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## SOME ASPECTS OF CRYSTALLIZATION AND MECHANICAL PROPERTIES OF LOW DENSITY POLYETHYLENE MODIFIED BY MALEIC ESTERS

### Summary

The object of investigation was low density polyethylene modified by following monoesters: allyl maleate, butyl maleate, dodecyl maleate, monoallyl tetrahydrophthalate. The obtained samples were characterized by: wide angle X-ray scattering (WAXS), small angle X-ray scattering (SAXS).

The influence of modifiers on some aspects of crystallization and mechanical properties of LDPE was discussed.

*Keywords:* polyethylene, chemical modification, mechanical properties, crystallization

### Introduction

The commercial importance of polyolefines and particularly polyethylene or polypropylene is one of the reasons for the attention devoted to all aspects of its solid-state organization. Degree of crystallinity has a great influence on mechanical properties of polymers.

In last years metal particles [1–3] or multifunctional modifiers, e.g. metal salts of organic acids are used for polymer modification [4–7]. The modification is usually carried out in the polymer melt and in the presence of free radical initiators, e.g. peroxides. Under such conditions the modifiers could be grafted onto polymer macromolecules. These additives form ionic clusters which fulfill the role of network knots (crosslinks).

In this paper, the main interest was in the molecular structure of the system, determined using wide angle X-ray scattering (WAXS) and small angle X-ray scattering (SAXS) techniques. It was also observed influence of modifiers on mechanical properties of compositions.

## Experimental details

### Materials

Low density polyethylene [LDPE], (Malen E, Petrochemia Płock Poland) (solubility parameter  $\delta = 15,4 \cdot 10^3 \cdot J^{0,5}/m^{1,5}$ ) was crosslinked with dicumyl peroxide 98% (Merck-Schuhardt, Germany) [DCP]. The following monoesters of maleic or tetrahydrophthalic acids: allyl maleate [AM], butyl maleate [BM], dodecyl maleate [DM], monoallyl tetrahydrophthalate [THFA], synthesized in our laboratory from maleic anhydride and corresponding alcohols, were used as modifiers. In addition, to some systems zinc oxide was added. The composition of compounds is given in table 1.

Tab. 1. Composition of compounds in weight parts [g]

	A1	A2	A3	A4	A5	A6	A7	A8	A9	A10	A11	A12	A13	A14	A15	A16	A17
LLDPE	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
ZnO	-	-	-	-	-	-	-	-	-	5	5	5	5	5	5	5	5
AM*	-	1,5	-	-	-	1,5	-	-	-	1,5	-	-	-	1,5	-	-	-
BM*	-	-	1,7	-	-	-	1,7	-	-	-	1,7	-	-	-	1,7	-	-
DM*	-	-	-	2,83	-	-	-	2,83	-	-	-	2,83	-	-	-	2,83	-
THFA*	-	-	-	-	2,1	-	-	-	2,1	-	-	-	2,1	-	-	-	2,1
DCP	-	-	-	-	-	1,5	1,5	1,5	1,5	1,5	1,5	1,5	1,5	1,5	-	-	-

\* modifier content about 10 mmol

Compounds were prepared, by means of a micro-mixer (Brabender, Plasti-Corder) at 155°C. The ready made compound was used to form a film by means of Plasti-Corder extruder at 125 – 130°C. Then, the prepared films were heated in metal moulds at 160°C for 30 min.

Tab. 2. Parameters of modifiers

Sample	Symbol	State	$\delta_D$ [J <sup>0,5</sup> /m <sup>1,5</sup> ]	$\delta_P$ [J <sup>0,5</sup> /m <sup>1,5</sup> ]	$\delta$ [J <sup>0,5</sup> /m <sup>1,5</sup> ]
Allyl maleate	MA	Liquid	15,51	5,89	17,49
Butyl maleate	MB	Liquid	16,84	4,70	19,61
Dodecyl maleate	MD	Solid	17,09	2,47	13,86
Monoallyl tetrahydrophthalate	THFA	Liquid	15,02	10,79	21,17

