined that the higher concentration of the fly ash in the PCM the higher the values of apparent density and the lower values of water absorption. This corresponds to the S. Anandhan's obtained data [23]. The values of apparent density and water absorption of the PCM samples with content of fly ash 65 % (treated by 5 % concentration H_2SO_4) are 1722 kg/m^3 and 0.19 %, respectively. For comparison, these values for the virgin rPET are 1410 kg/m^3 and 0.31 %, respectively.

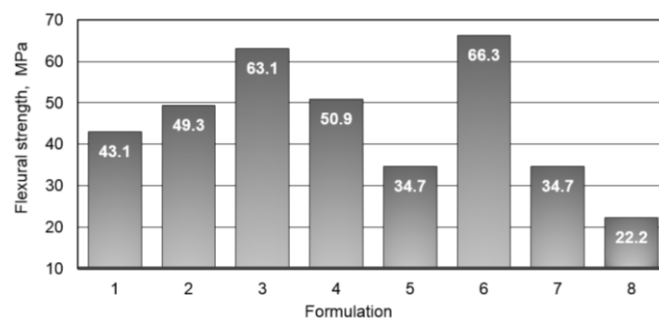


Figure 4. Flexural strength of PCM samples.

3.3. Phase analysis of pure rPET and PCM

Poly(ethylene terephthalate) is a semi-crystalline thermoplastic resin that in accordance with [21] is characterized by three intense Bragg diffraction peaks occurring at $2\theta = 17.5, 23.1, \text{ and } 26.1^\circ$ corresponded to (010), (110) and (100) lattice planes of triclinic crystal of PET. The broad peak $2\theta = 23.0^\circ$ points up the presence of an amorphous phase [24]. X-ray diffraction pattern of the pure rPET sample obtained is shown in Fig. 5. There are six characteristics intense peaks [25] on the diffractogram – 26.1° ($d = 0.341 \text{ nm}$, $IR = 100 \%$), 22.8° ($d = 0.389 \text{ nm}$, $IR = 81.8 \%$), 17.5° ($d = 0.506 \text{ nm}$, $IR = 79.9 \%$), 16.4° ($d = 0.540 \text{ nm}$, $IR = 79.8 \%$), 21.5° ($d = 0.413 \text{ nm}$, $IR = 78.4 \%$), 32.5° ($d = 0.275 \text{ nm}$, $IR = 48.4 \%$).

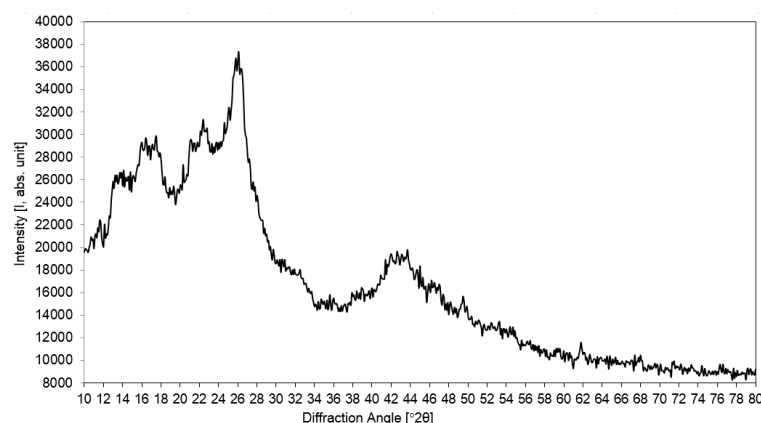


Figure 5. X-ray diffraction pattern of pure rPET.

Fig. 6 displays the XRD patterns of samples of PCM formulations 1, 3, 4, 6 (Table 2). By comparing the plots of the X-ray diffractograms of the fly ash (Fig. 2), pure rPET (Fig. 5) and the PCM samples (Fig. 6), it does not appear that the composite of the rPET matrix and the fly ash filler produced any new constituents. At the same time, it can be seen that the intensity of characteristic diffraction peaks of the rPET matrix is varied with the increment of the FA filler content. Setting the intensity of characteristic diffraction peaks of the PCM sample of formulation 1 (55 % FA content) at 100 %, the relative intensity of characteristic diffraction peaks of the PCM samples of formulations 3, 4 and 6 one can analyse in Table 3. It follows from these results that the intensity of characteristic diffraction peaks of the PCM sample of formulation 3 are higher in comparison with the sample of formulation 1. As mentioned above, fly ash filler is believed to act as a thermal insulator during molding. This reduces the cooling rate and increases the crystallinity of the rPET material by allowing the rPET molecules to arrange themselves in an ordered pattern. The highest values of relative intensity of diffraction peaks has the PCM sample of formulation 6 containing 65 % fly ash filler modified by sulphuric acid. On the other hand, when the content of FA filler is beyond 65 % the intensity of the diffraction peaks is the smallest among all the samples being investigated. Perhaps, in case of sufficiently thin layers of polymer between filler particles (high FA concentration) the crystallization process is inhibited. So, in our opinion it is clear that the XRD data are in conformity with the results of mechanical and physical properties of PCM.

