CrossMark

Characterization of piezoelectric films of foamed polyethylene obtained by extrusion

Halina Kaczmarek[1] · Ewa Klimiec[2] · Bogusław Królikowski[3] · Marta Chylińska[1] · Monika Machnik[2]

Abstract Foamed polyethylene (MDPE) films obtained by extrusion have been characterized by X-ray diffraction, thermogravimetric analysis and tensile tests. The piezoelectric properties have been determined by calculation of piezoelectric constant d_{33}, thermally stimulated depolarized current method and calculation of activation energy depolarization of electrets. It has been found that the crystallinity and internal morphology, including cellular structure, affect the possibility of an effective polarization in order to obtain a piezoelectric material from foamed MDPE. The conditions of processing have a great influence on the piezoelectric properties. The value of piezoelectric constant attains ~18 pC/N and ~75 pC/N for low stress range and diminishes for higher stresses, temperature T_m ~72 °C and ~82 °C, approximate activation energy attains 2.67 and 3.28 eV, for compacted and non-compacted film, respectively. Because of the simple and cheap method of foaming PE films of piezoelectric properties it is worthy to take care regarding their application for pressure sensors.

✉ Halina Kaczmarek
halina@umk.pl

[1] Faculty of Chemistry, Nicolaus Copernicus University in Toruń, Gagarina St. 7, 87-100 Toruń, Poland

[2] Institute of Electron Technology – Kraków Division, Zabłocie St. 39, 30-701 Kraków, Poland

[3] Institute for Engineering of Polymer Materials and Dyes – Toruń Division, M. Skłodowskiej-Curie St. 5, 87-100 Toruń, Poland

1 Introduction

Polyolefins have enjoyed for many years of sustained popularity thanks to a well-known technology of manufacturing, not high cost of production and the possibilities of structure modification leading to new beneficial properties [1, 2]. A large progress has been recently observed in the manufacturing of polyolefins (polyethylene—PE, polypropylene—PP and their derivatives) having a strictly planned, well-defined structure of macromolecules by using metathesis and specifically designed catalysts [2–5]. It is not without significance the polyolefin waste utilization in the recycling process [6]. Moreover, it is possible to obtain functionalized macromolecules of PE and PP, which contributes to the change of their properties and significantly expands the use in numerous industrial sectors. For example, the hydrophobic nature of the polyolefins may be modified by introducing of the polar groups to macromolecules in the process of copolymerization, which changes the surface properties, adhesion to various substances, printability and miscibility with other plastic components or polymers [3, 7, 8]. Of great significance in the planning of specific applications (medical, biotechnological, etc.) of polyolefins has a precise control of chemical structure and morphology, which is possible due to sophisticated, complementary instrumental techniques.

In common applications, dielectric properties of polyolefins are important and often used. These features are also necessary for obtaining piezoelectric materials.

The requirement for obtaining piezoelectric properties of electro-active polymers is their durable polarization. For polar materials such as poly (vinylidene fluoride), this is a lasting arrangement of molecular dipoles. In the case of non-polar materials such as polypropylene or polyethylene, it is a permanent arrangement of the charges

resulting from the structural defects of the material as well as the charge introduced into the material during the polarization process under the influence of strong electric field. The structural defects in polyolefins can be the residues of initiators or catalysts from the polymerization, incorporated into the macromolecules.

Permanently polarized materials exhibit an external electric field, and by analogy to magnets they are called electrets.

Recently, there appear reports on such materials based on polyolefin, which can be used for manufacturing of sensors and strain gauge for biomedical applications [9–11]. Particular attention was paid to research of semicrystalline polypropylene. It proved that the PP doped with inorganic substances forms stable electrets [12–16] due to the ordered polymer structure and some particular defects—the inner cavities (cells) filled with air or dopants of other substances. The detailed mechanism of trapping charges in polymer matrices is still under discussion. Generally speaking, it is believed that for the storage charge are responsible physical and/or chemical traps which may include impurities, structural disorders or free radicals captured in the polymer network.

New piezoelectrics based on polymers are still sought because of their valuable physicochemical properties (e.g. flexibility, durability, low density) and the possibility of forming any shapes and sizes of products in conventional molding processes. It has been repeatedly confirmed that good piezoelectric properties have semicrystalline polymers with a cellular structure [14, 17–20]. On the basis of reviewing the current literature shows that an isotactic polypropylene is already recognized as a potential piezoelectric material (besides of PVDF or PFTE) [12–16], however, other polyolefins, including polyethylene, are still not well investigated. In practice, there is no problem with obtaining cellular structure in PE, for example, through the corona discharge or use the foaming compound. Moreover, the degree of crystallization in PE film can be enhanced by orientation process or addition of nucleating agent.

In view of the scientific reports on the beneficial effect of cellular structure in the polymer on the piezoelectric properties, we decided to study whether the foamed polyethylene creates a structure providing formation of electrets. Thus, the aim of this study was to obtain and characterize properties (including piezoelectricity) of films prepared from medium density polyethylene (MDPE) containing chemical blowing agent. In this work few instrumental techniques have been used to determine the relationship between structure and properties of chosen MDPE. According to our knowledge it is the first study of foamed polyethylene from the viewpoint of its potential piezoelectric properties and application in sensors technology.

