PLA/PHA- BIODEGRADABLE BLENDS FOR PNEUMOTHERMIC FABRICATION OF NONWOVENS

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Abstract:

This study presents the results of research concerning fabrication of nonwovens from biodegradable polymer blends using the melt-blown method. The experiments performed within the framework of the research confirmed the possibility of obtaining polymer composites based on polylactide (PLA) with poly(hydroxyalkanoates) (PHA) and another aliphatic-aromatic copolyester. The obtained products were subjected to the analyses of chemical structure using the Fourier Transform Infrared Spectroscopy (FTIR) Attenuated Total Reflectance (ATR) method. The physical and mechanical properties of the fabricated nonwoven layers were also tested, which confirmed a wide spectrum of their applicability, depending on the polymer composition used in production.

Keywords:

Poly(hydroxyalkanoates) (PHA), polylactide (PLA), polymer composites, melt-blown nonwovens

1. Introduction

The first research studies aimed at application of biodegradable polymers for fabrication of new materials were started several decades ago. However, very high prices of such polymers posed a limitation on their use. The development of more inexpensive method of obtaining monomers for the production of polymers resulted in falling prices and growing interest in biopolymers. The studies of biodegradable polymers have developed in the recent years, primarily due to the search for an alternative for petroleum-derived materials. The products based on petroleum-derived materials are partially recyclable; however, their recycling is an energy-consuming process, which results in, unfortunately, a large proportion of such materials being disposed of in the landfills where they can last for many decades. The growing problem of disposal of petroleum-derived materials, associated with a very long time of their degradation, as well as energy consumption associated with the recycling process, has prompted various research centres to seek new materials that could successfully replace the plastics used to date. The continually increasing quantities of plastic waste have become a problem for humans, and in many cases, a source of adverse impact on the environment [1]. Other factors prompting intensification of the research include shrinking oil resources worldwide as well as legal restrictions applicable on the disposal of waste. During the recent years, products made of biodegradable materials have been introduced into the market, but they still fail to account for a large proportion in relation to all plastic products used at the moment [2]. Plastics are now applicable in almost all areas of life. Owing to their durability and chemical stability, they have been applied in many industrial sectors. At present, the best known biopolymers include polylactide (PLA) and poly(hydroxyalkanoates) (PHA) among which poly(hydroxybutyrate) (PHB) and poly(hydroxyvalerate) (PHV) arouse most interest. Generally, the biodegradable polymers

can be divided into two groups. The first one includes polymers obtained from petroleum-derived materials, whereas the other includes polymers obtained from renewable materials. The latter are often referred to as 'double green' because of the character of both raw materials and the obtained products. The examples of polymers of the first group are, among others, poly(ϵ -caprolactone) and poly(aspartic acid), whereas the most important representatives of the second one are PLA, poly(hydroxybutyric acid), PHA, as well as a hydroxybutyric acid and hydroxyvaleric acid copolymer, that is, poly(hydroxybutyric-co-hydroxyvaleric acid). It is also noteworthy that the cost of composting in the case of biopolymers is six-fold lower than that of recycling of petroleum-derived polymers. The aforementioned economic and environmental aspects pose currently a requirement for numerous research centres to undertake studies aimed at obtaining materials based on biopolymers [3]. At present, the best known and described biodegradable polymer is PLA, the largest manufacturer of which is Nature Works LLC (USA). PLA, known under the trade name of Ingeo [4], is produced from lactic acid, which, in turn, is obtained as a result of fermentation of glucose originating from plants. The polymer is produced, among others, using a synthetic method involving opening of the lactide ring. The polymerisation reaction with lactide ring opening proceeds by coordination and substitution mechanism, wherein two lactyl units are bound to the open lactide ring. The ring-opening process is initiated by nucleophilic compounds [5–8].

Figure 1. The scheme of polymerisation reaction with lactide ring opening [3]

Among many valuable properties such as biodegradability and biocompatibility, PLA is generally stiff and brittle, limiting possibilities of applying this polymer. To overcome these disadvantages, blends of PLA with other polymers have been formed, for example, with PHAs. PHAs have similar properties to conventional plastics such as polyethylene, polypropylene and some of them are elastomeric. Blending these polymers results in a material with a wider scope compared to the pure PLA and PHA. There are many studies on the blends of PLA and PHA. Investigated also adhesion between the two material phases PLA and PHA, was found that blends' adhesion and properties vary depending on the content of PHA in the PLA [9,10].

