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Investigation on the Melt Processing of Biodegradable Aliphatic-Aromatic Polyester into Fibrous Products

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Abstract
Research is described in the article concerning the melt processing of biodegradable aliphatic-aromatic copolyesters into fibrous products. Copolyesters containing 57 - 60% of a tri-component aliphatic portion (copolymers of butylene glycol and adypic-, succinic-, glutaric acid and terephtalic acid) prepared on a large laboratory scale were used in fibres and nonwoven from molten polymers. Fibres were made in a two-step process comprising spinning and drawing. Nonwovens were formed by the spunbond method. Main properties are given of the polymers and fibres, and the nonwoven made thereof. It was found that the aliphatic-aromatic copolyesters prepared reveal good spinability. Thermal properties: T_g < 0 °C and low T_m ~115 °C of fibres made of aliphatic-aromatic copolyesters limit their possible uses mainly to the production of disposables. A cheap method of making spunbond nonwoven which leads to ready textiles is recommended for the processing of the copolyesters.

Key words: *biodegradable polyester, fibrous products, spunbond nonwoven.*

Introduction

Aliphatic-aromatic copolyesters (AAC) with a random arrangement of the condensing components in their chain have been known for many years. AACs can be broken into two main groups: one with a prevailing number of aliphatic components and the other with prevailing aromatic segments. Both groups have found their specific application [1, 2]. One other more detailed division of AACs can be made on the grounds of the amount of acid and diol segments which form the copolyester structure. The use of substrates of varied structure has opened ways to the synthesis of numerous compounds with a rich palette of physical-chemical properties and possible applications [3]. The discovery of their biodegradability was a break-through in AAC research [4, 5]. It was found that the predominance of acidic aliphatic components in their structure is a precondition of the biodegradation of copolyesters during several weeks of composting at 60 °C. The outcome of the research was the elaboration by BASF of the synthesis of biodegradable AAC from terephtalic acid, adypic acid and 1,4-butandiol. It is an example of AAC with one acid aliphatic component and one acid aromatic [6]. It was given the trade name Ecoflex, and is put on the market in the amount of ca. 74 thousand tons a year. One more example is Eastar Bio made by the Eastman Chemical Corporation from the same substrates. Amongst the biodegradable AAC, there are examples which contain one [7, 8], two [9] or three acid aliphatic components in their structure [10]. Recently technology has been prepared and physical-chemical properties defined of a less known biodegradable copolyester with a tri-component aliphatic part: poly(butyleneadipate-co-succinate-co-glutarate-co-terephthalate) (PBASGT) [11 - 13].

A blend of methyl diesters of aliphatic dicarboxylic acids under the trade name Uniestrol was harnessed for the synthesis of biodegradable copolyester. Uniestrol is derived from post-crystallization lye which arises in the production process of adypic acid during its purification by crystallization [10]. The variable composition of the raw material does not impede the forming of the final macromolecular products with physical-chemical properties which come close together [14]. The copolyester is a potential source of valuable raw materials for biodegradable products by melt-processing.

PBASGT comprises a group of biodegradable copolyesters with a prevailing content of aliphatic segments in the macromolecule; however, coverage of their processing has not yet been given in scientific/technical literature.

Biodegradable copolyesters of that type belong to the group of statistic copolyesters whose macromolecules are composed of four acidic segments as structural elements. As in all statistic copolymers, the orderly chain arrangement of the macromolecules is disturbed, resulting in a decreased ability to crystallise, which causes problems in the forming of products at high speed and throughput since the material does not quickly solidify properly by crystallization. The drawback comes into play mainly in melt-blowing causing fibres stick together, thus deteriorating their bulkiness. Agglutination is also a problem in

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the casting of film. In short cycle extrusion moulding, insufficient solidification occurs as well as unsatisfactory dimension stability of the products. Agglutination of the granules is an obstacle to high-speed granulation. A more intensive quenching of the polymer at ambient temperature is not a remedy since the glass transition temperature falls much lower at about –27 °C.

When processing **P**BASGT, obstacles may be expected related with their poor crystallization. Much better results could be achieved with artificial nucleation [15].