2 Experimental part

2.1 Materials

A commercial medium density polyethylene (MDPE) containing blowing agent (Borcell™ ME 1244, Borealis AG) has been used. Purchased polymer is present in the form of a slightly yellow granules. The polymer films of 145 mm width and different thickness (100–200 μm) have been obtained by extrusion using single-screw lab extruder Plasti-Corder PLV 151 Brabender in the following conditions: extruder heating zones—225, 235, 235 °C, temperature of extrusion die head—245 °C, screw speed—75 s^{-1}. For thinner films, extruded samples were subjected to further compression in a hydraulic press (Graseby Specac, 9 cm diameter mold) at a temperature of 140 °C in time of 0.5 min with a load of approximately 2 tons.

2.2 Characterization

The morphology of received MDPE films has been observed by scanning electron microscope LEO 1430 working in controlled vacuum.

Crystallinity of samples have been studied by X-ray diffraction X'PERT Pro Philips Diffractometer using Cu $K_\alpha1$ radiation (wavelength 1.54056 Å), range 2θ 5°–90°, scan step size 0.020° and time per step 3.00 s. The method of determining the degree of crystallinity described in detail previously [16].

Thermogravimetric analysis was carried out using simultaneous thermal analyzer NETZSCH STA 449 F5 Jupiter® (NETZSCH-Gerätebau GmbH) in nitrogen atmosphere. This apparatus enables to record TG, DTG and DSC curves in one measurement. The heating rate and the gas flow rate were 10 °C min^{-1} and 100 mL min^{-1}, respectively. Proteus Thermal Analysis (Version 6.1.0) software has been used for results elaboration and presentation.

ATR-FTIR spectra have been obtained using Vertex 70v with RT-DLaTGS Wide Range detector and ATR device (Bruker Optics Gmbh, Ettlingen, Germany), with diamond crystal (in the vacuum below 100 Pa).

Raman measurements were performed at room temperature using confocal microRaman spectrometer (Senterra Raman microscope R200-L with laser safety enclosure, Bruker Optics Gmbh, Ettlingen, Germany) with a high resolution of 9 cm^{-1} and λ_{exc}=785 nm diode laser excitation in 400–3600 cm^{-1} region.

The study of the mechanical properties was performed using a tensile testing apparatus TIRAtest 27,025 equipped with a 3 kN head at room temperature. The feed speed of crosshead was V_1=1.0 mm min^{-1} (in the initial stage of the tensile, to 2% elongation) and V_2=100.0 mm min^{-1} (from 2% elongation to break). Dimensions of the samples

were 50 mm × 15 mm. Obtained results are the average of at least ten measurements.

Piezoelectric properties of foamed MDPE films were tested on extruded films and films additionally compressed at 140 °C. To manufacture the 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 upper temperature the voltage was switched on, and voltage value gradually increased. The polarization time was 1 h. The sample was then cooled down to room temperature and the voltage as switched off. The electric field and the temperature were selected for film basing on its breakdown voltage >100 V μm^{-1} at 85 °C. The density of the piezoelectric charge is proportional to stress and the piezoelectric constant d$_{33}$ is the coefficient of proportionality, whose value was calculated from dependence:

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

where q density of the piezoelectric charge, P stress, d$_{33}$ piezoelectric constant.

The stability of the electrets stored at room temperature has been systematically examined. The voltage and charge have been measured every few days (up to 38 or 82 days). Electrets durability was tested by the thermally stimulated depolarization current (TDSC) technique in the temperature range from room temperature to 120 °C. The activation energy for the depolarization process was calculated by taking the natural logarithm of Arrhenius' equation:

$$\ln(I(T)) = const - \frac{E}{kT} \tag{2}$$

where I is the current density, E is the activation energy, k is the Boltzmann constant and T is temperature in Kelvins.

Therefore, a plot of ln(I) versus 1/T gives a straight line, whose gradient can be used to determine activation energy E. This relationship is used in initial-rise method [21].

3 Results and discussions

3.1 Scanning electron microscopy (SEM)

The morphology of the film surface obtained by extrusion method varies depending on the side of the sample. The surface of the film that had direct contact with hot rollers, is smooth and glossy, while the opposite side is more matte and rough. SEM images of both sides of the film show further differences in the structure of the surface (Fig. 1). As can be seen in Fig. 1a, structure observed in microscale is typical for polymer obtained by rapid cooling of melt. The second side of film shows the chaotically scattered lamellar

structures in the polymer (Fig. 1b). However, in the same specimen elongated lamellar layers arranged in the plate are seen after higher magnification (such layout included in the Fig. 1c in brackets).

The cross-section of MDPE films shows cellular structure. Interestingly, this porous structure does not disappear after compression molding at 140 °C (Fig. 1d). On the basis of cross-sectional images of samples taken at various magnifications estimated cavity size in the range of 0.01–0.08 μm.

3.2 X-ray diffraction

X-ray diffraction pattern of the foamed polyethylene (Fig. 2) exhibits two main reflections in studied range at 2Θ: 21.4° and 23.7°, corresponding to the orthorhombic unit cell structure of (110) and (200) planes in PE crystallites, which is consistent with literature reports [22, 23]. The last small signal at 2Θ = 29.1° can be attributed to the residues of the foaming agent. This is very probable because it decreases after processing and almost completely disappears after additional compression molding of sample at 140 °C.

