

## BIODEGRADABLE POLYVINYLALCOHOL BASED SINGLE POLYMER COMPOSITES

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### **Abstract**

*Novel fully biodegradable polyvinylalcohol (PVOH) based single polymer composites (SPC) were prepared through melt compounding by using stapled fibres, differing for their melting temperature and tensile mechanical properties, and plasticized PVOH granules as matrix. Calorimetric tests on the constituents revealed the existence of an adequate processing window for the preparation of SPCs. On the other hand, the morphological integrity of the reinforcement was maintained only when high melting temperature fibres were utilized. PVOH fibres resulted extremely effective in increasing the elastic modulus, the stress at yield and the Vicat softening temperature of the matrix. Accordingly, dynamic storage modulus and glass transition temperature of SPC increased with respect to the neat PVOH. Also the creep stability was strongly improved, proportionally to the fibre content.*

### **1 Introduction**

The scientific and industrial interest toward the use of polymer matrix composites (PMCs) as replacements of more traditional structural materials, such as metals and ceramics, is continuously increasing [1]. In fact PMCs offer several advantages over conventional materials, such as outstanding specific mechanical properties, ease of processing and good chemical resistance. Recently, several environmental concerns have arisen on their use as reinforcement in composite materials, because Life Cycle Assessment (LCA) of traditional composite materials does not yield favorable results in terms of recyclability and energy requirements of the end-of-life processes [2]. Therefore, an increasing attention has been devoted to the use of natural fibres (wood flour, starch and natural cellulose fibres), that are abundant, relatively cheap and fully biodegradable. Even if these fillers derive from renewable resources and can be incinerated, natural fibre-based composites are hardly recyclable, and the limited thermal stability of natural fillers may lead to severe thermal degradation during subsequent recycling or reprocessing steps [3]. An effective way to improve composites recyclability can be represented by the development of single polymer composites (SPCs), also known as "one-polymer composites", "homocomposites", "all polymer composites", or "self-reinforced composites". In SPCs, both the reinforcing and the continuous phases are polymers with the same chemical composition, and the formation of a composite structure is possible if there is a proper processing windows, i.e. a difference between the melting point of the matrix and of highly oriented fibres. Unlike traditional

composites, SPCs are generally recyclable, because they can be entirely melted down at the end of the product life. Furthermore, interfacial bonding can be considerably improved when matrix and reinforcement are made of the same polymer [4]. Starting from the pioneering work of Capiati and Porter in 1975 [5], several efforts were devoted by materials scientists and engineers to explore new materials combinations, to extend the processing window and to develop new industrial processing and applications for SPCs. While the preparation of common thermoplastics based SPC systems (PE, PP, PET, PMMA, LCPs) has been often reported in literature [6], less attention was devoted to biodegradable single polymer composite systems. To the best of our knowledge, only Li and Yao [7] described the preparation of a poly(lactic acid) SPC constituted by amorphous sheets as matrix and highly crystalline fibres, while no papers dealing with the preparation of polyvinylalcohol (PVOH) based single polymer composites can be found in the open scientific literature.

Poly(vinyl alcohol) has recently attracted the attention as water-soluble biodegradable polymer, to be applied in a wide range of applications. Thanks to the hydroxyl groups present in its main backbone, PVOH possesses many good properties, such as high tensile strength, excellent adhesive properties, abrasion and chemical resistance and gas barrier properties [8]. Therefore, PVOH is widely used in several industrial applications, such as films, fibres, adhesives, textile sizing, emulsifiers, paper coating etc.. At the molecular level, different PVOH grades can be obtained varying the degree of hydrolysis (DH). Even if the increasing interest towards the production of PVOH films led to the development of new melt processing technologies, the main difficulty to overcome during the thermal extrusion processing is the close proximity of its melting point and decomposition temperature. In order to overcome this problem, several plasticizers (glycerol, ethylene glycol, amine alcohols, polyvalent hydroxyl compounds) can be added in order to enhance PVOH thermal stability [9]. The commercial production of PVOH fibers started in Japan after the second world war, and nowadays it is carried out by wet spinning or dry spinning, starting from aqueous PVOH solutions. In order to enhance the water resistance of the fibers, they can be treated by thermal and acetalization processes. PVOH fibers are characterized by a high affinity to water due to the hydroxyl groups present in PVOH, excellent mechanical properties because of the high crystallinity, and elevated chemical resistance. PVOH fibres can be also applied as concrete reinforcement, because they are effective in controlling the shrinkage and the fatigue cracking of traditional concretes. These fibres find application in rubber hosing reinforcement, geogrid reinforcement, paper and non-woven applications.