$\delta$  – solubility parameter

$\delta_D, \delta_P$ , – component of solubility parameter: dispersive and polar

## Techniques

X-ray examination was performed by means of an HZG-4 diffractometer (Seifert, Germany). WAXS investigation were carried out in the scattering angle range 4 – 60° with a step 0.1°. Each diffraction curve was deconvoluted into individual crystalline peaks and amorphous halo according to the procedure proposed by Hindeleh and Johnson [8]. Fitting was realized following the method described by Rosenbrock and Storey [9]. The degree of crystallinity was calculated according to the formula:

$$X_c [\%] = \frac{A_c}{A_c + A_a} \times 100$$

where:  $A_c$ - area under resolved crystalline peaks,  $A_a$ - area under amorphous halo.

SAXS investigation were performed in the scattering angle  $2\theta = 0,09 - 4,05^\circ$ , with a step of  $0,01^\circ$ . The small angle diffraction curves were smoothed and corrected for scattering and sample absorption by means of computer program 3 DVIEW (Anton Paar) and then corrected for collimation distortions, according to the procedure proposed by Hendricks and Schmidt [10,11].

## Results and discussion

The influence of modifiers on the structure of modified LDPE is presented in the tables 3 and 4.

Tab. 3. Degree of LDPE crystallinity calculated from WAXS

No.	Sample	Degree of crystallinity $x_k$ [%]	Magnitude of crystall area $D_k$ [nm]		Degree of bulk crystallinity $w_k$ [%]
			$D_{(110)}$	$D_{(200)}$	
A1	LDPE	35,2	19,4	12,2	30,8
A2	LDPE, MA	33,3	19,9	12,6	29,1
A3	LDPE, MB	35,0	17,9	12,6	30,1
A4	LDPE, MD	40,5	18,9	10,5	35,5
A5	LDPE, THFA	31,0	19,2	13,7	26,8
A6	LDPE, DCP, MA	31,6	19,5	11,3	27,7
A7	LDPE, DCP, MB	36,4	17,9	12,4	32,2
A8	LDPE, DCP, MD	32,4	18,2	11,4	28,0
A9	LDPE, DCP, THFA	29,2	17,9	13,2	24,9
A10	LDPE, DCP, ZnO, MA	32,8	19,1	13,1	28,5
A11	LDPE, DCP, ZnO, MB	30,6	18,9	13,5	26,7
A12	LDPE, DCP, ZnO, MD	29,8	22,3	11,7	25,2
A13	LDPE, DCP, ZnO, THFA	22,4	19,1	15,9	18,7
A1/2	LDPE, ZnO	30,0	20,4	12,9	-
A1/3	LDPE, DCP, ZnO	29	18,4	14,0	-
A7/2	LDPE, DCP	29,3	18,9	14,3	29,6

Tab.4. Apparent crystals sizes present in LDPE calculated from SAXS

No.	Sample	Average Lamellar layer thickness $I_c$ [nm]	Long period L[nm]		Thickness of transition layer E[nm]
			From correlation function L1	From one-dimensional function L <sub>2</sub>	
A1	LDPE	4,1	14,8	15,2	13,8
A2	LDPE, MA	3,6	12,6	12,9	22,3
A3	LDPE, MB	3,8	12,6	12,9	22,9
A4	LDPE, MD	3,7	14,0	15,4	26,7
A5	LDPE, THFA	3,6	12,2	12,6	14,0
A6	LDPE, DCP, MA	4,1	13,6	14,2	15,2
A7	LDPE, DCP, MB	3,8	13,4	15,0	15,1
A8	LDPE, DCP, MD	3,5	12,8	13,3	24,1
A9	LDPE, DCP, THFA	3,6	12,6	13,1	15,0
A10	LDPE, DCP, ZnO, MA	-	-	13,8	8,5
A11	LDPE, DCP, ZnO, MB	-	-	12,4	8,3
A12	LDPE, DCP, ZnO, MD	-	-	12,7	8,5
A13	LDPE, DCP, ZnO, THFA	-	-	12,4	11,0
A1/2	LDPE, ZnO	-	-	-	7,2
A1/3	LDPE, DCP, ZnO	-	-	-	7,0
A7/2	LDPE, DCP	4,7	16,3	16,3	12,5

Crystalline regions were found from the measurements of the diffraction width. In the case of samples containing ZnO, the diffractograms showed three sharp peaks within the angle range 30–40° derived from ZnO which were not taken into account in the calculation of the degree of LDPE crystallinity (Fig.1, 2).