To quantitatively estimate the degree of crystallinity (X, %) of MDPE, the recorded XRD curve has been deconvoluted for components assigned to the crystalline and amorphous phases using Voigt function, for which the best curve fitting has been achieved. The background has been described by a linear function. In diffraction angle range of 10–30°, the fraction of the integral intensity of the sharp peaks gives the degree of crystallinity similar to that determined by other experimental methods. The peak at 2Θ = 29.1° was not taken into account when calculating the degree of crystallinity of the polymer (its surface area was subtracted from the total area under the XRD curve). The result of XRD mathematical distribution is presented in Fig. 2.

The data listed in Table 1 shows that the degree of crystallinity slightly increases from 62.1 to 63.9% after molding at 140 °C although it was short-term heating (only 30 s). At the same time, on the basis of almost identical values of half-widths (FWHM) of signals at 21.4° and 23.7° it can be stated that crystallite size did not change at this time.

3.2.1 Thermogravimetric analysis

The thermal stability of extruded and additionally heated MDPE has been investigated by thermogravimetric analysis (TGA). Figure 3 shows TG, DTG and DSC curves for extruded MDPE. The main parameters determined from TGA for both type of samples (extruded and compacted) are collected in Table 2.

Fig. 1 SEM images of blown, extruded MDPE film: surface of gloss side (**a**), surface of mat side (**b**), details on mat side surface—*yellow brackets* indicate an ordered lamellar layer (**c**), cross-section of MDPE film after additional compacting at 140 °C (**d**). (Color figure online)
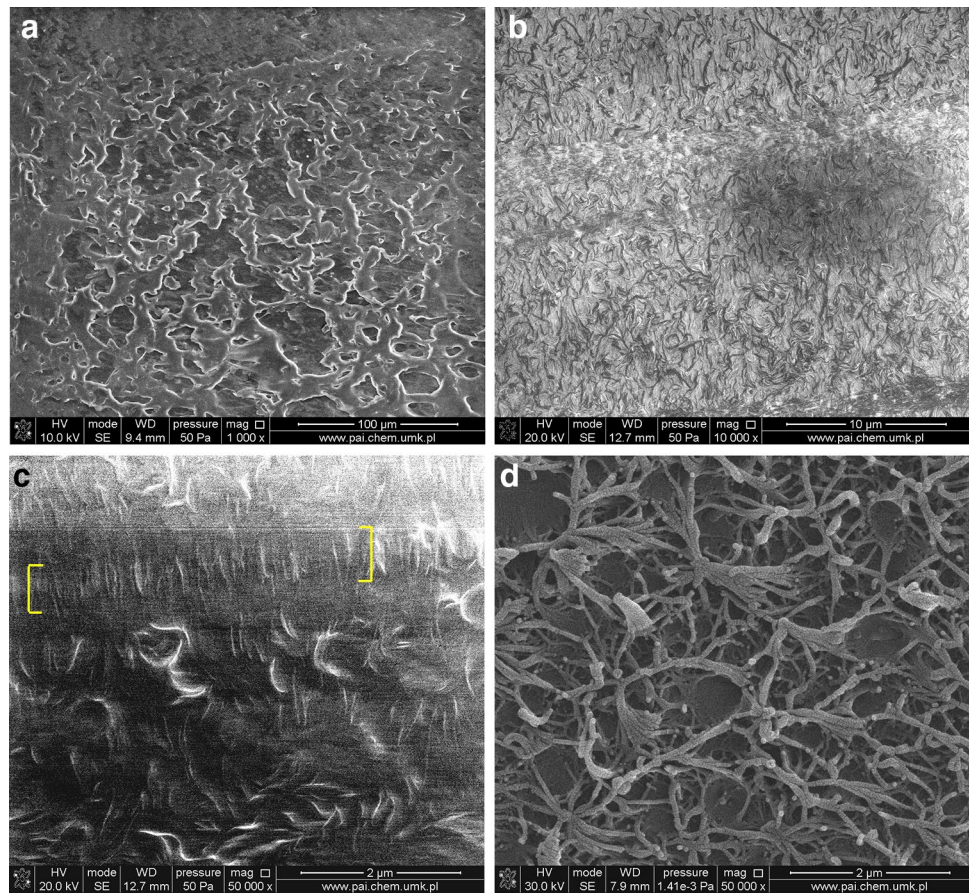
Fig. 2 XRD patterns of blown MDPE and curve fitting of experimental XRD data showing individual componet signals
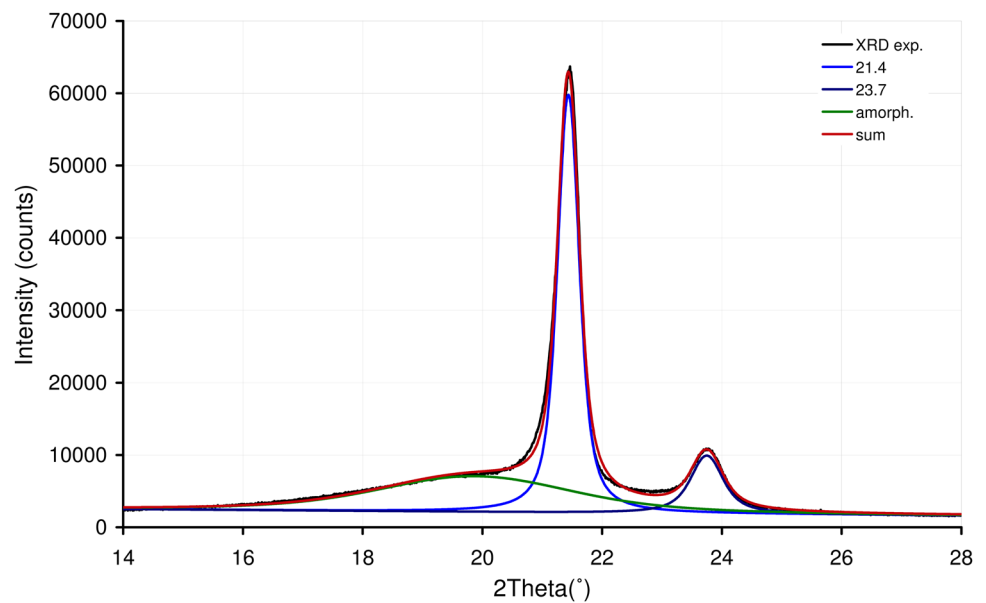

