Lucy Ciera[1],
Lynda Beladjal[2],
Xavier Almeras[3],
Tom Gheysens[4],
Lieve Van Landuyt[1],
Johan Mertens[2],
Vincent Nierstrasz[5],
Lieva Van Langenhove[1]

[1]Ghent University,
Faculty of Engineering and Architecture,
Department of Textiles,
Technologiepark 907, B-9052 Zwijnaarde, Belgium

[2]Faculty of Science,
Department of Biology, Terrestrial Ecology Unit,
Ledeganckstraat 35, B-9000 Ghent, Belgium.

[3]Devan Chemicals,
539, Klein Frankrijk, B-9600 Ronse, Belgium.

[4]ESA Advanced Concepts Team, ESTEC,
Keplerlaan, Noordwijk, The Netherlands

[5]The Swedish School of Textiles,
University of Borås,
Bryggaregatan 17, SE-501 90 Borås, Sweden

Morphological and Material Properties of Polyethyleneterephthalate (PET) Fibres with Spores Incorporated

Abstract

Owing to the current demand for textiles with new functionalities and improved properties, there has been a continuous effort to modify Polyethylene terephthalate (PET) materials. In our previous study, we demonstrated that Bacillus amyloliquefaciens spores can be incorporated into PET fibres during extrusion. However, the extent to which they can be incorporated without fundamentally changing the properties of the fibres is unknown. In this work, scanning electron microscopy (SEM), transmission electron microscopy (TEM), optical microscopy (OM), differential scanning calorimetry (DSC), a Favimat tensile tester, and Raman and Fourier transform infrared spectroscopy (FT-IR) were used to study the properties of PET/spore fibres. The tensile strength, Young's modulus and elongation at break were dependent on the spore concentration. Additionally the degree of crystallinity increased slightly, whereas the melting and crystallisation temperatures remained constant at all spore concentration levels. Nevertheless the properties of the fibres fall within the acceptable range of variation and are found to be as good as normal PET fibres.

Key words: *bacteria spores, PET fibres, extrusion, fibre properties.*

■ Introduction

Polyethyleneterephthalate (PET), popularly known as polyester, is a long-chain semicrystalline thermoplastic polymer that is widely produced, with a total production of 31.929 million tons in 2009 [1]. Due to its superior mechanical properties, ability to be recycled, low cost and ease of processing, PET fibres are extensively used in various textile and technical applications [2 - 4].

In order to meet the current need for multifunctional textiles with improved and specific properties, continuous effort is being made to modify PET fibres and materials. To date, various additives such as nucleating, antimicrobial, enzymes, colorants, cross-linking and matting agents have been incorporated in PET for applications in various fields [5 - 8]. Techniques for incorporating additives into PET fibres include the addition of compounds during the fibre production process or applying compounds on the material surface as a post-treatment process. The choice of technique depends on the functionality that is required as well as on the characteristics of the additives, like its migration to the surface during use [2, 9, 10]**.**

When additives are applied at the finishing stage, they are physically or chemically bonded to the surface of the material; however, their resistance to abrasion and washing are never guaranteed.

Furthermore finishing techniques like spraying can cause spills, which may be detrimental to the environment. Moreover badly applied coatings may lead to partial loss during use, care and storage [11]. In contrast, incorporating additives during fibre production entraps the additives in the polymer matrix during solidification of the fibre forming polymer and may take part in the crystallization process, resulting in a strong bond between the polymer and additives, as well as providing high resistance to abrasion [2, 10]. In addition the additive can migrate slowly to the surface, acting as a slow release mechanism, which guarantees an extended period of additive activity [12]. The release rate is influenced by the physical and chemical characteristics of the polymer in relation to the characteristics of the additive [13, 14]**.**

Earlier studies have shown that any additive incorporated into semi-crystalline polymers like PET during production can greatly influence the overall properties of the end product. The data available report effects on tensile properties like tensile strength, Young's modulus, flexural strength and elongation at break [3, 15, 16]. The results presented by Onuegbu & Igwe (2011) revealed an increase in tensile strength, Young's modulus and flexural strength with an increase in additive loading until a given level is reached where after a further increase in additives resulted in a decrease in the properties mentioned. This means that it is important to investigate the optimal concentration of additives that will give a good compromise for material properties and the functionality required.