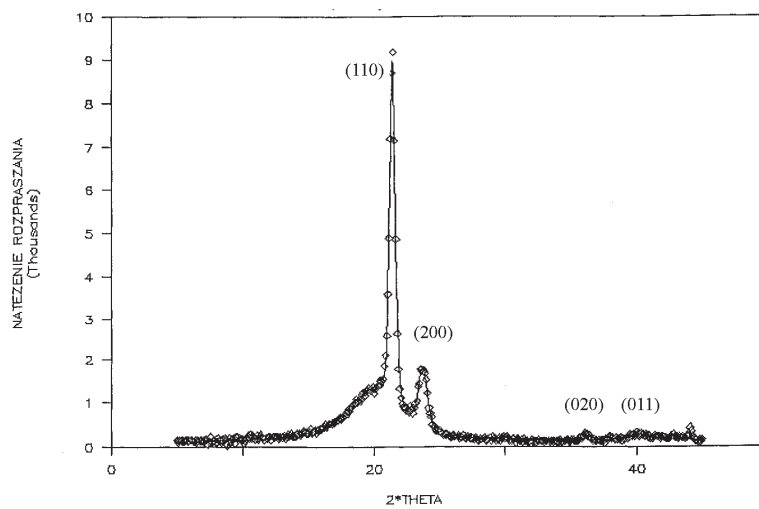


Fig.1. WAXS curve for LDPE

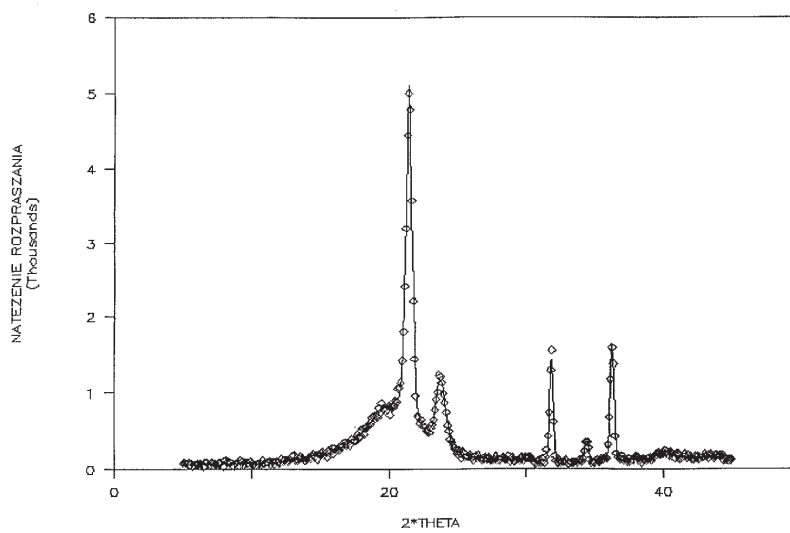


Fig.2. WAXS curve for LDPE/ZnO mix

It was stated, that all modifiers (except DM) decreased degree of crystallinity. The strongest influence, was noticed for THFA, which changed  $X_c$  from 35,2% for unmodified LDPE to 31,0% for LDPE/THFA sample. In this way manifests itself interaction between LDPE and molecules of modifiers. It is interesting to note that the addition of DM leads to increase in the degree of crystallinity to the 40,5%, which is not observed in other cases. It seems that longer aliphatic chains as contained in DM are able to cocrystallize with the macromolecules of LDPE. This is undoubtedly a reason for the advantageous effect of DM on the mechanical properties of LDPE which we described in our previous paper [12]. It is also observed that bulk crystallinity  $w_k$  was changing similar to  $X_k$  from 30,8% for LDPE to 35,5% for LDPE/MD. All modifiers (except THFA, which doesn't changed E value) increased thickness of transition layer between crystalline and amorphous region [E] as calculated according to the procedure proposed by Koberstein and co-workers [13]. The most effective was DM, which increased E value about 93,5%. In all cases we noticed decreasing of the average lamellar layer thickness  $I_c$  and value of long period (SAXS) corresponding to the position of the first maximum in the correlation function [ $L_1$ ] and to the peak in the Lorentz-corrected SAXS profile [ $L_2$ ] (Tab. 3). The crystal size D of LDPE in the direction perpendicular to the (110) and (200) crystallographic plane was calculated using Sherrer's equation [14]. In direction (200) only DM decreased crystal size, other coagents increased this parameter, most strongly THFA. In the second direction, only AM increased  $D_k$ .

