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INFLUENCE OF MALEIC ESTERS ON B-PHASE CONTENT IN ISOTACTIC POLYPROPYLENE

Abstract. The object of investigation was isotactic polypropylene modified by following monoesters: allyl maleate [AM], butyl maleate [BM], dodecyl maleate [DM], monoallyl tetrahydrophtalate [THFA]. Some samples were crosslinked by dicumyl peroxide [DCP]. The obtained samples were characterized by: wide angle X-ray scattering (WAXS), small angle X-ray scattering (SAXS) to characterize degree of crystallinity, coefficient of β-phase contents and its dimension. WAXS investigation were carried out in the scattering angle range 4–60^o with a step 0,1^o. Each diffraction curve was deconvoluted into individual crystalline peaks and amorphous halo according to the procedure proposed by Hindeleh and Johnson. SAXS investigation were performed in the scattering angle 2Θ=0,09–4,05^o with a step of 0.01o. It was observed, that DCP delays nucleation of β-phase. β-phase contents decreased about 50% in relation to the unmodified iPP. The addition of coagents to the iPP decreases β-phase content. The special case is BM, we didn't observe that phase at all. Only DM promotes nucleation of β-phase, value of K coefficient, proposed by Turner - Jones, was doubled. In the case iPP/DCP and coagents, the most usefull was AM and DM. Obtained results shows, that from technological point of view, the most interesting compositions are these containing DCP, and DM or AM.

Keywords: polipropylen, modyfikacja chemiczna, faza β, badania rentgenowskie

Introduction

Material's structure decides about properties of materials and the commercial importance of polyolefines is one of the reasons for the attention devoted to all aspects of their properties. Especially polypropylene in view of easiness of forming, modificability and trouble-free manufacturing is an interesting material. In recent years polyolefines are also used in nanotechnolgy as the matrix of nanomaterials doped with nanoparticles or with the bigger sized particles of metal oxides like ZnO, MgO etc.[1–5] . The modification is usually carried out

in the polymer's melt and in the presence of free radical initiators, e.g. peroxides (in our case, it was dicumyl peroxide) . 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.

Materials

The object of investigation was isotactic polypropylene [iPP] (Malen P, Petrochemia Płock, Poland) modified by following monoesters: allyl maleate, butyl maleate, dodecyl maleate, monoallyl tetrahydrophtalate. Some samples were crosslinked by dicumyl peroxide [DCP].

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

	P1	**P2**	**P3**	**P4**	**P5**	**P6**	**P7**	**P8**	**P9**	**P7/2**
iPP	100	100	100	100	100	100	100	100	100	100
AM		1,5				1,5				
BM			1,7				1,7			
DM				2,83				2,83		
THFA					2,1				2,1	
DCP						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 190^{o}C. The ready made compound was used to form a film by means of Plasti-Corder extruder. Then, the prepared films were heated in metal moulds at 160^{o}C for 30 min.

Tab. 2. Parameters of modifiers

Sample	Symbol	State	δ_D [$J^{0,5}/m^{1,5}$]	δ_P [$J^{0,5}/m^{1,5}$]	δ [$J^{0,5}/m^{1,5}$]
Allyl maleate	AM	Liquid	15,51	5,89	17,49
Butyl maleate	BM	Liquid	16,84	4,70	19,61
Dodecyl maleate	DM	Solid	17,09	2,47	13,86
Monoallyl tetrahydrophtalate	THFA	Liquid	15,02	10,79	21,17

δ -solubility parameter, δ_D, δ_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^o with a step 0,1^o. Each diffraction curve was deconvoluted into individual crystalline peaks and amorphous halo according to the procedure proposed by Hindeleh and Johnson [6]. Fitting was realized following the method described by Rosenbrock and Storey[7]. 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 2Θ=0,09 - 4,05^o with a step of 0,01^o. 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.

Results and Discussion

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

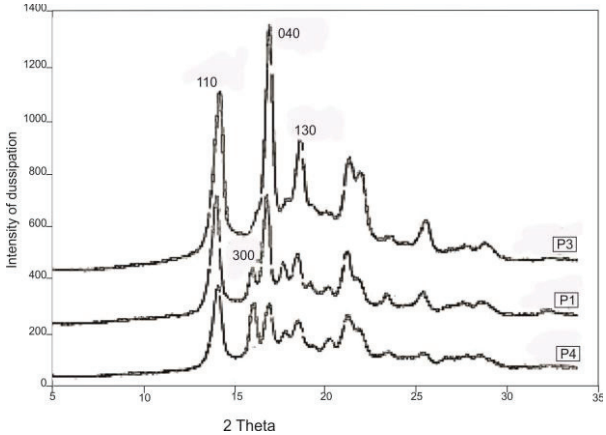

Fig. 1. WAXS curves for samples P1, P3, P4 (P1–iPP, P3–iPP, BM; P4–iPP, DM)

