ANALYTICAL TREATMENT AND MICROSTRUCTURAL CORRELATIONS OF PP BASED MODEL AND MACROCOMPOSITES

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SUMMARY: Estimation of the real spherulite shape and quantitative evaluation of microstructure parameters have been performed in order to analyse the microstructure/properties relations in the model composites. Investigations presented in this study include: i) analysis of microstructure parameters in model systems, ii) characterization of microstructure parameters in real composites, iii) microstructure correlation between the model and real composites. In the studied composites isotactic polypropylene, PP, was used as a matrix, and differently sized carbon fibres as reinforcement.

KEYWORDS: Composites, Polypropylene, Microstructure

INTRODUCTION

In the past decade, thermoplastic composites based on semicrystalline polymer matrix have been increased their importance as engineering materials [1,2]. Their properties depend strongly on the final microstructure of the matrix, which, in turn, is determined by the crystallization/processing conditions [3]. Microstructure is defined by the size, shape and boundaries of the spherulites that have been nucleated in the polymer matrix. The nucleation and growth conditions in the fiber reinforced composites are different from those in neat polymer. During the crystallization of fibre reinforced composites fibers are shown to have a dual effect, depending on the interplay between their enhancing impact on nucleation and the depressing effects on spherulites growth, caused by an impingement mechanism. Nucleation efficiency of the fibers can be generally tailored by chemical constitution of the sizing used, and by altering their surface morphology. In our previous investigation [4] it was shown that depending on the surface treatment glass fibers exhibit different nucleation effects, whereas unsized untreated fibers slightly depressed the nucleation of PP. Different analytical and numerical methods have been derived to investigate the relationship between the spherulitic microstructure of the polymer in fiber reinforced composites and the basic end-use properties of the composites. Among them most frequently used are dimensional, statistical, intercept, as well as Voronoi, arborescent, and front tracking methods [3-9]. Using these methods, the microstructure parameters at various nucleation and crystallization conditions can be predicted. Pyrz has investigated the quantitative parameters describing the microstructure of composites, including UD composites [9]. He has applied Dirichlet tessellation and second-order intensity function K(r) in order to calculate the important factors which characterize the microstructure. Deporter and Baird have established a simulation of the effects of thermal history on the morphology of thermoplastic composites [10], in order to predict the degree of crystallinity and the size of spherulites that arise during the cooling of semicrystalline polymer reinforced with continuous carbon fibres. Galeski and Piorkowska have analysed the growth of spherulites in a case of athermal, thermal and combined nucleation mechanisms. They examined the influence of nucleation mechanism on morphological peculiarities, calculating the spherulite size distribution for various types of nucleation [11]. Mehl and Rebenfeld have shown that computer simulation of polymer crystallization could be an effective tool for studying the influence of the reinforcing fibres on the crystallization kinetics and morphology of semicrystalline polymers [12].

In this paper, microstructure of PP-based composites was analysed by geometrical, intercept and diffuse-interface field methods. Geometrical method is concerned the parameters that characterise the grain sizes and shapes. Diffuse-interface field model, proposed by D.Fan et al., is based on the theory that grain boundaries are not just sharp interfaces having zero thickness, but they are assumed to be diffuse with finite thickness [6]. This method investigate the grain growth dependence on the grain size and various size distributions, as well as the local topological changes of the individual grains. Based on the

kinetic and relationships with the topological class, this model offers also the possibility to discuss the factors controlling the behaviour of spherulites grains. The area of the grains, A, at a certain time step is directly obtained from the microstructure by the grain radius, r, $A = pr^2$. The average grain size at a certain time is obtained by averaging the grain size over all grains in the system. The range of linearity of the averaged grain size dependence on topological class, n, indicates the most frequent grain sides number. If there is no clear linear relationship, the grain sizes depart from the average size and the degree of data fluctuation increases. According this model, the peak of the overall size distribution for all grains comes mainly from 5-, 6- and 7-sided grains. Also, for few-sided and many-sided grains, $5 > n > 7$, the distribution is more symmetric than those of 5- or 6-, 7- sided. The intercept method, proposed by A.Thorvaldsen, is one of the tools for evaluation of the grain shapes in various polycrystalline materials, including polymers [7]. This method based on the measurements of the total grain boundary area per unit volume, S_v, that can be measured on statistically representative sections through the material (eq.1):

