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Conference paper

Halina Kaczmarek*, Marta Chylińska, Ewa Klimiec, Bogusław Królikowski, Grzegorz Sionkowski and Monika Machnik

Piezo-electrets from polypropylene composites doped with mineral fillers

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Abstract: PP-based composites with two mineral fillers (perlite or glass beads) were manufactured by extrusion, and then subjected to orientation in a ratio of 3:1. Electrets were obtained in the polarization process under the influence of a constant electric field. Sample morphology was tested by SEM whereas the crystallinity was determined by XRD. Mechanical strength and thermal stability of composites was studied by tensile tests and thermogravimetric analysis, respectively. The piezoelectric characteristics were appointed by measurement of the electrical charge and current voltage in the polarized samples. The dependence of thermally stimulated depolarized current (TSDC) on temperature was also investigated. The piezoelectric coefficient (d_{33}), the electret stability over time as well as activation energy of depolarization process have been determined. It was found that low filler content (i.e. 2.5 and 5 wt.% of glass beads and perlite, respectively) significantly improve piezoelectric properties of isotactic polypropylene (i-PP).

Keywords: crystallinity; isotactic polypropylene; mechanical strength; morphology; piezoelectric properties; POC-17; polymer composites; thermal stability.

Introduction

Finding new, low cost piezoelectric materials, which can be easily molded into any shape using simple energy-saving methods is an important challenge for researchers. Durable electrets, which are the source of electric field, can be obtained not only from inorganic crystals or ceramics such as PZT (lead zirconate titanate) [1] but also from polymers of suitable internal structure [2–4]. The undisputed advantages of commonly used polymers are well known, and include inexpensive manufacturing technology, ease of processing, elasticity and the ability of various chemical and physical modifications to achieve the desired planned properties [5]. However, the piezoelectric effect in typical synthetic polymers is relatively weak for practical

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***Corresponding author: Halina Kaczmarek,** Chair of Polymer Chemistry and Photochemistry, Nicolaus Copernicus University in Toruń, Faculty of Chemistry, Gagarina St. 7, 87-100 Toruń, Poland, Tel.: +48 56 6114312, E-mail: halina@umk.pl
Marta Chylińska and Grzegorz Sionkowski: Polymer Chemistry and Photochemistry, Nicolaus Copernicus University in Toruń, Faculty of Chemistry, Gagarina St. 7, 87-100 Toruń, Poland
Ewa Klimiec and Monika Machnik: Department of Microelectronics, Institute of Electron Technology – Kraków Division, Zabłocie St. 39, 30-701 Kraków, Poland
Bogusław Królikowski: Institute for Engineering of Polymer Materials and Dyes – Toruń Division, M. Skłodowskiej-Curie St. 5., 87-100 Toruń, Poland

application. Therefore, new macromolecular materials or methods of their modification are sought, which may be exemplified by manufacturing hybrid composites [6, 7].

By nature, most polymers are dielectrics but the permanent internal dipole with electrostatic charges can be formed under constant electric field [8–12]. Polymeric piezoelectric composites are characterized by greater fracture toughness, lower density and lower dielectric constant than inorganic electrets. In addition, they are generally resistant to humidity, chemicals, oxidants and UV radiation which increases their application in various industries [13–17].

An attractive group of piezoelectrics are cellular, porous films based on polyolefins obtained under appropriate manufacturing conditions including electric discharge, orientation, foaming or by the addition of suitable fillers [18–20].

Recently, it has been found that in the isotactic PP a piezoelectric effect can be easily generated which is related to an ordered, semi-crystalline internal polymer structure [21, 22]. Additionally, the inorganic admixtures, for example, barium titanate [23] or calcium carbonate [22] enhance an initial charge density and its stability. Moreover, non-complicated chemical modification of PP also leads to improved thermal stability of electrets and greater piezoelectric activity [24, 25]. For this reason, and because of PP availability and low price, it is possible to predict the use of this polymer in electronics, e.g. for the manufacture of various sensors sensitive to electrical impulses or mechanical forces.

Our previous works indicate the accumulation of electrical charges in thin isotactic PP films modified by aluminosilicates from natural sources (Sillikoloid or Montmorillonite) [26–28]. Although these minerals are immiscible components with a polymer of typically hydrophobic nature, films with good mechanical properties can be obtained by extrusion.

The objective of this work was to investigate the effect of two different modifiers (perlite and glass beads) on the piezoelectric properties of isotactic polypropylene and to explain the influence of the composite structure on these properties. For this purpose, the fillers were added to the isotactic polypropylene matrix to obtain granulates, and then the films were extruded in carefully selected conditions. The motivation for using above mentioned mineral fillers was their availability and low price, as well as the results of initial research demonstrating the possibility of obtaining favorable physicochemical properties of PP modified in this way [29, 30]. The advantage of glass (or glass-like) fillers is their high chemical and thermal resistance as well as the increased processing ability of the filled polymers.

Perlite is a naturally occurring volcanic rock, which contains about a few percent of water. After mining, perlite is expanded at high temperatures, in which it obtains unique properties, of which the most important are high porosity, rigidity, large surface area, lower density and thermal conductivity. This allows its various applications in construction (as insulation, component of mortars and concretes), agriculture (subfloor for growing plants), filtration and adsorption materials (air and waste water treatment) [31, 32]. It is worth adding that perlite in this form is waste in production of building materials, so the advantage is its management, which contributes to the protection of the environment.

The second filler used in this work for PP are commercially available glass beads of a very regular shape and relatively uniform size. Although most published scientific reports concerning glass-modified PP is about composites filled with glass fibers, but recently, scientists have attracted a filler in the form of balls (solid or hollow inside) [33–35]. The addition of glass fillers to the polymer results in an increase in its mechanical properties such as tensile strength, Young's modulus, the stiffness and the toughness. Thermal conductivity of polypropylene filled with hollow glass-beads decreased with increase of the volume fraction of the beads, which clearly indicates the improvement of the heat insulation property of such composites [34]. This filler also improves material flow and changes the viscoelasticity of PP [35]. Moreover, it has been found that increase of bead content and diameter causes a reduction in polymeric composite shrinkage [36]. However, to our knowledge, the piezoelectric properties of PP glass-modified composites have not been described in the literature so far.

The appropriate choice of piezoelectric material for practical applications requires knowledge of the dependence of its properties on chemical structure, morphology and composition.

Experimental part

Materials

The commercial isotactic polypropylene, Moplen 456J type, produced by Basell Orlen Polyolefins (Poland) was used in this work. Mineral fillers were glass beads – MinTron 7™ (Rock Tron, UK; bulk density ~1.0 g/cm^3, melting temperature 1300–1317 °C, particle size <100 μm [37]), marked further with the abbreviation GB, and Perlite PEX-02/20 (Mining and Metal Works – Zakłady Górniczo-Metalowe Zębiec, Poland; bulk density 1.0–1.3 g/cm^3, melting temperature 950–1300 °C, particle size mostly <30 μm).