Several other studies have investigated factors that influence the material properties of additive-polymer products. It was found that interfacial bonding between the additive and polymer matrix and the dispersion of the additive in the matrix are the main determinants of properties of the end products [4, 18]. These factors depend on the characteristics of the additives, like size distribution, shape and loading. In a few works, smaller particles and good dispersion resulted in better tensile properties, while larger particles exhibited poor material properties [15, 19]. The additive size influences the stress transfer between the additives and the polymer, which increases with the decreasing size of the additives and decreasing void voiding intensity [20, 21]. Poor dispersion and agglomerates create voids and cracks in the polymer matrix that can result in reduced material properties and an ununiformed morphological structure [2, 22]. Therefore understanding the interfacial bonding and dispersion of additives is important while investigating the material properties of additive-polymer products.

Spores of the thermophile bacterial strain *Bacillus amyloliquefaciens* are known to be resistant to high temperatures and pressures [23, 24], making them good

Ciera L, Beladjal L, Almeras X, Gheysens T, Van Landuyt L, Mertens J, Nierstrasz V, Van Langenhove L. Morphological and Material Properties of Polyethyleneterephthalate (PET) Fibres with Spores Incorporated. *FIBRES & TEXTILES in Eastern Europe* 2014; 22, 4(106): 29-36.

29

candidates for extruding in polymers. In our previous work, we successfully incorporated spores in the polymer matrix during fibre formation [25]. However, the spores were used as proof of the concept and therefore did not add any functionality to the PET fibres. Nonetheless the extent to which the spores can be incorporated without fundamentally changing the properties of PET fibres is unknown. The present study investigated the morphological and material properties of PET fibres with spores incorporated to see if the fibres produced were different from normal PET fibres. PET fibres incorporated with 0 to 10% (w/w) spores were extruded in a single screw extruder. The spores-PET interaction and dispersion was studied with Scanning electron microscopy (SEM), Transmission electron microscopy (TEM) and optical microscopy (OM). Material properties like tensile strength, Young's modulus and elongation at break were studied on a Favimat tensile fibre testing machine, while thermal properties and crystallinity behavior were tested with Differential scanning calorimetry (DSC) and Raman and Fourier transform infrared spectroscopy (FT-IR).

Results from this study are expected to give an insight into how the micro-organisms incorporated affect the fibre properties. This knowledge will give new inspirations on how and where to improve the extrusion process in order to develop better quality fibres, which is valuable as the micro-organisms integrated could add a multitude of functions to textiles, creating novel and niche products.

■ Materials and method

Extrusion

Spores of *B. amyloliquefaciens* were extruded in Arnite thermoplastic PET pellets (Arnite A02 307) from Royal DSM N.V. (Netherlands).

Prior to extrusion, the PET pellets were dried in an oven for two days at 70 °C, after which pure *B. amyloliquefaciens* spores were added by gravimetric dosing during spinning to obtain a 0 (control), 2, 4, 6, 8 and 10% (w/w) concentration of spores to PET polymer. This mixture was extruded into multi-filament fibres by a single screw extruder (General extrusion technology, China). The three different heating zones of the barrel were set to 280 ± 10 °C for the feed stock (trans-

port of material), 290 ± 5 °C for plasticising (compression) and 295 ± 2 °C for pumping (metering). The die was heated at 295 °C; the pressure was around 6.0 ± 0.2 MPa, and the average residence time was approximately 5 ± 0.5 minutes. The resulting fibres had an average linear density of about 7 ± 0.5 dtex.

Characterisation methods
Tensile testing
Tensile properties like the tensile strength, modulus and elongation at break of resulting spores/PET fibres extruded were determined with a FAVIMAT-ROBOT (Textechno, Germany). All samples were kept in a conditioned room at 65 ± 2% humidity and temperature of 20 ± 2 °C for 24 hours before testing. An average of 50 single filaments was tested for each spore concentration level.

The two-sample Kolmogorov-Smirnov statistical test was used to determine how significantly the spores affected the tensile properties at each spore concentration level (0-10% w/w).

Microscopy characterisation
Morphological properties of the fibres were studied using an optical microscope (Olympus BX51), Olympus ocular and plan 100x/1.25 lens with oil, a scanning electron microscope (Joel Quanta 200 F FE-SEM) and a transmission electron microscope (Joel JEM 2200 FS-TEM).

To avoid electron loading on the SEM sample, the samples were placed on a stub and gold coated using a sputter coater (Balzers Union SKD 030). SEM micrographs were made under a high vacuum voltage of 20.0 kV, with a spot size of 4 to 6 nm, a dwell of 3000 μs and a working distance of 10 mm.