$$S_v = 2 P_l \quad (1)$$

where P_l is the number of intersections per unit test line on planar section made with grain boundaries. S_v represents a measure of the surface/volume ratio of the spherulite grains, A/V, that is characterised by the spherical aberration, k. The spherical aberration is the ratio between the surface area of the grain and the surface area of a sphere with equal volume (eq.2):

$$k = A/4 pr^2 \quad (2)$$

where r is the equivalent spherical radius. For non-spherical grains $k>1$. If all grains are sphere, $k=1$. In volume filling polycrystalline structures, k is increasing with decreasing the grain sizes. This concept has been also used for elongated spherulite grains and the eccentricity of spherulite grains, as a measure of the degree of elongation, is defined by the relation (eq.3):

$$e = (a^2 - c^2)^{1/2}/a \quad (3)$$

where a is the intercept with the x axis and c is the intercept with y axis. According this method, for eccentricities below 0.6, the spherical aberration is less than 1.01. The aberration is not significant before the eccentricity reaches levels of 0.8 or higher. Only higher degree of elongation has an impact on the surface/volume ratio of grains in polycrystalline materials.

EXPERIMENTAL

Isotactic polypropylene, iPP, (MT Daplen, MFI=12-14g/10min) was used as a matrix for the studied composites with differently sized carbon fibres as reinforcement (see Table 1). In our previous investigation [13] it was shown that carbon fibres (C-H and C-T) exhibit different surface morphology. In particular, C-H fibres have shown a smooth surface, while C-T fibres present roughness behavior.

Tabel 1. Basic characteristics of the carbon fibres and abbreviations used for the composites

Composite	Fibre	T [tex]	D [μm]	F [GPa]	E [GPa]	ρ [g/cm^3]
C-H/PP	C-Hercules AS4	800	7.5	4.0	241	1.80
C-T/PP	C-Torrayca	800	7.6	3.5	230	1.75

Microstructure of model composites was analysed during the nucleation and isothermal crystallization (T_c=124-130 °C) by using LEICA polarising microscope equipped with a hot-stage. Model composites were prepared by the following way. Very thin films of PP were prepared by melting small quantity of polymer between two microscope slides (18x18 mm) and then C-fibres were placed in the films. The samples were heated up to 205°C and then cooled to a given crystallization temperature. During the optical microscopy analysis of model composites, the same place was observed at all studied T_c. In the macro composites (PP reinforced with continuous caron fibers, consolidated at T=205°C, P = 3 MPa, t = 20 min), the final microstructure was studied by optical reflection microscopy (LEICA) and scanning electron microscopy (SEM Philips 301). Spherulities morphology was investigated on the etched surfaces. The surfaces were first ground successively with fine paper of 12.5 μm alumina on a selvyt cloth, the

same with 5 μm alumina, the same with 1 μm alumina; etching of PP was then performed for 2 h, in potassium permanganate (2 % vol), with the following composition of acid, 4 % vol orthophosphoric acis min 85 % (as supplied by Merc, UK) and 1 % vol water.

RESULTS AND DISCUSSION

***i*) Microstructure analysis in model composites C/PP**

Polymer microstructure in the model composites was analysed by the changes of the following parameters: the spherulite radius, r, the number of the spherulites sides, known as topological class, n, the spherulite area, A, and the shape factor, R_m. The distribution curve of the spherulites radius (determined by polarizing optical microscopy) during the isothermal crystallization at T_c=127 °C is given on fig. 1.