The addition of DCP or/and ZnO to LDPE actually reduced a degree of its crystallinity, and ZnO also a thickness of transition zone of about 50%. The presence of ZnO made impossible to count neither  $I_c$  nor L; there were no maxima on the respective curves. DCP influences on  $L_1$  and  $L_2$  changing them from 14,8 nm to 16,0 nm and from 15,2 nm to 16,3 nm respectively. Simultaneously, it increased  $D_k$  from 4,12 nm to 4,74 nm. The addition of modifiers to composition LDPE/DCP brought changes in  $X_k$  and  $w_k$ . It turned out that all coagents (except THFA, which doesn't influence on  $X_k$ ) increased degree of crystallinity in relation to sample LDPE/DCP, but only effect of BM was so strong that value of  $X_k$  was higher in comparison to unmodified LDPE. All modifiers increased thickness of transition layers - AM, BM, THFA of about 9%, while the influence of DM was the strongest. Value of E parameter increased of about 74% in relation to LDPE and 93% in relation to LDPE/DCP. Crystal size in the direction perpendicular to the (110) direction is less for all coagents, except AM, which is the one which increased this parameter. In the direction perpendicular to (200) direction we observed another dependencies: BM and THFA increased  $D_k$  to 12,4 nm and 13,2 nm; AM and DM decreased  $D_k$  to 11,3 nm and 11,4 nm respectively.

From technological point of view, the most interesting compositions are those containing DCP, ZnO and modifiers. In such the case modifiers increased  $X_k$  which was reduced by addition ZnO and DCP to LDPE. The most effective coagent was AM  $X_k = 32,8\%$ , then DM  $X_k = 30,6\%$  and DM  $X_k = 29,8\%$ . Only THFA reduced degree of crystallinity to the value 22,4%. Instead, their influence were not strong enough to exceed value of  $X_k$  for 'pure' LDPE. All esters increased thickness of transition zone in relation to the LDPE/DCP, ZnO sample, but for all modifiers value of E was less than for unmodified LDPE.

SAXS profiles for samples A10–A13 have not interfering maxima so we estimated value of long period from one-dimensional correlation function curve (Fig. 3). It was stated that coagents decreased values of the long period to the  $L = 13,8\text{ nm}$  for AM,  $L = 12,4\text{ nm}$  for BM and DM and  $L = 12,7\text{ nm}$  for DM. Because there were no reflexes from long period on the SAXS curves, we calculated structure parameter called average length of heterogeneity  $I_p$ . It was calculated from the three-dimensional correlation function profile (Fig. 4). The values of  $I_p$  are given in table 5.

Tab.5. Values of  $I_p$  calculated from three-dimensional correlation function

Symbol	Composition	$I_p$ [nm]
A1/3	LDPE, DCP, ZnO	24,9
A10	LDPE, MA, DCP, ZnO	20,2
A11	LDPE, MB, DCP, ZnO	22,8
A12	LDPE, MD, DCP, ZnO	25,5
A13	LDPE, THFA, DCP, ZnO	15,8

Only DM increased  $I_p$  to the 25,5 nm, instead other esters decreased  $I_p$  to 22,8 nm, 20,2 nm and 15,8 for BM, AM and THFA respectively. Values of  $I_p$  are well correlated with values of crystall size calculated from WAXS.