The usability of AAC polymers in the preparation of fibrous products has been described in a publication by German scientists [16, 17]. They investigated the process of producing POY fibres and spun-bond nonwoven from Eastar Bio polymer. At the Institute of Biopolymers and Chemical Fibres, works have confirmed the suitability of the polymer for use in the preparation of fibres and melt-blown nonwoven [18, 19]

The objective of the work was to assess the suitability of PBASGT copolyester as row material for fibrous products. In the article presented, research on the melt-processing of PBASGT copolyester into fibrous products is described. PBASGT was prepared on a large laboratory scale at the Institute of Biopolymers and Chemical Fibres. Shown are the main properties of the polymer and fibres and nonwoven made thereof.

Experimental

Raw materials

Dimethyl terephthalate (DMT) was purchased from Mogilevo (Belarus); 1,4-butanediol (BD) was obtained from PPH Standard Co., Ltd. (Poland), and Uniestrol was supplied by Pilot Plant ‘‘Organika’’ Co., Ltd. (Poland). Uniestrol is a mixture of dicarboxylic acid dimethyl esters: 31% of dimethyl adipate (DMA), 14% of dimethyl succinate (DMS), and 55% of dimethyl glutarate (DMG).

Tetrabutyl orthotitanate (Ti(OBu)4) and sodium carbonate were supplied by Sigma-Aldrich Co.

All chemicals were used without purification.

Research methods

Synthesis of a copolyester with a 57% mol part of the acidic aliphatic component

4200 g of dimethyl ester of terephtalic acid, 4600 g of a blend of dimethyl esters of aliphatic dicarboxylic acids (succinic, glutaric and adypic) with a medium molar mass of ca 160,

5500 g of 1,4-butandiol and 2.5 g of tetrabutyl orthotitanate were put into a 30 dm^3 autoclave (Fourne, Germany) heated to 140 °C.

The ester exchange reaction was conducted from 165 to 225 °C while carrying off the methanol delivered. 34 g of powdered Na_2CO_3 and 3.5 g of tetrabutyl orthotitanate were next added. The polycondensation process was conducted at 240 °C under a pressure of 0.053 kPa for 80 - 120 minutes to attain an assumed power consumption of the drive motor of the reactor shaft. Molten polymer was extruded in the form of a string and cut into granules.

Drying of copolyesters

Prior to the processing, the polymers were dried: for melt spinning - in a tumbler dryer (BT 50 type, by Fourne, Germany) for a minimum of 14 hours at 60 °C in a 0.027 kPa vacuum, for spun bonding - in a dehumidifying dryer (type HR50 by Piovan Co., Italy) for at least 7 h at 55 °C (dew point -30 °C)

Fibre formation

Fibres were formed from the molten PBASGT polymer in a two-step process comprising spinning and drawing. Multifilament fibre was spun on an experimental extruder spinning bank equipped with a 20 mm diameter extruder (Barmag, Germany) at a melt temperature of 220 - 240 °C with a capacity of 7 - 30 g/min and speed of 900 m/min through multihole (12, 17, 24) spinnerets. Spinning trials were also performed at the following speeds of the spinning bank godets: 1st godet - 500 m/min, 2nd godet - 900 m/min. Estesol TXB supplied by Bozzetto Group (Italy) in the form of a 15% emulsion in water was applied as the spinfinish. Multifilaments were next drawn (Rieter J2/2a type, Germany) at a speed of 496 m/min and draw ratio in the range of 2.0 - 3.1.

Preparation of the nonwowen

Nonwoven was formed by the spunbond technique from the melt on a laboratory stand constructed and built by the Research and Development Centre of Textile Machinery “Polmatex-Cenaro”.

The following parameters were varied in the course of the trials: the width of the forming channel, the extrusion output, pressure in the forming channel, temperature of the calender and the take-up speed of the nonwoven. The nonwoven was formed at a temperature range of 176 to 184 °C with a take-up speed of 2.6 to -3.7 m/min. A 210-hole spinneret was used with a hole diameter and capillary length of 0.3 and 0.9 mm, respectively. The extrusion output (on a single capillary) was varied in the range of 0.23 - 0.59 g/min, and the calender temperature - from 40 - 60 °C. Pressure in the forming channel was from 1200 to 1700 Pa.

Nonwoven was formed from dried polymer with a water content of ≤60 ppm. The polymer was kept at 55 °C (dew point was -30 °C) during the forming in the dehumidifier for resins of the HR50 type (Piovan Co.).

