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COMPOSITES THEORY AND PRACTICE

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MANUFACTURING ASPECTS OF THERMOPLASTIC SINGLE POLYESTER COMPOSITES BY FILM-STACKING METHOD

This paper presents the basic problems associated with the production of single polymer composite materials. The author has characterized the production of these materials and discussed the results of studies on the problems associated with manufacturing composites, that is the influence of the structure of the polymer material on the effect of moulding, as well as additives and the type of reinforcement fibres on its physical and chemical properties. The parameters of manufacturing single polymer polyester composites by the film-stacking method were determined empirically.

Keywords: **composite, single polymer composites, manufacturing, film-stacking method, thermoplastic polyester**

WYTWARZANIE TERMOPLASTYCZNYCH JEDNOPOLIMEROWYCH KOMPOZYTÓW POLIESTROWYCH METODĄ PRASOWANIA FOLII

Przedstawiono najważniejsze problemy związane z wytwarzaniem jednopolimerowych materiałów kompozytowych. Scharakteryzowano proces wytwarzania tych materiałów. Opisano wyniki badań dotyczące zagadnień związanych z wytwarzaniem kompozytów, czyli wpływ struktury materiału polimerowego na efekt formowania, dodatków i rodzaju włókien wzmacniających na jego właściwości fizykochemiczne. Zaprezentowano również wytwarzanie metodą prasowania folii. Określono w sposób empiryczny parametry procesu wytwarzania jednopolimerowych kompozytów poliestrowych „metodą film-stacking".

Słowa kluczowe: **kompozyt, kompozyty jednopolimerowe, wytwarzanie, metoda prasowania folii, poliestry termoplastyczne**

INTRODUCTION

Composites have been used since the initial period of development of our civilization, but the mass production of composites with a polymer matrix only started in the second half of the 20th century. The dynamic growth of the production of such composites has been mainly due to the development of polymer manufacturing and processing technologies, as well as the huge increase in demand for materials of this type in many areas of life [1-8].

Polymer-matrix composites are essential in the production of wind turbines. The shipbuilding industry uses them for boat hulls, superstructures and fuel tanks. These materials, mainly polyester-glass composites, are also used in boatbuilding and the machine industry [1-6].

Due to the increasing use of polymer matrix composites and stricter environmental policy in the European Union, the recycling of composite materials has become an important issue. Unfortunately, not all polymer materials are easily recycled. Theoretically, thermoplastic materials can be plasticized and solidified an infinite number of times, hence recycling thermoplastic composite material is easier than thermosetting matrix composites, even if thermoplastic remeltingdegrades their physical and chemical properties [2-3, 5-6]. The presence of additives or inclusions, such as glass fibers, limits further applications of the recyclate. In this connection, there is a demand for materials which at least consist of compatible polymer materials [1-7].

Attempts to satisfy this requirement have been made by developing single polymer composites (SPCs), in which both the matrix and reinforcement are made of the same or similar polymer material, where the components may differ from each other in molar mass, density and degree of branching [1-7, 9-11]. Unlike traditional heterogeneous composite materials, one advantage of SPCs is the similarity of the chemical properties of the matrix and reinforcement, which differ mainly in their mechanical and thermal properties. They do not require separation during recycling, which greatly simplifies the process and reduces the associated environmental impact. On the other hand, one of the main problems in the production of SPCs is the narrow temperature window [1-7, 9-11]. These authors have for several years investigated the issues under consideration, which are currently the subject of research at the Department of Polymer Materials, West Pomeranian University of Technology in Szczecin.

The aim of this study is to describe the results of research on issues related to SPCs production, particularly by the film-stacking method, for which the manufacturing process parameters were determined empirically.

MANUFACTURING SINGLE POLYMER COMPOSITES

The preparation of SPCs is related to the morphology, i.e. the related properties of polymers, in particular their characteristic temperatures, such as melt temperature and mould temperature. The temperature of transition of polymers to other states (from rigid to viscoelastic and others) depends on the degree of polymer crystallization (linear polymer), and on molecular weight. The higher the degrees of crystallinity and cross-linking of polymers, the higher the temperatures are at which the Young's modulus sharply drops, which proves that highly crystalline polymers have a higher heat resistance [1-7].