Test samples for studies were obtained by extrusion using a co-rotating twin-screw lab extruder of type Bühler BTSK 20/40D (the temperature of the subsequent zones in the extruder were in the range 190–195 °C) after thoroughly mixing of the components in the molten state. The fillers were added to the polypropylene matrix at 2.5, 5 and 10 % by weight.

The obtained films were further subjected to orientation (i.e. stretching 3:1) at a temperature 140 °C. The thickness of the samples obtained by extrusion was about 100–110 μm, and after orientation it diminished by half. Exceptions were samples with a 10 % filler content (in this case the thickness was reduced only by 10 %). The samples of different sizes were cut depending on the applied analysis method.

Polarization

For obtaining electrets, the films were polarized at constant electric field 100 V μm^{-1}, in a climatic chamber (VMT Heraeus-Vötsch). The samples were placed between two metal contact electrodes and then heated up to 85 °C. After reaching the proper temperature the voltage was switched on, and voltage gradually increased. The polarization time was 1 h. The sample was then cooled down to room temperature and the voltage switched off.

Characterization

The chemical structure of the resulting composites was monitored by FTIR spectroscopy using Vertex 70v with RT-DLaTGS Wide Range detector and ATR device, Bruker Optik, with diamond crystal.

Sample morphology was investigated by scanning electron microscope (SEM), model 1430 VP, produced by LEO Electron Microscopy Ltd., England.

The degree of crystallinity was determined by the XRD method using X'PERT Pro Philips diffractometer (Ni-filtered Cu $K_{\alpha 1}$ radiation, wavelength 1.54056 Å) at diffraction angle range $2\theta = 10°–50°$. In order to calculate the degree of crystallinity of the samples, the XRD curves were deconvoluted into components using mathematical functions analysis. XRD curves were fitted with Voigt function.

Thermogravimetric analysis was performed using the thermal analyzer NETZSCH STA 449 F5 Jupiter® (NETZSCH-Gerätebau GmbH) to determine the thermal stability of the composites. Nitrogen atmosphere, the heating rate 10 °C min^{-1} and the gas flow rate 100 mL min^{-1} were applied.

The standard tensile tests were used to evaluate the mechanical properties of composites using TIRAtest 27025 apparatus. The feed speed of crosshead at the beginning was 1.0 mm/min (for determination of Young's modulus) and then increased to 100.0 mm/min. The results of the tensile stress at breaking and ultimate elongation were averaged over a dozen measurements for samples of identical compositions.

Piezoelectric charge and voltage were tested on 10 cm^2 samples (thickness of ~100 μm), placing them between the contact electrodes on the actuator in the stress range up to 120 MPa. Measurements were carried out in quasistatic conditions. The interval for increasing and decreasing force was 1 s. The piezoelectric charge and voltage was measured using a charge amplifier and high impedance amplifier, respectively.

The piezoelectric coefficient d_{33} (pC/N) was calculated from dependence:

$$d_{33} = \frac{q}{P} \tag{1}$$

where: q is density of the piezoelectric charge (pC/cm^2) and P – stress (N/m^2).

The stability of polarized films kept at room temperature was determined by piezoelectric charge from time to time, up to about 120 days at 100 MPa strain. Process of electrets depolarization was determined by thermally stimulated depolarization current (TSDC) technique in the temperature range from room temperature to 120 °C. The temperature was increased at a rate of 0.018 °C/s.

The activation energy for the depolarization process was calculated by taking the natural logarithm of Arrhenius' equation:

$$\ln(J(T)) = \mathrm{const} - E / kT \tag{2}$$

where: J is the current density, E is the activation energy of depolarization, k is the Boltzmann constant and T is temperature in Kelvin.

Results and discussion

Extrusion process and visual assessment of i-PP composites containing fillers

The optimal extrusion conditions were chosen based on the trials performed. The temperature of extrusion die head equal to 245 °C and screw speed – 75 s^{-1} has been established. The temperatures of heating zones recommended for PP as well as investigated PP composites attain 190, 195, 195 and 190 °C, respectively.

Composite films with fillers were opaque and slightly stained in contrast to extruded under identical conditions neat PP (which was colorless). Darker were samples with glass beads (gray) than with perlite (cream color), however, all of them were still partly glossy. The higher filler content contributed to the hue increase. Visually no structural defects were observed on the surface of extruded film.

Oriented samples differ in surface – even by naked eyes one may see small parallel bands or wrinkles appearing as a result of stretching the film, additionally samples became more opaque. This can be caused by different direction of orientation of amorphous chains and highly ordered lamellae, which is also described in literature [38]. It has been suggested that disordered chains have tendency to orient towards the draw direction, contrary to crystalline ones.

Sample morphology studied by SEM

SEM images clearly show the differences in particle shapes of fillers selected for i-PP modification (Fig. 1). MinTron (i.e. GB) particles have predominantly regular spherical shapes of size in the range 1–10 μm (Fig. 1a). Only a few particles reach larger sizes (several dozen of μm), as confirmed by the manufacturer's declaration. Perlite is characterized by completely different structure (Fig. 1b) – this is a powder composed of very irregular, edged particles, resembling broken glass (or crushed bubbles). These structures arose from the process of expansion under the influence of considerable forces and collisions of particles with the walls of the processing device.

Surface testing with SEM allows to identify some imperfections in polymer samples resulting from the extrusion process. The initial, unmodified PP is homogeneous as opposed to composites containing fillers (Figs. 1c,d,e). In PP with MinTron filler, the glass beads are more or less regularly dispersed in the polymer matrix (in both oriented and non-oriented samples). Some of them are covered with a thin polymer shell. It is

