

## Investigations of the structure of composites of PP/GF by means of X-ray methods

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### Methodology of research

#### ABSTRACT

**Purpose:** This work aimed to identify the crystalline phases which appear in polymeric matrix as well as to determine the degree of crystallinity for composites based on the matrix of polypropylene reinforced with glass fibre. Moreover, the value of  $L_p$  (large period) of supermolecular structure in lamellar polypropylene has also been determined.

**Design/methodology/approach:** X-ray structural investigations of composites based on polypropylene matrix reinforced by glass fibre have been performed by means of X-ray diffraction (XRD) and small angle X-ray scattering (SAXS).

**Findings:** For investigated composites the presence of several types of polymorphous polypropylene has been found. The crystalline part of the matrix for the investigated composites is composed of  $\alpha$  phase which crystallizes in monoclinic lattice and  $\beta$  phase which crystallizes in hexagonal system. Moreover, it has been found that amorphous phase in the investigated composites is made of strongly oriented smectic phase of polypropylene.

**Research limitations/implications:** Continuation of the investigations by means of X-ray methods will enable an in-depth analysis and recognition of the structure of polymeric composites on the molecular and supermolecular level.

**Originality/value:** The work identified crystalline phases of polypropylene which made up the matrix for the investigated composites and the value of large period for supermolecular lamellar structure of polypropylene.

**Keywords:** X-ray phase analysis, Materials; Composites

### 1. Introduction

Main factors which determine the properties of a composite include the properties of its individual components. The quality of composites is determined by the internal structure of a polymer which makes up a matrix as well as the type of reinforced phase [1-3]. The structure of a polymer is of a crystalline-amorphous nature while better properties are obtained when the structure is predominated by the ordered crystalline phase fraction. The degree of crystallinity of thermoplastic polymers and the composites on the basis of polymeric matrix is a subject of numerous investigations [4, 5].

Arroyo and others [6], while investigating the kinetics of PP crystallisation in composites with glass fibre, found that glass fibre significantly influences the size of PP crystallites after crystallisation process. With the glass fibre fraction in the composites over 30% the size of spherulites in the matrix decreased. This could be caused by interaction of glass fibre as a factor limiting the creation of spherulitic structure. With the increase in percentage fraction of glass fibre in a composite, the melting point and the crystallinity degree of the composite increase, which means that glass fibre works as an agent for the heterogeneous nucleation of PP. Similar phenomenon was observed by other researchers [7].

Bogoceva - Gaceva and their associates [8], while investigating  $\beta$  - nucleating PP observed that glass fibre is favourable to crystallisation  $\alpha$  - PP, working as  $\alpha$  - nucleuses. The amount of  $\alpha$  phase in  $\beta$  - nucleating PP increased with the increase in percentage concentration of glass fibres in the alloy. The efficiency of nucleation on fibre glasses depends mainly on the surface energy and the size of the used fibre.

During analysis of the results of own investigations [9, 10], it was found that glass fibre can cause the decrease in the degree of crystallinity of composites on the basis of polypropylene matrix and the limitation in the development of spherulitic structure of the matrix.

## 2. Materials and experimental procedure

This work presents the results of investigations of composites made of the granulates by Polimarky (Rzeszow, Poland). These granulates contained polypropylene - Malen P J - 400 produced by Petrochemia Plock and glass fibres with E symbol. The glass fibres with final length 6 mm were covered by silane preparation.

Samples for investigations were prepared by means of injection with Krauss - Maffei injection machine (KM65 - 160C1 type). The investigations encompassed the composites on the polypropylene matrix which contained 30% and 50% of the glass fibre (GF). For the comparison purposes the matrix material was also tested. Part of the material was processed by heat treatment in the form of soaking at the temperature of 130 °C in the air. Soaking rate amounted to 0,015 °C/s, soaking time 900 s per mm of the sample thickness, cooling rate 0,010 °C/s.

Investigations by means of X-ray diffraction analysis method were performed using SEIFERT diffractometer of XRD 3003 T - T type. The filtered radiation of the copper anode lamp,  $\lambda = 0,154$  nm was applied. The stepped method of measurement within the range of scattering angles of  $2\theta$  from 1° to 40° with the step of 0,1° has been used. The measurements of the scattered radiation were performed both in crosswise ("r") and lengthwise ("s") orientation of the sample in relation to primary beam. The concentration of crystalline phase of polypropylene (i.e. crystallinity degree  $S_k$ ) was calculated in the form of the quotient of the total of integral intensities of crystalline reflexes to the integral intensity of diffraction curves.