Semi-crystalline materials always contain variously sized areas of regular arrangement of the macromolecules - crystallites - which affect the melt temperature (T_m). For this reason, in reference to such materials we use the term melt temperature range. The crystallite melting temperature range is used in the process of making SPC tapes from fibers with a high content of reinforcement phase. The process consists in melting the outer layer of the fibres and hot pressing. Another inherent characteristic of semi-crystalline polymers is their strong tendency to crystallize during modification. Modifying semi-crystalline materials changes the degree of crystallinity, and consequently its melt temperature also changes. This phenomenon is used in SPCs, where the matrix material has a lower T_m than the T_m of the polymer to be used as the reinforcement phase. By taking such an approach, we can prepare SPCs whose properties are similar to conventional glass fiber reinforced composites [1-7, 12-14].

Due to the variety of factors affecting the morphology of the polymer material, there are at present two main groups of diverse technologies of manufacturing SPCs [1, 3-7, 15]:
- indirect (ex situ) methods
- direct (in situ) methods.

Ex situ methods require many preparatory operations to produce the final composite. They include making reinforcement elements in the form of fibres, preparing their surfaces to assure proper connection with the matrix and appropriate fibre orientation. Failure to ensure a good surface area for fiber-matrix contact (chemical or mechanical damage) will weaken the composite strength. The basic difficulty in SPC manufacturing by ex situ methods is proper binding of the reinforcement with the matrix, while maintaining the mechanical strength of the reinforcement. The main reinforcing component in SPCs are fibers, including micro- and nanofibers, tapes and different textile assemblies made of material chemically the same as the matrix [1, 3-7, 15].

The preparation of a proper surface for matrix-reinforcement contact is not required in direct or in situ methods because the two phases precipitate simultaneously in the crystallization process, settling their chemical composition, coherence and consequently composite strength. Selecting the appropriate method depends on several factors: the intended working conditions of the composite, type of materials used, properties of these materials as well as the technical and financial capacities of the manufacturer [1-7, 9-18].

SINGLE POLYMER COMPOSITES WITH POLYESTER MATRIX

Hine and Ward [12] describe a method of manufacturing sheets by hot compaction of polyethylene terephthalate (PET) fibres. Tests of various processing parameters showed that the most important parameters were the temperature and time of compaction. Molecular weight measurement by means of intrinsic viscosity showed that fast hydrolytic degradation occurred rapidly at temperatures required for effective compaction, leading to embrittlement of the resulting materials with an increasing dwell time. The optimum manufacturing time is about two minutes, sufficient to melt enough of the material to enable binding of the composite, while the molecular weight changes slightly. The authors have used various methods, including mechanical tests, DSC (differential scanning calorimetry) and SEM (scanning electron microscopy), to evaluate the mechanical properties and morphology of the produced sheets. The results of these tests confirmed that the composite combined the properties of both components, that is originally oriented fibers and a recrystallized matrix.

Rojanapitayakorn et al. [13] made a single polymer PET composite by compacting arranged PET fibers under pressure and at a temperature slightly below their melting point. The tests showed an increase in the crystallinity of the original white fibre bundles and a simultaneous increase in their optical translucency after moulding. They investigated the crystalline orientation by Herman's orientation parameter from the WAXD data. It was found that there was no significant loss of orientation of the crystalline phase during pressing. The mechanical characteristics showed that increasing the compaction temperature causes a reduction in Young's modulus and increases the tensile strength. Along with that change, the material lost its optical transparency and theamorphous phase distribution changed, which was determined by means of SEM. The amorphous phase orientation rather than that of the crystalline phase had a greater effect on the mechanical properties of SPC-PET. Impact resistance tests using the Charpy test method showed a decline in the impact resistance as the process temperature was increased.

Zhang et al. [14] presented the production of an all-PET composite by the film-stacking method, prepared by proper positioning of PET tapes and copolymer PET (co-PET) films. The temperature window was determined through a number of tests (including DSC) for tapes and films. The tensile strength of PET tapes, co-PET films and PET-SPCs were compared with commercial co-extruded PP tapes. That work also identified the effects of temperature and process pressure on the tensile strength. Those studies were aimed at optimizing the processing parameters while maintaining good interfacial adhesion.