Therefore, the objective of the present work is to develop and thermo-mechanically characterize novel fully biodegradable PVOH based single polymer composites, with improved mechanical properties and dimensional stability.

## **2 Materials and testing methods**

### *2.1 Materials*

PVOH plasticized granules (Mowiflex TC, density =  $1.27 \text{ g}\cdot\text{cm}^{-3}$ , MFI at 2.16 kg and  $190 \text{ }^\circ\text{C}$  =  $39 \text{ g}\cdot(10 \text{ min})^{-1}$ ), supplied by Kuraray Specialties Europe GmbH (Frankfurt, Germany), were utilized as continuous matrix. Three kinds of Kuralon<sup>®</sup> stapled fibres (WN2, WN4, WN8), provided by Kuraray Co. LTD (Tokyo, Japan), were considered as reinforcement. These fibres have a mean length of 38 mm and a title of 1.7 dTex. They differ for the water dissolution temperatures ( $20 \text{ }^\circ\text{C}$  for WN2,  $40 \text{ }^\circ\text{C}$  for WN4,  $80 \text{ }^\circ\text{C}$  for WN8), while their density values, measured through an Accupyc 1330 helium pycnometer, are very similar (i.e.  $1.37 \text{ g}\cdot\text{cm}^{-3}$  for WN2,  $1.36 \text{ g}\cdot\text{cm}^{-3}$  for WN4, and  $1.39 \text{ g}\cdot\text{cm}^{-3}$  for WN8).

## 2.2 Preparation of the samples

In order to avoid moisture absorption, PVOH fibres were dried at 60 °C for 6 hours before to be compounded with PVOH chips in a Thermo Haake internal mixer operating at 180 °C for 6 min. In this way, square sheets of composite samples with a mean thickness of about 1 mm were prepared by compression moulding of the resulting materials at 180 °C for 5 minutes in a Carver laboratory press under a pressure of about 1 MPa. Immediately after the preparation, samples were sealed in vacuum plastic bags under vacuum. Samples were designated indicating the matrix, the kind of fibre and its relative weight amount. For instance, PVOH-WN2-20 denotes the composite sample filled with 20 wt% of WN2 fibres.

## 2.3 Characterization of the constituents

Differential Scanning Calorimetry (DSC) tests on the constituents (neat matrix and stapled fibres) were carried out through a Mettler DSC 30 apparatus. Samples were first heated from 0 °C to 280 °C at 10 °C·min<sup>-1</sup>, cooled down to 0 °C at the same rate and finally re-heated up to 280 °C. Samples were tested under a constant nitrogen flow of 150 ml·min<sup>-1</sup>. In this way, the melting ( $T_m$ ) and the crystallization ( $T_c$ ) temperatures of the constituents were evaluated, while the relative crystallinity degree ( $\gamma$ ) was computed dividing the specific melting enthalpy of the polymer ( $\Delta H_m$ ) by that of a fully crystalline PVOH ( $\Delta H_0$ ), taken as 161 J·g<sup>-1</sup> [10]. Quasi-static tensile tests on the constituents were carried out at room temperature through an Instron 4502 tensile testing machine. Tensile properties of the neat matrix were determined on ISO 527 1BA dumbbell specimens (width = 5 mm, thickness = 1 mm, gage length = 30 mm), punch-cutted from the compression molded sheets. Elastic modulus was evaluated at a lower crosshead speed (0.25 mm·min<sup>-1</sup>), and the strain was recorded through an Instron<sup>®</sup> model 2620-601 resistance extensometer (gage length = 12.5 mm). Tensile test at break were carried out at a crosshead speed of 50 mm·min<sup>-1</sup> without using the extensometer. At least five specimens were tested for each sample. Tensile properties of the fibres were determined by using the same machine, equipped with a 10 N load cell. Single filaments were extracted from the bundles and glued on paper mounting tabs. A cross-head speed of 1 mm·min<sup>-1</sup> and a gage length of 20 mm was utilized for all the samples. In this way it was possible to evaluate the elastic modulus (E), taken as the secant modulus between the deformation levels of 0.1 % and 0.5 %, the stress ( $\sigma_b$ ) and the strain ( $\epsilon_b$ ) at break of the fibres.