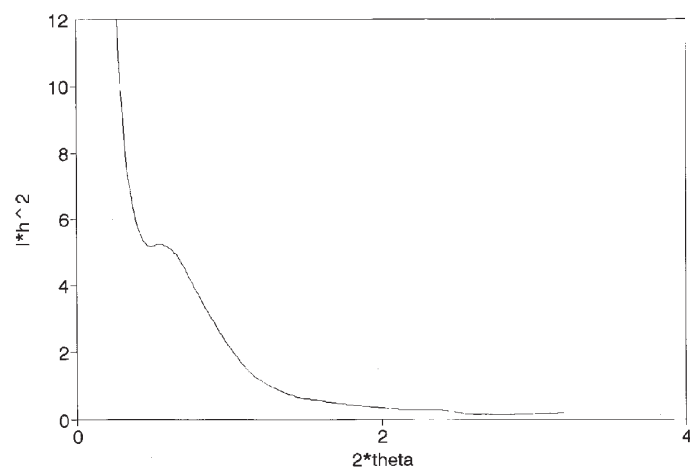


Fig. 3. One-dimensional correlation function for sample A11- LDPE, DCP, ZnO, BM

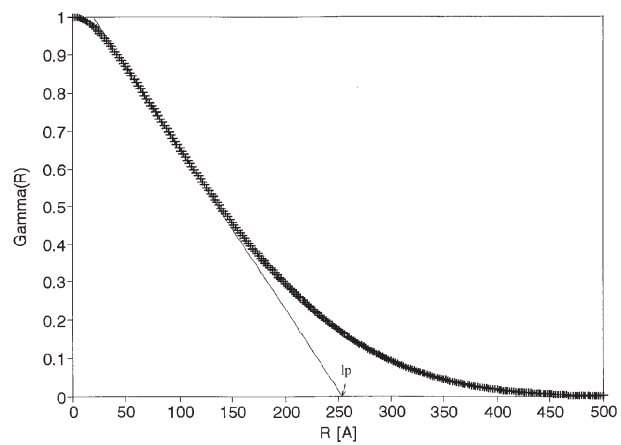


Fig. 4. Three-dimensional correlation function for sample A11- LDPE, DCP, ZnO, BM

The influence of modifiers on some mechanical properties of LDPE is presented in table 6.

Tab.6. Mechanical properties of LDPE

No.	Sample	$\sigma_1$ [MPa]	$\varepsilon_1$ [%]	$\sigma_2$ [MPa]	$\varepsilon_2$ [%]	E [MPa]
A1	LDPE	12,6	28	9,4	107	45
A2	LDPE, MA	12,1	27	8,9	120	44
A3	LDPE, MB	12,0	29	9,1	110	41
A4	LDPE, MD	12,9	27	11,7	180	47
A5	LDPE, THFA	12,3	28	8,7	115	44
A10	LDPE, DCP, ZnO, MA	8,3	31	8,7	233	32
A11	LDPE, DCP, ZnO, MB	8,7	17	9,5	276	50
A12	LDPE, DCP, ZnO, MD	9,2	21	13,2	424	44
A13	LDPE, DCP, ZnO, THFA	8,5	27	8,8	253	35
A14	LDPE, ZnO, MA	8,9	20	7,0	85	44
A15	LDPE, ZnO, MB	9,2	18	6,8	75	51
A16	LDPE, ZnO, MD	9,4	21	7,2	79	45
A17	LDPE, ZnO, THFA	8,7	19	6,7	80	46
A1/2	LDPE, ZnO	9,1	19	6,9	78	49
A1/3	LDPE, DCP, ZnO	6,9	20	8,6	366	34
A7/2	LDPE, DCP	9,5	20	12,9	480	48

$\sigma_1, \varepsilon_1, \sigma_2, \varepsilon_2$ — stress and elongation at flow limit and at break, E- Young's modulus

Crosslinking of LDPE caused the  $\sigma_1$  debasement and a growth of stress intensity on breaking the  $\sigma_2$ , as well as an elongation. DCP influenced on LDPE in two ways. On one hand it lowers the degree of the plastomer crystallinity, which leads to the  $\sigma_1$  debasement. At the same time it causes crosslinking action, which leads to the growth of the  $\sigma_2$  and  $\varepsilon_2$ . This interpretation does not really agree with the results of the E measurement. Nevertheless, the differences in the Young's modulus values of the A1 and A7/2 specimens are not big; they do not exceed 7%. Moreover, the Young's modulus was determined at a very small elongation, which did not exceed 1%. Thus, the mentioned difference is probably caused by inexact measurements.

