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COMPOSITES THEORY AND PRACTICE

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STRUCTURE ANALYSIS OF HELICALLY WRAPPED COMPOSITE PRESSURE VESSELS

This paper investigates the structures of composite overwrapped pressure vessels (COPV) intended for use as storage tanks for compressed gas fuels in automobiles and other vehicles. The objective of this work was to establish the use of mosaic patterns arising during winding in the helical layers. In the authors' opinion, the optimal mosaic pattern considering the behavior of reinforcement tows under loading is the one designated as N_r1 in the matrix method. It exhibits the lowest number of crossovers, as well as their most orderly array - linear. Crossovers are considered as local distortion of a composite structure, which has a negative effect on the development of damage in the material. This statement is the result of previous studies performed by the authors, as well as papers by other researchers. In total, 9 different type 3 and type 4 vessels produced by filament winding were studied. The studies encompassed an analysis of the mosaic patterns in selected helical layers only. This work contains neither information on the thickness, sequence or winding angle in the helical layers, nor on the number of longitudinal or circumferential layers. The work presents non-standard methods for the assessment and designation of mosaic patterns. The mosaic patterns in the helical layers were designated in accordance to the matrix method. The patterns were compared to the N_r1 patterns, which are optimal because of the lowest number of crossovers. The results of the study point to a lack of good engineering practices in the usage of specific mosaic patterns in responsible high-pressure constructions. In the opinion of the authors, the only rationale for the use of specific mosaic patterns now in use by the industry is the visual effect and attractive, rhombic character of the pattern. Each vessel had a unique composite layer template . Among the analyzed vessels, only one N_r1 mosaic pattern was found. It was used in the layer laid down at the angle of 14°.

Keywords: **high-pressure composite vessels, filament winding method, winding architecture, mosaic-shaped patterns, mosaic patterns, diamond patterns, diamond-shaped patterns, triangular repeating mosaic, triangular-shaped mosaic patterns, matrix method, structures of winding composites, interweaving, tow undulations, crossovers, CNG, CH2**

ANALIZA STRUKTURY KRZYŻOWO NAWINIĘTYCH WARSTW W KOMPOZYTOWYCH ZBIORNIKACH WYSOKOCIŚNIENIOWYCH

W pracy badano struktury zbiorników kompozytowych z pełnym oplotem (ang.: COPV - Composite Overwrapped Pressure Vessels) przeznaczonych do magazynowania wysokosprężonych paliw gazowych w pojazdach. Celem badań było ustalenie stosowania architektur nawijania w warstwach krzyżowych. Według autorów, optymalna jest architektura oznaczana w metodzie tablicowej jako N_r1. Charakteryzuje się najmniejszą liczbą przeplotów i ich największym uporządkowaniem. Przeplot jest uważany za lokalne zaburzenie struktury. Wpływa on niekorzystnie na rozwój uszkodzeń w materiale. To stwierdzenie jest wynikiem wcześniejszych badań autorów oraz innych doniesień literaturowych. W sumie zbadano 9 sztuk różnych zbiorników typu 3 i 4 wytwarzanych metodą nawijania. Badania polegały na analizie architektur nawijania użytych jedynie w wybranych warstwach krzyżowych. W pracy nie ma informacji na temat grubości, sekwencji czy kątów nawijania w warstwach krzyżowych oraz o ilości zastosowanych warstw obwodowych i wzdłużnych. Zaprezentowano niestandardowe metody badań do oceny architektur nawijania. Architektury warstw krzyżowych oznaczano zgodnie z metodą tablicową. Wyznaczone architektury odnoszono do architektury N_r1 jako optymalnej ze względu na najmniejszą liczbę przeplotów. Wyniki przeprowadzonych badań świadczą o braku tendencji w stosowaniu konkretnej architektury nawijania. Każdy zbiornik charakteryzował się indywidualnym sposobem wykonywania warstw kompozytowych. W badanych zbiornikach znaleziono tylko jedną architekturę, określaną według metody tablicowej jako N_r1. Była ona użyta w warstwie wykonanej pod kątem 14°.