Test methods

Thermal analysis

Thermal characteristic of the copolyester samples was prepared by the method of differential scanning calorimetry (DSC) and use of Diamond (Perkin-Elmer) eqThermal cuipped apparatus with a cooler for work at moderately low temperature - Introcooler II and microscale AD-2Z. The DSC - tested samples, 5 - 15 mg by weight, were airtight closed in standard aluminum vessels under nitrogen. The speed of heating and cooling was 20 °C/min. Measurements were made in the temperature range of - 60 to +160 °C in the cycle: heating I, cooling, heating II.

The melting temperature T_m was estimated iat the maximum point of the endothermic peak of melting. The temperature of crystallization T_{cc} and crystallization from the melt T_c were estimated at the minimum point of the relevant exothermic peak of crystallization.

Parameters of the physical transformations proceeding in the course of the DSC examination were estimated by means of standard software - “Pyris**”.**

Mass loss during the heating of the polymer at 240 °C for 30 min. and the temperature of the maximum weight loss speed

Table 1. Thermal properties of aliphatic-aromatic polyester for melt spinning.

Symbol of sample	DSC				TGA
	T_g, °C	T_m, °C	T_c, °C	T_{cc}, °C	T_{max}, °C
A	- 31.0	103.2	27.1	11.6	417.7
B	-29.2	114.6	49.4	-	414.4

*Table 2. Thermal properties and MFI of aliphatic-aromatic polyester for the preparation of spun- bond nonwoven. *) by method A.*

Symbol of sample	T_C, °C	ΔH_C, J/g	T_m, °C	ΔH_m, J/g	MFI*, g/10 min
C	53.7	-18.9	118.8	18.9	35
D	50.7	-18.9	118.9	19.0	33
E	65.9	-18.9	117.8	19.0	37
F	59.6	-20.2	114.7	20.6	35
G	57.6	-20.4	115.1	20.4	34
H	50.0	-20.2	114.8	20.2	35

T_{max} were tested by the TGA method; TGAs were recorded on a TA Instruments 2950 TGA HR V5.4 thermogravimetric analyser under an inert (N_2) carrier flow at a heating rate of 20 °C min^{-1}

Estimation of inherent viscosity

Viscosity was measured in chloroform at 25 °C using a viscometer - Ubbelohde with capillary 0Ak = 0.00498. The inherent viscosity was calculated from:

$$\eta_{inh} = \ln \eta_{rel}/c$$

where, η_{rel} – relative viscosity, c – polymer concentration 0.1 g/dl.

Estimation of water content in the copolyester.

The moisture content in the polymer was measured by the coulometric -Karl Fischer method with DL39X apparatus by Mettler Toledo.

Melt flow index

The melt flow index (MFI) of the polymers was established according to method A in accordance with Standard ASTM D1238 Standard Test Method for Melt Flow Rates of Thermoplastics by Extrusion Plastometer (with a spinneret hole of 2 mm, at a temperature of 190 °C, and method B, developed on the basis of the above standard at IBWCh for fibre-forming polymers (using a spinneret hole of 0.5 mm, within the temperature range of 210 to 250 °C).

Physical-mechanical properties of fibrous products

Physical-mechanical properties of the fibre and spunbond nonwoven were measured using Instron 5540 apparatus according to following Polish-ISO standards:

for filaments:

linear density PN-EN ISO 2060:1997
tenacity PN-EN ISO 2062:1997
elongation PN-EN ISO 2062:1997
initial modulus PN-EN ISO 2062:1997
elastic recovery PN-84/P-04667