SAXS investigations were performed on the Kratky camera combined with the SWAXS optical system by Hecus-MBraun (Austria) with the resolution of 81nm. The X-ray copper anode lamp  $\lambda=0,154$  nm was used for investigations. The primary beam was monochromatized by means of nickel filter.

Small angle diffraction curves SAXS were used for determination of one-dimensional function of small-angle scattering of  $I(q)q^2$  [11, 12]. The analysis of SAXS scattering function was performed by means of computer software of PS by Hecus-MBraun; on its basis the location of diffraction maximums ( $q_m$ ) and the values for identity period of the supermolecular structure  $L_p$  have been determined using Bragg's rule:

$$L_p = \frac{2\pi}{q_m} \quad (1)$$

where:

$L_p$  - identity period for the supermolecular structure,  
 $q_m$  - location of diffraction maximum.

## 3. Results and discussion

Examples of comparison of X-ray diffraction patterns determined for the samples positioned crosswise - "r" and the lengthwise - "s" in relation to primary beam have been presented in the picture 1. On the diffraction patterns "r" (Fig. 1a) and "s" (Fig. 1b) the experimental curve has been determined by the dotted line while the continuous line is a 'fitting curve'. The analysis of X-ray diffraction patterns was based on the literature data concerning characteristic diffraction reflexes for polymorphous  $\alpha$  types (monoclinic) or  $\beta$  (hexagonal) of polypropylene and polypropylene smectic phase [13, 14].

In most of the obtained diffraction patterns a few strong diffraction reflexes are to be seen (Fig. 1). They come from the lattice planes: (110), (040), (130) and also (111) and (131), characteristic for the  $\alpha$  form and from the crystallographic plane (300) - for  $\beta$  form (Fig. 1a, b). While comparing diffraction patterns obtained for the crosswise and lengthwise samples in relation to the primary beam it can be assumed that the amorphous phase in composites both for polypropylene and for polypropylene domains is composed of strongly oriented smectic phase of polypropylene. The manifestation of this fact is a diametrically different course of the envelope through local minimums of the scattered radiation intensity, located between diffraction reflexes of the crystalline phase. The most appropriate example of such a diffraction effect are curves in the diffraction patterns "r" and "s" determined for the composite on the basis of the polypropylene matrix which contain 50% of glass fibre (Fig.1).

Moreover, distinct dislocation of diffraction reflex can be observed. This proves a very high degree of orientation of crystallites of polypropylene in relation to longitudinal axis of the investigated samples. This causes the differences between literature values of diffraction reflexes for the matrix of the investigated composites and the values determined in own investigations.

Determined values of the crystallinity degree (Tab. 1) should be treated as an estimation since due to the strong orientation of crystallites, diffraction reflexes and maximums shapes are deformed as compared to the reflexes determined by the samples with isotropic crystalline orientation.

Taking the abovementioned into consideration as compared to the results of the investigations performed for the composite which contains 30% of glass fibre after soaking it should be observed that very low intensity of the diffraction reflex which comes from the (300) plane or virtually non-existence of such a diffraction reflex can be connected with the effects caused by the orientation rather than by lack of  $\beta$  type in this individual case.

Hence, during diffraction pattern analysis of this sample the existence of  $\beta$  polypropylene was also taken into consideration. Moreover, changes in intensity of the reflex (300) which come from the  $\beta$  form show that this form is less stable than monoclinic type of the  $\alpha$ .

From the analysis of the crystallinity degree compared in the Tab. 1 it results that soaking causes the increase in crystallinity phase fraction which occur in polymeric matrix of the investigated composites.