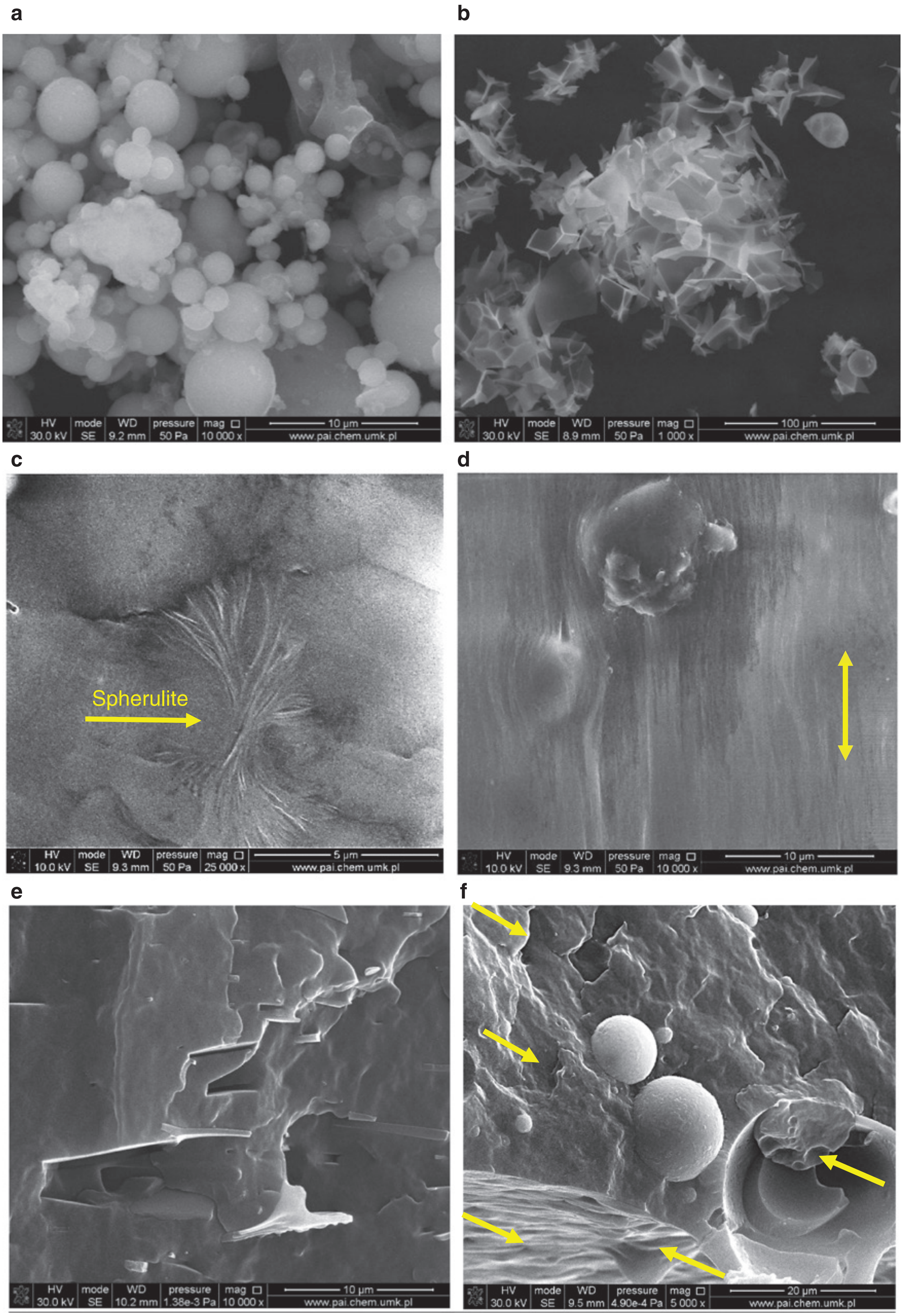

Fig. 1: SEM images of studied systems: (a) glass beads (GB); (b) perlite filler; (c) surface of non-oriented i-PP + 5 % GB, (d) oriented i-PP + 5 % GB (the arrow indicates the orientation direction); (e) iPP + 5 % perlite (non-oriented); (f) film cross-sections of PP + 5 % GB (the arrows indicate the cavities).

interesting that formed spherulites can be observed at sample surface in filled i-PP (Fig. 1d), although on the surface of neat i-PP film such crystallities were invisible.

The surface of the oriented samples indicates the alignment of the lamellae in parallel with the direction of stretching, an example of which is shown in Fig. 1d. At the same time, the elongated voids of about 10 μm in length and 1 μm in width are formed, some of them are empty and some are filled. These slots (micro-cavities) formed during orientation are typical for both types of PP composite containing perlite or glass beads.

In order to check the internal structure, the sections of films obtained by fragile fractures in liquid nitrogen were also observed by SEM (Fig. 1f). Regular glass balls dispersed throughout the PP matrix are clearly visible on the cross sections. Moreover, the numerous cavities of different sizes and shapes are seen – some of them are spherical, while other part has an elongated shape, and in addition they are often arranged parallel.

The smaller, irregularly shaped particles of perlite can also be observed in the second type composites. Significant differences in internal morphology appear after the sample stretching. In addition to the characteristic parallel ribbons resulting from orientation, numerous extended crevices appear. It can be seen that some of the filler particles have fallen out of their initial positions forming small holes (i.e. cellular structure) necessary for electric charge accumulation.

Observed structure is caused by the poor adhesion of the filler particles to the PP macromolecules due to the different properties of the components (both fillers are hydrophilic, while PP is typical hydrophobic polymer). The lack of adhesion is probably a reason for the complicated cellular-layered structure formation during sample orientation.

XRD analysis

Isotactic polypropylene is a semi-crystalline polymer, whereas fillers are completely amorphous, which is confirmed by XRD studies (Fig. 2). The addition of glass beads or perlite generally causes an increase of polymer crystallinity, however, the changes are not higher than 5 % (Table 1). These results suggest that added fillers are rather poor nucleating agents, contrary to other fillers described in literature [39].

All XRD patterns clearly indicate that ordered PP occurs in the form of monoclinic α-crystals as evidenced by the values of the main reflections at $2\Theta \sim 14°$ (1), 17° (2) and 18.6° (3) attributed to (110), (040) and (130) Miller indices. This is a favorable morphological structure having the least energy [40]. When calculating the degree of crystallinity, it also takes into account minor signals at 2Θ 11.5, 21–22 and 25.6°.

Full-width at half maximum of signals in XRD of PP and filled PP also alter insignificantly and irregularly. It means that size of crystallites is practically independent on the presence of fillers (up to 10 wt.% content).

As expected, the degree of PP crystallinity increases with film stretching. This also applies to i-PP samples with added glass beads but not perlite (exception are composites with 2.5 % filler).

XRD of tested films were recorded again after current polarization and aging at room temperature for 4 months to check if these processes have an effect on macromolecular arrangement. There was a slight increase in the degree of crystallinity in PP samples containing GB caused by electric field and aging (Table 1). This suggests that the action of constant electrical field may contribute to the alignment of PP chains, probably because of enhanced relaxation processes.

FTIR spectroscopy

Infrared spectra of obtained composites do not differ significantly from pure spectrum of i-PP alone. However, after films orientation small changes in fingerprint region were detected (Fig. 3). The band at 997 cm^{-1} is an index of PP isotacticity and it is characteristic for regular i-PP conformation in helix form 3_1 [41]. Thus, the little changes of absorption bands ratio A_{972}/A_{997} indicates slight increase in alignment. It confirms the small increase of crystallization degree determined by XRD.

