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Evaluation of the Influence of Glass Fibre Distribution in Polyamide Matrix During the Consolidation Process on the Mechanical Properties of GF/PA6 Composites

Abstract
This paper presents the relationship between the glass fibre arrangement in a polyamide 6 matrix during the consolidation process and the mechanical properties of GF/PA6 composites. Three specially designed hybrid yarns were used to produce the composites. The different structure of yarns and the different level of blending of the reinforcing and thermoplastic fibres in yarns give different conditions of fibre impregnation and of the matrix crystallisation process. The thermal conductivity and micro-thermomechanical behaviour of the polyamide matrix at selected places of the composite surface were studied by means of micro-thermal analysis. Differences in the supermolecular structure of the matrix described by μTMA influence the mechanical properties of the composites.

Key words: *glass fibres, textiles composites, mechanical properties, localised micro-thermal analysis μTMA.*

Introduction

Modification of the composite manufacturing process, consisting in utilising textile hybrid prepreg products made from commingled thermoplastic and reinforcing fibres, leads to an improvement in the mechanical properties of composites. The introduction of hybrid prepregs for the manufacturing of thermoplastic composites was based on the hypothesis that the close contact of reinforcing filaments with thermoplastic filaments subjected to the melting process would create impregnation conditions sufficient to guarantee the good wettability of reinforcement fibres by molten polymers. Consequently, an improvement in the mechanical properties of the composites was expected. A review of the literature indicates that many research activities were undertaken to elucidate issues arising during the commingling process of hybrid yarns [1 - 12]. Up to now little attention has been paid to explaining the physico-chemical phenomena that take place during the consolidation of the thermoplastic matrix of hybrid composites.

Let us consider the rule of mixture [13], according to which the composite strength during the unidirectional tension test depends on the matrix strength and reinforcing fibre strength. This relationship is shown by the following equation:

$$\sigma_c = \sigma_f V_f + \sigma_m(1-V_f) \qquad (1)$$

where:
σ_c – the tensile strength of the composite material,
σ_f – the tensile strength of the reinforcing fibres,
σ_m – the tensile strength of the matrix,
V_f – the volumetric contents (dimensionless fractional value) of reinforcing fibres,
$(1 - V_f)$ – the volumetric contents (dimensionless fractional value) of matrix.

The matrix strength depends on the matrix molecular structure (crystalline structure, the orientation of the amorphous regions), especially on the degree of crystallinity. The crystalline structure results from the thermodynamic conditions occurring in the whole reinforcement / molten polymer system during the consolidation process. The arrangement of reinforcing fibres in molten polymer depends on the structure of hybrid yarns used for the manufacturing of composites. It is possible that this structure has an influence on the conditions of heat exchange inside the system and, at the same time, affects the process of matrix crystallisation.

The approach presented results from the Ziabicki theory [14], according to which the degree of polymer crystallinity increases with a decrease in the difference between the temperature of the polymer and temperature of the surrounding medium. Based on this theory, the following hypothesis can be formulated: considering the glass fibre/polyamide 6 (GF/PA6) system, the degree of crystallinity of polyamide 6 decreases towards the surface of the glass fibre. This hypothesis is due to the fact that glass fibre has a lower coefficient of thermal conductivity than poliamide 6, and probably during crystallisation in the cooling process of glass fibre / polyamide 6 matrix composites, the glass fibre has a higher temperature than the surrounding polyamide matrix, and the heat can be transferred to the polyamide. In this situation, close to the glass fibre, a higher temperature gradient appeared then further away from the fibre.

Studies completed and presented by us earlier [15] showed that the thermal conductivity of the polyamide matrix in GF/PA6 composites depends on the distances between glass fibres. The shorter the distance between the fibres, the lower the thermal conductivity of the polyamide matrix is. Hypothetically, this could mean that the degree of crystallinity of the matrix could be lower when fibres in the composite are spaced closely together, and higher when the fibres are placed far from each other. The changes concern the degree of crystallinity both at some distance from the fibre and near the fibre surface.

