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INVESTIGATIONS ON NUCLEATED POLYPROPYLENE WITH USING THERMAL ANALYSIS METHOD

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Abstract

In the following essay the results of the research on nucleation of polypropylene obtained in PKN Orlen SA were presented. Both, organic (Millad 3988, ADK NA21) and non-organic (talc) mediums were used in the process. The main aim of the examination was to measure the influence of the above-mentioned mediums on the structure and physicochemical features of polypropylene. It has been proved that the organic nucleation mediums are more efficient as not only did polypropylene become more transparent, its structure more homogenous but his melting temperature increased as well. All those changes demonstrate that the nucleation process has taken place. The favourable changes in the polymer macrostructure were enabled by the process of nucleate molecules in the process heteronucleation.

Keywords: nucleation, nucleating mediums, polypropylene

Introduction

Polypropylene in one of the plastics used for modifications with nucleating mediums, mostly obtain suitable optical properties with keeping or improvement the resistance parameters. Low transparency that is appreciable opacity of the plastic are the effect of the presence of large-size crystalline areas in the polypropylene structure. As a result of modification by nucleation, which changes the method of polypropylene crystallization, is possible to obtain fine-crystalline structure with high homogeneity. It ensures the high transparency and resistance of polypropylene. The effect of the heterogeneous nucleation is the increase of the crystallization temperature and the increase of the fusion temperature of formed crystalline structures with more perfect ordered state. It is also favourable for decreasing of the fusion temperature. That is why the important is to determine the fusion temperature and stages of thermal decomposition of nucleated polypropylene, which can be one of the criterion of the nucleation effects estimation [1–7].

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The aim of the research was to measure the impact of nucleating mediums on both the structure and physicochemical features of polypropylene.

Experimental

In the study, polypropylene nucleated by nucleating mediums with different properties was used. Polypropylene used in the investigations was modified by following additions:

– organic derivative of phosphate salt ADK NA-21 from 'Asahi Denka Kogyo K.K.' (Japan), which is recognized as the most effective nucleating medium for polypropylene,

– derivate of sorbite Millad 3988 from 'Milliken Chemicals Co.' (USA),

– talc A5 and A30 from 'Luzenac Naintsch Mineralwerke GmbH' (Austria).

The amount of the organic nucleating mediums was 0.1, 0.2, 0.3% by mass.

Nucleated polypropylene was produced in PKN ORLEN S.A. from stabilized polypropylene powder by mixing with nucleating mediums and then extrusion moulding on screw extruder under the temperature of 200–220°C, what is shown in Fig. 1.

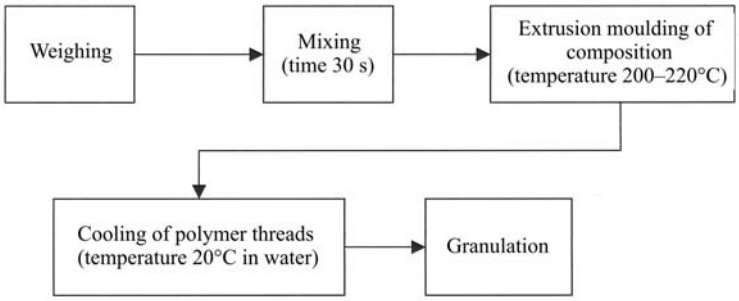

Fig. 1 Scheme of producing the nucleated polypropylene

The following resistance properties was measured: yield point, breaking stress, elongation at rupture, breaking modulus of elasticity, bending modulus of elasticity, mass melt flow index.

The research on the structure of the polypropylene has been conducted with the use of the optical microscope Alphaphot 2. As far as the examined sample is concerned (app. 0.1 cm thick foil), it has been obtained as a result of crystallization of a melted polymer. The structure and the degree of homogeneity has been observed in a polarized light.

Thermal transformations of nucleated polypropylene were also investigated with using thermobalance SDT 2960TA Instruments. The temperature of samples with mass of 20–25 mg were registrated, with heatup rate of 10°C min^{-1} under the temperature of 20–500°C and under the atmospheric pressure.

Results and discussion

The results of the studies showed that the addition of the nucleating mediums influences had an influence on properties changes and opacity degree of nucleated polypropylene. These changes were depended on kind and amount of the nucleating medium. It was found that the nucleating mediums Millad 3988 and NA21 had the advantageous influence on PP properties. The maximum effect of the polypropylene transparency improvement, of about 64%, was obtained with the amount of 0.2% by mass of Millad 3988 and 0.1% by mass of NA21. Resistance properties of nucleated polypropylene improved with using all the nucleating mediums (Table 1).

Besides the properties change and opacity of polypropylene, the effect of the nucleation was the increase of crystalline structure homogeneity of nucleated polypropylene. It was confirmed by microscopic investigations (Fig. 2).