The studied polyethylene undergoes the single-stage thermal decomposition, which starts above 450 °C and ends about 500 °C. Decomposition is almost complete—carbonaceous residue at 600 °C is no more than 2%.

As is known from the literature, the main products secreting during thermal decomposition of PE are saturated or unsaturated hydrocarbons containing different number of carbon atoms [24–26]. This is the result of random chain

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 crystalline signals						X, %
		2Θ	FWHM	%	2Θ	FWHM	%	
Borcell extruded	37.9	21.4	0.43	51.1	23.7	0.58	11.0	62.1
Borcell compacted	36.1		0.45	49.5		0.57	14.4	63.9

Fig. 3 Thermogravimetric analysis of foamed, extruded MDPE
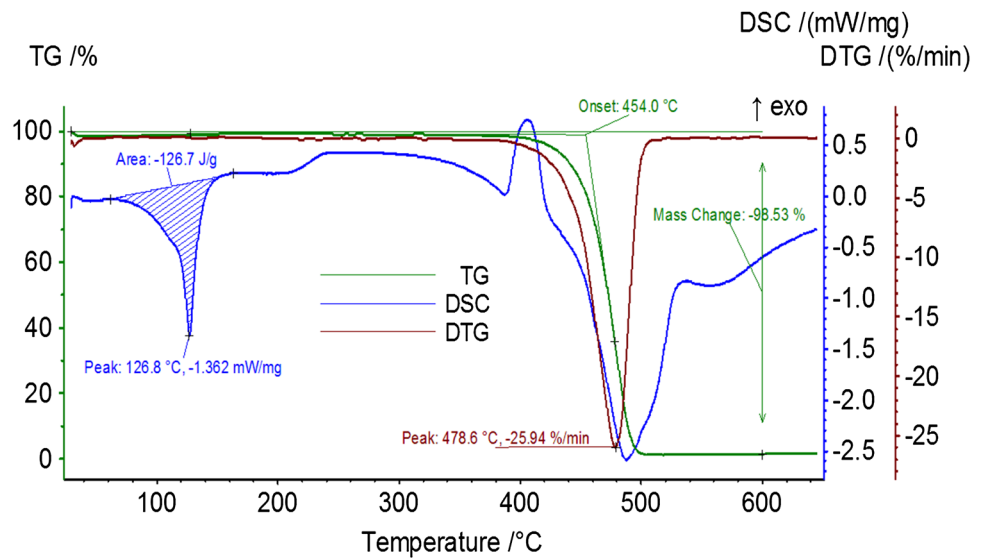
Table 2 Main parameters determined from thermogravimetric analysis of foamed MDPE (extruded and additionally heated)

Sample	T_m, °C	ΔH_m, J/g	T_o, °C	T_{max}, °C	T_{end}, °C	Δm, %	Residue at 600 °C
Borcell extruded	126.8	126.7	454.0	478.6	491.4	98.53	1.47
Borcell compacted	130.5	292.9	459.7	477.9	492.7	98.44	1.64

scission of PE chains to shorter hydrocarbons. It was also found the evolution of significant amounts of hydrogen and the creation of nanocarbon structures (e.g. graphite-like) during PE thermal degradation in the inert gas atmosphere [26].

In the temperature range of 100–150 °C, on the DSC curve appears an endothermic melting peak (Fig. 3b). The heat of fusion (ΔH_m) of the crystalline phase is 126.7 J g^{-1} for extruded sample. Unexpectedly, the ΔH_m value increases more than twice after the sample heating, although the change in crystallinity, determined by XRD, was small.

It is interesting that at approximately 410 °C an extra small exothermic peak appears in extruded sample, which almost disappears in the compacted film. The origin of this peak is not clear, maybe it is caused by a reaction of residues, which remained after decay of the blowing agent.