The objective of this paper is to prove the formulated hypothesis concerning the influence of the structure of hybrid yarns based on glass fibres/polyamide 6 on the crystallinity of the matrix, and how the difference in crystallinity influences the mechanical properties of composites manufactured from designed hybrid yarns. In particular, during the course of the research, the influence of the distances between reinforcing fibres in hybrid prepregs on the supermolecular structure of the matrix was studied.

Materials

Fibres

As thermoplastic materials, both PA 6 multifilament and staple polyamide fibres, produced by "Stilon" Co. Gorzów Wielkopolski, Poland, were used. The PA 6 fibres were coated with an anti-electrostatic preparation.

The glass multifilament EC9, produced by Krośnieńskie Huty Szkła, Poland, was used as reinforcing fibres. The glass fibres

were sized with an aminosilane coupling agent and a dispersion of polyurethane resin, as published elsewhere [10]. Characteristics of the materials used are given in ***Table 1***.

Hybrid yarns

In order to investigate the influence of the structure of hybrid yarns of the GF/PA6 type on the crystallinity of the matrix and the resulting mechanical properties of the composites, the following yarns of different structure were manufactured: friction-spun yarns, twisted yarns and pneumatic textured yarns. The technologies chosen should guarantee diversification of the distances between reinforcing fibres during the process of manufacturing composites.

For comparative analysis the following hybrid yarns were manufactured:

- friction-spun yarns of a linear density of 135.0 tex, composed of glass multifilament of 68 tex, and PA 6 staple fibres; the mass content of the glass fibres was equal to 51.4 wt.%,
- twisted yarns of a linear density of 115.0 tex, composed of glass multifilament of 68 tex, and 2 × PA 6 multifilament yarns of a linear density of 26 tex; the number of twists was equal to 90 twists/m and the glass fibres were of 56.6 wt.%.,
- air textured yarns of a fineness of 119.0 tex, consisting of glass multifilament of 68 tex, 2× PA 6 multifilament yarns of a fineness of 26 tex, and glass fibres of 55.2 wt.%.

Composites

The composites were made using unidirectional oriented yarns on a hydraulic press with a water-cooling system and an additional system supplying nitrogen. The optimal thermal and pressure conditions, favourable for a good impregnation of reinforcing filaments by the molten polymer at low degradation of polyamide, were determined in a separate study [16]. The dried yarns wound on a metallic plate were pressed using the following conditions:

- a consolidation time of 15 min, the pressure during the consolidation was equal to 0.012 MPa, and the temperature was adjusted to 260 °C,
- the cooling time was equal to 15 min, the pressure during cooling was 0.012 MPa, and the temperature decreased to 20 °C.

Approximately 0.1 mm thick composites were made out of an equal amount of yarn.

Table 1. *Characteristics of test material.*

Fibre type	Yarn fineness, tex	Tensile strength ± s.d., cN/tex	Elongation ± s.d., %	Number of filaments	Filament fineness, dtex
EC9 glass multifilament	68	48.7 ± 6.08	2.12 ± 0.31	420	1.6
Polyamide 6 multifilament	26	41.2 ± 1.6	39.0 ± 1.69	192	1.3
Staple PA 6 fibres, 38 mm long	-	44.8 ± 13.89	68.5 ± 17.8	-	2.8

Table 2. *Distances between fibres in hybrid yarn composites.*

Composites made of	Sample number	Distance between fibres, µm		
		mean	minimal	maximal
friction spun yarn	1.	2.21	0.20	11.14
	2.	2.79	0.29	14.97
	3.	2.64	0.20	9.52
twisted yarn	1.	5.30	0.20	20.87
	2.	5.29	0.40	18.30
	3.	4.66	0.40	16.22
	4.	5.20	0.57	14.73
	5.	4.74	0.20	15.14
textured yarn	1.	7.00	0.40	31.27
	2.	6.68	0.45	28.29
	3.	5.30	0.45	16.06

The application of all three types of hybrid yarns in the manufacturing process of composites results in different interspace regions between reinforcing fibres in the composites obtained. The arrangement of the glass fibres in the cross-section of the composites was observed by means of an Olympus BX51 optical microscope, equipped with a colour video camera/ccd – Iris and PC computer . The distances between neighbouring fibres on the surface of all the composite cross-sections were manually estimated and measured by a Lucia Programme. The mean distances oscillated in the range of 2 to 7 µm, as shown in ***Table 2***. The data given comprises results of 100 single values for each fibre/matrix arrangement.