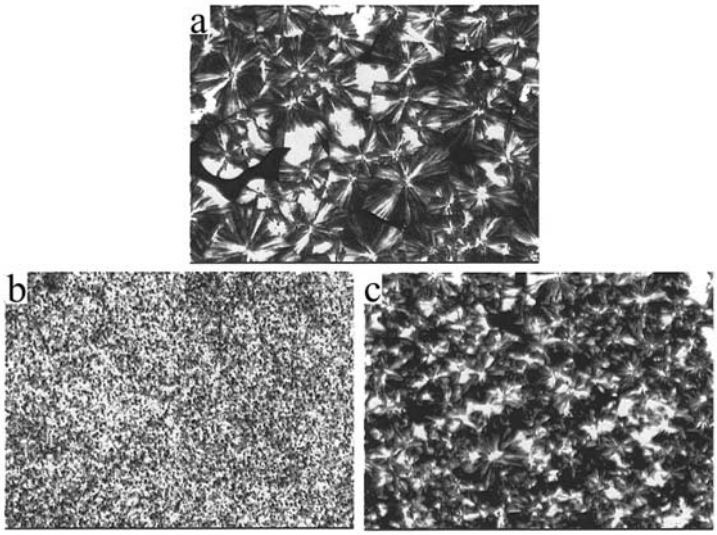

Fig. 2 Structure of polypropylene (300×): a – non-nucleated, b – nucleated by 0.1% by mass of ADK NA21, c – nucleated by 0.1% by mass of Millad 3988

The melting point, as an endothermic peak on DTA curve, and the thermal decomposition, as an exothermic peak on DTA curve (the temperature of the beginning and the end of sample decomposition), were determined by different ways from thermal curve of initial and nucleated polypropylene. Examples of thermal curves are shown in Fig. 3.

The analysis of non-nucleated polypropylene and polypropylene nucleated by nucleating mediums with diversified chemical specification showed, that the curves runs were closed and determined melting points were insignificantly diversified. The increase of nucleation on the polypropylene melting point was found, in comparison to non-modified polymer. The addition of the nucleating medium raises the polypropylene melting point of about 5°C with dependence on kind and amount of the nu-

Table 1 Characteristics parameters of nucleated polypropylene

Properties (Polish standard)	Non-nucleated polypropylene	The amount of nucleating medium/% by mass					
		NA21			Millad 3988		
		0.1	0.2	0.3	0.1	0.2	0.3
MFR/g 10 min^{-1} (PN–93/C–89069)	3.89±0.06	5.14±0.07	5.07±0.07	4.58±0.07	6.18±0.88	4.88±0.08	3.84±0.07
Yield point/MPa (PN–81/C–89034)	35.5±0.3	40.5±0.1	41.0±0.2	41.0±0.3	38.4±0.1	39.4±0.2	40.3±0.2
Breaking stress/MPa (PN–81/C–89034)	20.3±0.8	23.5±0.1	23.6±0.7	25.2±0.3	22.4±0.7	22.6±0.9	25.3±0.6
Elongation at rupture/% (PN–81/C–89034)	761.7±8.6	19.3±0.8	23.9±1.3	21.4±0.7	136.3±6.1	26.6±2.0	18.0±1.7
Breaking modulus of elasticity/MPa (PN–81/C–89034)	1596.4±69.3	2182.7±76.1	2219.5±65.2	2225.7±70.7	1923.2±77.0	2179.7±39.9	2151.0±67.4
Bending modulus of elasticity/MPa (PN–82/C–89054)	1455.3±0.5	1960.6±0.6	2250.2±0.5	2090.2±0.4	1620.3±0.6	1772.5±0.5	1920.0±0.4
Opacity degree/% (PN–84/C–89100)	97.6±0.1	54.5±0.1	45.5±0.1	39.4±0.1	81.3±0.2	35.5±0.1	32.9±0.1
Melting point/°C (Thermal analysis method)	156	160	160	161	160	160	161