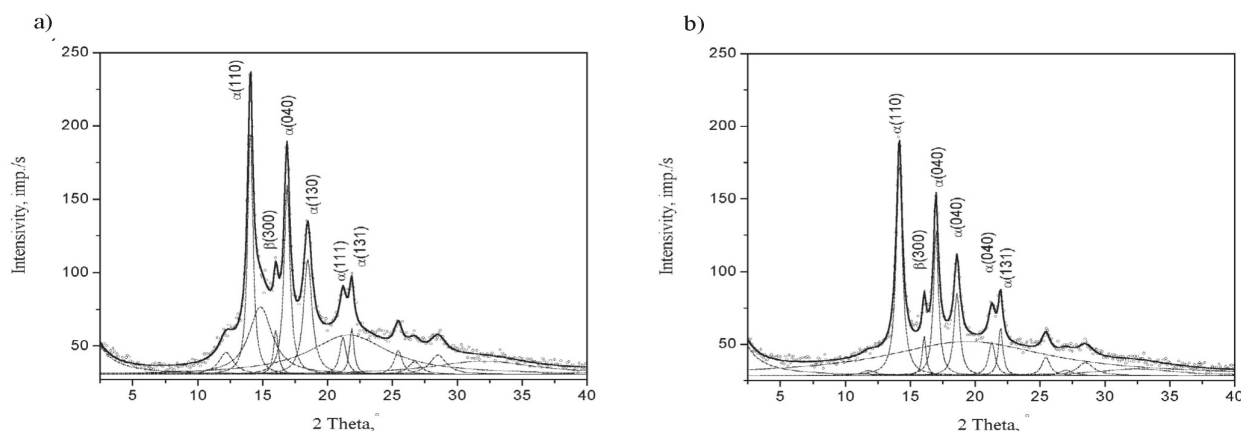


Fig. 1. Diffraction curve for the composites: PP + 50% GF ob.: a) PP+50%GF ob – ‘r’, b) PP+50%GF ob – ‘s’ (—●— experimental curve, — fitting curve, ---- reflexes from crystalline and amorphous phase)

The reason of this fact is a repeated crystallization which takes place during heating and soaking of the sample at the temperature within optimal crystallization rate and as a result slow cooling.

Table 1. Values of  $S_k$  and  $L_p$  of the investigated samples determined by X-ray methods

Material		$S_k$ , %	$L_p$ , nm
PP	„I”	67,8	13,6
	„S”	73,7	
PPob.	„I”	71,8	17,0
	„S”	79,5	
PP+30% GF	„I”	53	15,4
	„S”	46,8	
PP+30% GF ob.	„I”	70	21,0
	„S”	59,4	
PP+50% GF	„I”	32,8	12,2
	„S”	29,4	
PP+50% GF ob.	„I”	43,4	16,7
	„S”	37,2	

The energy transmitted during heating causes the increase in mobility of macromolecules and the reconstruction of the crystalline structures in the matrix, mainly spherulites. Implementation of the fibres into the polymeric matrix caused the decrease in crystallinity degree determined by the X-ray method (Tab.1). This proves that glass fibre does not work as a factor which causes nucleation of the matrix crystallites.

Investigations by means of small-angle X-ray scattering (SAXS) enabled to determine the value of the large period of lamellar supermolecular structure [10-12]. Lamellar structure is characterized by the identity period  $L_p$  (‘large period’) which is equal to the total of thickness of crystalline lamella,

amorphous layer and the width of the transient area which separates these domains [15].

Example of one-dimensional scattering function of  $I(q)q^2$  has been presented in the Fig. 2 with the scattering functions for the sample before and after heat treatment for comparison.

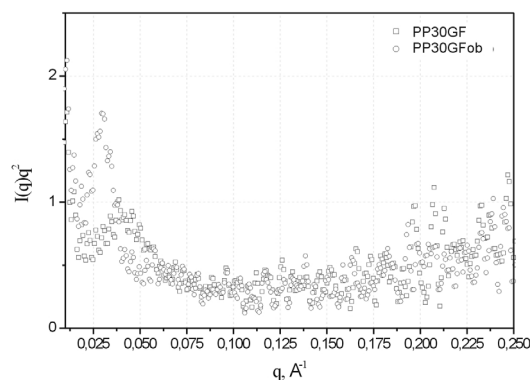


Fig. 2. One-dimensional scattering function for PP+30% GF composites

Angular location of the diffraction maximum is closely connected with the value of the large period. Analysing of the value of the large period  $L_p$  of the supermolecular lamellar structure of polypropylene and polypropylene domains in composites compared in Tab. 1 it can be observed that due to the thermal treatment the large period of supermolecular lamellar structure of the investigated samples increases by 25÷37% as compared to the initial value. The amorphous phase which occurs in the matrix of the investigated composites is a smectic type of polypropylene. This is proved by the results of X-ray diffraction investigations. It can be predicted that in case of the composites the smectic polypropylene most probably contains an insignificant amount of glass fibre.

Lack of visible diffraction maximum for the composites of PP+50% of glass fibre and appearance of the same maximum after heat treatment proves the increase in contrast of electron

density between crystalline and amorphous phase or change in volume fractions of these phase or appearance of both effects at the same time.

Considering the results of X-ray diffraction (XRD) investigations which prove distinct increase in crystallinity degree caused by heat treatment (Tab. 1) one can assume that the change in volume fraction for crystalline and amorphous phase is in this case a predominant factor.

The tendency of changes in large period observed during investigations is consistent with the results of investigations of X-ray diffraction – XRD, which proves the increase in crystallites size and the crystallinity degree after heat treatment. However, the reason of the increase in large period can not be clearly determined. It can be caused both by the increase in thickness of crystalline layers of lamellar structure as well as the increase in the distance of crystalline ‘arms’ in case of spherulitic structure.