The shortest mean distance between glass fibres can be observed in friction spun yarn composite. There are visible concentrations of fibres in the core of friction spun yarns. In both twisted and textured yarn composites, the distances between fibres are longer. In twisted yarn composites the fibre arrangement is more uniform, and almost each fibre is coated by matrix. In textured yarn composites, glass fibres come into contact with each other very often, and the distances between them are different.

Methods

Microthermal analysis of the composites

Differences in the thermal conductivity and micro-thermomechanical behaviour[1)] of the polyamide matrix in composites manufactured from hybrid yarn of different structure were examined us-

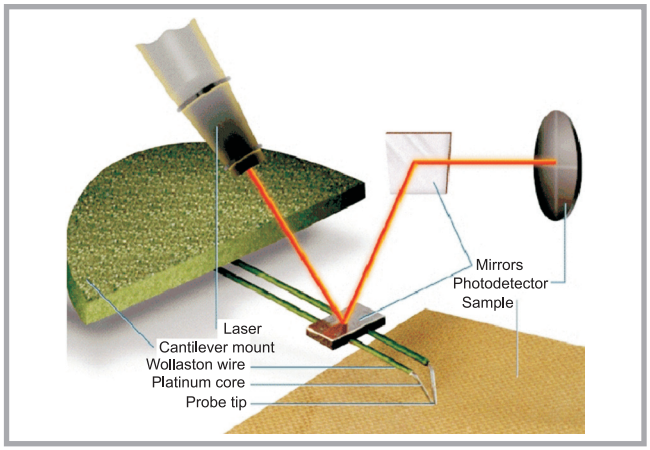

Figure 1. *Schemating designe of µ-TA™ 2990 (product folder of TA Instruments, Inc.).*

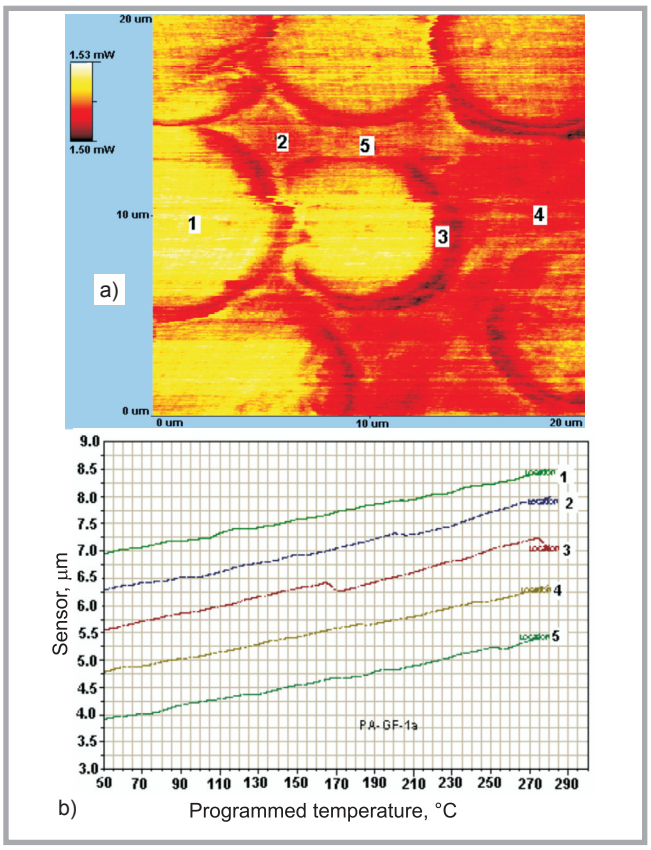

Figure 2. Localized micro-thermomechanical analysis of friction spun yarn GF/PA 6 composite (cf. description in [23]); a) thermal image, b) temperature-displacement curves.