Słowa kluczowe: **kompozytowe zbiorniki wysokociśnieniowe, metoda nawijania, architektura nawijania, metoda tablicowa, struktura kompozytu nawijanego, przeploty, skrzyżowania wiązek, CNG, CH2**

INTRODUCTION

With increasing crude oil prices, it is becoming increasingly common to use highly-compressed gaseous fuels, such as natural gas and hydrogen (CNG and CH2, respectively), for consumption by vehicle engines. In those vehicles, the gaseous fuel is stored in light composite storage vessels. High-strength composite vessels are manufactured by wet filament winding. The process involves winding resin-impregnated tows of fibers onto a rotating liner, which serves as a kind of mold or mandrel (Fig. 1). The composite material thus obtained is composed of highly compacted, fiber tows that are interconnected and placed in layers according to a preplanned program. Many parameters are used to describe the winded structure, the foremost among them: tow width (tow composed of several roving strands), tow thickness, distance between parallel tows, layer count, winding angle in each layer etc. The important aspect in designing the composite vessel structure is the selection of a suitable mosaic pattern in the helical layers. The multitude of mosaic patterns is inherent to filament winding technology [1-3]. The choice of pattern is connected to the number and placement of fiber crossovers. The crossovers (fiber undulations) become the sites of stress concentration and fracture initiators. This is caused by local deviation of fiber axes from the original direction. In the vicinity of the crossovers, the differentiation of resin content and defects such as voids may also be seen. The crossover and its vicinity constitute a disturbance in the structure and may be considered a flaw, a defect, a fracture initiator, etc. Research works [1-5] confirm the described phenomenon. Previous research work by the team indicates the importance of the mosaic pattern influence on the initiation and propagation of cracks in the composite material [3, 4]. In deference to the matrix method, the cited works declare mosaic pattern N_r1 of the helical layer to be the most beneficial, as the one with the lowest number of crossovers in the unit cell of one winding lead length *s*. Figure 2 presents the scheme of an exemplar N_r1 mosaic pattern from matrix 11 [4, 5] with highlighted characteristic sites. In the matrix method, this pattern is labeled as 11/1, with 80 crossovers (see Table 2, vessels I, IV and VIII). The matrix number is connected to the number of tows in a mosaic pattern on the vessel circumference. For each matrix with a natural number, an N_r1 mosaic pattern exists[4, 5].

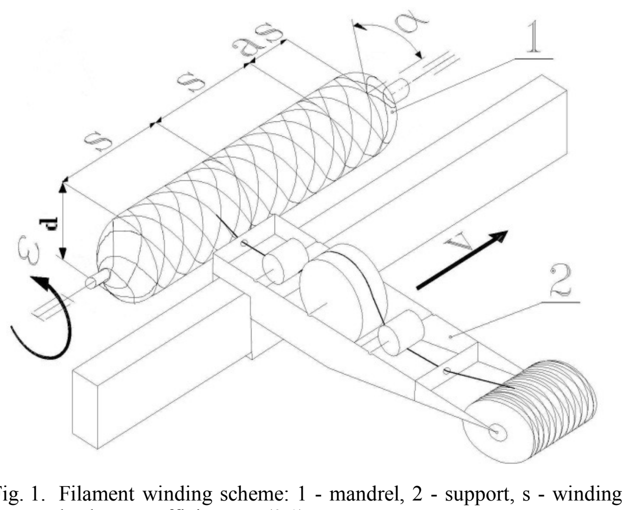

Fig. 1. Filament winding scheme: 1 - mandrel, 2 - support, s - winding lead, a - coefficient, a ϵ(0,1)

Rys. 1. Schemat nawijania: 1 - rdzeń, 2 - suport, s - skok nawijania, a - współczynnik, a ϵ(0,1)

Presented below are the results of a study of the structures of composite vessels for vehicle onboard highly-pressurized gaseous fuels storage. The most important goal of the study was to verify the application of mosaic structures in the helical layers of commercial composite vessels. In total, 9 different type-3 and type-4 composite overwrapped pressure vessels (COPV) were studied. The study included microscopic investigation of microsections in order to evaluate the void content, fiber and resin fraction. The fiber and resin fractions were also evaluated via calcination, and the density was determined via mass estimation.