## 2.4 Characterization of the composites

Scanning electron microscopy (SEM) images of the fracture surfaces of the composites were obtained through a field emission Zeiss Supra 40 microscope at different magnifications levels. Samples were cryofractured in liquid nitrogen and metalized before observations. DSC and tensile mechanical tests were performed by using the same equipment described in Paragraph 2.3. Vicat Softening Temperature (VST) was determined through a HDT-Vicat mod. MP/3 (ATS FAAR) apparatus, according to ASTM D1525-07 standard. Rectangular specimens (thickness = 3.2 mm, length = 10 mm, width = 5 mm) were tested under a load of 10 N and setting a heating rate of 50 °C·h<sup>-1</sup>. At least three specimens were tested for each sample. Dynamic-mechanical tests were performed through a DMA Q800 (TA Instruments) apparatus in tensile configuration, setting a clamp distance of 12 mm, a frequency of 1 Hz, a preload of 0.01 N and a strain amplitude of 64  $\mu$ m. Specimens were tested in a temperature interval between 0 °C and 170 °C, at a heating rate of 3 °C·min<sup>-1</sup>. Creep tests were performed by using an Instron 4502 testing machine at various temperatures (from 30 °C to 90 °C), applying at a constant stress of 3 MPa. Rectangular specimens (length = 40 mm, width = 5 mm, thickness = 0.8 mm) were tested for 3600 s, and tensile creep compliance D(t) was computed by dividing the time dependent strain  $\epsilon(t)$  by the applied stress ( $\sigma_0$ ). A time-temperature superposition principle was adopted to analyze the creep data [10]. In this way, creep compliance master curves at a reference temperature ( $T_0$ ) of 30 °C, describing the creep response over a wide time scale, were obtained.

### 3 Results and Discussion

#### 3.1 Characterization of the constituents

The main results of DSC tests on PVOH chips and on the different reinforcing fibres, collected during the two heating stages, are summarized in Table 1. It can be noticed that PVOH granules are characterized by a melting temperature (176.5 °C) and a crystallinity content (about 16 %) much lower than those of PVOH fibres. It can be inferred that chain alignment produced during the spinning process and the subsequent drawing operations increased the crystallinity of the fibres, with the formation of a more regular and stable crystalline phase. It is also interesting to note that both the melting temperature ( $T_{m1}$ ) and the crystallinity values ( $\chi_1$ ) of the PVOH fibres, evaluated after the first heating stage, remarkably increase moving from WN2 to WN4 and WN8 type of fibres. Considering DSC results from the second heating stage, it can be noticed that crystallization during the cooling stage induces some changes in the microstructure of the materials under investigation. The observed changes for PVOH chips are relatively small, being both the melting temperature ( $T_{m2}$ ) and the relative crystallinity ( $\chi_2$ ) values only slightly increased with respect to the first heating stage. On the other hand, in the case of PVOH a remarkable decrease of both melting point and crystallinity content can be observed in the second DSC heating stage. Among the investigated fibres, WN8 still manifest the highest  $T_m$  and  $\chi$  values among the tested fibres even after the second heating stage. This means that the differences in the thermal properties of the tested fibres are not only due to the drawing conditions, but probably also to possible differences in the molecular weight and/or hydrolysis degree of the parent polymers. In fact, in literature it is widely reported that both the thermal and the mechanical properties of polyvinylalcohol are strongly influenced by the above mentioned parameters [11]. Interestingly, DSC tests demonstrate the existence of a thermal processing window for the preparation of PVOH based single polymer composites by using the three PVOH fibres.