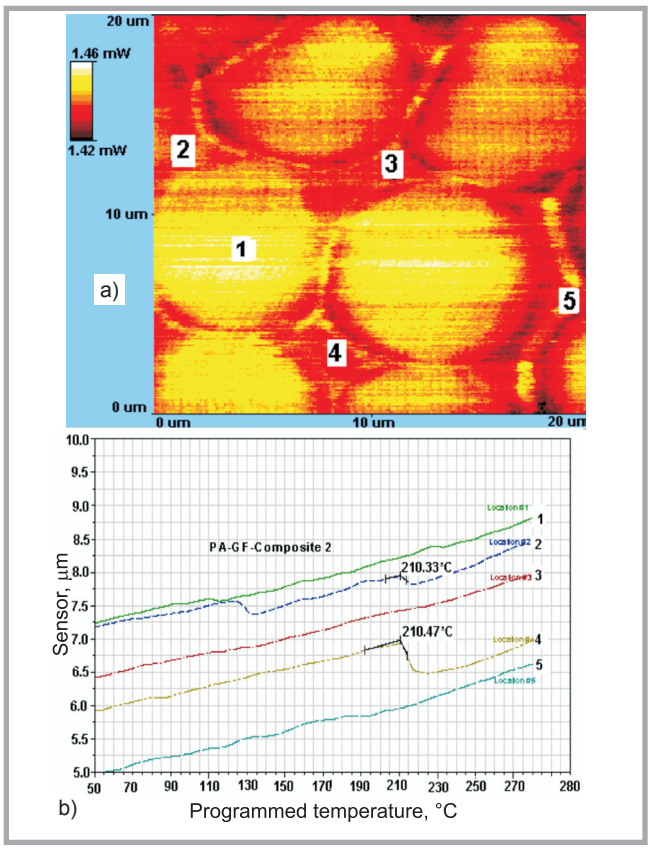

Figure 3. Localized micro- thermomechanical analysis of twisted yarn GF/PA 6 composite; a) thermal image, b) temperature-displacement curves.

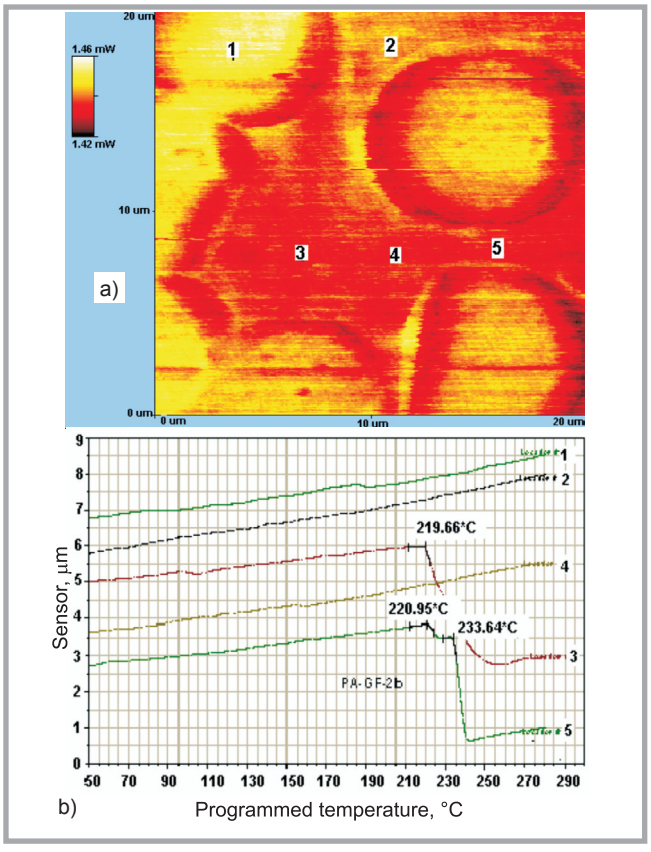

Figure 4. Localized micro- thermomechanical analysis of twisted yarn GF/PA 6 composite – another area of sample; a) thermal image, b) temperature-displacement curves.