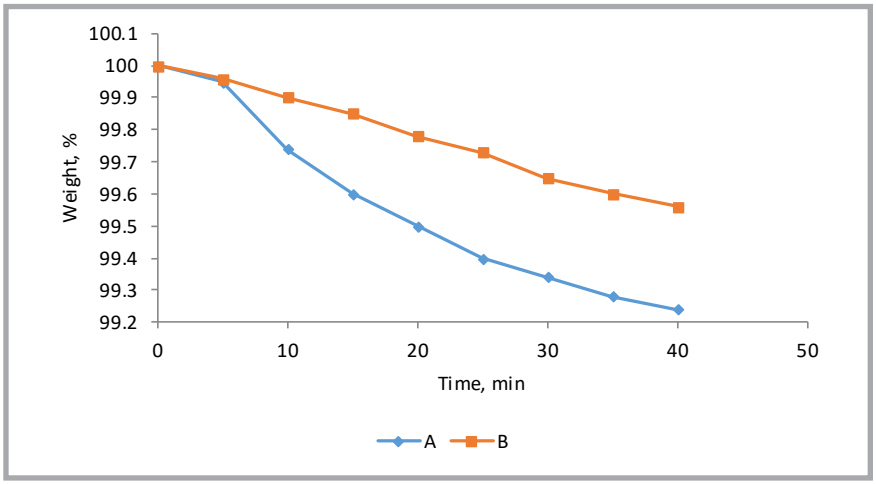

Figure 1. TGA thermogram of mass loss (heating rate 20 °C/min) of the polymer after annealing during 30 minutes at 240 °C.

for nonwoven:

surface density PN-EN 29073-1:1994,
tenacity PN-EN 29073-3:1994,
elongation at break PN-EN 29073-3:1994.

Results and discussion

Characteristics of the aliphatic-aromatic copolyester

Several tens of syntheses of the PBASGT polymer were completed in the course of research which lasted a couple of years. One synthesis trial on a large laboratory scale yielded 6 to 8 kg of the polymer with a content of 57% - 60% of the aliphatic component. Physical-chemical properties of the material are described elsewhere [13].

In research concerning the melt-forming of fibres, copolyester PBASGT with 60% of the aliphatic component (A in ***Table 1***) and copolyester B with 57% of the aliphatic acidic component were used. Polymer A was obtained in a similar synthesis from 3880 g of DMT and 4800 g of Uniestrol. Nonwovens were made of copolyesters C – H containing 57% of acidic aliphatic component.

Given below are only the basic characteristics of the copolyesters (samples A – H) used in the processing to fibrous materials.

Thermal properties of the polymers used in the forming of fibre are presented in ***Table 1*** and ***Figure 1***.

Thermal properties and melt flow indices (by method A) of polymers used in the preparation of the nonwoven are shown in ***Table 2***.

Melt spinning

The objective of the work was to:

- assess the suitability of poly(butylene-co terephtalate-co-glutarate-co-adipate-co succinate) prepared on a big laboratory scale for the forming of fibres,
- assess physical-mechanical properties of the fibres obtained

The melt flow index (MFI) at varied temperature was chosen as a measure of the spinability of the aliphatic-aromatic polyesters. Several spinning trials on an experimental line were also made for the purpose of preparing a multifilament yarn. Polymers **A** and B differing

in the content of aliphatic and aromatic components were used in the trials:
A: 60 aliphatic/40 aromatic,
B: 57 aliphatic/43 aromatic components.

Physical-mechanical properties of the fibre were estimated; and the impact of the proportion of the aliphatic and aromatic portions upon the susceptibility of the polymer to thermal degradation was investigated.

Figure 2 presents the dependence on temperature of the MFI measured by method B. The dependence indicates how to tentatively adopt a suitable spinning temperature. Both polymers have a similar MFI, that of polymer B being slightly higher. The temperature range of 220 – 240 °C proved suitable for the spinning of both polymers.

