RESEARCH ON THERMALLY INDUCED SHAPE MEMORY NONWOVEN FABRICS BASED ON BIODEGRADABLE POLYESTERS

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ABSTRACT

The aim of conducted research was to produce polylactide based nonwoven fabrics using melt-blown technology, having one-way shape memory effect triggered by temperature near human body temperature. In the current studies, thermal, morphological and shape memory properties of fabrics made from two polylactide based polymer blends with addition of atactic, low molecular weight polyhydroxybutyrate are compared. Thermally induced shape memory effect was evaluated in the thermomechanical experiments where the temperature and time of transition were measured.

Key Words: shape memory polymers (SMPs), nonwoven fabrics, copolymer poly-l-lactide with glycolide, poly-l-lacyde, polyhydroxybutyrate

1. INTRODUCTION

In the recent studies, the scientist`s attention is increasingly drawn to shape memory textiles based on biodegradable polyesters for biomedical applications. The main reasons for this growing trend are such properties of these polymers like: low molecular weight, easiness of processing, ability to program controlled biodegradability and high shape recovery ratio [1]. What is more, on the contrary to shape memory alloys, shape memory polymers are considered as safer for human organism and more favourable from economical point of view.

The thermally induced shape memory effect is the result of the phase transition in characteristic material temperature and change of entropy during deformation. Shape memory polymers have possibility to cyclic triggered by temperature shape recovery after the deformation. The transition temperature T_{trans} is the temperature where the shape change starts, the shape fixation occurs below T_{trans} and shape recovery is induced automatically above T_{trans} [2,3]. The behaviour of shape memory in polylactide was tested in thermomechanical analysis [4].

Shape memory effect induced thermally in polymers may find its vast application in medicine [5-6] as self-tightening sutures or implants, self-deploying stents [7], neuroprosthesis to increase brain activity [8] or scaffolds in minimal invasive surgery [9].

2. MATERIALS AND METHODS

The materials used in the present research were two polymeric blends described below:

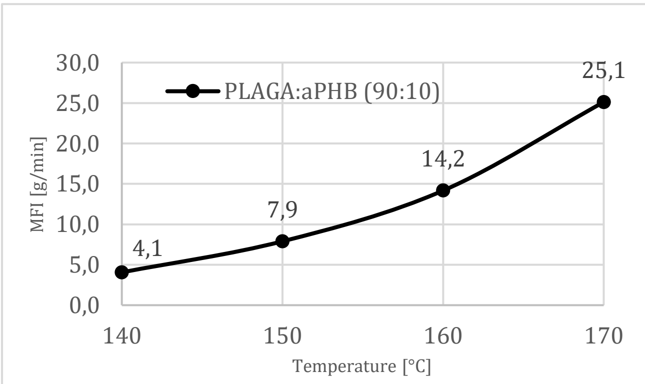
A: PLAGA: aPHB (90:10) – copolymer poly-l-lactide with glycolide, were the amount of lactide units was 86% and glycolide 16%, blended with atactic polyhydroxybutyrate with mass ratio 90: 10;
B: PLLA: aPHB (90:10) – poly-l-lacyde blended with atactic polyhydroxybutyrate with mass ratio 90: 10.

In table 1 are gathered polymers' basic characteristics. Thermal analysis, in which characteristic temperature points were examined, was conducted using differential scanning calorimetry. Weight average molecular weight was determined in Gel Permeation Chromatography (GPC) analysis.

Table 1. Characteristics of polymers used in research

Materiał/Parametr	Glass transition temp. Tg, ◦C	Melting temp. Tm, ◦C	Weight average molecular weight Mw, Da
PLLA	61	168	227 512
PGLA	54	-	130 000
aPHB	-9	-	4051
PLLA:aPHB	47	163	-
PGLA:aPHB	42	-	-

In order to determine optimal parameters for polymer processing rheological properties were assessed using mass melt flow index (MFI) (figure 1).