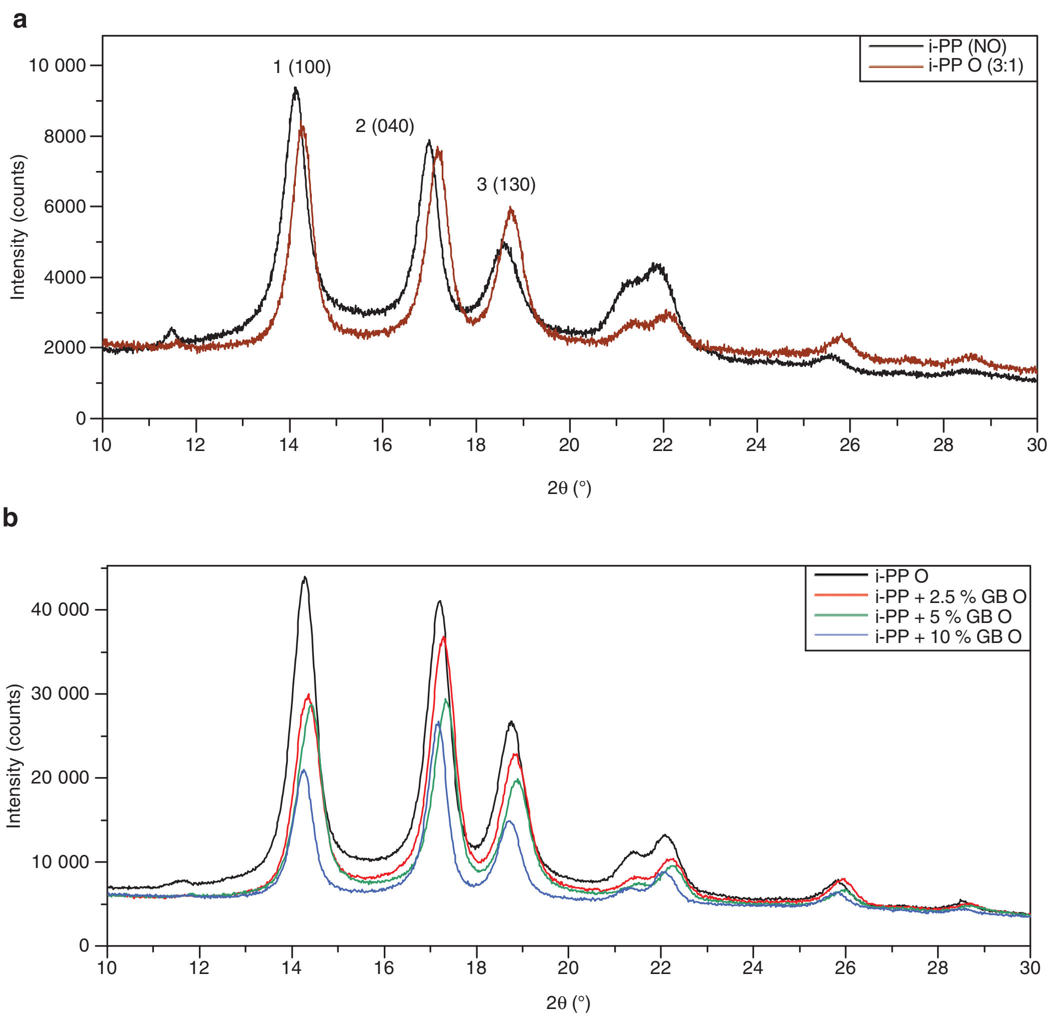

Fig. 2: XRD patterns of pure i-PP – oriented and non-oriented (a), oriented film of i-PP modified by glass beads of varying content (b).

It should be added that process of polarization in electric field does not cause any modification of the chemical structure of studied composites as was indicated by the fact that no change was observed in the FTIR spectra.

Mechanical properties

The following parameters characterizing mechanical properties: maximal stress (σ_M), stress at break (σ_B), elongation at maximal stress (ε_M), ultimate elongation at break point (ε_B) and Young modulus (E_t) have been assigned from strain-stress curves for all studied samples. The course of stretching curves was typical for thermoplastic polymers – after reaching the maximal stress, the formation of neck has been observed in most cases.

As one can see from the results presented in the Table 2, σ_B of non-oriented PP little decreases in the presence of fillers (exception is PP + 2.5 wt.% glass beads), while σ_M increases slightly in composites containing 2.5 and 5 wt.% filler (but decreases in sample with 10 wt.%). However, E_t increases in PP doped with perlite and GB up to 10 wt.% content in polymer matrix, indicating the reinforcing effect of applied mineral fillers at low stresses. There are no simple correlation E_t with filler content.

Table 1: Main signals at 2Θ range of 10–30° and their percentage contribution in the total surface area under the XRD curve, full-width at half-maximum (FWHM,°), as well as crystallinity degree of sample (X, %) calculated after deconvolution of XRD curves.

Sample	Amorphous halo share, %	Position (2Θ,°), FWHM (°) and share (%) of main crystalline signals									X, %
		1			2			3			
		2Θ	FWHM	%	2Θ	FWHM	%	2Θ	FWHM	%	
i-PP NO	31.2	14.0	0.46	17.9	16.8	0.43	25.6	18.5	0.55	10.9	68.8
i-PP O	29.4	14.3	0.50	22.0	17.2	0.49	20.5	18.7	0.58	13.1	70.6
PP + 2.5 %GB NO	30.7	14.0	0.49	14.9	16.8	0.38	36.0	18.5	0.46	5.9	69.3
PP + 5 %GB NO	36.7	14.2	0.66	17.6	17.1	0.56	19.7	18.7	0.66	9.7	63.3
PP + 10 %GB NO	26.9	14.1	0.42	13.5	16.9	0.37	29.4	18.6	0.46	9.0	73.1
PP + 2.5 % GB O	30.9	14.3	0.64	19.7	17.3	0.59	24.8	18.8	0.63	12.9	69.1
PP + 5 % GB O	28.5	14.4	0.59	23.6	17.3	0.54	23.3	18.9	0.61	13.8	71.5
PP + 10 %GB O	21.4	14.2	0.51	21.4	17.2	0.47	29.5	18.7	0.55	12.9	78.6
PP + 2.5 %perlite NO	31.6	14.1	0.51	17.0	17.0	0.45	26.6	18.6	0.59	10.1	68.4
PP + 5 %perlite NO	27.9	14.0	0.44	13.6	16.9	0.37	35.7	18.5	0.47	8.2	72.1
PP + 10 %perlite NO	26.8	14.0	0.44	13.9	16.9	0.37	32.6	18.5	0.45	9.1	73.2
PP + 2.5 %perlite O	25.3	14.1	0.56	21.0	17.0	0.51	26.1	18.6	0.56	13.8	74.4
PP + 5 %perlite O	30.6	14.2	0.60	17.3	17.2	0.55	27.5	18.8	0.61	11.2	69.4
PP + 10 %perlite O	28.1	14.3	0.61	19.3	17.2	0.56	25.0	18.8	0.60	11.3	71.9
After polarization at electric field of 100 V μm^{-1} and aging											
PP + 2.5 %GB NO	23.4	14.1	0.41	14.9	16.9	0.38	38.9	18.5	0.47	9.9	76.6
PP + 5 %GB NO	25.8	14.0	0.42	17.8	16.9	0.39	26.6	18.5	0.50	10.5	74.2
PP + 10 %GB NO	25.2	14.1	0.39	13.5	16.9	0.36	37.4	18.5	0.43	8.4	74.8

NO and O denote samples non-oriented and oriented 3:1, respectively.