Sample	$T_{m1}$ [°C]	$\Delta H_{m1}$ [J·g <sup>-1</sup> ]	$\chi_1$ [%]	$T_{m2}$ [°C]	$\Delta H_{m2}$ [J·g <sup>-1</sup> ]	$\chi_2$ [%]
PVOH	176.5	25.2	15.7	180.0	19.1	11.9
WN2	202.4	50.5	31.3	198.2	36.8	23.4
WN4	220.3	79.1	49.1	211.3	50.7	31.5
WN8	238.6	99.4	61.7	222.3	67.9	42.2

**Table 1.** Results of DSC tests on PVOH chips and on WN2, WN4, WN8 PVOH fibres.

Relative tensile mechanical properties of neat PVOH sheets and of the three kind of PVOH fibres are collected in Table 2. Neat PVOH matrix presents a ductile behaviour, with a relatively low elastic modulus and elevated deformation at break. As expected, the PVOH fibres present much higher elastic modulus and stress at break with respect to the neat matrix, with a progressive increase passing from WN2 to WN8, and a parallel reduction of the deformation at break.

Sample	E [GPa]	$\sigma_y$ [MPa]	$\sigma_b$ [MPa]	$\epsilon_b$ [%]
PVOH	0.3 ± 0.1	33.6 ± 2.4	43.6 ± 6.4	280 ± 80
WN2	9.6 ± 1.1	-	425.9 ± 95.7	19 ± 2
WN4	12.5 ± 2.5	-	673.0 ± 119.8	14 ± 3
WN8	22.4 ± 1.5	-	883.6 ± 112.4	9 ± 1

**Table 2.** Tensile mechanical properties of neat PVOH compression molded sheets and of WN2, WN4 and WN8 PVOH fibres.

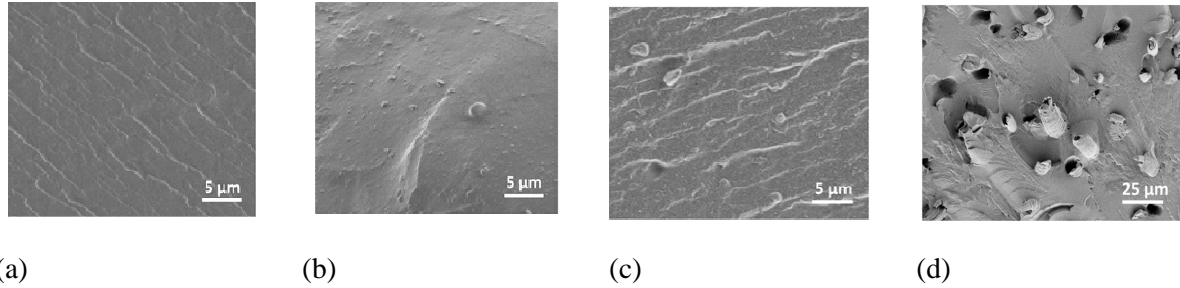
### 3.2 Characterization of the composites

Results of DSC tests on neat PVOH and on the relative composites with a fibre content of 20 wt% are summarized in Table 3. The melting endothermal signals of two distinct phases can be clearly distinguished in DSC scans of SPCs under investigation (not reported for brevity). It is interesting to note that both the melting temperature ( $T_{mF}$ ) and the crystallinity degree ( $\chi_F$ ) of the compounded fibres are lower than the values reported in Table 2 for the unprocessed constituents. This clearly means that the selected processing conditions induced a partial melting of low crystallinity fractions of the fibres. This phenomenon could have been enhanced by a possible overheating produced by the high shear stresses generated during the melt compounding process. A reduction of the fibre crystallinity could limit their reinforcing capability in the composites. However, this hypothesis should be supported by a direct evaluation of the effect of the thermo-mechanical degradation induced by the melt compounding on the mechanical properties of the fibres.