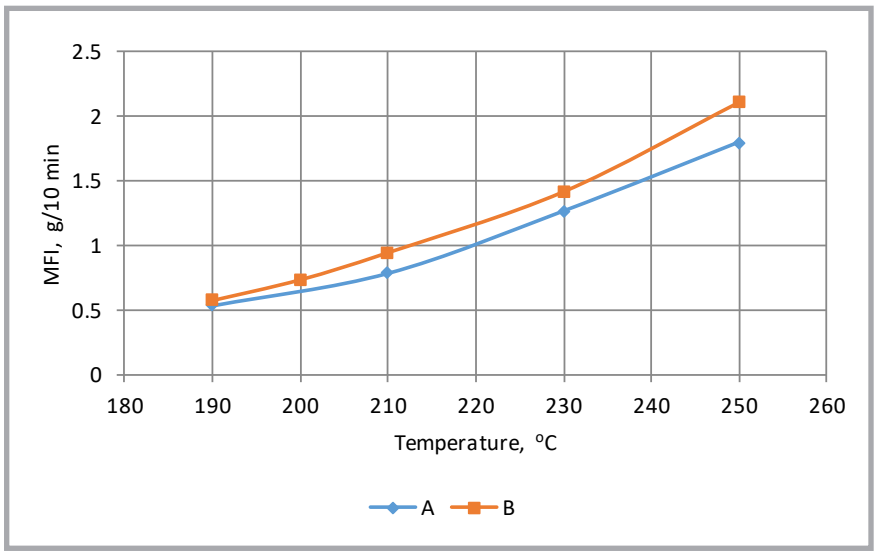

Figure 2. *Dependence of the melt flow index (MFI) on temperature for copolyesters A and B (according to method B).*

Physical-mechanical properties of continuous yarn made of polymers A and B under varied conditions are shown in ***Table 3***. The fibres were formed in two separate steps: spinning and drawing. Some problems emerged with the building of the yarn packing on the winder. An additional spinning trial was made with a varied speed of the two godets on the spinning bank: 1st godet - 500 m/min, 2nd godet 900 m/min. The pre-oriented yarn thus prepared was of a much better quality (trial A/2, ***Table 3***).

Characteristic of all fibres made of the aliphatic-aromatic PBASGT copolyesters is a rather low tenacity, high elasticity and low initial modulus. Their elastic properties are closely related to their structure, characterized by the low temperature of glass transition, which falls below 0 °C. Hence the fibres are elastic at ambient temperature.

Due to their thermal properties, low glass transition and melting temperature (~115°C), the PBASGT fibres can be harnessed for limited applications, primarily in disposable products. These, in turn, favour the cheap spunbond or melt-blown technique, which yield ready textiles in one operation.

In the course of the melt-processing of polymers, their molecular mass is reduced due to the impact of high temperature. A lower molecular mass leads to the deterioration of mechanical properties. In the processing of thermally unstable polymers, a temperature as low as possible is therefore applied and a the shortest possible residence time of the resin in a molten state. A significant lowering of the temperature in the spinning of fibres is impracticable. The conditions at spinning promote degradation of the polymer. In comparison to film casting or extrusion moulding, the contact surface between the molten polymer and equipment and air is larger. To prevent hydrolysis during processing, the polymers were dried to a water content below 50 ppm. In the course of processing the degradation degree was controlled by assessing the inherent viscosity of the polymer and as-spun fibre. Fibre was spun on an experimental single-spinneret spinning bank. In such an arrangement, the low throughput of extrusion implies prolonging of the polymer melt residence time. The residence time in the experimental machine is no longer than 5 minutes with a maximal spinning throughput of 30 g/min; it reaches 15 minutes when thin fibres are spun at the minimal throughput.

Table 3. *Physical-mechanical properties of continuous fibres spun from aliphatic-aromatic copolyesters PBASGT under varied conditions. n.e. – not examined.*

Polymer sample/ spinning sample	Tempera-ture, °C	Otput, g/min	Linear mass of the as-spun fibre/number of filaments, dtex	Draw ratio R_C	Linear density, dtex	Tenacity of fibre, cN/tex	Elongation, %	Initial modulus of extension, cN/tex]	Elastic recovery at elongation 20%, *30%, %	Shrinkage at 80 °C in water, %
A/1	240	12.0	138/12	-	138 ± 5	13.0 ± 0.6	86 ± 3	n.e.	92* ± 1	n.e.
A/2	240	20.0	224/12	-	224 ± 3	18.4 ± 0.7	181 ± 6	n.e.	94* ± 3	n.e.
A/3*	240	30.0	322/17	3.09	104.2 ±	19.1 ± 0.5	67 ± 2	29.6 ±	96* ± 2	n.e.
A/4	219	29.7	345/17	2.56	154 ± 4	15.5 ± 0.3	69 ± 3	29.6 ± 4	n.e.	n.e.
B/1	240	29.6	337/24	2.93	141 ± 5	16.3 ± 0.3	63 ± 2	24.5 ± 3.0	90 ± 3	71 ± 5
B/2	240	23.1	266/24	2.79	110 ± 8	19.5 ± 0.3	39 ± 4	31.3 ± 3.6	85 ± 4	73 ± 2
B/3	240	14.1	166/24	2.93	64.8 ± 3.3	24.4 ± 1.0	23 ± 1	70.6 ± 13	- n.e.	70 ± 4
B/4	240	7.1	86/24	2.17	44.8 ± 1.4	13.9 ± 0.7	40 ± 4	41.2 ± 7.8	94 ± 1	61 ± 3
B/5	220	29.5	334/24	2.79	138 ± 2	18.2 ± 0.5	68 ± 3	33.3 ± 4.4	95 ± 1	65 ± 6
B/6	220	23.4	267/24	2.79	113 ± 3	17.8 ± 0.4	69 ± 2	23.6 ± 3.0	94 ± 0.4	64 ± 3
B/7	220	14.4	165/24	2.79	67.2 ± 2.8	21.3 ± 0.9	44 ± 4	46.3 ± 7.8	86 ± 2	70 ± 0
B/8	**220**	7.1	87/24	2.17	46 ± 1.8	14.7 ± 0.5	44 ± 4	37.8 ± 5.5	94 ± 2	59 ± 1