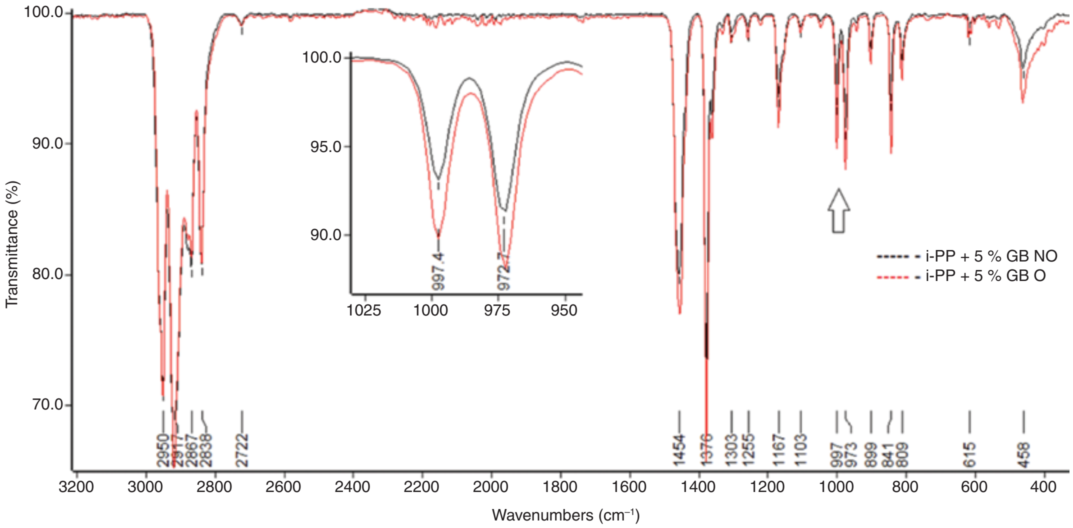

Fig. 3: Changes in FTIR spectra of i-PP film containing 5 % glass beads after orientation. The insert contains a magnified fragment of the spectrum containing the band assigned to the crystalline structure (indicated also by arrow).

Elongation (ε_M and ε_B) of composite samples drops significantly compared to respected parameters in neat PP.

Orientation leads to an improvement of mechanical parameters (σ_M, σ_B and E_t) in all type of samples comparing to non-oriented ones.

Changes in ultimate elongation in filled samples after orientation show a different trend than that in pure i-PP, in which both ε_M and ε_B decreases about four times when stretching.

Table 2: Mechanical properties of i-PP film and its composites with perlite and glass beads (GB).

Sample		σ_M [MPa]	σ_B [MPa]	ε_M [%]	ε_B [%]	E_t [MPa]
i-PP	NO	30.5	30.1	638	627	1065
i-PP	O	177	150	155	159	1967
PP + 2.5 % GB	NO	35.2	32.8	6.2	10.1	1185
PP + 5 % GB	NO	34.3	26.7	6.2	53.9	1117
PP + 10 % GB	NO	28.5	25.3	7.4	31.0	1143
PP + 2.5 % GB	O	130	35.2	21.1	41.7	2245
PP + 5 % GB	O	113	31.9	68.9	90.2	1760
PP + 10 % GB	O	109	38.5	40.4	53.6	1882
PP + 2.5 % Perlite	NO	31.0	27.8	6.4	58.2	1163
PP + 5 % Perlite	NO	33.5	26.0	7.4	12.3	1267
PP + 10 % Perlite	NO	28.3	24.9	5.6	8.4	1225
PP + 2.5 % Perlite	O	122	91.1	56.1	91.1	1961
PP + 5 % Perlite	O	114	21.1	67.2	20.5	2101
PP + 10 % Perlite	O	94.4	28.3	21.9	23.2	1853

NO and O denote samples non-oriented and oriented 3:1, respectively.

The improved mechanical properties of the samples with lower additives content (2.5 or 5 %) are due to their relatively good dispersion in the PP matrix but the effect is not very significant. When 10 wt.% of filler was incorporated, the dispersion gets worse and the particles can agglomerate, what negatively affects the mechanical strength at break. However, this does not affect Young' modulus.

The lack of a simple relationship between the parameters illustrating mechanical properties and the filler content may be due to the heterogeneity of the samples and poor adhesion of inorganic phase to macromolecules. This is consistent with the results obtained for PP with other mineral fillers [42].

Thermal stability

Knowledge about the thermal resistance of PP and its composites is important both from the point of view of processing and applications at elevated temperatures. The thermogravimetric analysis allows us to find a safe temperature range for the filled PP composite and, owing to the ability to simultaneously register DSC, also provides information on phase transformations, in this case melting of the polymer crystallites.

From simultaneously recorded TG, DTG and DSC curves, the following parameters have been determined: T_o – temperature onset (determined from the point at which TG begins to deviate from the straight line at a mass level of 100 %), T_{max} – temperature at maximum process rate (it is the inflection point on the TG curve), T_{50} – temperature at 50 % weight loss, Δm – weight loss at the process end (at 600 °C) as well as temperature and heat of melting (T_m, ΔH_m).

Examples of TG, DTG and DSC curves are shown for selected samples in Fig. 4a–c. As one can see the thermal degradation of PP-based materials is a one-step process. Neat polymer decomposes almost completely in the temperature range of 400–500 °C (the carbonaceous residue at 600 °C is about 5 %), which is consistent with the literature data [43]. DSC curve shows two main endothermic peaks connected with melting of PP crystalline phase (in the range of 140–180 °C with maximum at 164–167 °C) and main decomposition process (350–480 °C).

The mechanism and kinetics of PP thermal decomposition have been the object of many previously published works [43–46 and refs cited therein], so it will not be discussed here again. Just be reminded that under the influence of heat there is a statistical cracking of the main chains, depolymerization and the secretion of volatile, low-molecular weight products, including monomer. The undecomposed polymer residue contains stable, mostly crosslinked systems.