Sample	$T_{mM}$ [°C]	$T_{mF}$ [°C]	$\Delta T_m$ [°C]	$\chi_M$ [%]	$\chi_F$ [%]
PVOH	176.5	-	-	15.7	-
PVOH-WN2-20	176.2	194.5	18.4	7.3	10.5
PVOH-WN4-20	173.7	195.0	21.3	6.6	29.5
PVOH-WN8-20	173.2	221.2	47.9	5.3	21.0

**Table 3.** Results of DSC tests on neat PVOH and relative composites (fibre content = 20 wt%)

In order to investigate the fibres morphology within the SPCs, microstructural analyses were carried out by electron microscopy. FESEM images of the fracture surfaces of neat PVOH matrix and of SPC with a fibre content of 20 wt% are reported in Figure 1. While fracture surface of neat PVOH matrix is relatively smooth, in PVOH-WN2-20 and PVOH-WN4-20 samples the fibrous morphology is almost completely lost. According to DSC measurements, this probably means that the selected processing parameters cannot prevent a partial melting of these fibres. Only in WN8 filled composite the fibrous morphology of the reinforcement is maintained, and some cavities due to debonding phenomena can be clearly detected. The length of the protruding fibres is lower than 20 microns, thus indicating that a relatively good level of fibre-matrix interfacial adhesion has been reached [12]. As reported in the introduction, the good interfacial bonding can be attributed to the fact that both matrix and fibres have the same chemical nature.



**Figure 1.** FESEM images of the fracture surfaces of neat PVOH and relative composites. (a) PVOH, (b) PVOH-WN2-20, (c) PVOH-WN4-20, (d) PVOH-WN8-20.

From these preliminary results it clearly emerges that WN8 fibres is the optimal choice for the preparation of PVOH based SPCs, with fibrous morphology, possessing suitable thermal and dimensional stability. Therefore, WN8 fibres were selected for the preparation of composites with different fibre contents (10, 20 and 30 wt%).

The most important results from quasi-static tensile tests on neat PVOH matrix and relative WN8 filled composites are collected in Table 4. First of all, the addition of the fibres produces an interesting stiffening effect, with an increase of the tensile modulus by a factor of about 6 when 30 wt% of WN8 fibres are added to the neat matrix. PVOH sample shows a ductile behaviour, with a relatively low yield point and elevated strain at break. Stress at yield values ( $\sigma_y$ ) are interestingly enhanced by fibre addition, while strain at break ( $\epsilon_b$ ) is heavily reduced (about seven times). In order to evaluate the dimensional stability of the prepared composites, Vicat softening temperature (VST) measurements were carried out. As reported in Table 4, VST noticeably increases with the fibre loading. For instance, PVOH-WN8-10 composite shows a VST about 30 °C higher than that of the neat PVOH, while PVOH-WN8-30 composite reaches a VST value very close to the melting temperature of the neat PVOH (172.3 °C).

Sample	$E_c/E_m$	$\sigma_{yc}/\sigma_{ym}$	$\epsilon_{bc}/\epsilon_{bm}$	VST [°C]
<b>PVOH</b>	$1.00 \pm 0.06$	$1.00 \pm 0.07$	$1.00 \pm 0.29$	$126.4 \pm 1.5$
<b>PVOH-WN8-10</b>	$1.90 \pm 0.24$	$1.10 \pm 0.08$	$0.23 \pm 0.07$	$156.9 \pm 3.3$
<b>PVOH-WN8-20</b>	$2.64 \pm 0.28$	$1.28 \pm 0.19$	$0.15 \pm 0.07$	$161.1 \pm 1.0$
<b>PVOH-WN8-30</b>	$5.72 \pm 0.69$	$1.52 \pm 0.10$	$0.13 \pm 0.06$	$172.3 \pm 2.2$