3.3 ATR-FTIR and Raman spectroscopy

FTIR and Raman spectroscopies provide information about the chemical structure of polyethylene. As shown in Fig. 4, in FTIR spectrum, the absorption band characteristic for groups CH/CH$_2$/CH$_3$ are present both in the stretching (2915, 2847 cm^{-1}) and the bending (1472, 1462, 730, 719 cm^{-1}) vibration range [27]. There was no branching, vinyl groups or other functional groups which could indicate the presence of impurities. Moreover, the spectra do not show any chemical changes during sample extrusion and heating, which proves that processing does not cause chemical modification of macromolecule structure. Similarly, the Raman spectra of PE do not point to any structural differences or changes in the crystallinity of the samples. The bands at 1418 and 1169 cm^{-1} (CH$_2$ bending and rocking, respectively) are attributed to the crystalline phase,

Fig. 4 ATR-FTIR (*a*) and Raman (*b*) spectra of MDPE extruded film (the *vertical axis* for the FTIR spectrum corresponds to the transmission (%), and for the Raman spectra—to the intensity of radiation)
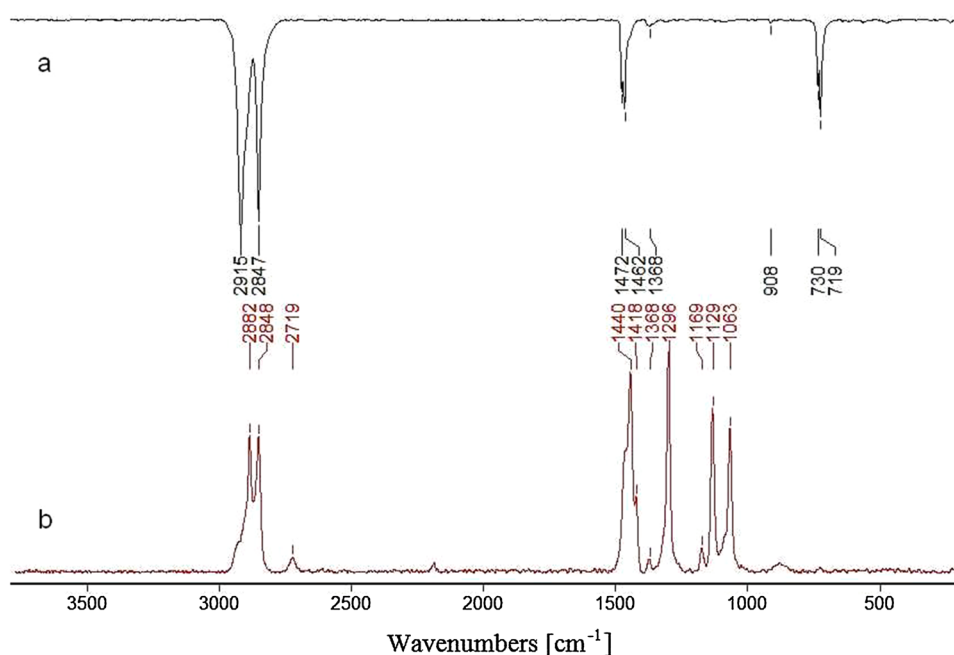
Table 3 Mechanical parameters for extruded, foamed MDPE film

σ_m, MPa	σ_b, MPa	ε_m, %	ε_b, %	E_t, MPa
15.4	14.6	878	888	364

whereas, bands at 1368 and 1063 cm^{-1} (CH$_2$ wagging and C–C stretching) to amorphous phase of PE. On the basis of the obtained spectra one cannot identify the presence of residue of blowing agent either because of its low content in the sample or the decomposition during extrusion/compacting process.

3.4 Mechanical properties

The mechanical parameters, strictly speaking tensile stress at break—σ_b; maximum stress—σ_m; elongation at break—ε_b; elongation at maximum stress—ε_m and Young's modulus—E_t, determined from standard tensile test are presented in Table 3. It should be added, that E_t has been determined from the straight line range of stress–strain relationship at the low stretching rate ($V_1 = 1.0$ mm min^{-1}). The values of σ_b and ε_b determined in this work are even somewhat higher than those given by Borcell ME 1244 manufacturer, which according to the technical data sheet are 11 MPa and 500%, respectively [28]. This may be a result from a different method of preparation of samples for testing and other measurement conditions.

It should be added that the mechanical properties of the samples subjected to additional pressing using a laboratory press were not investigated because of the too small

size of the obtained films. However, it can be assumed that the change in the initial stretching range should not be significant.

3.5 Piezoelectric properties

The measurements of piezoelectric charge and voltage at pressure 100 kPa were carried out using electrets made of extruded and compacted films of thickness ~120 μm and ~80 μm, respectively.

In the research the contact electrodes of surface 10 cm^2 were applied. Dependence voltage—charge as a function of storing time at room temperature shows Fig. 5.

The TDSC tests were made on the same samples (Fig. 6) and an approximate activation energy of electrets depolarization processes was determined. As we can see from Fig. 6, the maximum of the current density for depolarization (T_m) corresponds to 72 and 78 °C in extruded and compacted MDPE films, respectively.

Initial rise method results [29, 30] is accurate when considering the small fraction of the peak where the current density starts to increase. On the other hand, the current density in this temperature range is often related to a small signal-to-noise ratio or the occurrence of overlapping processes. In the case of the current density graphs of the tested materials, the first shows the presence of a process of a different nature in the initial phase of peak growth. For this reason, it was decided to set the temperature of the peak rise TL to 5 and 0% of peak height on its left side of curve obtained for extruded and compacted sample,