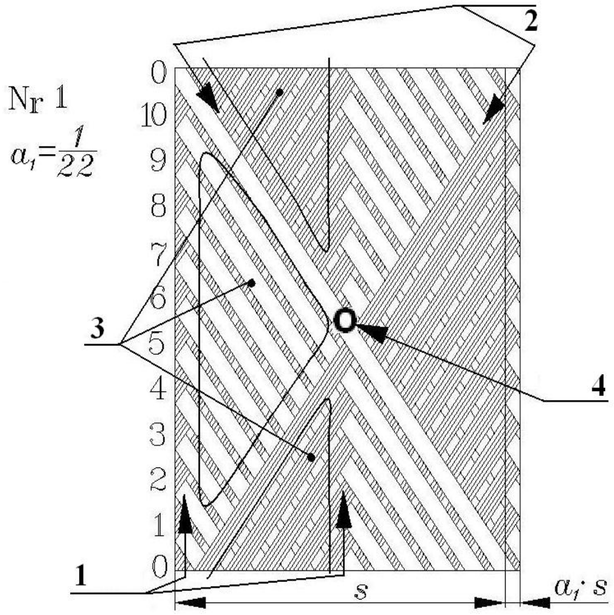

Fig. 2. N_r1 mosaic pattern scheme with characteristic areas: 1- crossover lines (circumferential band), 2 - fibre undulation line (helical band), 3 - areas without crossovers (undulations), 4 - central point, s - winding lead, a_1 - coefficient

Rys. 2. Schemat wzoru mozaikowego N_r1 z zaznaczonymi miejscami charakterystycznymi: 1 - linie przeplotów, 2 - linie uskoku, 3 - obszary bez przeplotów, 4 - punkt centralny, s - skok nawijania, a_1 - współczynnik

TESTING METHODS AND SAMPLE DESCRIPTION

High-pressure composite type-3 and type-4 vessels intended for vehicle onboard storage of compressed methane and hydrogen at between 200 and 700 bar pressure, with carbon-fiber or hybrid reinforcement, constituted the objects of the study. All of the vessels exhibited a layered wall structure. Layers without mosaic patterns, e.g. circumferential, were excluded from the analysis. Table 1 provides information on the operational parameters of the vessels - energy storage capacity per unit mass (P_BV/W), which testifies to a high class of objects and their composite overwrap. The P_BV/W coefficients correlate neither to the division between type 3 and type 4 cylinders, nor to the intended working pressures. According to this criterion, the vessels are comparable.

TABLE 1. **Collation of energy storage capacity per unit mass. P_B - burst pressure, V - capacity (volume), W - unit mass**

TABELA 1. **Zestawienie tzw. pojemności przechowywanej energii na jednostkę masy, P_B - ciśnienie niszczące, V - objętość, W - masa zbiornika**

Vessel	P_BV/W [MPa·l/kg]
A	108
B	110
C	124
D	132
E	139
F	149
G	154
H	173
I	179

MICROSCOPIC EXAMINATION

The mosaic patterns were imaged under a microscope at 50x magnification, and the obtained images were used to determine the fiber and resin fractions, and the void content. An occurrence with a detrimental effect in the wet winding process is the introduction of a large number of voids into the material. These voids are considered to be material defects. Their number may be constrained by careful choice of the impregnating system, the use of special additives and other technological means, but voids will exist nonetheless. In microsections, the voids (dark regions) were discerned as a different phase by SAO quantitative image analysis software. Evaluation of the component fractions in the composite material was performed in the helical layers because in comparison to the circumferential and longitudinal layers, the epoxy resin fraction and void content in the helical layers should be different. The percentage of void content was compared to the scale given by Purslow [6-8]. The samples exhibited inordinate porosity, with void content in the range of 4 up to 10%, which according to Purslow's classification qualifies as mediocre (< 5%) and poor (> 5%) [7]. Purslow's classification pertains only to the porosity, and not to the parameters connected to the strength or safety of exploitation of vessels for CNG and CH2 storage. As far as the authors know, there is no standard pertaining to composite high-pressure vessels for the storage of highly-compressed gaseous fuels, which would include the methodology for determining the structural wall porosity. Based on the microscopic images, the resin and fiber fractions in individual layers were also established. The evaluation of microsections (and their images) of the composites with carbon fibers constituted some difficulty. Therefore, the fiber diameter was estimated and the contrasting circles were hand-added to the processed image as exemplified in the upper left corner of the image in Figure 3. The results were compared to those from other, described below, methods. The results obtained for the same vessels were concurrent.