Tab. 3. Degree of iPP crystallinity calculated from WAXS

No.	Sample	Degree of crystalli-nity x_k [%]	Magnitude of crystall area z_k [nm]		Degree of bulk crystallinity w_k [%]
			$D_{(110)}$	$D_{(040)}$	
P1	iPP	51,6	17,0	21,2	49,0
P2	iPP, AM	56,2	16,9	21,0	53,7
P3	iPP, BM	46,5	14,9	20,9	44,0
P4	iPP, DM	57,4	15,5	18,4	54,6
P5	iPP, THFA	52,1	16,1	19,5	49,6
P6	iPP, DCP, AM	52,0	17,1	24,6	49,5
P7	iPP, DCP, BM	49,1	12,7	18,8	46,6
P8	iPP, DCP, DM	54,3	15,0	20,4	51,8
P9	iPP, DCP, THFA	52,0	15,1	21,6	49,5
P7/2	iPP, DCP	55,7	16,9	22,3	53,2

It was stated, that all modifiers (except MB) increased degree of crystallinity. The strongest influence, was noticed for DM, which changed xk 51,6% for unmodified iPP to 57,4% for iPP/DM sample. In this way manifests itself interaction between iPP and molecules of modifiers. Only MB decreased xk to 46,5%, solwatation of iPP macromolecules by modifiers molecules is the reason of such behavior. The same correlation was observed in the case of crosslinked samples. It is also observed that bulk crystallinity wk was changing similar to xk from 49,0% for iPP to 54,6% for iPP/DM.

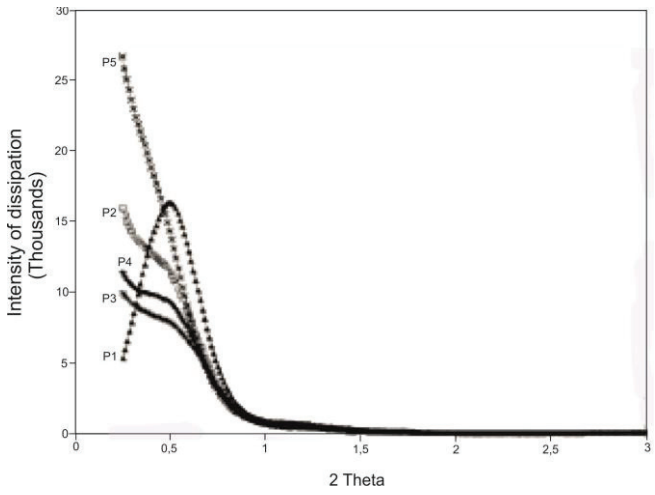

Fig. 2. SAXS curves for samples P1, P5 (P1–iPP, P2–iPP, AM; P3–iPP, BM; P4–iPP, DM; P5–iPP, THFA)

Tab.4. Apparent crystals sizes present in iPP 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 L_1	From one-dimensional function L_2	
P1	iPP	11,0	14,3	14,5	0,5
P2	iPP, AM	10,7	14,4	14,5	0,4
P3	iPP, BM	11,4	14,4	14,1	0,4
P4	iPP, DM	10,6	14,0	14,4	0,5
P5	iPP, THFA	12,4	16,2	16,2	0,8
P6	iPP, DCP, AM	9,0	12,6	12,9	0,9
P7	iPP, DCP, BM	10,8	13,9	14,1	0,8
P8	iPP, DCP, DM	9,2	12,0	12,3	0,8
P9	iPP, DCP, THFA	9,5	12,6	12,9	0,6
P7/2	iPP, DCP	9,6	12,4	12,5	0,6

Modifiers, also changed an average lamellar layer thickness.