Duhovic et al. [18] using the experience gained in the development of polymer composites reinforced with nanofibres attempted to make a PET matrix/PET nanofibre composite. For this purpose, PET nanofibres were placed between PET films having a lower melt temperature than that of the nanofibres and pressed at 120°C. Improved tensile strength and Young's modulus were observed in the composites compared to the matrix material alone.

J.C. Chen et al. [17] made a PET composite using a modified film pressing method. The reinforcement was composed of high strength PET yarn, and the matrix material was biodegradable polyester with a low melting point. The difference in the melting point of both components was about 56°C. The study included tests of sheets made at various consolidation temperatures (215, 225 and 235°C) and at a constant holding time (6.5 min), and at different holding times (3, 6.5, and 10 min), but at a constant consolidation temperature of 225°C. Analysis of the test results shows substantial improvement of the mechanical properties of the composite compared to the matrix material.

Donggang Yao et al. [16] investigated composites obtained from highly crystalline fibres and amorphous PET films. By using materials with much different melt temperatures, they managed to broaden the temperature window. The composite was made at 180°C in 90 seconds, at a pressure of about 0.7 MPa. In addition, the investigation showed that when the heating rate is decreased, the quality of fibre-matrix binding substantially deteriorates.

EXPERIMENTAL PROCEDURE

Materials

The materials were produced by film-stacking on a test bench at the Faculty of Mechanical Engineering and Mechatronics, West Pomeranian University of Technology in Szczecin.

Single polymer polyester composites were made as follows:

- reinforcement phase: stretched polyester fiber with enhanced strength and low shrinkage, purchased from the Polish company TORLEN,
- matrix material: glycol-modified polyethylene terephthalate (PET-G) film 0.5 mm thick, from VIVAK. The composite plates made for testing had the dimensions: 150x100x1 mm, ordered and disordered reinforcement fibres differing in weight: 5, 10, 15 and 20%.

Film-stacking method of manufacturing single polymer composite materials

One of the oldest ex situ methods of making SPC was initiated by Capiati and Porter [3]. The advantages of this method include relatively easy selection of the matrix and reinforcement materials made of the same type of polymer, low production costs, possibility of using reinforcing components in various forms: fibre, tape, yarn or fabric.

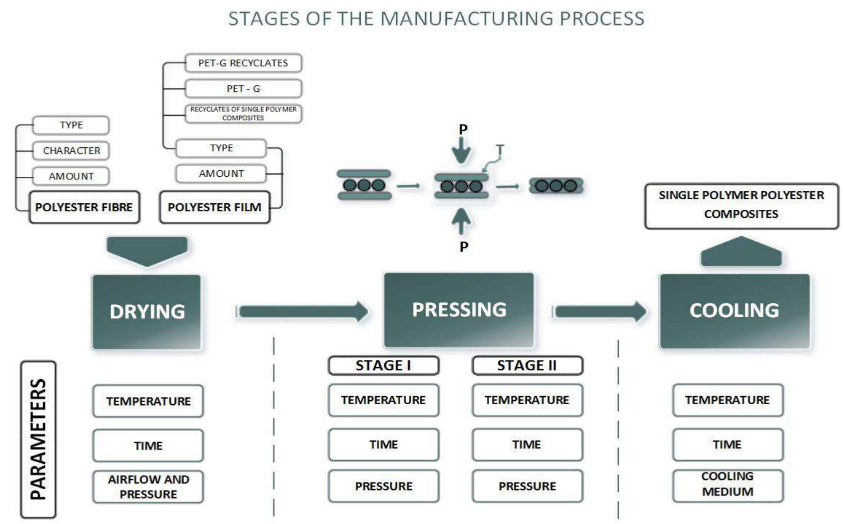

Fig. 1. Stages of single polymer polyester composite manufacturing [2]

Rys. 1. Etapy otrzymywania jednopolimerowych kompozytów poliestrowych

This method can make use of many polymer materials to produce composites [1-7]. The reinforcement phase component is laid between two films made of the same polymer as the reinforcement, but having a lower melt temperature. The thus prepared material is hot pressed under conditions allowing plasticizing of the film without melting the reinforcement phase. The pressure must be sufficiently high for the melted matrix polymer to completely fill the free spaces between the polyester fibres. In addition, in order to avoid degrading the reinforcing fibre properties, the time of heating and cooling should be appropriately short [1-7].

