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THE INFLUENCE OF DODECYL MALEATE ADMIXTURE ON THE DIELECTRIC AND ELECTRIC PROPERTIES OF POLARIZED POLYETHYLENE

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The aim of this paper is to discuss dielectric and electric properties of low density polyethylene (LDPE) modified by dodecyl maleate (DM). For determining trap parameters and obtaining information about molecular motion of the modifier, the thermally stimulated depolarization currents method (TSDC) and dielectric analysis in range of frequencies 10^{-2}–10^{7} Hz were used. Cells were prepared with and without presence of electric field. For polarized cell in temperature range 353–373 K the high increasing in real part of permittivity has been detected.

Key words: dielectric and electric properties, polyethylene, dodecyl maleate.

Thermoplasts and especially polyolefines such as polythene whether polipropylen are an interesting group of organic materials in view of easiness of forming, modificability and trouble-free manufactureing. In view of accessibility and easiness of receiving of polythene it is purposeful to search modifiers, which can improve its electric properties and dielectric parameters. Dodecyl maleate (DM) applied as admixture in principle way modifies properties of polyethylene. Essential interest is in mobility of coagent molecules and its influence onto polymer matrix, researched in wide range of temperatures and frequencies.

Low density polyethylene (LDPE), Malen E – made by Pertrochemia Płock, was investigated. Dodecyl maleate (DM) as lattice additive was used. Mentioned monoester was synthesized from maleic anhydride and appropriate alcohol. The modifier content was equal to 10 mmoles per 100g of LDPE (2,83%). For determining trap parameters, for non-polarized cells, was used the well known Thermally Stimulated Depolarization Currents technique (TSDC) with temperature range from 15 to 325 K. The measurements have been made in vacuum. We used steady voltage values, 70–7 V, correspondingly to injection and external polarization. Aluminium electrodes were evaporated on the special thermal foils and then welded with material placed between electrodes (sandwich like, Fig. 1) in a own-made pressure welding for 30 minutes at the temperature 433 K.

Thermally stimulated processes are most useful for measurement but we need to have some theoretical dissolves for practical analyses. Last three decades we can find some experimental and theoretical papers based on thermally stimulating processes [1, 2]. This information is needed for making computer programs for automating analyses of measured data. Information obtained from sequences of TSDC curves was numerically analyzed and deconvoluted using Genor (General Order Kinetics Model ver. 0,33 – A.Mandowski 1998) computer program.

For material studied by dielectric relaxation spectroscopy (DRS), polarized and non polarized cells, dielectric analysis in range of frequencies 10^{-2}–10^{7} Hz and temperature range 173K-383K have been performed, using Solartron 1260 with dielectric interface. The same electrodes geometry (Fig. 1) was chosen for enable material polarization (external field attendance) during cell's welding. Cells were prepared with copper electrodes, evaporated on the glassy discs, which were welding (sandwich like) with modified polyethylene in order to provide a good electrical contact with polymer material. The sample thickness was about 0,2 mm. 100 V external DC voltage during preparation was applyed. The same welding process have been apply for non polarized cells build also with copper electrodes. Experimental details obtained from measurement in frequencies domain were analized and approximated on ground of Havriliak-Negami equations using Novocontrol WinFit program.

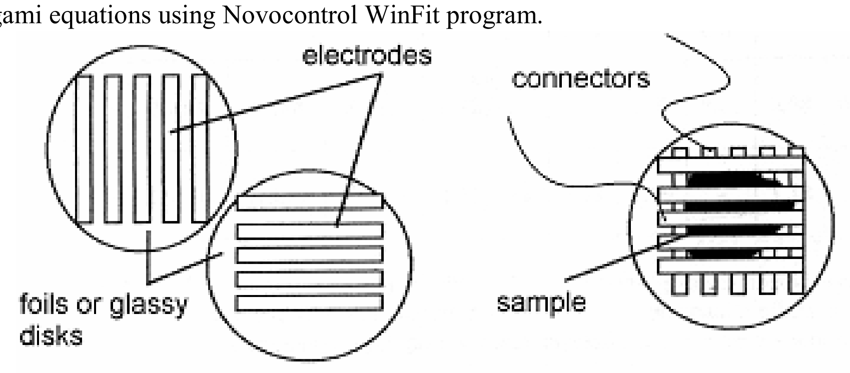


Fig. 1. Cell preparation and electrode space for TSDC and DRS measurements

Estimated parameters from Genor program for pure LDPE and LDPE/DM mixture are shown in Table 1. All parameters were calculated with First Order Kinetics [3] parameter b=1.