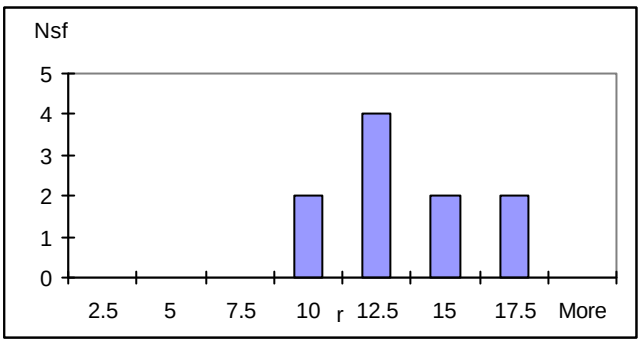

Fig.1 Distribution of spherulities radius at T_c = 127°C

The changes of the radius were in accordance with the known kinetic dependence, *i.e.* r increased with the time and decreased by increasing T_c. It was found that the distribution of the number of spherulites by r was wider at lower T_c. For the studied range of crystallization temperture, it was noticed that by increasing of r, the number of spherulites sides, n also increased. Using the ratio of the radius of two neighbour spherulites, an attempt was made to predict the spherulite shape and the number of the grain sides, n. Mathematically calculated values and the experimentally obtained ones have shown pretty high percent of compatibility (almost 98 %). Higher discrepancy was noticed at lower T_c (T_c=124°C). The obtained data, for the same period of crystallization (t = 9 min), are shown in table 2: n is in the range of 5 to 8.

Table 2. Number of spherulites sides
(mathematically predicted and experimentally determined)

	n	
T [°C]	Mathematically calculated	Experimentally determined
124	6 6 6 8	7 8 6 8
127	6 6 6 6	6 6 6 6
130	5 6 5 7	5 6 6 6

Consequently with the changes of the spherulites raduis, the spherulites area was changed: for model composites (both systems) A was in the range of 100-400μm^2, and it increased by increasing the n.
The spherulites shape factor, R_m, is in the range 0.7 - 0.95 for the studied T_c. R_m increased by increasing the crystallization time and by increasing the topological class of the spherulites.
Concerning the spherulite growth front the following conclusions can be drawn: (i) the impingement of spherulites, having almost the same radius, produced a grain boundary similar to a straight line. On the contrary, if the spherulites have different radius, the grain boundary assumes a concave or convex shape; (ii) the impingement of 5 or more spherulites can produce interspherulite fractures or pores, which are suppose to be a defect place in the microstructure.
Obviously, in the investigation of model composites the nucleation of the spherulites represents a combination of thermal and athermal mechanism [10,11].

***ii*) Microstructure analysis of macro composites**

Microstructure analysis of the macro composites includes the same parameters, r , A, n, R_m, and they were compared for the composites produced from both types of the fibres (C-H and C-T). Spherulites morphology of the polymer matrix, obtained by SEM, is presented on fig. 2 (C-H/PP) and fig.3 (C-T/PP). Spherulites grain boundary, as obtained by optical reflection microscopy, is presented on fig. 4 (for C-H/PP).