Fig. 3. Window of SAO software for determining composite material component fractions. In upper left corner of processed picture, effect of manual carbon fiber marking is presented. Magnification 500x

Rys. 3. Widok okna programu SAO do określania udziałów składników materiału kompozytowego. W lewym górnym rogu obrabianego zdjęcia przedstawiono efekt ręcznego zaznaczania włókien węglowych. Powiększenie 500x

SAMPLE PREPARATION FOR MATERIAL COMPONENTS FRACTION DETERMINATION

The components fraction was determined two-fold: according to a standard [9] for calcination, and through density determination by the estimation of mass. Because of carbon fiber reinforcement and concerns regarding possible destruction of the fiber in the calcination method, calcination at a lower temperature, ca. 400°C, was attempted. Due to the long time of calcination at such a low temperature, the authors decided to perform calcination true to the standard [9]. No carbon fiber destruction was noted at 625°C. Calcination was performed in two stages. In the first one, the crucible containing the specimen was heated using a burner up to the ignition temperature of the resin. After self-extinguishing, the crucible and its content was moved to a muffle furnace pre-heated to 625°C, and heated there until a stable mass was reached. The time the specimen spent in the furnace depended on the size of the specimen, on average ca. 2.5 hours. Examples of the specimens after calcination are presented in Figure 4.

Fig. 4. Examples of specimens with carbon and glass (hybrid) fibers after calcination

Rys. 4. Widok przykładowych próbek materiału kompozytowego wzmocnionego włóknem węglowym i szklanym (próbka hybrydowa) po kalcynowaniu

After the described procedure, the component fractions were determined. The fiber volume fraction in the composite materials tested in the study fell in the range of 51 to 68%. In the hybrid vessels, the thickness of glass and carbon layers was measured. Based on this proportion, the fractions of carbon and glass-fiber were established.

DETERMINATION OF MOSAIC PATTERNS

The mosaic patterns were determined according to the matrix method [4-6]. To this end, the results of the microscopic investigation and the residual material after calcination were analyzed. Taking into consideration such data as tow width, placement angle, vessel circumference, etc., the probable site of occurrence was determined for characteristic features of the particular mosaic pattern. From this site, samples 100x100 mm, or larger if deemed necessary, were taken. The samples were then subjected to calcination according to the already described method. In order to obtain better and faster resin burn-out, as well as better positioning of the characteristic regions of mosaic patterns, 3 mm holes were drilled in the specimens. Figure 5 presents a view of an exemplar sample after the first stage of calcination. After the burn-out, consecutive fiber tows were peeled away. The process was documented with photographs. Characteristic sites in the structure were noted and compared to the drawings in a catalogue of mosaic patterns included in the appendix to [10]. Table 2 presents the mosaic patterns, labeled according to matrix method prescriptions, i.e. matrix number / mosaic pattern number (T/N_r). Matrix number T means the number of tows on the circumference of the cylindrical part of the vessel, and mosaic number N_r means the shift of consecutive tows necessary for filling-in the circumference of the cylindrical part of the vessel. Figure 2 presents the N_r1 mosaic pattern from the T11 matrix - 11/1 (11 divisions of vessel circumference, the tow is shifted by 1). Table 2 also presents the number of crossovers counted on the area of the pattern - a rectangle with the dimensions of s - the winding lead and πd - the circumference of the cylindrical section of the vessel. The number of crossovers may also be calculated from the equation: $L_p = 8\ N_p\ (T-N_p)$ - a product of an octupled pattern number N_p (from the series arranged according to a rising number of crossovers) and a matrix number minus the pattern number arranged according to the number of crossovers. $N_p = T/N_r$, N_p **N** - pattern number from the sequence arranged according to the crossover number - N_p belongs to the set of natural numbers. Table 2 gives values for N_p for the patterns found in the study. Mosaic patterns 27/11, 44/7, 28/11, and 53/15 are exceptional cases for which N_p is calculated by a different method - more unequivocal, but also more complicated, which was presented in [10]. The maximum value of N_p may be calculated from the equation: $N_{p\ max} = T/2$. Comparing N_p to $N_{p\ max}$, an implication arises indicating that in commercial vessels mosaic patterns with pleasant patterns of rhombi are used, and they arise at a low N_r number, but the N_r1 pattern is not used. In the last column of Table 2, the number of crossovers in the N_r1 pattern from the same matrix is presented. Comparing the column presenting the number of crossovers in the actual pattern used by the vessel manufacturer to the number of crossovers for the obtainable N_r1 pattern, one may see a significant difference. There is a great potential for reducing the crossover (undulation, i.e. material defect) number through application of the N_r1 pattern.