The composite production process consisted of the following technological stages (Fig. 1): preparation of reinforcement and matrix phases, drying, pressing (two stages), cooling, removal of the product from the mould and finishing.

SUMMARY

In practice, the process parameters for making single polymer polyester composites are set by the trial and error method because we still do not have a complete mathematical description of the relationships between the different variables of the process, which prevents the use of classical optimization methods [19]. The author's work focuses on the process of manufacturing SPC composed of PET-G polyester films and reinforced with high strength PET fibres. The composites were prepared as shown in Figure 1, using the film-stacking method. The manufacturing process was implemented on a Collin P 200 E hydraulic press.

Relatively simple devices are required to make single polymer polyester composites by film-stacking, but the process of moulding these materials is physically complex. To obtain a composite with an optimized number of defects requires the necessary know-how, including the characteristic temperatures.

Therefore, during the moulding process the following requirements should be borne in mind:

- The reinforcement phase of the polymeric material used in the form of fibres should have a homogeneous structure, uniform weave, and a higher degree of crystallinity than the matrix material (Fig. 2a).
- The matrix phase polymer used in the form of a film or plate should have a homogeneous structure and thickness (Fig. 2b).

Uniform distribution of the reinforcement phase in the mould should be maintained in the process and the final product.

No moisture in the materials to be processed; moisture in the polymeric material may result in destruction or degradation by water during the moulding process; besides, moisture causes defects in single polymer composites - local delamination (Fig. 3a) local or porosity (Fig. 3b). The process parameters of vacuum drying, i.e. temperature and time depend directly on the polymer material used.

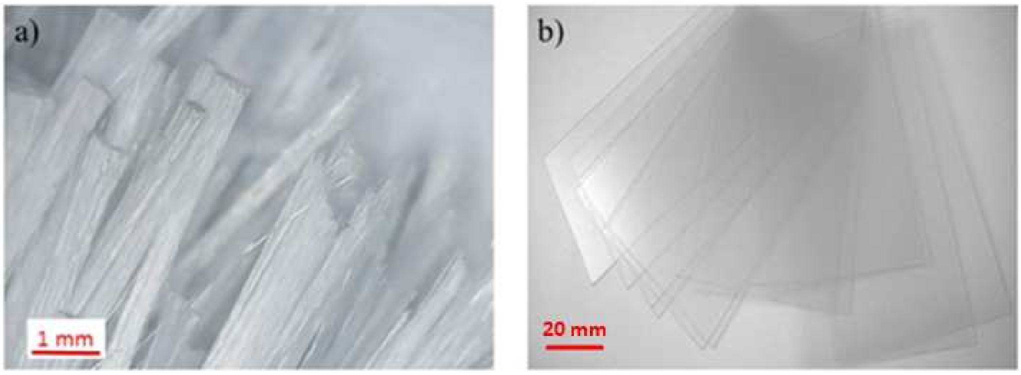

Fig. 2. Components used for a single-polymer composite material: a) reinforcement; b) matrix

Rys. 2. Komponenty zastosowane do jednopolimerowego materiału kompozytowego: a) materiał umocnienia, b) materiał osnowy