Fig. 5 Dependence voltage—charge versus storing time at room temperature, 1—extruded samples, 2—samples compacted at 140 °C
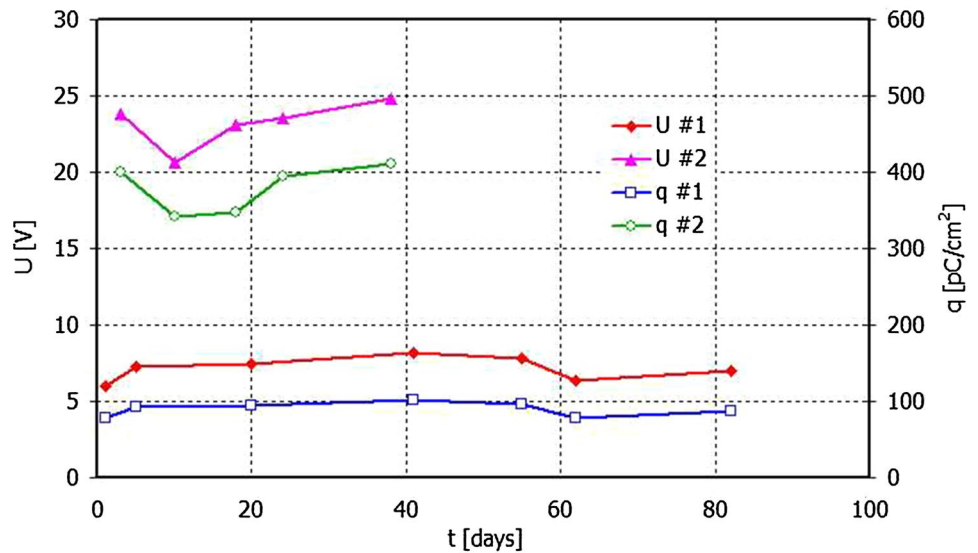
**Fig. 6** Courses of TSDC currents for samples: 1—extruded, 2—compacted at 140 °C
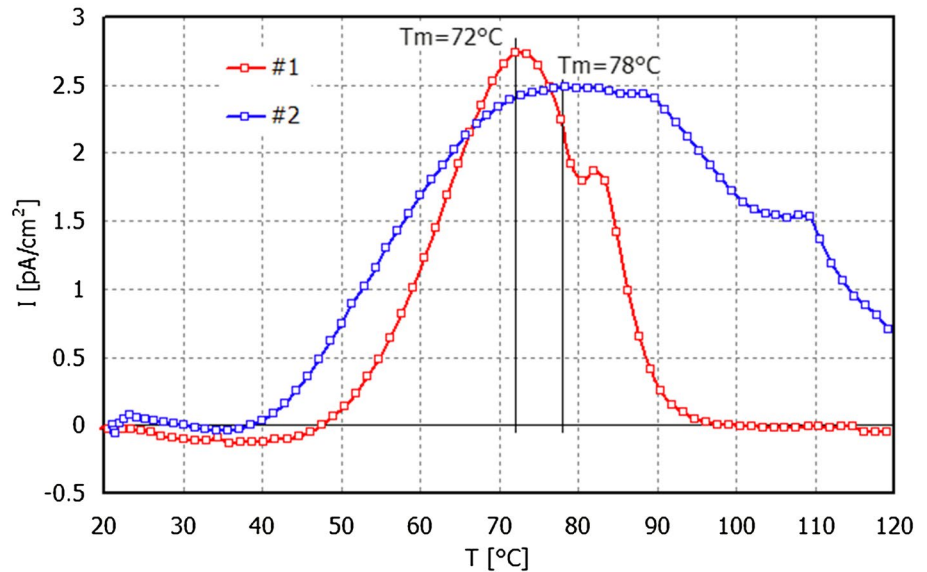
respectively. The upper limit of temperature range TR was set to 25% of peak height (Figs. 7, 8).

Since function ln(I(T)) over that range is not linear in practice, and therefore the computation of the slope is not unique, it was decided to modify the initial-rise method algorithm. The modification bases on determining a set of tangent lines with corresponding slopes and calculating their weighted average. The procedure for obtaining the weights was as follows. Using least squares method a trend lines were fitting to 3, 4, etc. points from the start point TL until a match over the whole temperature range (to a temperature TR) was reached. The standard error (SE) and the correlation coefficient (R^2) was calculated for each line giving the weight $(R^2)^2/SE$. The relationship between weighted slope and calculated activation energy is

described by the Eq. (2). The Figs. 7 and 8 show initial-rise method plot with tangent line corresponding to calculated activation energy for electrets made of extruded and compacted films attains 2.67 and 3.28 eV, respectively.

Piezoelectric constant d_{33} was calculated from dependence piezoelectric charge density versus stress what was shown in Fig. 9. As we can see from this the piezoelectric constant values were ~18 pC/N and ~75 pC/N for extruded and compacted film, respectively at low stresses and diminishes twice within higher stresses. The test made for comparative purposes for piezoelectric PVDF film attained values from 16 to 50 pC/N, which is consistent with the literature data [31]. The compacting process of foamed PE advantageously influences the piezoelectric properties and durability of electrets.