Presence of dodecyle maleate (DM) modified the energy structure of LDPE. The energy of traps is too small and relaxation times are too short for joining it with side-group movements or dipole reorientation.

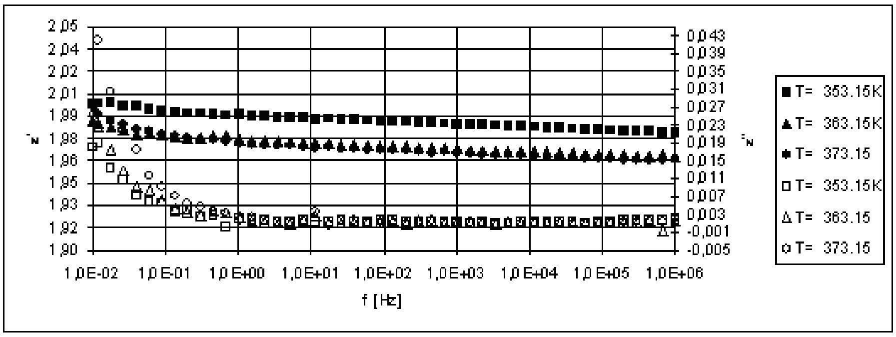
Table 1

Sample	Tm [K]	E [eV] b=1	ν [s^{-1}]	τ_0 [s]	S_t [m^2]
LDPE	118	0,10	-	-	-
	163	0,09	-	-	-
	227	0,17	-	-	-
	317	0,76	$2,12 \cdot 10^{10}$	$4,71 \cdot 10^{-11}$	$7,29 \cdot 10^{-20}$
LDPE+DM	180	0,33	$4,10 \cdot 10^{7}$	$2,44 \cdot 10^{-8}$	$4,36 \cdot 10^{-22}$
	228	0,27	-	-	-
	261	0,34	-	-	-
	289	0,83	$6,87 \cdot 10^{12}$	$1.45 \cdot 10^{-13}$	$2,83 \cdot 10^{-17}$
	315	0,51	$1,72 \cdot 10^{6}$	$5,80 \cdot 10^{-7}$	$5,98 \cdot 10^{-24}$

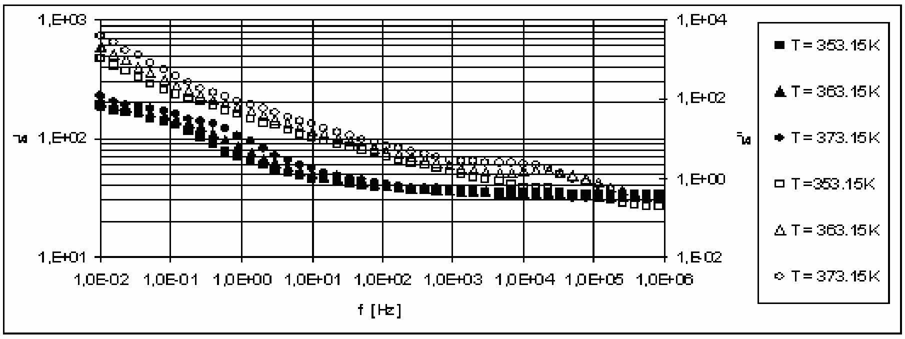
Where: Tm – temperature of peak's maximum, E – energy depth of the trap ν - carrier escape frequency, τ_0 – relaxation time, S_t – capture cross-section

Low activation energies in the wide range of temperature suggest hopping as a carrier's transport mechanism. So we should notice the electron relaxation in this case.