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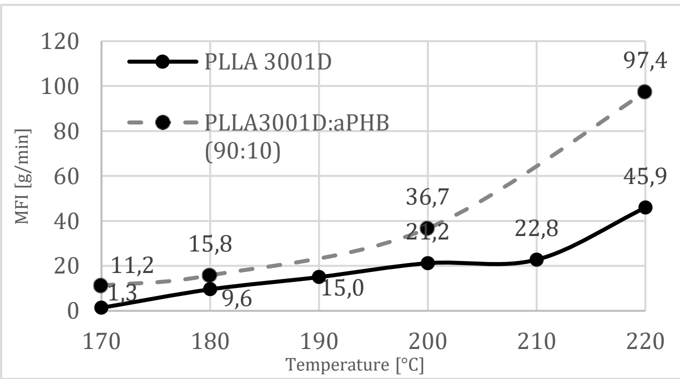

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Figure 1. Melt flow index for polymeric blends: A – PLAGA:aPHB (90:10), B – PLLA oraz PLLA:aPHB (90:10)

Nonwoven fabrics have been manufactured applying melt-blown technology. In case of the blend A was used the laboratory stand with the twin-screw extruder MiniLab, the die and the collector made by Haake/Germany. Nonwoven fabrics from the blend B were produced using the technological line equipped in the twin-screw extruder ended with fibres making dies, the extruder and air temperature control panel and the collector of controlled speed.

The nonwoven fabrics obtained after the spinning process showed high thermal shrinkage, which was completely eliminated as a result of multidirectional thermal stabilization conducted at temperature of 80°C and time of 30 min in air condition determined on the basis of the previous tests.

In the next research stage, in order to characterize nonwoven fabrics before and after the thermal stabilization, thickness of nonwoven fabrics was measured using a thickness gauge and surface mass of the investigated samples was determined. Nonwoven fabrics before and after stabilization were subjected to the thermal analysis using DSC method (differential scanning calorimetry) and the structural analysis applying SEM method (Scanning Electron Microscopy).

The stabilized nonwoven fabrics have been examined in thermomechanical shape memory experiments in which the samples firstly have been deformed above its glass transition temperature T_g, then sample's shape was fixed below T_g, and the shape recovery occurred in water at temperature in range 40-45°C.

3. RESULTS

3.1 Thermal properties

The results of differential scanning calorimetry are presented in table 2.

Table 2. Summary of the characteristic temperature points of polymeric blends and produced nonwoven fabrics after stabilization

Material/Parameter	Glass transition temp. Tg, °C	Cold crystallization temp. T_c, °C	Melting temp. Tm, °C
PLLA	61	100	168
PGLA	54	-	-
PLLA:aPHB	47	93	163
PGLA:aPHB blend	42	-	-
Nonwoven PLLA:aPHB stabilized	50	99	166
Nonwoven PGLA:aPHB stabilized	49	105	143, 162

The analysis conducted indicates that polymeric blends processing influences their thermal properties. After polymer processing the values of glass transition temperature of the both nonwoven fabrics are higher and in the case of PLGA: aPHB nonwoven fabrics additionally a melting peak occurred what is characteristic for presence of the crystalline phase.

3.2 Physical and structural properties

Thickness of the produced nonwoven fabrics before and after the stabilization process was close to 1 mm; however its surface mass varied. The PGLA: aPHB fabric was characterized by surface mass of 45.5 g/m^2 and the PLLA:aPHB fabric by 48.1 g/m^2 before thermal stabilization. After thermal stabilization the values of surface mass increase to 57.6 g/m^2 and 49.2 g/m^2 respectively. The views of the obtained nonwoven fabrics are presented in figure 2.

Produced nonwoven fabrics in melt-blown technique are characterized by irregular fibres orientation and thickness. After the thermal stabilization process fibres entanglements increases and fibres are more packed what proves higher surface mass of the fabrics obtained after thermal treatment.