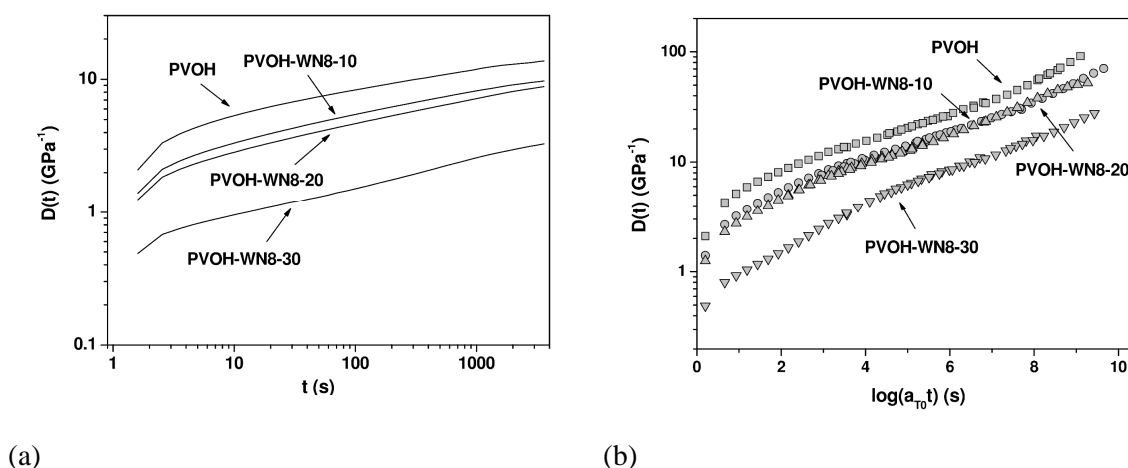
**Table 4.** Relative tensile mechanical properties and VST of neat PVOH and WN8 fibre filled composites.

The contribution of PVOH fibres on the viscoelastic properties of SPCs composites has been investigated through dynamical mechanical and creep tests. The values of the storage modulus ( $E'$ ) at different temperatures and of the glass transitions temperature ( $T_g$ ), taken as the loss tangent ( $\tan\delta$ ) peak, are reported in Table 5. As it commonly happens for semicrystalline polymers, a drastic drop of the storage modulus is observed in correspondence of the glass transition temperature. The presence of WN8 fibres increases the storage modulus over the entire range of testing temperatures. Also the glass transition temperature progressively increases with the fibre amount. The improvement of these viscoelastic properties is probably associated to the immobilizing effect provided by the fibres on the PVOH matrix.

Sample	E' 0 °C [MPa]	E' 25 °C [MPa]	E' 70 °C [MPa]	T <sub>g</sub> [°C]
PVOH	4257	1809	238	38.9
PVOH-WN8-10	5294	3309	237	47.5
PVOH-WN8-20	5915	4111	159	49.9
PVOH-WN8-30	6866	4666	241	52.0

**Table 5.** Storage modulus (E') at different temperatures and glass transition (T<sub>g</sub>) values of neat PVOH and WN8 fibre filled composites.

Isothermal creep compliance curves of neat PVOH and relative WN8 filled composites at ambient temperature (30 °C) are reported in Figure 2a. Also in this case, the stabilizing effect provided by PVOH fibres leads to an important reduction of the creep compliance values. After a loading time of 3600 s, neat PVOH shows a creep compliance of about 14 GPa<sup>-1</sup>, while PVOH-WN8-30 composite reaches a D(t) value of only 3 GPa<sup>-1</sup>. This results could be particularly important for those application for which a good dimensional stability under constant loads is required at ambient temperature. Creep tests at various temperatures, were carried out under a constant stress of 3 MPa, with the aim to determine the effect of the temperature on the creep stability of these materials and to describe the viscoelastic behaviour of the tested materials over a wide time scale. Therefore, creep compliance master curves at a reference temperature (T<sub>0</sub>) of 30 °C and a reference stress (σ<sub>0</sub>) of 3 MPa were generated on the basis of a time-temperature superposition principle. In Figure 2b the obtained master curves are reported. It is evident that a good superposition can be obtained for both neat PVOH and for filled samples, and the dramatic reduction of the creep compliance with the fibre content is confirmed over an extended time interval. For instance, while neat PVOH matrix reaches a creep compliance of 20 GPa<sup>-1</sup> after a loading time of 1 day, for PVOH-WN8-30 sample a time period of about 12 years is needed to reach the same creep compliance.