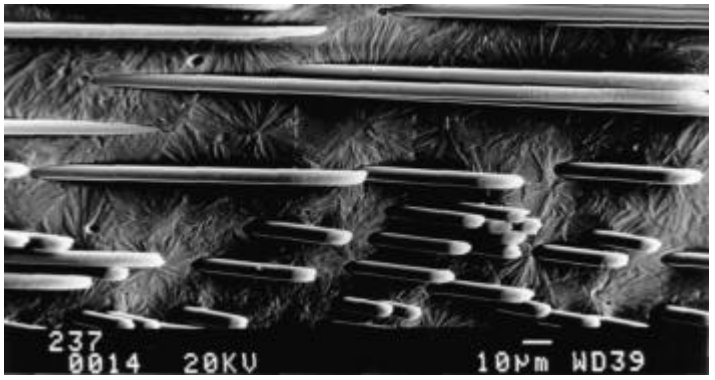

Fig. 2. SEM photographs of UD C-H/PP (x 500) composites

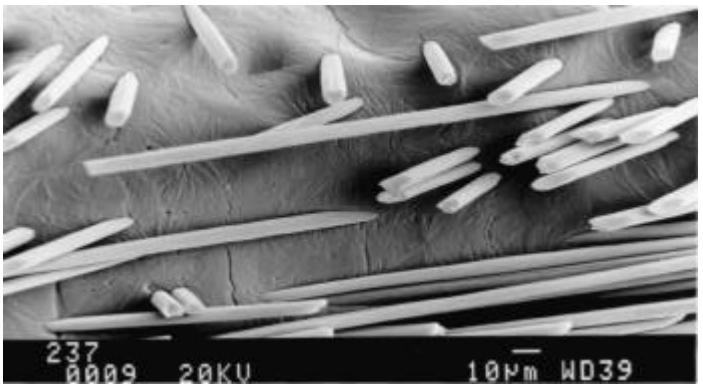

Fig. 3. SEM photographs of UD C-T/PP (x 500) composites

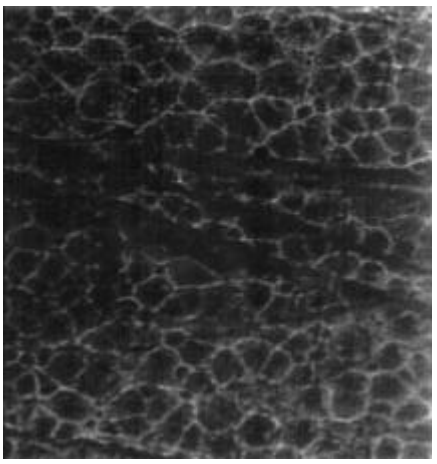

Fig. 4 Optical reflection microscopy of UD C-H/PP (x100) composites

It was found that spherulities distribution by *r* is wider in the presence of C-H fibers, where most of the spherulites have *r* up to 25 μm, while in the presence of T-C fibers, *r* is in the range of 35-45 μm. For both composites, *r* increased by increasing the number of grain sides (see fig. 5).

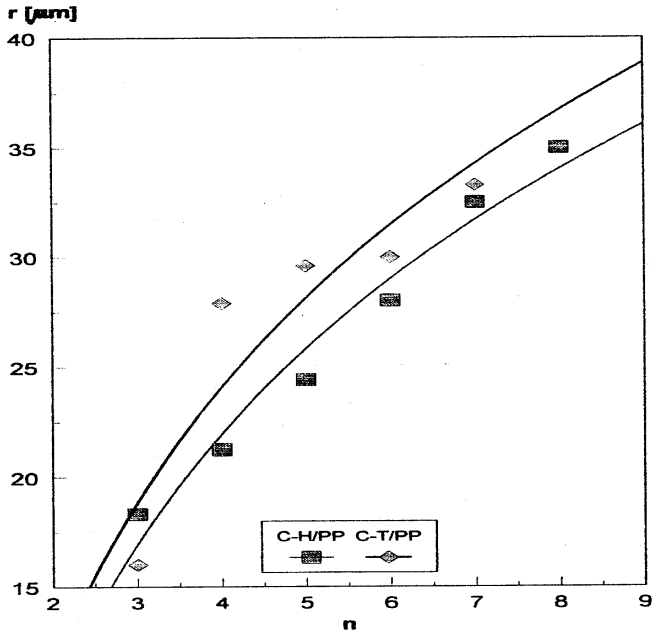

Fig. 5 Changes of the average radius with the topological class n
(final microstructure of the composites)

The analysis of the spherulites distribution by the area has shown that it is narrow for C-H/PP composites (*A* is in the range of 500-3000μm^2), while for C-T/PP composites it is wider (*A* is in the range of 500-4000 μm^2). The average value for *A* was calculated, and A_{av} = 2000μm^2 (see fig.6).