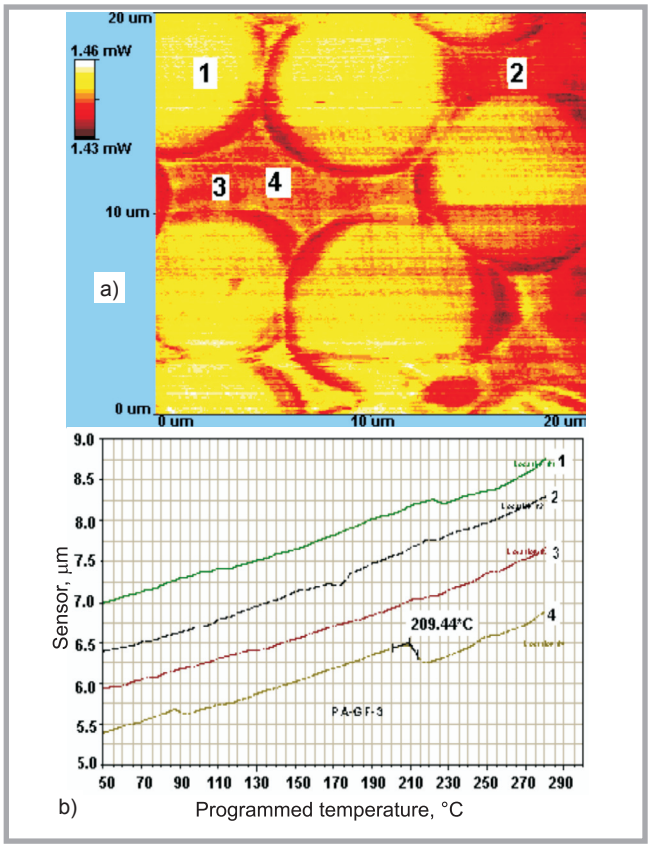

Figure 5. Localized micro- thermomechanical analysis of textured yarn GF/PA 6 composite; a) thermal image, b) temperature-displacement curves.

Table 3. Results of tensile tests for both hybrid yarns and composites manufactured from hybrid yarns.

Composite symbol	Tensile strength of hybrid yarn, cN/tex	Elongation of yarn, %	Ratio of tensile strength of hybrid yarn to tensile strength of reinforcing multifilament yarn	Tensile strength of composite σ_{tw}, MPa	Young's modulus E, GPa	Elongation of composite, mm
Friction	26.1	2.66	0.53	152.3	4.5	0.85
Twisted	I 27.0 II 17.9	2.0 33.7	0.55	400.3	12.5	0.73
Textured	I 16.3 II 16.0	2.2 26.6	0.33	348.0	7.2	1.24

ing a μ-TA™ 2990 Micro-Thermal Analyser (TA Instruments, Inc.) (***Figure 1,*** see page 82) [17 - 26]. During the scanning process, the probing tip measuring the heat flow is in direct contact with the sample surface, and the tip temperature value is constant. Changes in thermal conductivity across the material surface cause a different heat flow between the tip and sample.