**Figure 2.** Creep compliance of neat PVOH and WN8 fibre filled composites. (a) Creep curves at 30 °C and (b) creep compliance master curves according to the time-temperature superposition principle.

#### 4 Conclusions

For the first time, fully biodegradable polyvinylalcohol (PVOH) based single polymer composites (SPC) were prepared and thermo-mechanically characterized. Calorimetric tests on the constituents demonstrated the theoretical possibility to prepare single polymer composites with an adequate processing window, while FESEM micrographs evidenced how the reinforcement morphology was maintained only when high melting temperature fibres (i.e. WN8) were used. The introduction of PVOH fibres revealed extremely effective in increasing the stiffness, the yield properties and the Vicat softening temperature of the neat PVOH matrix, proportionally to the fibre content. On the other side, a progressive reduction of the elongation at break, accompanied by an heavy embrittlement, was encountered for the filled samples. The stabilizing effect due to fibre introduction was confirmed by marked improvements of the viscoelastic properties of the composites. Storage modulus and glass transition temperature of SPC increased with respect to the neat PVOH, while creep compliance values were strongly decreased at all the testing temperatures.

#### References

- [1] Gay D., Hoa S.V., Tsai S.W. *Composite materials. Design and applications*. CRC Press, Boca Raton (USA) (2003).
- [2] Henshaw J.M., Han W., Owens A.D. An overview of recycling issues for composite materials. *Journal of Thermoplastic Composite Materials*, **9**, pp. 4-20 (1996).
- [3] Houshyar S., Shanks R.A. Morphology, Thermal and Mechanical Properties of Poly(propylene) Fibre-Matrix Composites. *Macromolecular Materials and Engineering*, **288**, pp. 599-606 (2003).
- [4] Alcock B., Cabrera N., Barkoula N., Spoelstra A., Loos J., Peijs T. The mechanical properties of woven tape all-polypropylene composites. *Composites Part A : Applied Science and Manufacturing*, **38**, pp. 147-161 (2007).
- [5] Capiati N.J., Porter R.S. The concept of one polymer composites modeled with high density polyethylene. *Journal of Materials Science*, **10**, pp. 1671-1677 (1975).
- [6] Pegoretti A., Ashkar M., Migliaresi C., Marom G. Relaxation processes in polyethylene fibre-reinforced polyethylene composites. *Composites Science and Technology*, **60**, pp. 1181-1189 (2000).
- [7] Li R., Yao D. Preparation of single poly(lactic acid) composites. *Journal of Applied Polymer Science*, **107**, pp. 2909-2916 (2008).
- [8] Chen N., Li L., Wang Q. New technology for thermal processing of poly(vinyl alcohol). *Plastics Rubber and Composites Processing and Applications*, **36**, pp. 283-290 (2007).
- [9] Dickstein J., Bouchard R. *Polyvinyl Alcohol. Manufacture of Plastics*. Reinhold Publishing Co., New York (1964).
- [10] Riande E., Calleja R.D., Prolongo M.G., Masegosa R.M., Salom C. *Polymer Viscoelasticity*, Dekker, New York (2000).
- [11] Finch C.A. *Polyvinyl Alcohol. Properties and Applications*. John Wiley and Sons, Bristol (UK) (1973).
- [12] Pegoretti A., Accorsi M.L., Di Benedetto A.T. Fracture toughness of the fiber-matrix interface in glass-epoxy composites. *Journal of Materials Science*, **31**, pp. 6145-6153 (1996).