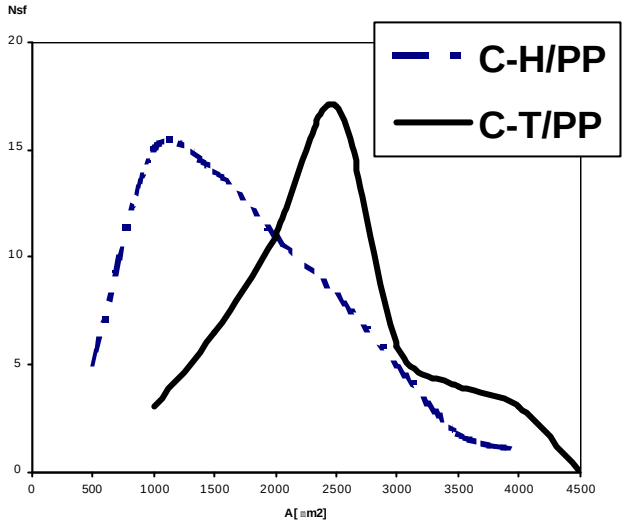

Fig. 6. Surface area distribution in the microstructure of composites

For C-H/PP composites most of the spherulites have A<2000μm^2 and for C-T/PP composites, most of the spherulites have A>2000 μm^2. All these parameters suggest that in C-H/PP composites, the spherulite network was siever, with higher spherulites density. Spherulites distribution by the grain sides number has shown that it is almost symmetric in the presence of both fibres, n was in the range of 3 to 7. The number of spherulites for n=5 is the same (22) in both composites (see fig.7). The shape factor, R_m was in the range of 0.6-0.9, and it differs with the topological class, n.

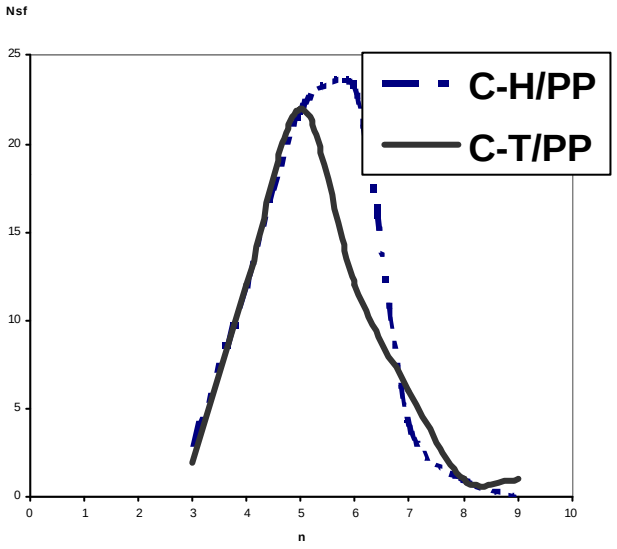

Fig.7. Grain sides distribution in macro-composites

iii) Microstructure correlation

Comparison of the characteristic microstructure parameters for model and macro composites has shown that the spherulites radius in model composites were up to 15 μm, while in real composites it was higher (up to 35 μm). Consequently, in model composites the spherulites surface area was lower, in the range of 200-400 μm^2, while in real composites it was up to 3500 μm^2. R_m was in the same range, for both model and real composites (0.6-0.9). Topological class, n was also in the same range for model and real composites, 4-7.

The upper comparison of microstructure parameters for both type of composites, model and real, has shown that the effect of H-carbon fibers was more evident, obviously due to the created interface.

Distribution of the microstructure parameters for model and real composites were analysed according to diffuse-interface filed method (fig.1,5,6,7). It should be pointed out that that experimentally obtained values and relations for normalised average grain area and radius versus topological class, *n* have shown linear dependence, which is in agreement with the theoretical background of this method (see fig. 8 and fig.9).