To obtain more information about material's structure and make verification of our observation the dielectric measurements were performed. The dielectric properties of LDPE and LDPE+DM samples are explicitly different. The high temperature measurement results for polarized LDPE+DME are presented in Fig. 2 At lower temperatures investigated phenomenon is less visible.



a



b

Fig. 2. Frequency dependence of the complex dielectric constant of polarized LDPE/DM for different temperatures, adequately for *a* – non-polarized and *b* – polarized sample. Where filled marks correspond to real part and unfilled correspond to imaginary part of ε^*

Table 2

The Havriliak-Negami equation parameters for three chosen temperatures (Fig2-b)

Temp. [K]	σ_{dc} [S/cm]	n	$\Delta\varepsilon_2$	τ_{HN2} [s]	ε_{inf}
373,0	$2{,}34\cdot10^{-11}$	1,00	3,760	$4{,}23\cdot10^{-5}$	30,800
363,0	$1{,}22\cdot10^{-11}$	1,00	2,540	$1{,}06\cdot10^{-5}$	30,800
353,0	$6{,}08\cdot10^{-12}$	1,00	1,120	$5{,}73\cdot10^{-5}$	32,500

α2	β2	$\Delta\varepsilon_1$	τ_{HN1} [s]	α1	α1
1,000	0,555	129,000	$4{,}24\cdot10^{-1}$	0,976	0,469
1,000	0,646	134,000	$1{,}08\cdot10^{0}$	1,000	0,434
0,603	0,361	136,000	$1.93\cdot10^{0}$	1,000	0,451

We can observe that real part of permeability increasing from about 2, for non-polarized, to 35 for polarized sample. It has been suggested [4] that DM lattice may elevate the cristallinity of the LDPE. At frequencies about 10^4Hz appeared explicit dielectric looses peak. So in this case we can try approximating measure data using Havriliak-Negami equations [5]. Estimated parameters include Table 2. It was clearly shown that it is almost independent on temperature. But we can not say that there are no relaxation. In paper [6] we can find relaxations which looks similar to ours. We can say that it is not ionic relaxation. In case of high ionization potential of electrodes (not extracted electrons) during sample preparation at high temperature the electrons were pulled out from material of sample. So we can suggest the high holes concentration. We also suggest the relaxation process at 0,2 Hz.

Hyper Chem simulations shows that this holes can be situated on the DM molecules. Dielectric relaxations processes will be related to rotation or movement of parts of grafted polyethylene chains pulled by DM molecules. Melting of crystalline phase of pure DM take place at temperature about 315 K. Furthermore dodecyle maleate molecules are too big to participate in crystalline phase of polymer. Probably the polyethylene chains movement is possible at amorphous area of the material bulk.

For lower temperatures range we suggest hopping as a carriers transport mechanism. This should have effect with electron relaxation in this case.

During the dielectric measurements we observed:

- polarization of electrodes phenomenon at frequencies below 1Hz;
- relaxation near 0,2 Hz;
- relaxation with very strong losses peak at frequency about 10^4Hz;

Observed height of real part of permeability can be connected with movement of particles of polar modifier in non-polar matrix.

For more information about electrical structure of this material some electrical conductivity or carriers' mobility measurements have to be performed.

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ВПЛИВ ДОМІШКИ ДОДЕЦИЛМАЛЕІНАТУ НА ЕЛЕКТРИЧНІ ТА ДІЕЛЕКТРИЧНІ ВЛАСТИВОСТІ ПОЛЯРИЗОВАНОГО ПОЛІЕТИЛЕНУ

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У статті досліджено електричні та діелектричні властивості поліетилену низької густини з доданим додецилмалеінатом. З метою визначення параметрів пастки та дослідження молекулярного руху домішки використовували метод термостимульованих деполяризаційних струмів та діелектричні вимірювання в частотному діапазоні 10^{-2}–10^{7} Гц. Зразки готували як за наявності, так і за відсутності електричного поля. Для поляризованих зразків було виявлено значний ріст дійсної частини діелектричної проникності в температурному діапазоні 353–373 K.

Ключові слова: електричні та діелектричні властивості, поліетилен, додецилмалеінат.

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