Fig. 7 Dependence of lnI as a function of 1/T and the fitting straight line for electrets made of extruded film
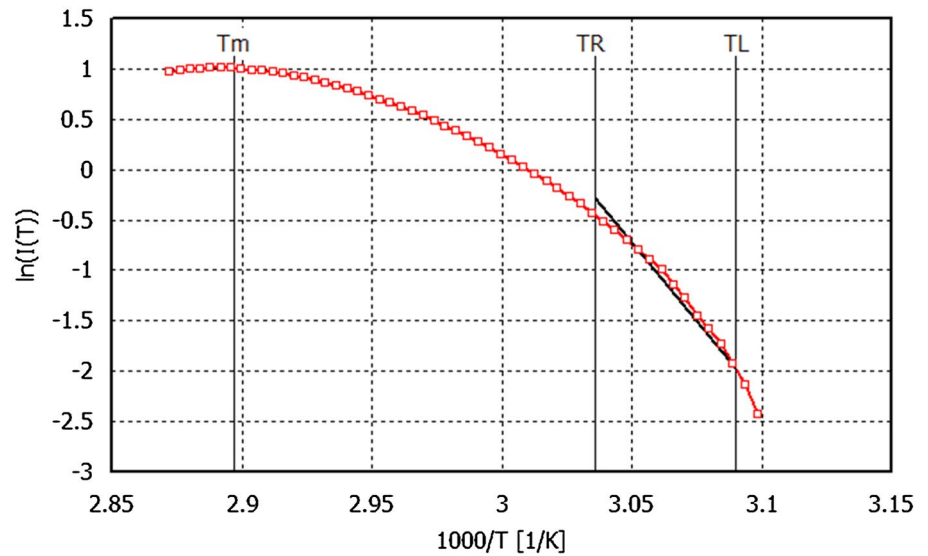
Fig. 8 Dependence of lnI as a function of 1/T and the fitting straight line for electrets made of film compacted at 140°C
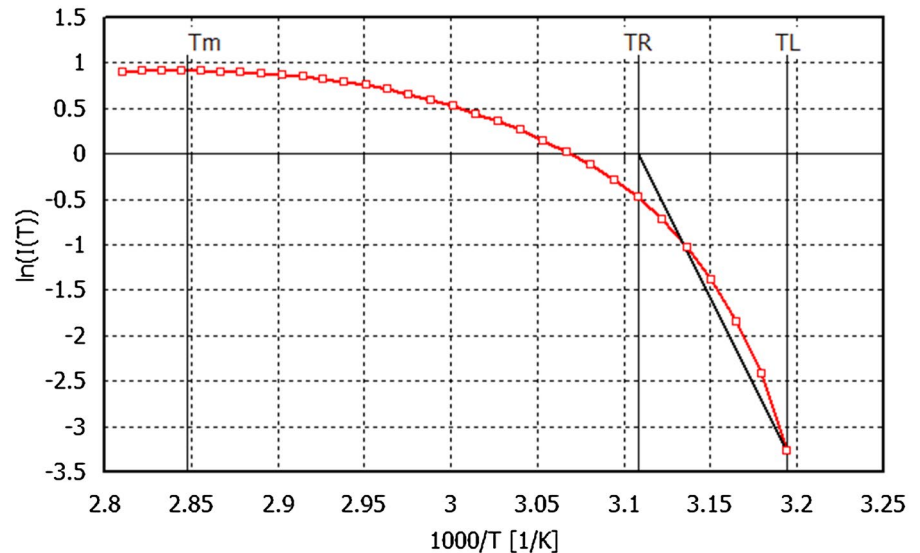
4 Conclusions

Physicochemical properties of foamed MDPE has been characterized by few instrumental methods. XRD allowed to determine the degree of crystallinity and monitoring changes in arrangement of the macromolecules in the samples subjected to processing. FTIR/Raman spectroscopy showed the purity of polyethylene studied. SEM revealed internal and surface morphology. The presence of voids in polymer film enabled the creation of electrets under the electric field of constant intensity. Piezoelectric effect in cellular MDPE depends on film heat treatment and structure as well as on temperature of polarization. The durability of this system is satisfactory.
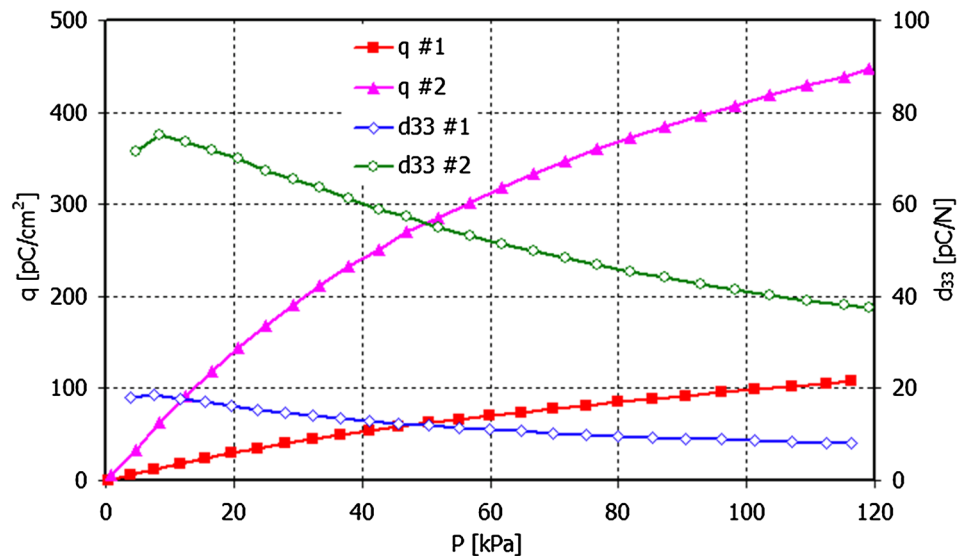
The research showed that film compacting process positively influences the growth of the crystallinity of the tested material as well as its mechanical strength and considerable growth of the piezoelectric constant d_{33}.