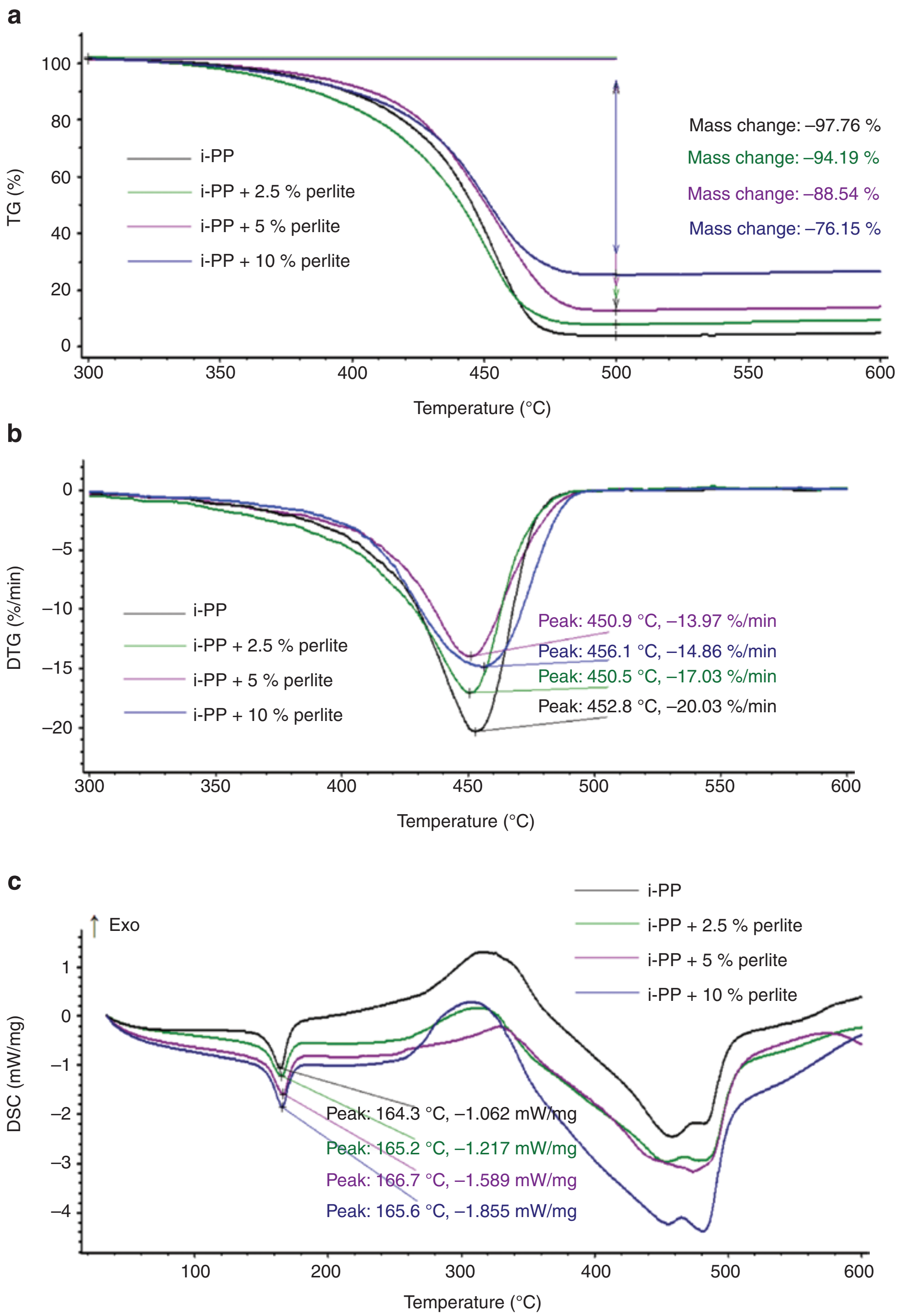

Fig. 4: TG (a), DTG (b) and DSC (c) curves of non-oriented films of i-PP with different content of perlite.

The orientation of PP causes a significant decrease in the temperature onset, but the temperature of T_{max} and T_{50} decreases only by about 9 and 5 °C, respectively. Also, the carbon residue is several percent higher in oriented virgin PP. Moreover, DSC curve exhibits additional exothermic peak (at ~270–350 °C range) and much broader endothermic peak above 350 °C corresponding to decomposition. Such altered DSC curves are observed in all composites, irrespective of the type and amount of filler. It suggests that further reorganization takes place and more crosslinked structures are formed in ordered crystalline phase upon heat thanks to close location of segments in PP lamellae.

Influence of fillers and orientation process on PP degradation can be discussed on the basis of the parameters presented in the Table 3. It should be noted that up to 600 °C neither perlite nor glass beads do

Table 3: Thermal parameters determined from TGA analysis in nitrogen for i-PP composites with glass beads (GB) and perlite.

Sample		T_o, °C	T_{max}, °C	T_{50}, °C	Δm, %	T_m, °C/ΔH_m, $J \cdot g^{-1}$
i-PP	NO	360	453	441	98	164/73
i-PP	O	333	442	436	93	163/78
i-PP + 2.5 % GB	NO	359	449	445	92	166/76
i-PP + 5 % GB	NO	373	452	451	87	167/75
i-PP + 10 % GB	NO	372	452	452	75	165/78
i-PP + 2.5 % GB	O	350	438	434	89	165/79
i-PP + 5 % GB	O	354	440	428	89	164/82
i-PP + 10 % GB	O	361	445	446	86	165/80
i-PP + 2.5 % perlite	NO	348	450	453	94	165/67
i-PP + 5 % perlite	NO	365	451	447	89	167/78
i-PP + 10 % perlite	NO	370	456	454	76	166/77
i-PP + 2.5 % perlite	O	338	435	434	77	165/93
i-PP + 5 % perlite	O	340	450	440	88	163/79
i-PP + 10 % perlite	O	352	431	433	76	163/81

(nonoriented – NO and oriented – O).

not undergo any thermal changes, apart from a slight loss of adsorbed water (2.5 % and 7 % for glass beads and perlite, respectively).

The filler added to PP causes increase of T_o and T_{50} in non-oriented films, with exception of samples containing 2.5 % of GB or perlite. No effect on the temperature of maximum process rate (T_{max}) was observed. Larger undecomposed residue (in comparison to pure PP) is due to the presence of mineral fillers, resistant at least to temperature of 600 °C.

Interestingly, the rate of thermal decomposition decreases in the presence of fillers comparing to pure PP what has been read from the maximum DTG curves. It is illustrated for PP with perlite in Fig. 4b.

GB and perlite addition causes a drop of T_o, T_{max} and T_{50} by about few or over a dozen degrees in oriented samples, but not as big as in pure PP (where, for example, the difference in T_o is 27 degrees). It clearly indicates the destabilizing effect of orientation in filled PP samples.

Melting point in modified but not oriented PP is practically unchanged, while ΔH slightly increases in the presence of fillers (except 2.5 % perlite) and after sample orientation. This is in accordance with XRD experiment and proves the growth of macromolecular order.

Generalizing, on the basis of this analysis, it can be stated that the addition of selected fillers does not markedly affect the thermal stability of PP systems. Despite the high thermal resistance of glass beads and perlite, they do not show any effective stabilizing effect on the composite. From the other hand, the heterogeneity of the samples has no negative influence on theirs thermal properties.

Piezoelectric properties

Voltage and charge measurements in the samples with fillers show a significant improvement in piezoelectric properties compared to neat polymer polarized under identical conditions (Figs. 5 and 6). As previously described, SEM images have shown the presence of cavities in samples with modifiers. In these internal gaps, the electric charges may accumulate.