3.4. Thermal analysis of the rPET and PCM samples

The thermal behaviour as well as the crystallization behaviour of the rPET and PCM samples has been characterized by the thermogravimetric (TGA) and differential thermal analysis (DTA). DTA/TG curves of thermal decomposition of pure rPET and PCM sample of formulation 6 (35 % rPET : 65 % the modified FA filler) are presented in Fig. 7 and Fig. 8, respectively. TG curves show that above 350 °C the mass is decreased by thermal decomposition.

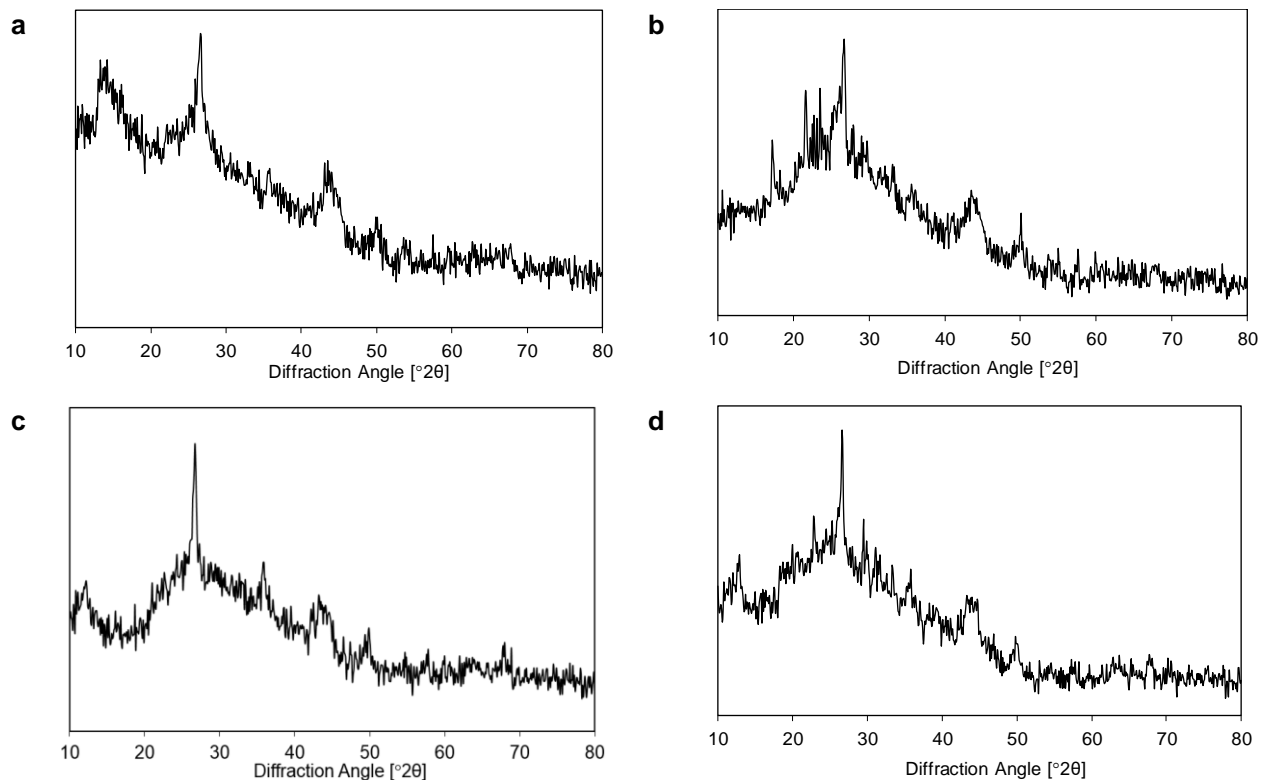


Figure 6. X-ray diffractograms of PCM:
a – 55 wt.% FA; b – 65 wt.% FA; c – 70 wt.% FA; d – 65 wt.% FA modified.

Table 3. The relative intensity of characteristic diffraction peaks of the PCM samples.

Formulation	Intensity of characteristic diffraction peaks, 2 theta, deg.											
	32.5		26.1		22.8		21.5		17.5		16.4	
	a.u.	%	a.u.	%	a.u.	%	a.u.	%	a.u.	%	a.u.	%
1 (Fig. 6 a)	13832	100	17136	100	15632	100	14912	100	16128	100	16376	100
3 (Fig. 6 b)	14440	104	17976	105	15864	101	16984	114	16184	100	16528	101
4 (Fig. 6 c)	14480	105	16656	97	14944	95.5	13989	94	12888	80	13228	81
6 (Fig. 6 d)	14960	108	18728	109	17352	111	17145	115	16376	101.5	14256	87

The value of mass loss comprises 35 and 33 % for pure rPET and PCM, respectively. In turn, DTA curves show a glass transition temperature T_g – 75 °C for pure rPET and 97 °C for PCM. In accordance with [18, 19] polymers with high crystallinity have a higher glass transition temperature T_g , higher modulus, toughness, stiffness, tensile strength, hardness and are more resistant to solvents, but have less impact strength. The rPET sample has an endotherm peak at 250 °C while the PCM one – at 251 °C.