It can be concluded that foamed PE films can be used for manufacturing valuable, piezoelectric materials which opens perspectives for production new low-cost sensors or strain gauges for biomedical application.

Thanks to these favorable properties, the discussed modified MDPE is the subject of a patent application (no. P.422119 from July 4th, 2017).

Fig. 9 Dependence of charge density and piezoelectric constant d_{33} versus stress

References

1. P.S. Chum, K.W. Swogger, Prog. Polym. Sci. **33**, 797–819 (2008)
2. M. Stürzel, S. Mihan, R. Müllhaupt, Chem. Rev. **116**, 1398–1433 (2016)
3. N.M.G. Franssen, J.N.H. Reek, B. de Bruin, Chem. Soc. Rev. **42**, 5809–5832 (2013)
4. G. Rojas, E.B. Berda, K.B. Wagener, Polymer **40**, 2985–2995 (2008)
5. M.D. Schultz, N.F. Sauty, K.B. Wagener, Appl. Petrochem. Res. **5**, 3–8 (2015)
6. J. Hopewell, E.R. Dvorak, Kosior. Philos. Trans. R Soc. Lond. B Biol. Sci. **364**(1526), 2115–2126 (2009)
7. L.S. Boffa, B.M. Nowak, Chem. Rev. **100**, 1479–1493 (2000)
8. T.C. Chung, *Functionalisation of Polyolefins* (Academic Press, London, 2002)
9. P. Ciselli, L. Lu, J.C.J. Busfield, T. Peijs, e-Polymers **14**, 1–13 (2010)
10. Y. Yang, H. Zhang, X. Zhong, F. Yi, R. Yu, Y. Zhang, Z.L. Wang, ACS Appl. Mater. Interfaces **6**, 3680–3688 (2014)
11. K.T. Chong, X. Su, E.J.D. Lee, S.J. O'Shea, Langmuir **18**, 9932–9936 (2002)
12. A. Mellinger, F.C. Gonzalez, R. Gerhard-Multhaupt, Appl. Phys. Lett. **82**, 254–256 (2003)
13. X. Zhang, G.M. Sessler, J. Hillenbrand, J. Electrostat. **65**, 94–100 (2007)
14. M. Tang, Z. An, Z. Xia, X. Zhang, J. Electrostat. **5**, 203–208 (2007)
15. E. Klimiec, B. Królikowski, M. Machnik, W. Zaraska, J. Dzwonkowski, J. Electron. Mater. **44**, 2283–2291 (2015)
16. H. Kaczmarek, B. Królikowski, E. Klimiec, J. Kowalonek, J. Mater. Sci. (2017). doi:10.1007/s10854-016-6329-9
17. A. Qaiss, H. Saidi, O. Fassi-Fehri, M. Bousmina, Polym. Eng. Sci. **52**, 2637–2644 (2012)
18. Z. An, M. Mao, J. Cang, Y. Zhang, F. Zheng, J. Appl. Phys. **111**, 024111 (2012)
19. H. Gilbert-Tremblay, F. Mighri, D. Rodrigue, J. Cell. Plast. **48**, 341–354 (2012)
20. A. Mohebbi, F. Mighri, A. AJjji, D. Rodrigue, Adv. Polym. Tech. (2016). doi:10.1002/adv.21686
21. T. Krause, Rozkład ładunków swobodnych i wolnorelaksacyjnej polaryzacji w materiałach aktywnych (Distribution of free charges and slow relaxation polarization in active materials), Doctoral Thesis, Wroclaw University of Technology, (Wrocław, 2006) pp. 57–61
22. M. Psarski, E. Piotrowska, A. Galeski, Macromolecules **33**, 916–932 (2000)
23. W. Li, H. Yang, M. Shang, T. Chen, W. Wang, Ind. End. Chem. Res. **55**, 8719–8725 (2016)
24. K. Tomaszewska, J. Kałużna-Czaplińska, W. Jóźwiak, Polimery **55**, 222–226 (2010).
25. S. Kumar, R.K. Singh, J. Pet. Eng. **987568**, 1–7 (2013). doi:10.1155/2013/987568
26. S.A. Deshmukh, G. Kamath, V.G. Pol, S.K.R.S. Sankaranarayanan, J. Phys. Chem. **118**, 9706–9714 (2014)
27. T. Furukawa, H. Sato, Y. Kita, K. Matsukawa, H. Yamaguchi, S. Ochiai, H.W. Siesler, Y. Ozaki, Polym. J. **38**, 1127–1136 (2006)
28. Technical data sheet: Borealis Borcell™ ME1244 Medium Density Polyethylene http://www.matweb.com/search/datasheettext.aspx?matguid=a1b2fa83c9d248a49716946999a31db9 (Accessed 10 April 2017)
29. N.S. Rawat, M.S. Kulkarni, D.R. Mishra, B.C. Bhatt, C.M. Sunta, S.K. Gupta, D.N. Sharma, Nucl. Instrum. Methods Phys. Res. B **267**, 3475–3479 (2009)
30. T. Krause, Rozkład ładunków swobodnych i wolnorelaksacyjnej polaryzacji w materiałach aktywnych, Thesis, Wroclaw University of Technology, Wrocław, 2006, pp. 57–61 (**in Polish**)
31. Measurement Specialties Inc., Piezo Film Sensors Technical Manual. http://www.tufts.edu/programs/mma/emid/piezo.pdf (Accessed 17 July 2017)