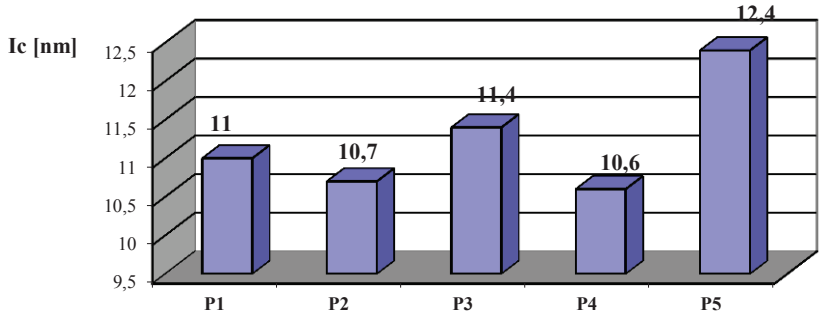

Fig. 3. Influence of modifiers on an average lamellar layer thickness (Ic) in iPP. P1 – iPP; P2 – iPP, AM; P3 – PP,BM; P4 –PP,DM; P5 – iPP, THFA

All modifiers (except THFA) decreased average lamellar layer thickness.

Thickness of transition layers was changed in all crosslinked samples. The most effective was AM, which changed E from 0,5 nm to 0,9 nm.

WAXS method shown, that samples were polimorfic. Characteristic peak from atomic plane (300) was observed on WAXS curves.

Tab. 5. Influence of modifiers on β–phase in iPP

No.	Sample	Coefficient of β–phase content K	Magnitude of crystall area D(300) [nm]
P1	iPP	0,110	20,5
P2	iPP, AM	0,046	13,5
P3	iPP, BM	0	-
P4	iPP, DM	0,261	21,6
P5	iPP, THFA	0,028	17,2
P6	iPP, AM, DCP	0,600	14,6
P7	iPP, BM, DCP	0	-
P8	iPP, DM, DCP	0,074	15,5
P9	iPP, THFA, DCP	0,053	22,4
P 7/2	iPP, DCP	0,059	23,8

It was observed, that DCP delays nucleation of β-phase. β-phase content decreased about 50% in relation to the unmodified iPP. The addition of co-agents to the iPP decreases β-phase content. The special case is BM, we didn't observe that phase at all.

Only DM promotes nucleation of β-phase, value of K coefficient, proposed by Turner – Jones [8], was doubled.

In the case of iPP/DCP and coagents, the most effective was AM. K coefficient changed from 0,110 in iPP and 0,059 in iPP/DCP to the 0,600 in iPP/AM/DCP. Influence of other modifiers was smaller, for DM K = 0,074, and for THFA K = 0,053. BM interaction was as strong as in earlier cases- the β–phase decayed.

In the sample iPP/DM (without DCP) increasing of β–phase content was observed K = 0,261.

Only in three cases, magnitude of crystall area increased. In the presence of DM in iPP z_k increased to 21.6 nm, in iPP/DCP z_k = 23,8 nm, and in iPP/THFA/DCP z_k = 22,4 nm. In other samples, magnitude of crystall area decreased.

Conclusions

The influence of modifiers on the crystallinity structural phase content in iPP has been observed. Distinct symptoms of nucleation and a growth of crystallinity structural constituent in the case of applying DM have been detected. One can come to the conclusion, that DM can cocrystallize with iPP increasing the content of crystallinity structural constituent in the configuration.

In samples monoclinic form α is dominated, but also β-phase appears.

The modifiers' ability, for nucleation and to build in the crystallinity structural constituent of polymer decreases significantly when there is dicumyl peroxide.

Obtained results shows, that from technological point of view, the most interesting compositions are these containing DCP, and MD or MA.

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WPŁYW ESTRÓW KWASU MALEINOWEGO NA ZAWARTOŚĆ FAZY *B* W IZOTAKTYCZNYM POLIPROPYLENIE

Streszczenie

Przedmiot badań był izotaktyczny polipropylen modyfikowany estrami kwasu maleinowego. Niektóre próbki były dodatkowo usieciowane za pomocą nadtlenku dikumylu. Materiał badano, wykorzystując metodę wąskokątowego i szerokokątowego rozpraszania rentgenowskiego. Do wyznaczenia zawartość fazy β w iPP wykorzystano natężenie refleksu od płaszczyzny (300), obliczając wskaźnik zaproponowany przez Turnera-Jonesa. Zaobserwowano, iż obecność DCP w materiale wpłynęła na nukleację fazy β, której zawartość wzrosła o 50% w stosunku do niemodyfikowanego iPP. Z zastosowanych estrów najskuteczniejszymi okazały się maleinian mono allilowy oraz maleinian mono dodecylowy. Uzyskane wyniki prowadzą do wniosku, że z technicznego punktu widzenia najlepszy jest układ zawierający DCP i DM.

Słowa kluczowe: polipropylen, modyfikacja chemiczna , faza β badania rentgenowskie