Differential Scanning Calorimetry (DSC)
Thermal analysis of the PET fibres incorporated with spores was conducted using a DSC (Q 2000, TA-Instruments, DA, USA) in a nitrogen atmosphere heat flow of 50 ml/min and calibrated with pure indium, tin and sapphire. Fibre samples weighing 5 ± 1 mg were placed in aluminum DSC pans (Tzero Pan) and sealed with an aluminum lid (Tzero lid) using a TA crimping tool. An empty pan was used as reference. The samples were then equilibrated to 50 °C for 10 minutes and then heated at 2 °C/min run, isothermal conditioned for 5 minutes at 290 °C

and then cooled down to 0 °C. Two heatings were recorded: the first investigated the effects of spores on the melting temperature and heat fusion, which is defined as the area under the melting curve, while the second heating used as an intrinsic material reference.

The modulated mode of the DSC instrument was used to study the glass transition and onset temperatures of the PET samples. The heat flow of the materials was monitored over the range of 0 to 290 °C with a temperature modulation of ± 0.2 °C/min superimposed on a 2 °C/min run. Universal Analysis 2000 software was used for t interpretation of the thermographs.

The degree of crystallinity was calculated from the enthalpies obtained using the following **Equation 1**:

$$\text{Crystallinity} = \frac{\Delta Hx1 - \Delta Hy1}{\Delta Hx0 \cdot (1 - \frac{wt\%}{100})} \cdot 100, \% \quad (1)$$

Where $\Delta Hx1$ is the melting enthalpy of the sample and $\Delta Hy1$ the crystallisation enthalpy, while $\Delta Hx0$ is the melting enthalpy of a perfect crystalline PET sample and wt% the total weight percentage of spores. An enthalpy of 140 J/g was used for perfect crystalline PET.

Spectroscopic analysis
To investigate the crystallinity and bonding quality of PET fibres incorporated with spores, Raman and FT-IR spectroscopy was used.

Raman spectra were obtained by using a Perkin-Elmer Spectrum GX 2000 spectrometer with a Raman beam splitter, a diode-pumped YAG infrared laser (1064 nm and laser power of 800Mw) and InGaAs detector. The measurements were recorded in the back-scattering mode (180° excitation optics) for 64 scans, a resolution of 4 cm^{-1}, and a data-interval of 1 cm^{-1} from 200 to 3200 cm^{-1}. The samples were aligned on a sample holder and spectra taken in a random orientation.

For the FT-IR studies, a Perkin-Elmer Spectrum GX 2000 with a Peltier-cooled DTGS Mid-IR detector, Mid-IR source, extended KBr beam splitter and diffuse reflection (DRIFTS) accessories was used. All samples were studied with 64 scans, a resolution of 4 cm^{-1} and a data-interval of 1 cm^{-1} from 400 to 4000 cm^{-1} in
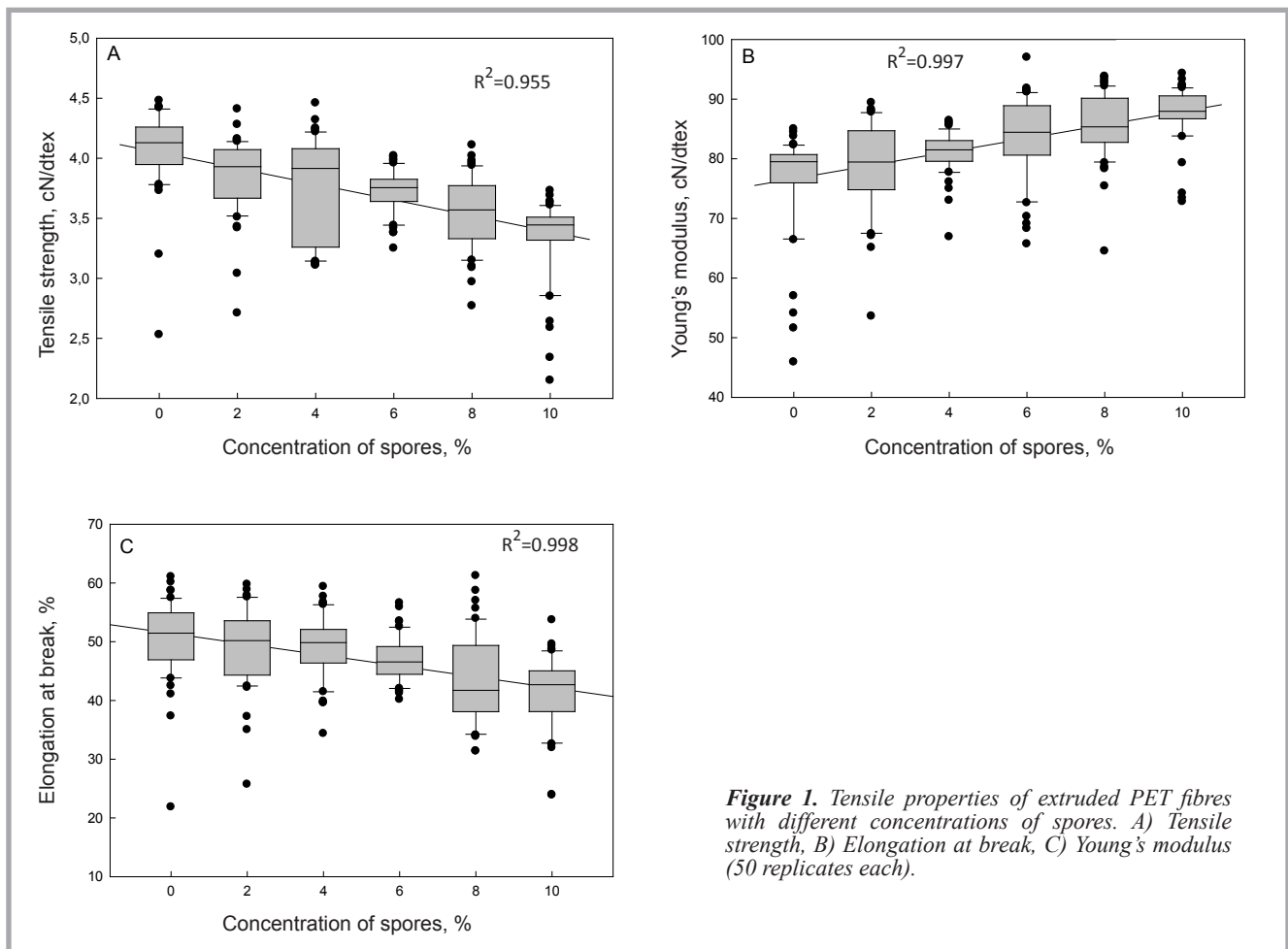
Figure 1. *Tensile properties of extruded PET fibres with different concentrations of spores. A) Tensile strength, B) Elongation at break, C) Young's modulus (50 replicates each).*