It turned out that oriented films of i-PP with fillers were characterized by worse piezoelectric properties (lower charge and voltage values) or they were completely unsuitable for testing. Piezoelectric properties were only determined for non-oriented samples. This negative influence of orientation on piezoelectric properties in this case can be explained by higher deformation of voids created in filled PP during stretching.

The dependence of piezoelectric voltage and charge on storage time at room temperature of i-PP with glass and perlite fillers is shown in Figs. 5 and 6. Only PP with 2.5 % addition of perlite exhibits slightly lower U and q values than for the neat polymer itself (up to 60 days). In this case, perlite content was too small

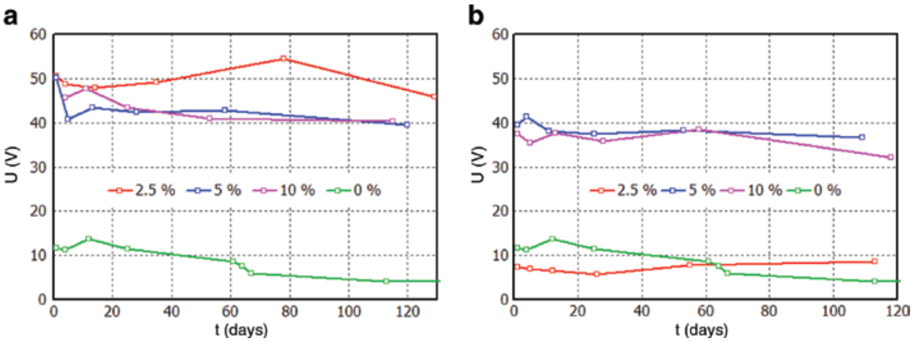

Fig. 5: Dependence of piezoelectric voltage versus storage time at room temperature for neat (0 %) and modified i-PP films: (a) with glass beads, (b) with perlite.

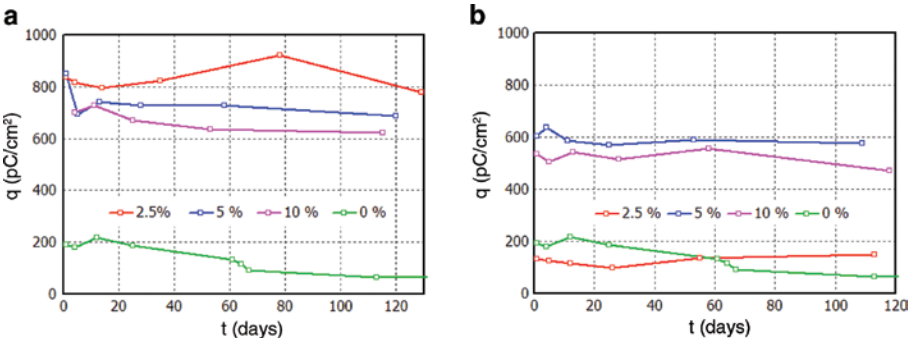

Fig. 6: Relationship of piezoelectric charge from storage time at room temperature for neat (0 %) and modified i-PP films with: (a) with glass beads, (b) with perlite.

and insufficient to improve the piezoelectric properties of i-PP film. Higher addition (5 or 10 %) of this filler produces a significant increase of U and q but the differences between the PP with 5 % and 10 % perlite are rather negligible. This effect can be explained by the polymer arrangement – similar crystallinity in these samples (72–73 %) has been observed, while PP + 2.5 perlite has a degree of crystallinity almost identical to the unmodified polymer (68 %).

In all samples, changes in voltage and charge values after about 120 days of storage at room temperature are low. Electrets formed in composites with glass beads exhibit higher voltage and piezoelectric charge values at the same pressure (100 kPa).

TSDC curves for the neat and modified i-PP film with glass beads and perlite are shown in Figs. 7a and b, respectively. Depolarization temperatures (T_m = 75–78 °C) differ slightly in the samples tested. The effect of the small amount (2.5 %) of GB or perlite causes small increase of this value, while 10 % has opposite effect. This may be due to the greater heterogeneity of this sample. This contributes to the formation of more pores, and it can result in depolarization of the sample at slightly lower temperatures.

Highest T_m value is obtained for composite films with 2.5 % glass beads and 5 % perlite, thus, we decided to calculate the activation energy of depolarization for these two selected samples.

Because in the course of thermostimulated depolarization currents for i-PP with glass beads (Fig. 7a), we observed two overlapping processes, the sample was additionally aged at 60 °C for 30 min. After aging, this first small effect disappears, thus, it was possible to calculate approximate activation energy from the slope of $\ln(|J(T)|)$ vs. $1/T$ (an example of the course of this function is shown in Fig. 8). Normalized root-mean-square error of fitting a straight line to measurement series in Fig. 8 is 3 %. This provides an upper bound on the error of determination of the line slope, and thus the uncertainty of the activation energy is ≤3 %.

Activation energy value is 4.03 eV for i-PP film with 2.5 % glass beads and 4.48 eV for i-PP with 5 % perlite. Differences between E values for both samples do not exceed the experimental error. It can be concluded that

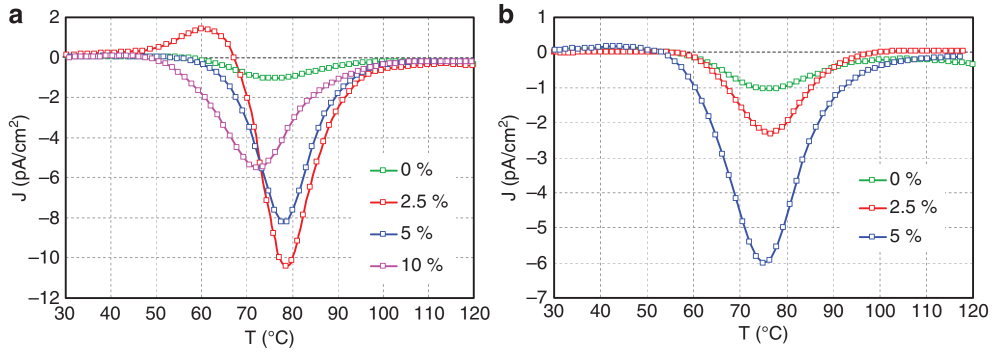

Fig. 7: TSDC currents for neat (0 %) and modified i-PP films with: (a) the glass beads, (b) perlite.

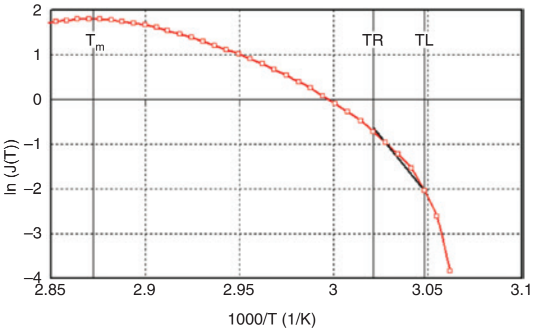

Fig. 8: Dependence of the logarithmic discharge current density versus the temperature reciprocal for i-PP film with 2.5 % glass beads. The section between TR and TL indicates the straight line fitted in the beginning of the temperature rise, corresponding to 0–10 % of the absolute value of the maximum current density in Fig. 7.

the durability of these films is similar, which also confirms approximately the same temperature value T_m, in which the change in the absolute value of the discharge current density is maximal.