In order to improve the properties of biodegradable polymers, there are formed also blends with aliphatic-aromatic polymers because of their, for example, elastomeric properties [11]. In this study was prepared compound PLA/biomass. The biomass is aliphatic-aromatic copolyester and is characterised by the properties typical of elastomers, that is, materials capable of dimension changes as a result of tensile or shear stresses.

On the other hand, polymers belonging to the PHA group are aliphatic polyesters produced by biofermentation process, where due to the lack of sufficient amount of food, bacteria start to accumulate it in cells as a reserve material storing energy and providing a carbon source. The process yielding PHA as a result of bacterial fermentation consists of the following stages: fermentation, isolation and purification. The carbon sources for PHA production include: glucose, fructose, sucrose, methanol, glycerine, organic acids [12,13]. The promising substrates for PHA production by biofermentation in the future are, among others, molasses, starch, waste from biodiesel production, fats obtained from plant and animal waste, as well as lactic acid from dairy industry [14]. PHA can also be produced from materials other than petroleum-based ones. One of the methods by which they are obtained is polymerisation reaction with opening of the β -lactone ring described in [14].

Figure 2. The scheme of PHA structure [3]

A representative of PHA is PHB, a natural aliphatic polymer produced as a reserve material by such bacteria as: *Pseudomonas*, *Bacillus*, *Azotobacter* [15,16]. Biologically, PHB is synthesised by bacterial fermentation of glucose, most commonly as a result of sugarcane sucrose processing, and less frequently, both for technical and economic reasons, from maize starch glucose. Synthesising PHB by using bacteria allows to obtain a polymer with highly regular structure [17,18]. Currently, the largest manufacturer of PHB is Telles (USA), producing that polymer under the trade name of Mirel [19]. The polymers of that group undergo degradation, among others, as a result of exposure to sunlight or microorganisms (bacteria of different species and fungi), both under aerobic and

anaerobic conditions; however, in anaerobic environment, their biodegradation is slower. The degradation rate is dependent on the type and number of microorganisms present, temperature and pH of the environment in which the degradation process occurs. The structure of the material made of the biopolymer, its porosity, but also the presence in the degradation environment of various pollutants and amounts of food sufficient for the microorganisms to multiply are also important factors affecting the process [20, 21].

One major advantage, besides biodegradation and the capability of producing biopolymers from renewable raw materials, is the possibility of processing biopolymers with the machinery used for processing conventional polymers, after minor modifications [22, 23]. This is due to the thermal and mechanical properties of the analysed polymers.

The aim of the study was to determine the effect of the basic technological parameters of the formation of melt-blown fibrous structures based on biodegradable polymers compositions. Three types of biodegradable polymers were used in the research. PLA was the main component used in the composition, and the second polymer component used in the mixture was PHA, or, alternatively, a copolyester (Pripol 1009 -co- butyl terephthalate) known under the biomass acronym. At the same time, the study analysed the effect of the proportions of individual polymers on chemical structure, macroscopic structure and physico-mechanical properties of the obtained nonwoven layers.

Figure 3. The scheme of biomass structure [24]

2. Experimental

2.1. Materials and research methods

Biodegradable polymers were used in production of melt-blown nonwovens. The first polymer was PLA, a commercial product known as Ingeo 6400D, with glass transition temperature of 55–60°C and melting temperature of 160–170°C. The density of PLA was 1.24 g/cm³. The second of the used polymers was PHA, a commercial product known as Mirel M4100 with glass transition temperature range from –20 to –11°C and melting temperature at the 164–166°C level. The density of the used PHA was at the level similar to that of PLA and amounted to 1.22 g/cm³. The third biodegradable polymer used in the study was a synthesised aliphatic-aromatic copolymer (Pripol 1009 -co- butyl terephthalate) described in [25]. In the prepared synthesis, the acid aromatic component was dimethyl terephthalate (DMT), whereas Pripol 1009™ consisting of fatty acid dimers was used as an acid aliphatic component. The melting temperature of this polymer was 106°C.

The polymer composites used in the study were prepared in the Institute of Industrial Chemistry in Warsaw using a ZE 25AX51D twin-screw extruder with 120 min⁻¹ screw rotations, composite preparation temperature of 180–195°C, and 10 kg/h output.