Micro-thermal analysis measurements were performed on polished surfaces of the composite cross-sections. For this analysis the composite samples cross-sections should be polished perfectly. The samples were prepared in the following way. Small rectangular samples in the direction of the yarn axis were cut out from composite plates. Then the samples, which were of a thickness of 0.1 mm, were embedded in epoxy resin. This composite thickness was big enough in order that the boundary conditions did not play an important part in the results obtained for the regions studied (20 μm × 20 μm). The surface of the block obtained, which is perpendicular to the yarn axis, was polished with high precision by means of Phoenix Beta apparatus using successive polish media, for example paper, woven fabric and finally SiO_2/Al_2O_3 masterpolish of 50 nm grain size. The surface smoothness obtained was high, but not enough to make thermal conductivity images of the composites. Because of the big difference between the hardness of the composite components, the surface topography was non-uniform, and it was impossible to illustrate correctly the thermal conductivity changes of the matrix as a function of the distances between glass fibres. The quality of the surface polishing enabled to perform localised thermal analysis of selected matrix places using a new thermal technique: Micro-Thermomechanical Analysis (μTMA™). In this mode the vertical displacement of the cantilever tip as a function of the tip temperature is measured. The tip is heated in contact with the sample, and when the temperature is raised and the sample softens, a downward deflection of the cantilever is observed. Temperature-displacement (in the Figures: Programmed Temperature, °C – Sensor, μm) curves are obtained. In this method heat was provided by an ultra-miniature thermal probe, and the heating rate of the material surface was realised at a speed of 10 K/s. Heating was applied once for each place selected, which was within the range of 50 and 280 °C. As a result of localised micro-thermomechanical measurements, phase diagrams characterising the crystalline structure of the matrix were obtained.

Mechanical properties of the composites

To study the influence of the hybrid yarn structure on the mechanical properties of the composites, unidirectional tensile tests were performed with - an 'INSTRON' tensile tester series 4204 equipped with PC control. The first series of tests was to determine the mechanical properties of the hybrid yarns according to the standard [27].

The second series of tests were performed to determine the mechanical properties of the composite material according to the Standard ISO 527-4 [28] . Samples of 58 mm × 10 mm were cut from the model composites in the yarn direction. The gauge length was 20 mm, and the cross-head velocity was equal to 50 mm/min.

Results

Microthermal analysis of the composites

Application of localised Micro-Thermomechanical Analysis (μTMA™) to investigate heat processes generated locally on the surface of a composite cross-section allows to obtain displacement-temperature diagrams illustrating changes in the position of the heating tip in the investigated area as a function of the temperature of the small heated region. Any change in the position of the tip of the Micro-Thermal Analyser results from changes in the physical state of the material investigated, which takes place in the heated polymer. This analysis, performed at selected places with dimensions of several micrometers, allows to indirectly and compare the crystalline structure of composite matrix using the melting temperatures in relation to the distances between fibres. The places tested were chosen on the basis of the thermal images obtained in areas where the topography was rather uniform, because contact between the heating probe and the sample surface was required. ***Figures 2 - 5*** (see page 83) show the localised micro-thermomechanical analysis of each type of composite. These figures illustrate thermal images of selected regions of the sample together with places tested, which are marked with numbers (a), and a diagram illustrating phase changes in the matrix polymer at selected places (b).

The small sharp peaks, which are related to changes in the phase signal on the μTMA curves arising at melting temperatures of particular crystalline forms of polyamide 6, exhibit only the existence of these forms. If there is no change in the phase signal at a given temperature, the quantity of the corresponding crystalline form is too low, or this specific crystalline form does not exist in test composite.

The thermal image of a selected region of friction spun yarn composite (***Figure 2.a***) reveals very tightly packed fibres. In this composite distances between glass fibres are very short (about 2 μm, according to ***Table 2,*** see page 82). The curves (***Figure 2.b***) do not show any deviation from a linear plot. Thus, the cantilever tip is expected to touch the glass fibres tightly packed in the friction spun composite when a μTMA investigation is performed, or the quantity of crystalline forms of PA 6 is too low to be exhibited during micro-thermomechanical analysis.

For composites manufactured from twisted yarn, where the fibres are arranged uniformly and the distances between fibres are much longer than in friction-spun yarn composites, averaging about 5 μm,

the presence of two different peak positions on the temperature-displacement curves could be identified by μTMA investigation (***Figures 3.b, 4.b***). Temperature values of 220 °C and about 210 °C allowed to identify the existence of α and γ forms in the composite matrix. Similar results were obtained using DSC studies presented in paper [29].

In a composite manufactured from textured yarn, where distances between fibres are similar to distances in twisted yarns composites but their arrangement being less uniform, the existence of only the γ form in the composite matrix was observed. As ***Figure 5.b*** shows, a maximum displacement appeared only at a temperature of 210 °C, which corresponds to the γ form. A lack of signal changes in the phase diagram at the point where the temperature is 220 °C does not eliminate the presence of the α form. As mentioned above, the quantity of this form is probably too low to be identified.