It is well known that melting of pure PET happens in the range 225–260 °C with peak melting temperature at 255 °C [26, 27]. Broad exotherm with two peaks at 398 (rPET) and 417 °C (PCM) indicates a decomposition of polymer. Thus, the sample with fly ash filler has higher values of temperature of glass transition (97 > 75 °C), melting (251 > 250 °C) and decomposition (417 > 398 °C) in comparison with virgin rPET sample.

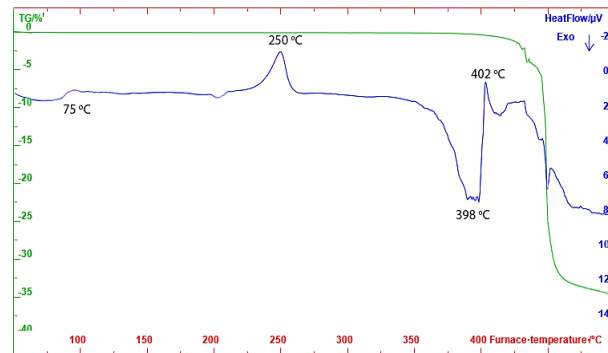


Figure 7. DTA/TG curves of rPET sample.

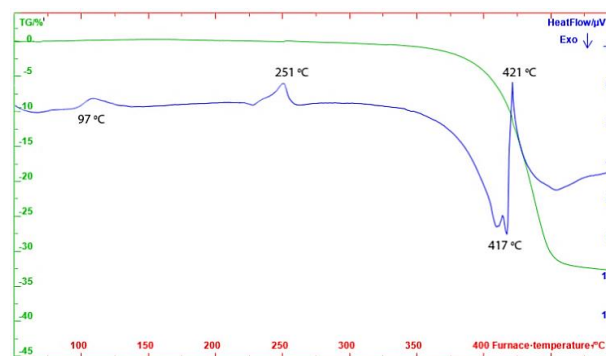


Figure 8. DTA/TG curves of PCM sample with 65 % fly ash concentration.

Effect of increasing temperature of glass transition and decomposition presumably stated because the filler particles drain thermal energy during PCM heating. A slight increase in the melting temperature of the PCM sample compared to the rPET sample indicates an increase in the degree of crystallinity due to the filler addition.

4. Conclusions

The properties of poly(ethylene terephthalate) composite material with the fly ash filler modified by sulphuric acid have been investigated. The results of the presented study can be formulated as follow:

1. The element and oxide composition of original (as received) fly ash is affected by the modification of sulphuric acid of 5 % concentration solution. It is displayed by decreasing content of the major oxides (silica, alumina, and ferric). At the same time, the presence of significant increment in SO_3 concentration can be seen. It is due to a corresponding chemical reaction of free inorganic composition of FA with acid, which damages aluminosilicate vitreous structure of particles surface and leads to the Si–O and Al–O bond tetrahedron structure flabby and fractured with soluble SiO_2 and Al_2O_3 increasing and forming new cavities. As a result, chemical modification of FA by sulphuric acid brings the variations in the particle size distribution of filler. In particular, the modified FA filler has an increased content of fine particles.

2. The XRD pattern of as received fly ash indicates the presence both of crystalline (25 %) and of amorphous phases (75 %). The main phases are quartz SiO_2 (19.6 %), hematite $\alpha\text{-Fe}_2\text{O}_3$ (5.4 %), and amorphous substance (75.0 %). On the other hand, XRD pattern of FA after chemical modification points to the fact that the content of crystalline phase has been increased up to 40 % while the content of amorphous phase has been decreased up to 60 %. In comparison with the unmodified sample the main crystalline phases are represented by the weaker diffraction peaks of quartz SiO_2 (11.8 %) and hematite $\alpha\text{-Fe}_2\text{O}_3$ (3.3 %).

Besides, some new substances in the crystalline state have been detected: magnetite Fe_3O_4 (8.7 %), gypsum (calcium sulphate) (8.1 %), and alunogen (8.1 %).

3. The results of mechanical and physical properties of PCM with various content of unmodified fly ash (55, 60, 65, 70, 75 %) filler indicate that compressive and flexural strength tends to increase from 57.7 to 73.3 MPa and from 43.1 to 63.1 MPa, respectively, with increasing concentration of FA from 55 to 65 percent. In the certain case when the fly ash filler is modified by sulphuric acid of 5 % concentration, the values of compressive and flexural strength of PCM sample at 65 % FA loading are higher on 18.9 percent (87.2 MPa) and on 5.1 % (66.3 MPa), respectively, as compared with PCM sample on the base of unmodified filler. The strength gain may be attributed to the increasing crystallinity in the rPET matrix of the composite material as the fly ash content is increased. Fly ash filler is believed to act as a thermal insulator during molding. This reduces the cooling rate and increases the crystallinity of the rPET material by allowing the rPET molecules to arrange themselves in an ordered pattern. The XRD, DTA/TGA data of pure rPET and PCM are in conformity with the results of mechanical and physical properties of PCM.

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