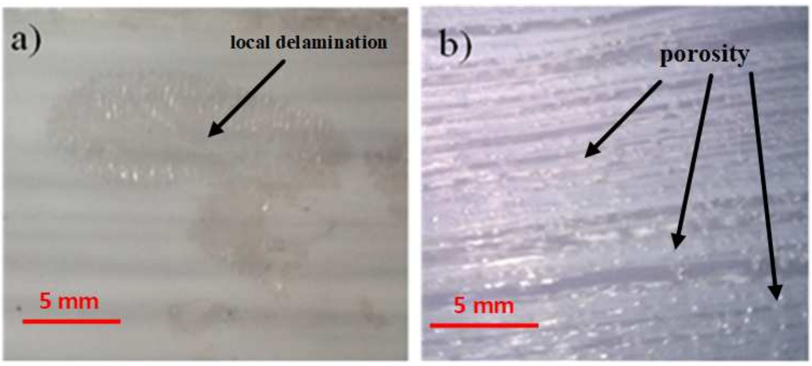

Fig. 3. Defects of single polymer composite: a) local delamination, b) porosity

Rys. 3. Wady jednopolimerowych kompozytów poliestrowych: a) delaminacja miejscowa, b) porowatość

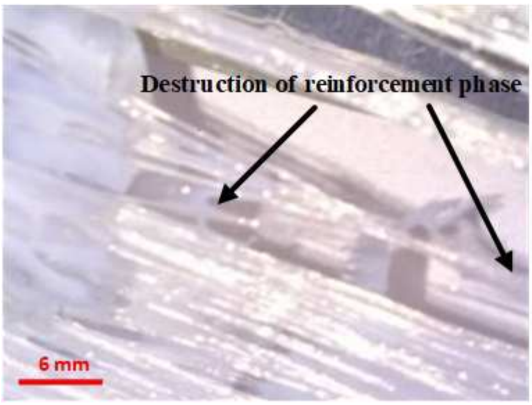

Fig. 4. Destruction of reinforcement phase

Rys. 4. Zniszczenie fazy umocnienia

The optimum time of heating the polymeric material depends on the thickness of the matrix. The thicker the polymer film or plate is, the longer the heating time should be to equalize the temperature across the matrix volume. The heating time also depends on the power of the heaters. If we shorten the heating time by increasing the heater power, the moulding process efficiency will also increase. This, however, results in undesired local temperature differences in the film or plate, which can lead to mechanical stresses degrading the quality and reliability of the composite material.

The hot pressing temperature depends on the properties of the matrix and reinforcement phase materials. The moulding temperature of a single polymer composite must be within the temperature-processing window. It is assumed that at the lowest temperature enabling hot pressing, the resultant composite meets the predefined requirements, and at the highest moulding temperature, additionally thermal and mechanical damage to the composite components must not occur (Fig. 4). The moulding temperature also depends on the process pressure.

The applied pressure depends primarily on the type and quantity of the reinforcement phase. Fibres oriented perpendicular to the matrix flow direction impose the need to increase the process pressure because the fiber is an obstacle to the flow of the matrix. It is assumed that the minimum pressure is the one that allows uniform infiltration of the matrix material in the mould, and that the produced composite meets the predefined requirements, such as matrix continuity. The maximum moulding pressure, in addition to the above requirement, should be such as to prevent mechanical damage of the components, e.g. reinforcement deformation in the composite material (Fig. 5).

The approriate time and method of cooling the moulded object depend on the type of material, especially its specific heat and thermal conductivity, as well as the thickness of the composite being made, the amount and type of reinforcement phase, the process temperature and the mould material.

The choice of the method of separating the moulded composite from the remaining film or plate and removing it from the mould mainly depends on the composite thickness. Using an inappropriate technique and tools cause damage to the object edges, mostly micro-cracks or cracks. These cracks are places of mechanical stress concentration and are generally the source of further damage development when the object is in use. For this reason, research is also focused on separating the object from the rest of the material and the associated tools [20, 21].

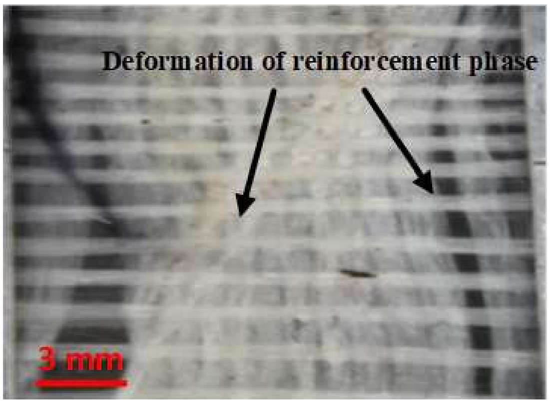

Fig. 5. Deformation of reinforcement phase

Rys. 5. Deformacja fazy umocnienia

From the research results, analyses of the structure (Fig. 6) and tests connected with SPC manufacturing, the author has established the best conditions for the production of SPCs.