the DRIFT accessory. Before recording the DRIFT spectrum, a background spectrum to correct the atmospheric H_2O and CO_2 bands was recorded using standard sandpaper samples provided, after which the sample was focused and the energy analysed.

■ Results

Tensile testing

A negative trend can be noted whereby an increase in spore concentration results in a decrease in tensile strength and elongation at break, as shown in ***Figures 1.A*** and ***1.C***. However, Young's modulus increases with the spore concentration (***Figure 1.B***). These trends are further emphasised by their R-squared values of 0.955, 0.997 and 0.998 for tensile strength, modulus and elongation, respectively.

The tensile properties of fibres extruded with spores (2 - 10% (w/w)) were compared with those of virgin PET fibres (0% (w/w)) using two-sample Kolmogorov-Smirnov statistical tests. The results presented in ***Table 1*** show that incorpo-

rating spores in PET fibres had a significant effect on the tenacity and modulus at all concentration levels. However, the effect on the elongation at break at 2 and 4% (w/w) spore concentration did not have a significant effect since their p-values (0.5440 and 0.1780 respectively) were more than the significance threshold level of 0.05. Nevertheless a significant effect on the elongation at break was noted at 6, 8 and 10% (w/w) spore concentration levels, which means that the spores interact with the fibres in the amorphous regions, filling them up; hence, with a reduced elongation at break.

Optical characterisation

Optical micrographs of blank PET-fibres show a smooth appearance (***Figure 2.A***), whereas the samples extruded with spores are very characteristic in that they exhibit cracks parallel to the fibre axis (***Figure 2.B***), which suggests that the spores are heterogeneously distributed throughout the fibre. Conclusively the SEM micrograph of the blank PET fibres confirmed a smooth fibre surface (***Figure 3.A***), whereas the fibres incorporated with spores showed visible spore agglomerates on the surface (***Figure 3.B***).