2.2. Nonwoven formation

The nonwovens were produced using a large-scale laboratory stand for melt-blown nonwoven formation (manufactured by ZAMAK), a part of the equipment of the Department of Materials and Commodity Sciences and Textile Metrology of Lodz University of Technology (Figure 4). This device allows to produce finished fibrous structures directly from polymer melts by blowing them with hot air at high speed. It is also equipped with temperature setting controls for the individual heating zones of the extruder and other process parameters. Products made of short fibres or microfibres are obtained in this way. Additionally, as demonstrated by previous studies, the device makes it possible to process various types of thermoplastic polymers, which was confirmed [26, 27].

Figure 4. A large-scale laboratory stand for melt-blown nonwoven formation

2.3. Research methodology

The study used the following methodology in order to identify the conditions of processing of biopolymers used in the research, and to determine the properties of melt-blown nonwovens obtained from the investigated polymer blends.

Mass flow indexes (MFI) of polymers used for the preparation of composites was determined by means of a Melt Flow Indexer 4010 apparatus (Hanatek). This parameter was determined for the 180–200°C temperature range.

The analyses of the chemical structure of polymers were based on the spectra obtained using a Thermo Scientific Nicolet 6700 FTIR spectrometer. Each sample was scanned with following parameters: 32 scans at resolution 4 cm⁻¹. Samples were used in the form of pellets.

The thermal properties of the polymers were determined using a DSC Q2000, TA Instrument.

DSC analyses were performed at heating, cooling and heating rate equal 10°C·min⁻¹.

The surface mass of the obtained nonwovens was determined according to DIN EN 29073-1.

The thickness of the obtained nonwoven fabrics was determined using a DM 100 thickness gauge, in accordance with PN-EN ISO 9073-2.

The mechanical properties of the nonwovens were determined using an Instron 3119 testing machine, in accordance with PN-EN 29073-3.

The macroscopic structure of the nonwovens was analysed on the basis of images obtained with a Nova NanoSEM 230 scanning electron microscope manufactured by FEI (FEG-type field emission gun).

3. Results and discussion

3.1. Thermal properties of polymers and polymer composites

Based on the results obtained from the analysis of the mass flow index (MFI) (Table 1), it was found that similar MFI values for the polymers used in the polymer compositions are observed for a temperature of 180°C. There was a trend towards growing differences between the MFI values with increasing temperature of the material. At the same time, it was found that 180°C is the lowest possible PLA processing temperature for the melt-blown technique. The results of analysis are shown in Table 1.

Table 1. Results of MFI determination for the used polymers MFI: Mass flow index.

Polymer	Temperature, °C	Melt flow index, g/10min
PLA 6400D	180	2
PHA M4100	180	3.8
PLA 6400D	190	3.2
PHA M4100	190	9.7
PLA 6400D	200	9.3
PHA M4100	200	45.3
BIOMASS	180	26

The analysis of DSC thermograms of the studied polymers and blends presented in Figures 4–10 allows to observe the occurrence of characteristic glass transition at –14°C for PHA, 59°C for PLA and –30°C for biomass aliphatic-aromatic copolyester. Notably, PLA is characterised by the highest glass transition temperature T_g . The thermograms obtained for all samples contain the melting point of the crystalline phase transition. For PHA, the melting temperature determined on the basis of the thermogram (Figure 5) is 169°C, whereas analogous analysis of the DSC thermogram for PLA demonstrates the melting temperature of 167°C. The lowest temperature of phase

change - melting of the crystalline phase - was observed for the biomass copolyester, for which that value equals $T_m = 106^\circ\text{C}$. Only the thermogram of PHA demonstrates an exothermic effect with ca. 62°C maximum, responsible for susceptibility of the material to secondary crystallisation, and thermogram of PLA demonstrates cool crystallisation with ca. 138°C .

The cold crystallisation takes place faster due to the increased primary nucleation when heating from the glassy state and crystallisation in lower temperature than cooling from the melt state [28].