TABLE 2. **Observed mosaic patterns determined according to matrix method. Number of crossovers (undulations) occurring in area of winding lead s related to number of crossovers in *N_r1* mosaic patterns is presented**

TABELA 2. **Zaobserwowane wzory mozaikowe oznaczone zgodnie z zasadami metody tablicowej. Przedstawiono także ilości występujących przeplotów w obszarze skoku nawijania w odniesieniu do liczby przeplotów wzoru mozaikowego *N_r1***

Vessel	Mosaic patterns found (matrix/ mosaic pattern number)	Number of pattern in sequence according to number of crossovers	Number of crossovers	Number of crossovers for N_r1
I	11 / 4	3	192	80
	19 / 9	2	772	144
	29 / 4	7	1232	224
	31 / 15	2	464	240
II	15 / 4	4	352	112
	26 / 5	5	840	200
	34 / 5	7	1512	264
	39 / 10	4	1120	304
III	14 / 1	1	104	104
	23 / 4	6	816	176
	25 / 6	4	672	192
	26 / 5	5	840	200
	27 / 11	**5**	880	208
IV	11 / 5	2	144	80
	25 / 8	3	528	192
	37 / 9	4	1056	288
	41 / 8	5	1440	320
V	44 / 9	5	1560	344
VI	44 / 7	**19**	3800	344
VII	7 / 3	2	80	48
	28 / 11	**5**	920	216
	35 / 12	3	768	272
	45 / 11	4	1312	352
	51 / 13	4	1504	400
VIII	11 / 5	2	144	80
	33 / 16	2	496	256
	39 / 10	4	1120	304
	49 / 12	4	1440	384
	53 / 15	**7**	2576	416
IX	25 / 6	4	672	192
	29 / 6	5	960	224
	33 / 8	4	928	256

Fig. 5. Exemplary sample after first stage of calcination

Rys.5. Widok przykładowej próbki po pierwszym etapie kalcynowania

CONCLUSIONS

1. The goal of the presented method of analysis was to verify whether there is any tendency to use specific mosaic patterns, or principles of overwrap preparation based on the number and placement of fiber crossovers in composite high-pressure vessels. The results of the analysis bear witness to the lack of any directed selection of a particular mosaic pattern. Each vessel exhibits unique mosaic patterns in the helical layers.
2. As mentioned in the introduction, crossovers (undulations) constitute a defect in a wound composite material for high-pressure vessels. In the analyzed vessels, only one helical layer exhibiting the pattern with the smallest number of crossovers, labeled N_r1 according to matrix method, was found. It was present in a layer wound with low angle, ca. 14°. Probably the motive for this pattern was something other than minimizing the number of undulations.
3. There is a possibility to considerably reduce the number of undulations, which is the same as reducing of the number of material defects in the wound composite, through application of the N_r1 pattern. This may lead to improved fatigue strength of high-pressure composite vessels.
4. In commercial vessels, pleasant mosaic patterns with a nice array of rhombi, which arise at a low N_p number, are used. This is evidenced by comparing number N_p, collated in Table 2, with values for $N_{p\ max}$ - the maximum value for N_p may be determined from the equation: $N_{p\ max} = T/2$. The authors believe that the criterion of an attractive appearance is the deciding factor in mosaic pattern selection for high-pressure vessels.
5. It was possible to remove the resin from all of the samples. The drilling of the samples proved to be an advantageous idea. Just after the first stage of calcination performed on the burner, it was already possible to analyze the mosaic patterns in the composite material. The second stage of calcination, performed at 625°C, did not lead to any significant degradation of the carbon fibers, as evidenced by the lack of mass loss at the final stage of heating.
6. Comparison of the fiber fractions in different samples taken did not lead to any interesting results. The samples exhibited considerable void content, from 4 even up to 10%, which qualifies as mediocre and poor in Purslow's classification. Purslow's classification, or any other similar one is not used by the standards pertaining to CH2 and CNG storage vessels. The fiber fraction in the structure consistently fell in the range of 51 to 68%. Through the application of mosaic pattern N_r1, a reduction in void content and number of resin pockets in the undulation regions may be expected, as well as a reduction in the overall wall thickness by ca. 1%. This would lead to obtaining a composite material with a higher fiber volume fraction.

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