#### 4. Conclusions

On the basis of X-ray diffraction analysis the existence of several polymorphous forms of the polypropylene has been observed in the investigated composites. The crystalline part of the matrix of the investigated composites composes of  $\alpha$  phase which crystallizes in monoclinic lattice and the  $\beta$  phase which crystallizes in hexagonal system. Moreover, it has been stated that the amorphous phase in the investigated composites is in the form of strongly oriented smectic phase of polypropylene. As a result of soaking, in the structure of the investigated composites the increase in fraction of crystalline phases which appear in polymeric matrix occurs. The introduction of fibres into the polymeric matrix has caused the decrease in crystallinity degree. The existence of small-angle diffraction maximum for the investigated samples is connected with the existence of ordered supermolecular structure formed by crystalline and amorphous phases of polypropylene (smectic form). Changes in intensity and angular location of the interference maximums prove significant changes in structure of matrix caused by the existence of glass fibre.

#### References

- [1] W. Dziadur, A. Tabor, The effect of wood filler behaviour on structure and fracture of polyethylene, *Journal of Achievements in Materials and Manufacturing Engineering* 17 (2006) 53-56.
- [2] A. Gnatowski, O. Suberlak, P. Postawa, Functional materials based on PA6/PVP blends, *Journal of Achievements in Materials and Manufacturing Engineering* 18 (2006) 91-94.
- [3] J. Koszkuł, D. Kwiatkowski, The influence of annealing on dynamical mechanical properties of polyamide 6/fiber glass composites, *Journal of Achievements in Materials and Manufacturing Engineering* 19/2 (2006) 16-20.
- [4] J. Myalski, J. Śleziona, Influence of preparing of GFR recyclates on the properties of polyester matrix compopsites, *Journal of Achievements in Materials and Manufacturing Engineering* 18 (2006) 163-166.
- [5] S. M. Zebajrad, S.A. Sajjadi, M. Tahani, A. Lazzeri, A study on thermal behaviour of HDPE/CaCO<sub>3</sub> nanocomposites, *Journal of Achievements in Materials and Manufacturing Engineering* 17 (2006) 173-176.
- [6] M. Arroyo, M.A. Lopez-Manchado, F. Avalos, Crystallization kinetics of polypropylene: Effect of the addition of short glass fibres, *Polymer* 38/22 (1997) 5587-5593.
- [7] E. Mader, H.J. Jacobasch, K. Grundke, T. Gietzeld, Influence of an optimized interphase on the properties of polypropylene/glass fibre composites, *Composites Part A* 27A (1996) 907-912.
- [8] G. Bogoceva-Gaceva, A. Janevski, E. Mader, Nucleation activity of glass fibres towards iPP evaluated by DSC and polarizing light microscopy, *Polymer* 42 (2001) 4409-4416.
- [9] Z. Nitkiewicz, R. Sobczak, J. Koszkuł, Microstructure and X-ray diffraction of polypropylene and polypropylene with glass fibre, *Composites* 2 (2001) 127-129 (in Polish).
- [10] R. Sobczak, Z. Nitkiewicz, J. Koszkuł, Supermolecular structure and thermal properties of polypropylene composites reinforced glass fibre, *Composites* 8 (2002) 343-348 (in Polish).
- [11] K. Suchocka-Gałaś, C. Ślusarczyk, A. Włochowicz, The state of ion aggregation in ionomers based on copolymers of styrene and acrylic acid, 1. Small- angle X-ray scattering studies, *European Polymer Journal* 36 (2000) 2167-2174.
- [12] R. Sobczak, Examinations of the supermolecular structure of polypropylene composites reinforced glass fibres with using saxs method, *Polymer amaterials and their manufacturing*, Czestohowa University Press, Czestohowa 2004, (in Polish).
- [13] F. Auriemma, O.D. De Ballesteros, C. De Rosa, P. Corradini, Structural disorder in the  $\alpha$  form of isotactic polypropylene, *Macromolecules* 33 (2000) 8764-8774.
- [14] M. Naiki, T. Kikkawa, Y. Endo, K. Nozaki, T. Yamamoto, T. Hara, Crystal ordering of  $\alpha$  phase isotactic polypropylene, *Polymer* 42 (2000) 5471-5477.
- [15] M. Ijima, G. Strobl, Isothermal crystallization and melting of isotactic polypropylene analyzed by time and temperature dependent small – angle X – ray scattering experiments, *Macromolecules* 33 (2000) 5204-5214.