In the figures 7–10, we can observe changes of glass transition and crystallisation temperatures; however, the cold crystallisation temperature of PLA in blends was not observed. The increase of the PHA fraction causes the increasing of the glass transition temperature of PHA from -14°C to -6°C and also a slight decrease in glass transition temperature of PLA. The cold crystallisation of PLA does not appear in blends. We observed that blends crystallise almost at the same time and temperature of crystallisation, which is different than of the pure polymers. On this basis, we assume that in PLA/PHA blends, the same type of the macromolecular interaction occurs that means that these polymers may be partially mixed. In the literature, we can find works on the miscibility of PLA and PHA [28]. In PLA/PHA, blends are examined in terms of the interfacial adhesion occurrence. In other research, it was proven that blends prepared by melt-blended technique at high temperature present evidence of the increasing miscibility of PLA and PHA [29,10]. Miscibility of the used polymers will be the subject of our further research.

3.2. Chemical structure analysis

As it follows from the analysis of the FTIR spectrum presented in Figure 12, characteristic vibration signals of the C=O band at 1719 cm^{-1} for PHA, 1748 cm^{-1} for PLA and 1712 cm^{-1} for biomass copolyester are visible in all spectra. The shifts of these bands maxima result from interactions with the adjacent groups, different in the case of the used polymers.

The spectrogram in Figure 13 presents the FTIR ATR of various PLA/PHA blend compositions. As it can be observed in the

presented spectra, increasing the PHA proportion in the polymer mixture to 50% results in the appearance of considerable overlap of the carbonyl signals corresponding to both PLA and PHA. In contrast, 10% content of PHA in the polymer blend is insufficient for manifestation of that phenomenon.

Figure 14 presents a range of FTIR ATR spectra for PLA/biomass aliphatic-aromatic copolymer composite. Similarly, as in the case of PLA/PHA composite, 10% content of biomass copolyester in the blend did not result in the appearance of signals originating from that copolymer. The spectrum of the blend containing 10% biomass copolyester is similar to that of baseline PLA spectrum, or possibly the biomass copolymer signals overlap with the PLA bands and are invisible in the FTIR ATR spectrum.

3.3. Formation of fibrous structures by melt-blown method

On the basis of preliminary research on processes of forming fibrous structures from the polymer composites described above by melt-blown method, the optimum conditions of temperature distribution in the heating zones of the extruder were selected. The temperature values for the extruder heating zones and the spinner head are presented in Table 2.

Figure 6. DSC thermogram for PLA 6400D sample

Figure 5. DSC thermogram for PHA M4100 sample

Figure 7. DSC thermogram for biomass aliphatic-aromatic copolyester sample

Figure 8. DSC thermogram for PLA 6400D/PHA M4100 90:10 sample

Figure 10. DSC thermogram for PLA 6400D/PHA M4100 70:30 sample

Figure 9. DSC thermogram for PLA 6400D/biomass 90:10 sample

Figure 11. DSC thermogram for PLA 6400D/PHA M4100 50:50 sample

Figure 12. Spectrograms of the studied polymers: (a) PHA M4100, (b) PLA 6400D, (c) Biomass

Figure 13. Spectrograms of PLA/PHA polymer composites: (a) PLA6400D/PHAM4100 90:10, (b) PLA6400/PHAM4100 70:30, (c) PLA6400/PHAM4100 50:50.

Figure 14. Spectrograms of biomass copolyester and PLA 6400D/biomass aliphatic-aromatic copolyester composite

The nonwoven formation experiments demonstrated the possibility to obtain fibrous structures from PLA/PHA and PLA/biomass copolyester blends keeping the maximum proportion of PHA or biomass copolyester in the blend composition not higher than 30%. Increasing the proportion of, for example, PHA to 50% resulted in process instability and consequently, made it impossible to obtain representative, reproducible structures.

The microstructure of the obtained nonwovens was visualised with scanning electron microscopy (Figure 15).

As it follows from the microscopic images presented in Figure 15, nonwoven materials differ in the fibre diameter depending on the blend they have been made of. The largest fibre diameter was obtained in the melt-blown spinning process from the PLA6400D/PHAM4100 70:30 blend, whereas the PLA6400D/PHAM4100 90:10 blend yielded the smallest one. The above experiments indicate that increasing the content of PHA in the polymer composition results in a twofold increase in the diameter of the obtained fibres, whereas the introduction of biomass copolyester in 10% quantity did not cause a significant increase in the fibre diameter. Additionally, it is noteworthy that considerable scatter of fibre diameters is observed in the case of all nonwoven types. The obtained fibrous structures were analysed with respect to their physical and mechanical

properties. Table 3 presents the most important parameters of the obtained melt-blown nonwovens.