In each position the existence of the crystalline forms of polyamide 6 were revealed at places far from the glass fibres. The farther the distance between the fibre and measurement location, the more stable the form observed was. For example, a high quantity of the α form was observed in areas where the fibres were placed at longer distances from each other. According to literature [30], composites of high quantity in this form should be characterised by a high tensile strength.

Mechanical properties of the composites

The results of investigations of the mechanical properties of hybrid yarns and respective composites are presented in ***Table 3***. The symbol "I" given in ***Table 3*** is related to the first break resulting from damage to more rigid fibres i.e. glass fibres in hybrid yarns, and the symbol "II" is related to the second peak, describing the break of polyamide fibres.

The results presented in ***Table 3*** indicate that the different conditions that occur during the manufacturing of hybrid yarns influence the mechanical properties of reinforcing and matrix fibres. However, it is impossible to determine the range of these changes for each component because a hybrid yarn constitutes an inseparable unity. Thus, to determe the level of utilisation of reinforcing fibres in the yarn, the ratio of the breaking strength of a hybrid yarn to the breaking strength of a reinforcing multifilament was calculated. The results presented in column four of ***Table 3*** shows that the value of this coefficient changes from 0.33 to 0.55. The lowest values occur for texturing technology and the highest for twisting and friction spinning techniques. For the last two techniques the values are 0.55 and 0.53, respectively.

Analysis of the results presented in column five and six shows that there is no direct relationship between the tenacity of hybrid yarns and the tensile strength of composites made out of these three types of yarns. The lowest value of tensile strength was achieved by the composite made from friction-spun yarn not from textured yarn. In the first case the tensile strength was equal to 348.0 MPa, whereas in the second case the tensile strength decreased to a value of 152.3 MPa. The highest value of tensile strength, equal to 400.3 MPa, was obtained for composites made from the strongest twisted yarn. The highest tensile strength of this yarn, a uniform arrangement of reinforcing fibres in the composite and an almost full coat of the reinforcing fibres by the polyamide matrix, cause that the twisted yarn composite is also characterised by the highest value of Young's modulus, with a value of 12.5 GPa.

Discussion

The results presented in ***Table 3*** indicate that the application of the hybrid yarns, characterised by a different structure and consisting of the same content of reinforcement fibres, had a great influence on the mechanical properties of resultant composites. The study of friction yarns and texturing yarns indicates that there is no simple proportional relationship between the mechanical properties of the hybrid yarns and the mechanical properties of composites manufactured out of these yarns. The mechanical properties of composites are dependent on both the tensile properties of the reinforcement fibres and on the properties of the matrix. The properties of the matrix can be varied during the solidification process and are influenced by the arrangement of fibres in the hybrid yarns.

The formation of polyamide 6 matrix of a different crystalline structure is connected with the existence of different thermal conditions in local fibre/matrix systems during the composite manufacturing process, especially during cooling. At a temperature of 260 °C the polyamide fibres melt within 15 min and their crystalline regions are destroyed by the heat delivered . During the next step, the cooling of the whole system to room temperature, the polymer alloy consolidates and a composite is formed. During this process, the glass fibres with a lower thermal conductivity than that of polyamide 6 maintain a higher temperature relatively longer than the matrix. This is the reason why the first crystal nuclei appear at some distance from the fibre surface, where the polymer temperature decreases to the value required for the commencing of nucleation. Approaching the fibre, the temperature gradient of the matrix rises, and according to Ziabicki's theory, the degree of crystallinity of the polymer matrix in such regions should be smaller than in regions of the matrix far away from fibres in the bulk matrix. This phenomenon was confirmed by tests, completed at various locations of the composite matrix both distant and close to the reinforcing fibres, using μTMA. A localised heating procedure allows to illustrate physical changes in the state of the matrix in relation to its supermolecular structure. If the quantity of particular crystalline forms was big enough to produce a change in the phase signal, a sharp peak would appear in the diagram, indicating the local melting point of this region.