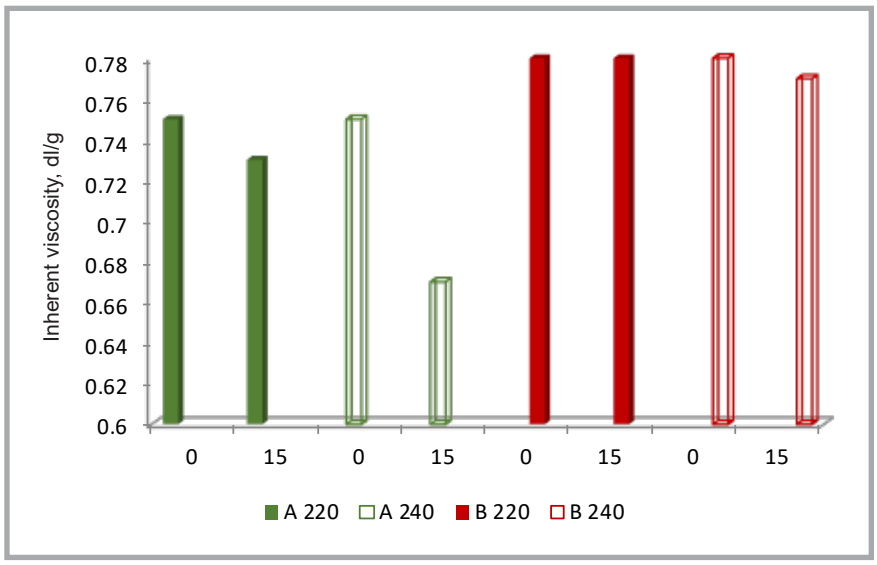

Figure 3. *Change in polymer inherent viscosity during spinning; residence time in molten state - 15 min, temperature 220 and 240 °C.*

Examples of the change in the inherent viscosity of polymers A and B occurring after processing into fibres under varied thermal conditions are presented in ***Figure 3***.

A distinct drop in the inherent viscosity of the polymers could be observed with increasing temperature and prolonged residence time in a molten state.

The polymer with a lower content of the aliphatic portion (sample B) shows a better thermal stability than polymer A in the processing to fibre.

Forming of spunbond nonwoven

Spunbond nonwoven finds use in the production of disposable medical and hygiene devices and in technical materials like filters [20]. They are also applied in the manufacture of underwear and clothes. They also are widely used in agriculture for plant protection and mulching and in the preparation of biodegradable seedling pots, which after germination are planted in soil. In the building industry nonwoven is used in roofing and in the protection of houses against humidity.

It was aim of the work to assess the possibility of forming spunbond nonwoven from aliphatic–aromatic copolyesters synthesized at IBWCh. Trials to prepare the nonwoven were accomplished with the use of blended PBASGT's from various syntheses denoted as C+D, E+F and G+H. The joining of the polymers from two syntheses was necessary because of the minimal amount of the material needed for one spinning trial on the equipment in possession

Nonwoven was formed from a polymer first dried to a water content ≤ 60 ppm. From each of the polymers, several changes in the nonwoven were formed at varying process parameters. The surface density of the nonwoven was from 75 to 100 g/m^2. The impact was estimated of the take-up speed of the nonwoven and temperature of calendaring on selected structural and physical-mechanical properties of the product.