Addition of ZnO to LDPE results in the  $\sigma_1$ ,  $\sigma_2$  and  $\varepsilon_2$  debasement, whereas the Young's modulus value is slightly higher. Such behavior shows, that ZnO fulfills here the function of an inactive filler. Analyzing the data referring to the LDPE/DCP/ZnO composition, one can notice the  $\sigma_1$ ,  $\sigma_2$ ,  $\varepsilon_2$ , E debasement as well as a growth of the stress intensity on breaking  $\varepsilon_2$ . Addition of modifiers to such a configuration in the case of MA and THFA results in the reduction of the Young's modulus and  $\varepsilon_2$ . The presence of MB and MD causes a growth of mechanical properties in comparison to the crosslinked LDPE containing only ZnO.

In the case of the LDPE/ZnO/modifiers composition no significant influence of the modifiers on the mechanical properties of the composition is observed. They remain on the level of the values received in the case of LDPE/ZnO.

The presence of the modifiers in LDPE (without the DCP or ZnO content) only in the case of MD caused a growth of tensile strength, what is probably connected with the growth of the level of LDPE crystallinity.

## **Conclusions**

The influence of modifiers on the crystallinity structural phase content in LDPE has been observed. Distinct symptoms of nucleation and a growth of crystallinity structural constituent in the case of applying MD have been detected. One can come to the conclusion, that MD can cocrystallize with LDPE increasing the content of crystallinity structural constituent in the configuration. As far as the other modifiers are concerned, it was observed the participation in the LDPE crystallinity in the case of MB. The modifiers' ability, both n-butyl maleate and n-dodecyl maleate, for nucleation and to build in the crystallinity structural constituent of polymer decreases significantly when there is dicumyl peroxide or zinc oxide, or the two substances together in the configuration. Chemical bonding by covalent bond, grafting or a reaction with the surface of zinc oxide molecules impedes the absorption of appropriate arrangements by ester molecules, and also the arrangements participation in crystallization of polyethylene.

It was observed, that heating of LDPE with DCP caused on one hand the  $\sigma_1$  debasement, and on the other hand a growth of the stress intensity and elongation on breaking the specimen. This is probably an indication of crosslinking, which causes a limited ability of macromolecules for a mutual arrangement, and as a result, a reduction of  $x_k$ . Adding esters to LDPE caused a growth of tensile strength of the specimens only in the case of MD. It confirms the thesis on its cocrystallization with LDPE. If, apart from the modifiers, there was DCP and ZnO in the configuration, in all the cases there was a distinct growth of the

specimens' elongation on breaking from 100% up to 400% (in the case of MD). It looks like this result was achieved by the presence of ionic bonds in a polymer net, which fulfill a role of slide bonds.

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## **WYBRANE ASPEKTY WPŁYWU ESTRÓW KWASU MALEINOWEGO NA KRYSTALIZACJĘ I WŁAŚCIWOŚCI MECHANICZNE MODYFI- KOWANEGO POLIETYLENU MAŁEJ GĘSTOŚCI**

### Streszczenie

Przedmiotem badań był polietylen małej gęstości modyfikowany estrami kwasu maleinowego maleinianem monoallilowym, maleinianem monobutylowym, maleinianem monododecylovym oraz tetrahydroftalanem monoallilowym. Metodami rentgenowskimi małego (SAXS) i dużego kąta (WAXS), zbadano wpływ modyfikacji na budowę krystaliczną polietyleny. Określono również jak modyfikatory wpływają na właściwości mechaniczne materiału. Najskuteczniejszy okazał się maleinian monododecylovym, otrzymane wyniki sugerują jego kokrystalizację z matrycą polimerową.

*Słowa kluczowe:* polietylen, modyfikacja chemiczna, właściwości mechaniczne, krystalizacja