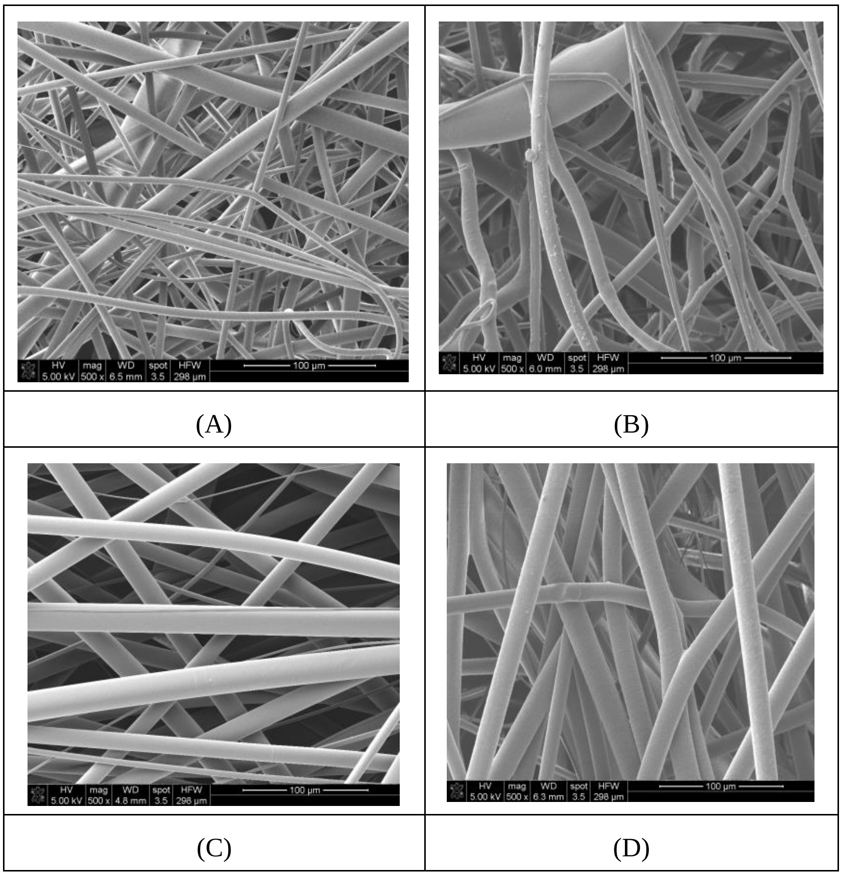


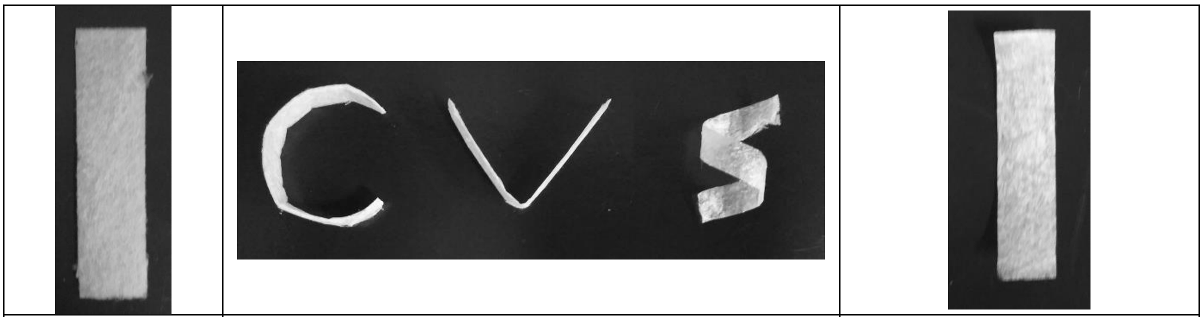
Figure 2. Images of surface morphology of: PLAGA:aPHB nonwoven fabrics before (A) and after (B) thermal stabilization, PLLA:aPHB aPHB nonwoven fabrics before (C) and after (D) thermal stabilization. Magnification 500x

3.3 Shape memory effect

The results of the thermomechanical shape memory experiments were illustrated in table 3 and in figure 3.

Table 3. Shape memory results with deformation in shape C, V, S (Figure 2B)

Material	Transition temperature, ◦C	Recovery time, s	Shape recovery ratio
PGLA:aPHB	40	15	100 % (Figure. 3C)
PLLA:aPHB	45	150	100 %



A: Origin shape	B: Temporary shapes	C: Shapes after recovery

Figure 3 Shape memory results

Independently on the temporary shapes of the nonwoven fabrics after implementation transition temperature the fabrics return to the origin shapes.

4. CONCLUSIONS

- The present studies prove that the addition of atacitc polyhydroxybutyrate decreases glass transition temperature of the polymeric blends and improves their rheological properties, important for polymer processing using a melt-blown technique.
- The polymeric blends processing influences their thermal properties. After polymer processing the values of glass transition temperature of the both nonwoven fabrics are higher and in the case of PLGA: aPHB nonwoven fabrics additionally a melting peak occurred what can indicate the development of crystalline phase.
- The deformed shapes after glass transition temperature characterize stable in time structure under transition temperature thanks to the successful shape fixation after immediate sample cooling. The shape recovery ratios in the shape memory experiments varied depending on transition temperature and time. In the table 2 are gathered the optimal conditions for both type of the nonwoven fabrics for which shape recovery ratios were equal to 100%. Both tested polymer blends exhibit a thermally induced shape memory effect, however, for PGLA: aPHB nonwoven fabrics, it occurs at a lower temperature equals to 40^{o}C, close to human body temperature.

5. REFERENCES

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