For each of the fleece variants (obtained at a given width of the lead channel and pressure in the channel), the take-up speed was calculated from the formula:

$$V = W/(d\pi r^2)$$

where, V – take-up speed of the fibre, W – mass extrusion output (g/min/capillary), r – radius of the filament (μm), d – density of the polymer melt (g/cm).

The diameter of the fibre changes in the course of the thermal bonding of the fleece on the heated calender. Samples of fibre for diameter measurement were therefore taken before the calender to eliminate the influence of calendering.

Mechanical properties of the spunbond nonwoven

Mechanical properties of the polymeric material depend largely upon its internal structure (molecular order) and crystallization form. Tenacity and elongation at break were measured in the nonwoven prepared both along and across the fabric. ***Figures 4*** and ***5*** illustrate changes in the mechanical properties of the nonwoven occurring at varied take-up speeds and constant temperature of the calender (40 °C).

Figures 4 and ***5*** present dependences of the tenacity as a function of the fibre take-up speed for nonwoven made of the PBASGT (C+D) and (E+F) polymers. The dependence of the elongation at break as a function of the fibre take-up speed was also analyzed for the E+F blend. The nonwoven was formed at a constant calender temperature (40 °C). As expected, the tenacity is up and elongation is down with the increasing take-up speed of the fibre. Nonwoven formed at 40 °C does not reveal the anisotropy of tenacity, At a given take-up speed of the fibre, the tenacity is comparable both in the along and across directions of the fabric, while some differences can be noted in the values of elongation at break. Elongation measured across the fabric was higher than that along in the product made of E+F polymer.

The tenacity of the nonwovens made at a higher calendering temperature (50 - 65 °C) depends upon the measurement direction; substantial differences between across and along measurements appear (***Figure 6***). The along value is about 15% higher than the across one.

The change in mechanical properties observed as a function of the take-up speed issues from the morphological and molecular ordered state of the polymer. A high-speed take-up leads to better orientation of the polymer chains and causes morphological changes in the nonwoven like in the thickness and diameter of the fibres. Thus an increase in the take-up speed results in a stronger nonwoven. The anisotropy of tenacity of nonwoven calendered at a temperature in the range of 50 - 65 °C probably ensues from thermal degradation of the nonwoven at the point of contact with the calender. The same proceeds in the nonwoven made of polylactide [21].

Conclusions

PBASGT with content of acidic aliphatic components of 57 – 60 % having an inherent viscosity of 0.75-0.78 g/l, and MFI $_{190\ oC}$, =31-37 g/10 min and prepared on a big laboratory scale at the Institute of

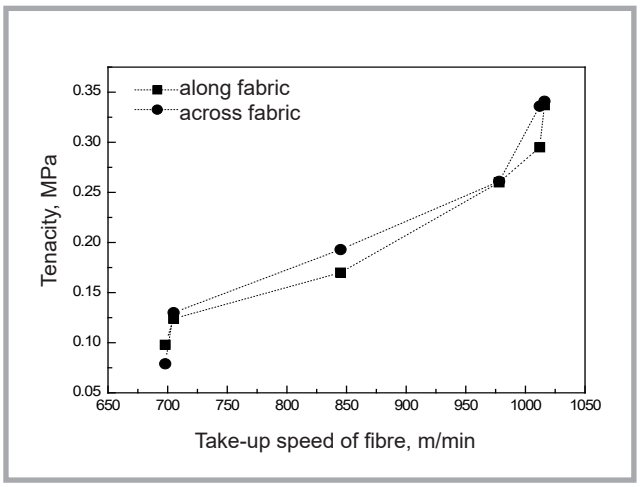

Figure 4. *Dependence of the tenacity on the fibre take-up speed of nonwoven made of PBASGT (C+D).*