Studies of the influence of the properties of nonwoven material with different physical and mechanical properties on the composition has been conducted. Those nonwovens have been made from biopolymers composition similar to elastomeric. Nonwoven material produced from PLA/PHA 90/10 is characterised by following mechanical and physical properties: maximum breaking force 1.27N, relative elongation with maximum force 4.03% and tenacity 0.02cN/tex. Nonwovens produced from composition PLA/PHA 70/30 have better physical and mechanical properties: maximum breaking force 1.65N, relative elongation with maximum force 4.96% and tenacity 0.03cN/tex. The introduction of biomass to PLA results production of nonwoven characterised by the best properties among all nonwoven material produced from composition PLA/second biopolymer.

The biomass copolyester used in the PLA6400D/biomass 90:10 blend was characterised by the properties typical of elastomers, that is, materials capable of dimension changes as a result of tensile or shear stresses. The introduction of that copolyester to PLA resulted in obtaining the composition with the highest relative elongation and breaking force. Among the PLA6400D/PHAM4100 blends, the 70:30 one was characterised by a higher breaking force, elongation and tensile stress.

Table 2. Conditions of fibrous structure formation by melt-blown method

	Z1	Z2	Z3	Z4	Z5	Z6	Z7	H	Screw rotation speed	Receiving speed	Air temperature
	°C	°C	°C	°C	°C	°C	°C	°C	rpm	rpm	°C
PLA	190	190	200	200	220	220	240	240	10	0,3	250
PLA/PHA 90/10	170	180	180	190	195	195	220	220	10	0,3	230
PLA/PHA 70/30	170	180	180	190	195	195	220	220	10	0,3	230
PLA/copolyester 90/10	170	180	180	190	190	190	190	200	10	0,3	210

where: H - head, Z₁-Z₇ - extruder heating zones.

Table 3. Physical and mechanical properties of the obtained melt-blown nonwovens

Polymer blends	Surface mass g/m ²	Nonwoven-forming fibres diameter µm	Thickness mm	Maximum breaking force N	Relative elongation with maximum force %	Tenacity cN/tex	Tensile stress at maximum force (MPa)
PLA6400D	68±3.4	3.27±1.99	0.93±0.05	2.03±0.43	6.14±1.83	0.03±0.0009	0.14±0.03
PLA6400D/PHAM4100 90:10	113±5.65	2.85±1.72	1.05±0.05	1.27±0.26	4.03±1.17	0.02±0.0006	0.09±0.02
PLA6400D/PHAM4100 70:30	91±4.55	6.04±2.76	1.19±0.06	1.65±0.14	4.96±1.01	0.03±0.0009	0.12±0.01
PLA6400D/biomass 90:10	151±7.55	3.36±2.43	1.41±0.07	2.62±0.17	9.12±1.51	0.04±0.0012	0.19±0.02

Figure 15. The microscopic structure of melt-blown nonwovens: (a) PLA6400D, (b) PLA6400D/PHAM4100 90:10 (c) PLA6400D/PHAM4100 70:30, (d) PLA6400D/biomass 90:10

4. Summary and Conclusion

The experiments performed within the framework of the research confirmed the possibility of obtaining polymer composites based on PLA and PHA and aliphatic-aromatic copolyesters applicable for production of nonwovens by pneumothermic method. Additionally, the possibilities of processing composites with various contents of the individual polymer components were verified by technological studies. It was demonstrated that the use of PLA compositions with the aforementioned polymers in 50:50 proportions made it impossible to obtain homogeneous fibrous structures by melt-blown method. The course of the fibre-forming process in the case of such content of another copolymer was unstable, impaired by disturbances, such as clogging of the spinner head openings, as well as composite outflow over the head. In contrast, no such phenomena were observed in the case of polymer composition where the proportion of PLA in the blend was at the level of 70%. The analyses of chemical structure using the FTIR ATR method demonstrated no significant differences in the spectra of the obtained polymer composites.

It is associated primarily with similar chemical structure of the used polymers and overlapping of the characteristic bands in the spectrograms. The obtained nonwoven layers were also subjected to tests of physical and mechanical properties, which confirmed a wide spectrum of applicability of the obtained nonwovens, depending on the polymer composition used in production.

Biodegradation dynamics of produced materials will be the subject of further research.

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