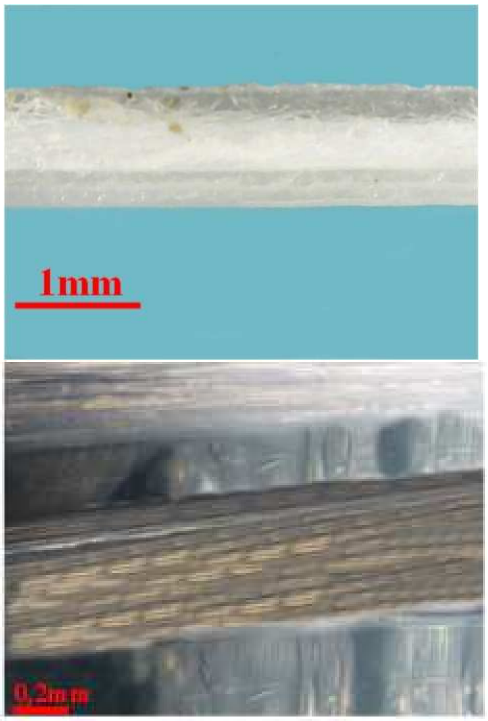

Fig. 6. Structure of single polymer polyester composites

Rys. 6. Struktura jednopolimerowych kompozytów poliestrowych

The ranges of the basic parameters (temperature, time, infiltration pressure) are shown in Table 1.

TABLE 1. **Empirical parameters of polyester composite manufacturing by film-stacking method**
TABELA 1. **Empiryczne parametry procesu wytwarzania jednopolimerowych kompozytów poliestrowych metodą prasowania folii**

Parameter	Drying	Pressing		Cooling
		Stage I	Stage II.	
Temperature	60°C	234÷237°C	234-237°C	to room temperature
Time	more than 6 h	15÷60 s	15-60 s	200÷360 s
Pressure	in vacuum	15÷20 bar	20-25 bar	-
Other	-	pressed in air atmosphere		pressed in air atmosphere

The composites made according to the above described parameters show good mechanical properties. Example properties are shown in Table 2.

TABLE 2. **Properties of example thermoplastic single polymer polyester composites**
TABELA 2. **Właściwości jednopolimerowego termoplastycznego jedynopolimerowego kompozytu poliestrowego**

Materials	Density	Water absorption	Tensile strength	Impact strength
	[g/cm^3]	[%]	[MPa]	[J/cm^2]
SPC - PET/ 20%PETG	1.20±0.01	1.16±0.04	48±4	5.0±1.5

CONCLUSIONS

- A review of the literature shows single polymer polyester composites prepared at a low compaction pressure still possess a set of practical mechanical properties. It implies that SPC can be prepared by simple techniques, which is a cost effective processing method for thermoplastic composites.
- Thermoplastic single polymer polyester composites were manufactured by the film stacking method using PET fiber in combination with PETG films. High matrix compatibility will provide strong interfacial strength, therefore allowing load transfer between the matrix and fibres.
- The film stacking method based on PETG films provided a large processing temperature window in the composite preparation.
- The use of two-step compression eliminates the incidence of defects (defects of the reinforcement phase: deformation or destruction; matrix defects: incorrect structure; internal defects: failure to fill the space of the reinforcement phase).
- Adequate interfacial bonding was achieved when the PET/PETG assembly was consolidated in a hot press at 234÷237°C and a compaction pressure of around 15÷25 bar. The composites (reinforcement fibres 20% weight) made according to the above described parameters show good mechanical properties - a tensile strength in the range of 44÷52 MPa and a Young's modulus of 1000÷1500 MPa.
- PET/PETG has results close to the characteristics of polyetylen/fiberglass composites, which is conducive to the substitution of this material.
- PET/PETG usage will be the beginning of using modern single-polymer materials in the shipbuilding industry, e.g. for building vessel hulls and signaling buoys.

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