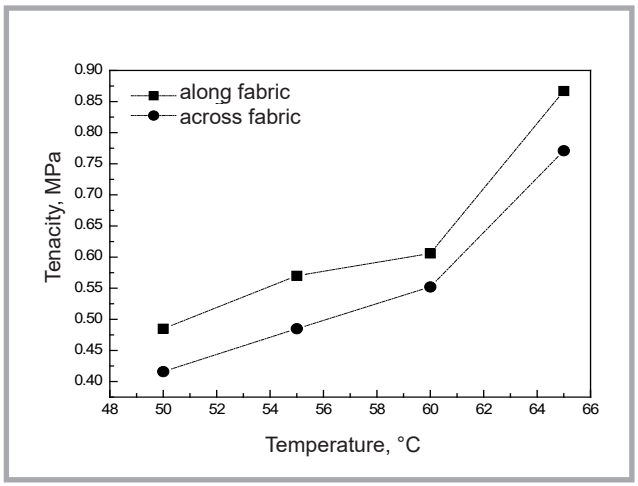

Figure 6. *Dependence of the tenacity on the calandering temperature of nonwoven made of PBASGT (G+H).*

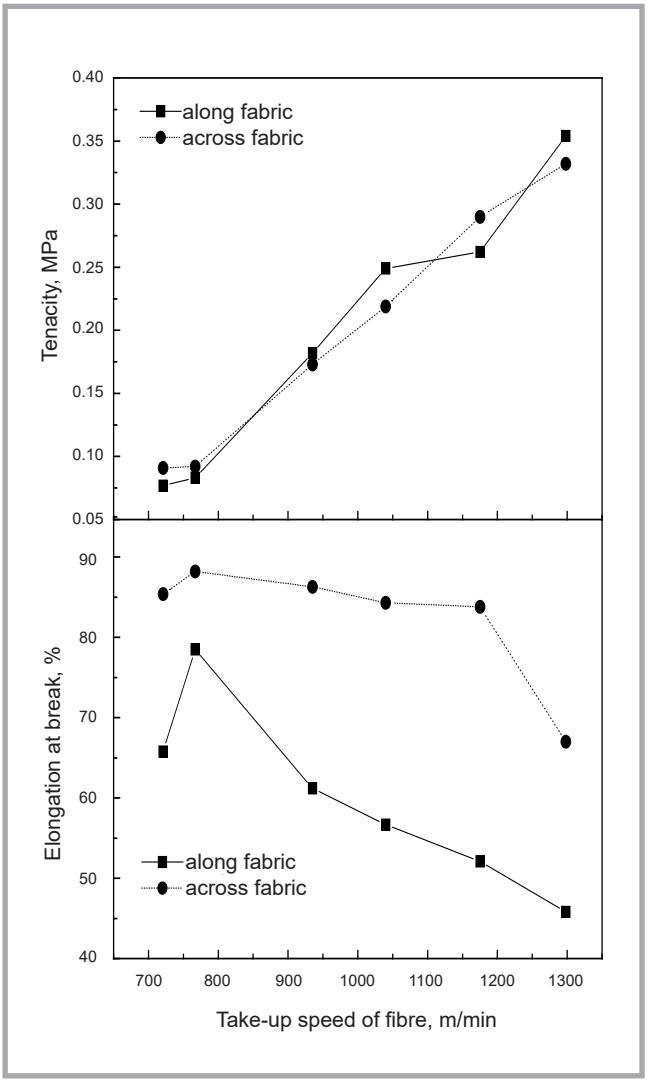

Figure 5. *Dependence of the tenacity on the fibre take-up speed of nonwoven made of PBASGT (E+F).*

Biopolymers and Chemical Fibres, Lodz, Poland revealed spin-ability.

In the processing to fibre, polymer with a lower content of the aliphatic portion (sample B) shows a better thermal stability than polymer A.

Fibres of PBASGT are characterized by a low tenacity, high elasticity and low initial modulus. They count as elastic-type fibres due to the structure of the polymer (glass transition temperature below 0 °C). The fibres of the polymer remain in an elastic-plastic state at ambient temperature.

The aliphatic-aromatic copolyesters investigated lend themselves to the forming of spunbond nonwoven. The tenacity and elongation at break largely depend upon the process parameters, primarily the take-up speed and temperature of calendering. A high take-up speed and calendering temperature in the range of 40 - 65 °C provide high tenacity and low elongation of the fibre. The tenacity of the nonwoven calendered at 40 °C does not depend on the direction of measurement (across or along the fabric). Calendering of the nonwoven at higher temperature causes the anisotropy of the tenacity.

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