In the case of friction spun yarn, where the composite is reinforced with fibres closely packed in the matrix, the existence of crystalline forms of polyamide could not be detected by μTMA. However, it is obvious that crystalline forms may exist. However, the μTA™ 2990 Micro-Thermal Analyser is unable to characterise regions of < 2 μm because of its tip geometry and boundary effect, as described in detail elsewhere [20]. Furthermore, there seem to be other influences of thermal conductivity.

Both in twisted and textured yarn composites, where reinforcing fibres are placed farther from each other than in friction-spun yarn composites, the γ crystalline form was found. A sharp peak was observed in the diagram at a temperature of 210 °C, corresponding to the melting point of this form. Moreover, in twisted yarn composites, besides the γ crystalline form, the α crystalline form was also detected. The results of local thermal analysis were confirmed by an analysis of the supermolecular structure completed by means of Differential Scanning Calorimetry (DSC) and Wide Angle X-ray Scattering (WAXS), as described in [31].

The results achieved by both methods confirmed that the degree of crystallinity

of matrix achieves the highest value in twisted yarn composites, where glass fibres are distributed evenly and distances between fibres are relatively longer then in textured and friction spun yarn composites. Additionally, the DSC analysis indicated the presence of two main crystalline forms, α and γ, in the composites investigated. The highest ratio of the α to γ form was found for the twisted yarn composite, the textured yarn composite having second highest, and friction yarn composite the lowest. The diversified supermolecular structure of matrix obtained for the composites investigated had an influence on the tensile properties of the test material.

Composites of friction spun yarn of compact structure with a weak intermixing of constituent fibres is a special example of that. In spite of a very high tensile strength of the yarn, with a value of 26.1 cN/tex , the friction spun yarn composite exhibited the lowest tensile strength among the three kinds of composites, with a value of 152.3 MPa. However, the supermolecular structure of the hybrid yarn composite matrix exhibited the lowest degree of crystallisation in comparison with other composite samples, which finally had a negative influence on the tensile strength of the composites. The textured yarn composite manufactured from the yarn with the lowest tensile strength had the relatively high tensile strength of 348.0 MPa. The matrix of this composite had a higher degree of crystallinity than that of the composite made of friction spun yarn. The twisted yarn composite with the highest matrix crystallinity and the biggest content of α phase in the matrix, made of the yarn with reinforcing fibres of the highest tensile strength, exhibited the highest tensile strength in the direction of the yarn axis.

Conclusions

The discussion presented allows to draw the following conclusions:

1. The architecture of continuous glass fibre distribution in polyamide matrix caused by the structure of hybrid yarns possesses a great influence on the mechanical properties of resultant composites.
2. Local thermo-mechanical analysis using the μTA ™ 2990 Micro-Thermal Analyser showed that the degree of crystallinity of polyamide matrix, depending on the architecture of the glass fibre distribution in the polyamide matrix, leads to different melting points. It was proven that in twisted yarn composites, where the fibres are distributed uniformly in the matrix and placed at relatively long distances from each other, the polyamide matrix is characterised by the highest degree of crystallinity and the highest content of the α crystalline phase. In the case of friction spun yarn composite reinforced with glass fibres, closely packed in matrix, the existence of a crystalline form of polyamide was not detected.
3. Among the composites obtained from the hybrid yarns parallelly placed, the twisted yarn composite is characterised by the highest tensile strength in the direction of the yarn axis, equal to 400.3 MPa. It results from the highest crystallinity of matrix, the highest content of the α crystalline phase in the matrix and the highest residual tensile strength of reinforcing fibres after the commingling process.
4. Among the hybrid yarns studied, the twisted yarn is the most suitable textile structure for manufacturing reinforced composites.

Editorial note

1) The notation 'micro-thermomechanical' is related to function of the Micro-Thermal Analyser apparatous and the measuring method performed by it, and not to the mechanical tensile strength testing of the samples by an Instron tensile tester.

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