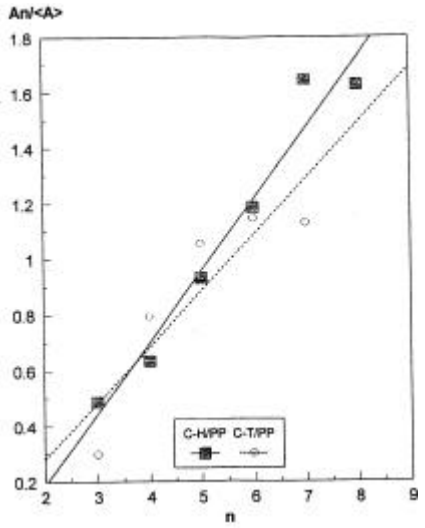

Fig. 8. Relationship between the normalised average grain area *An/<A>* and topological class *n* in the final microstructure of composites

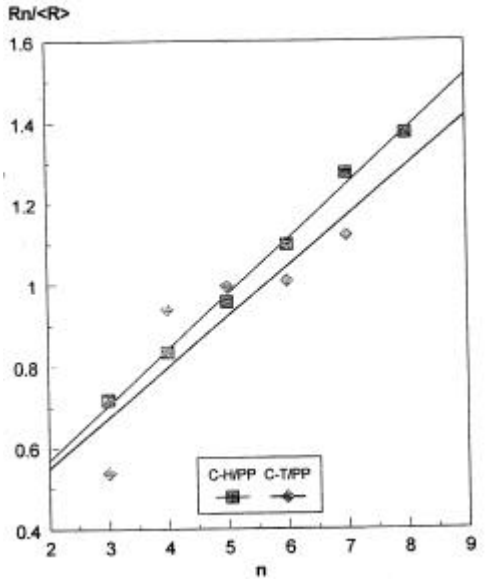

Fig.9. Relationship between the normalised average grain radius *Rn/<R>* and topological class *n* in the final microstructure of composites

Microstructure parameters obtained by the evaluation of the spherulites geometry and grain shape, fitted by the intercept method, are presented in table 3 and table 4. Higher values for the total grain boundary area per unit volume, S_v, was found for C-H composites.

Table 3. Microstructure parameters of spherulities geometry

Sample	P_l	N_l	L_3	D	S_v
PP	**11**	**10**	**0.09**	**0.13**	**22**

C-T/PP	**14**	**13**	**0.07**	**0.10**	**28**
C-H/PP	**18**	**17**	**0.07**	**0.08**	**36**

P_l - number of intersections per unit test line
N_l - number of grains per unit test line
L_3 - test line along base direction
D - average volume diameter of the grains
S_v - total grain boundary area per unit volume

Table 4. Grain shape analysis of the spherulities in the final microstructure of composites

Sample	n	R_m	K	e
w15 IPP	5.0	1.000	0.08	0.38
C-T/iPP	5.0	0.735	0.19	0.68
AltC-H/iPP	6.0	0.736	0.18	0.76

n – grain sides
R_m – grain shape factor
k – spherical aberration
e – spherical (ellipsoid) eccentricity

Due to the higher total grain boundary area per unit volume , S_v, obtained for C-H composites, higher degree of spherical elongation, e ($e_{C\text{-}H/iPP} = 0.76 > e_{C\text{-}T/iPP} = 0.68$) for this system was determined. The obtained results for this system have shown smaller spherulites surface and radius, but higher surface density, due to the better compatibility of C-H fibers with PP, which indicate on the siever spherulities network.
The results for microstructure evaluation confirmed the significance of the correlation between microstructure parameters and mechanical properties of the composites. Namely, the microstructure parameters determined for C-H/PP macro composites suggested better mechanical properties of the composites, which was experimentally confirmed by the measured mechanical properties of the composites: transverse tensile strength and modulus for this system were higher for 30% in comparison to C-T composites [12,13].

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