The dependence of charge and piezoelectric constant d_{33} from the pressure acting on the film in a direction perpendicular to the plane of the sample and in the direction of the electrical field in the electrets obtained is shown in Figs. 9 and 10. For comparison, the results for neat i-PP obtained and polarized in the same conditions as the composite samples, are also shown. The d_{33} value of neat i-PP attains ca. 15 pC/N for small stresses and ca. 6 pC/N for bigger ones.

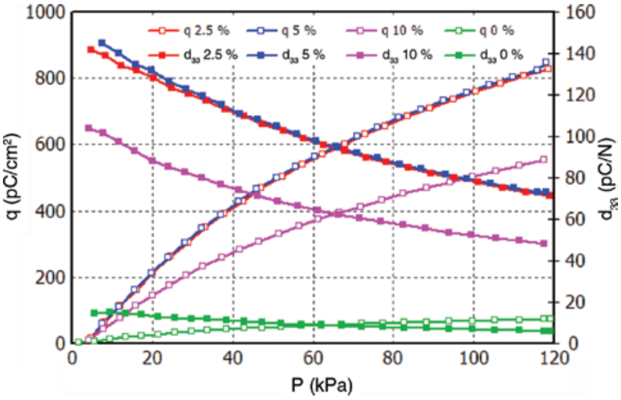

Fig. 9: The dependence of charge and d_{33} on the stress for neat (0 %) and modified i-PP with glass beads.

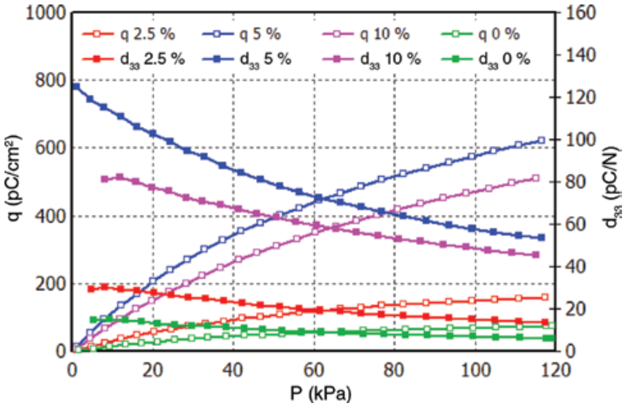

Fig. 10: The dependence of charge and d_{33} on the stress for neat (0 %) and modified i-PP with perlite.

Also in compositions d_{33} depends on the value of acting stress. In the low stress area, the maximum value of d_{33} is ~140 and ~130 pC/N, for PP + GB and PP + perlite, respectively. At higher stresses (~120 kPa), these values decrease to ~70 and ~55 pC/N, respectively, but still exceed the d_{33} of poly(vinylidene fluoride) film (PVDF), which, according to our research and literature data, ranges from ~20 to ~50 pC/N.

It should be noted that PVDF is a polymer which, due to its piezoelectric properties, is already used in practice for production of sensors, gauges or transducers and can be treated as reference. The i-PP based systems described in this paper, however, can be an economic alternative to this rather expensive polymer.

Final discussion

From the thermodynamic point of view silica-based fillers are immiscible with polyolefins but the physicochemical properties (including mechanical and piezoelectric) of the composites depend on the size and concentration of the particles incorporated into the matrix [47–49]. A small amount of filler with micrometric particle size allows its good dispersion during processing, which contributes to material reinforcing and improvement of certain properties. Higher filler content may cause agglomeration of the particles, or even lead to phase separation, which generally results in the deterioration of the mechanical strength. Modification of the internal composite structure is possible, for example, due to the functionalization of the filler surface or grafting, which promotes the improvement of adhesion between the components [50]. The situation changes when the particles have a nanometer dimensions – then the ratio of the surface to the volume of the particle is very large and the developed filler surface leads to stronger molecular interactions, thus the structure enhancement appear at low filling degree [51].

It is also necessary remember that due to high molecular weight of polymer, the high melt viscosity impedes accurate distribution of filler particles throughout the matrix during processing [52].

In studied samples the fillers with average diameter of 20–30 µm (GB) and ~10 µm (perlite) have been used. The resulting microcomposite materials have the heterophase structure containing inorganic inclusions and voids, necessary to the storage of electric charge and formation electrets. The advantage is also the lack of the need for additional filler modification or compatibilizer addition. The best effect was obtained for samples with 2.5–5 % filler content. Higher filler content (10 %) weakens the polymer structure, especially for samples oriented to increase the degree of crystallinity. Moreover, piezoelectric effect was also lower in this case.

Although both modifiers are characterized by non-uniform particle size and similar chemical composition, perlite contains dusty fraction and irregular shape as opposed to GB. This can affect the boundary interactions and conditions of charge trapping.

Conclusions

This work presents the possibility of manufacturing of durable piezo-electrets on the base of modified isotactic polypropylene by relatively simple method. The effect of applied fillers on the properties of i-PP composites, in particular the piezoelectric properties, has been determined by complementary instrumental techniques.

Both used fillers – glass beads and perlite, despite different origin, are characterized by a similar chemical composition. The main difference is the shape and size of the filler particles, influencing the composite structure, thus also its properties.

SEM micrographs of outer and inner layers of both types of i-PP composites exhibited that filler particles dispersed in the polymer matrix are characterized by rather poor adhesion. Simultaneously, the voids are formed around the filler particles.

Both addition of filler and orientation process influence the crystallinity degree of i-PP. The effect of the fillers on the tensile strength is small, the elongation decreases but the Young's modulus in the composites is growing. The orientation of the samples has greater effect on the mechanical properties of tested films.

It was found that the improvement of the piezoelectric effect of PP composites is closely related not only to the filler content, but also to their microstructure and the presence of free spaces within the matrix that allow the accumulation of electric charges.

The best piezoelectric properties have been obtained in non-oriented films of i-PP containing 2.5 % glass beads or 5 % perlite. The activation energy of depolarization process (~4–4.5 eV) and temperature at maximal current density determined from TSDC experiment ($T_m = 75–78\ ^\circ C$) is similar in these samples. An important achievement is the high piezoelectric constant d_{33} both in area of small (10–20 kPa) and large (120 kPa) stresses. It should be added that both specified samples are characterized by crystallization degree about 70 % and similar Young modulus (~1200 MPa).

Finally, it can be concluded, that composites based on i-PP modified by about 2.5–5 % studied fillers are a potential piezoelectric materials due to theirs favorable piezoelectric properties, electrets durability, beneficial mechanical and thermal properties as well as predicted low production costs.

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