Table 1 Continued

Properties (Polish standard)	Non-nucleated polypropylene	The amount of nucleating medium/% by mass					
		Talc A5			Talc A30		
		0.1	0.3	0.5	0.1	0.3	0.5
MFR/g 10 min^{-1} (PN–93/C–89069)	3.89±0.06	4.68±0.06	4.84±0.05	4.51±0.03	4.67±0.04	5.61±0.04	4.76±0.1
Yield point/MPa (PN–81/C–89034)	35.5±0.3	37.9±0.3	38.5±0.3	38.6±0.2	37.2±0.3	37.9±0.2	37.5±0.3
Breaking stress/MPa (PN–81/C–89034)	20.3±0.8	21.8±0.5	23.8±0.7	23.8±0.8	22.0±0.7	22.8±0.7	23.5±0.4
Elongation at rupture/% (PN–81/C–89034)	761.7±8.6	128.3±12.5	27.9±1.3	28.0±2.4	156.4±14.0	29.5±5.6	27.1±2.3
Breaking modulus of elasticity/MPa (PN–81/C–89034)	1596.4±69.3	1861.2±77.2	2005.7±58.3	2116.8±70.2	1896.9±109.3	1959.2±32.0	2003.9±107.9
Bending modulus of elasticity/MPa (PN–82/C–89054)	1455.3±0.5	1628.3±61.0	1691.0±16.0	1745.8±21.5	1683.5±23.8	1785.5±23.1	1805.4±45.2
Opacity degree/% (PN–84/C–89100	97.6±0.1	54.5±0.1	45.5±0.1	39.4±0.1	54.5±0.1	45.5±0.1	39.4±0.1
Melting point/°C (Thermal analysis method)	156	158	159	159	159	157	159

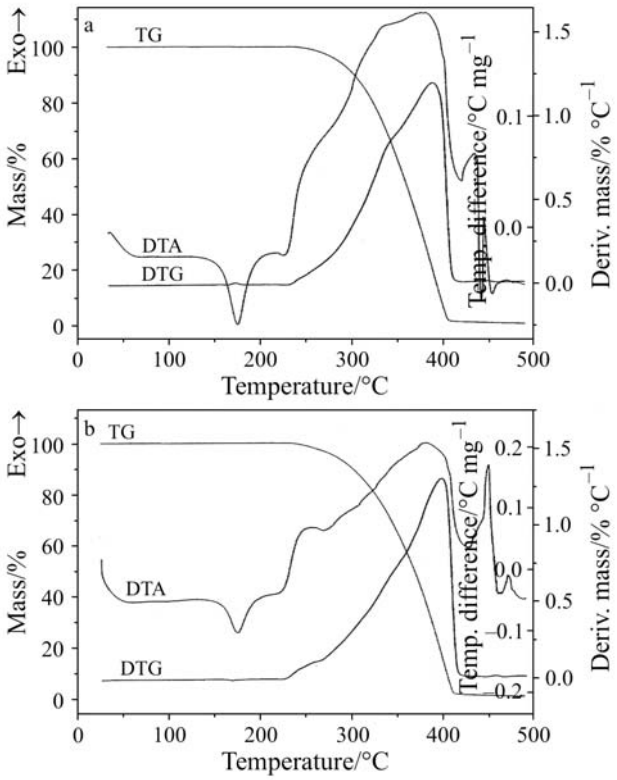

Fig. 3 Examples of thermal curves of a – non-nucleated polypropylene, b – polypropylene nucleated by 0.3% by mass ADK NA21

cleating medium. The highest increase of the melting point was found for polypropylene nucleated by organic nucleating mediums ADK NA21 and Millad 3988 in amount of 0.3% by mass. The decomposition temperatures of most of the samples were between 236–420°C. The highest temperatures of the decomposition beginning were found for polypropylene nucleated by ADK NA21.

The increase of the melting point of the nucleated polypropylene in relation to non-nucleated polypropylene confirmed that the course of the nucleation process (observed increase of the polymer crystallization temperature). It could be accepted that the advantageous changes in polymer macrostructure were proceeded, which were possible by hetero-nucleation carried out with the portion of nucleation medium molecules.

Conclusions

- The results of the research prove the organic mediums as Millad 3988 and ADK NA21 used to polypropylene nucleation to be much better nucleates than the non-organic ones like talc.

- The results of the polypropylene is increase in melting point, considerable decrease in opacity degree and improvement of the crystal structure homogeneity.
- Owing to the process of nucleation of polypropylene, it is possible to obtain a product with specific optical features as well as favourably increased temperature of crystallization, hence the processing time can be limited.

References

1 R. Schlotmann and R. Walker, Kunststoffe, 86 (1996) 1002.
2 R. D. Maier, C. Friedrich and R. Mülhaupt, Kunststoffe, 89 (1999) 89.
3 C. B. Park, L. K. Cheung and S. W. Song, Polymer, 17 (1998) 731.
4 A. Bukowski, B. Osowiecka and J. Zieliński, J. Thermal Anal., 43 (1995) 271.
5 K. Nagarajan, K. Levon, A. S. Myerson, J. Therm. Anal. Cal., 59 (2000) 497.
6 E. S. de Medeiros, R. S. Tocchetto, L. H. de Carvalho, I. M. G. Santos, A. G. Souza, J. Therm. Anal. Cal., 66 (2001) 523.
7 E. S. de Medeiros, R. S. Tocchetto, L. H. de Carvalho, M. M. Conceicao, A. G. Souza, J. Therm. Anal. Cal., 67 (2002) 279.