Table 1. *Two-sample Kolmogorov-Smirnov tests showing the statistical significance of incorporating spores for material properties like tensile strength, Young's modulus and elongation at break (n - number of replicas = 50).*

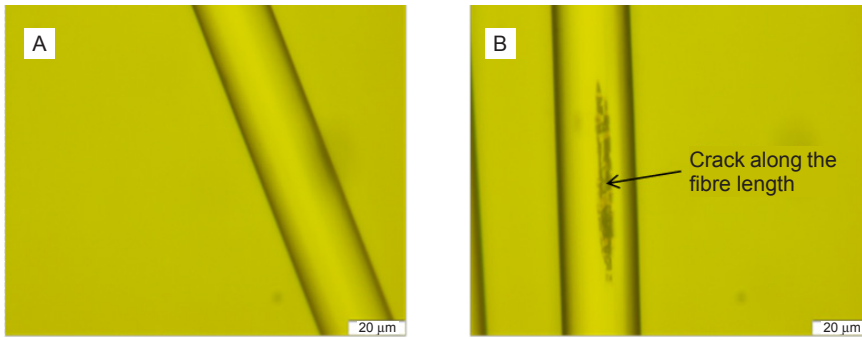| Spore content, % w/w	Tensile properties			Spore content, % w/w vs. control	P-Values		
	Tensile strength, cN/dtex	Young's modulus, cN/dtex	Elongation at break, %		Tensile strength, cN/dtex	Young's modulus, cN/dtex	Elongation at break, %
2	3.9 ± 0.3	85.7 ± 5.4	49.2 ± 6.6	2	0.0010	0.0010	0.5440
4	3.8 ± 0.4	83.8 ± 6.8	48.9 ± 5.3	4	0.0010	0.0001	0.1780
6	3.7 ± 0.2	81.2 ± 3.5	46.9 ± 3.8	6	0.0001	0.0001	0.0001
8	3.6 ± 0.3	78.8 ± 7.5	43.8 ± 7.3	8	0.0001	0.0001	0.0001
10	3.3 ± 0.3	76.6 ± 8.3	41.4 ± 6.1	10	0.0001	0.0001	0.0001

Figure 2. *Two representative optical micrographs of PET fibres. A) Blank PET fibre (control), B) PET fibre incorporated with 2 wt% spores exhibiting cracks parallel to the fibre axis (shown by arrow).*
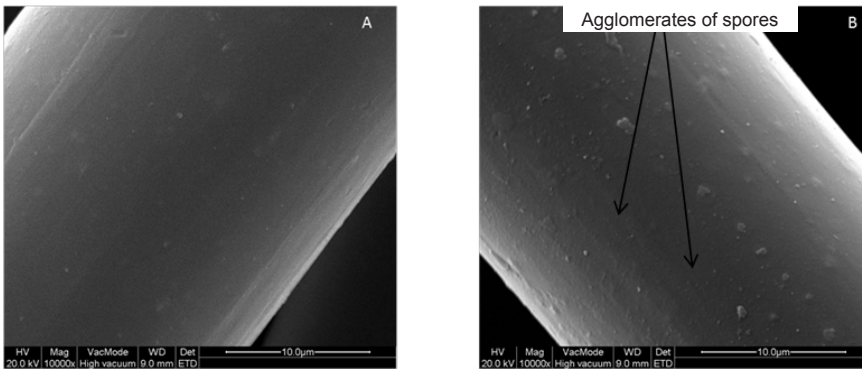

Figure 4. *TEM micrographs for PET fibres incorporated with 6 wt% spores showing spore agglomerates in the polymer matrix.*

Figure 3. *SEM micrographs for PET fibres. A) Blank PET fibre (control), B) PET fibre incorporated with 2 wt% spores exhibiting spore agglomerates on the fibre surface (shown by arrow).*

No preferential orientation was seen of the spores in the PET-fibres, suggesting a heterogeneous distribution. Additionally there seems to be a good adhesion bond between the spores and polymer matrix (**Figure 4**).

Differential scanning calorimetry (DSC)

DSC results of thermal properties of the fibres incorporated with spores are shown in **Figures 5.A - 5.C**. The addition of spores leads to a slight increase in the endothermic melting peak (melt temperature) and exothermic peak of cold crystallisation (crystallisation temperature). However, the crystallisation percentage increases with the concentration of spores, which shows that the spores may

Transmission electron microscopy (TEM) was used to look at the roughness on the surface of the fibres induced by the inclusion of spores noticed by optical and SEM microscopy. The electron dense spots (black) are most likely spores embedded into the PET-matrix, as they were not found in the blank fibres.
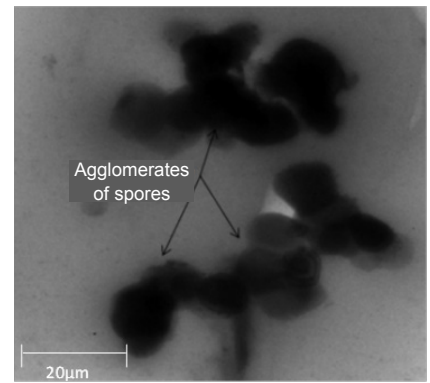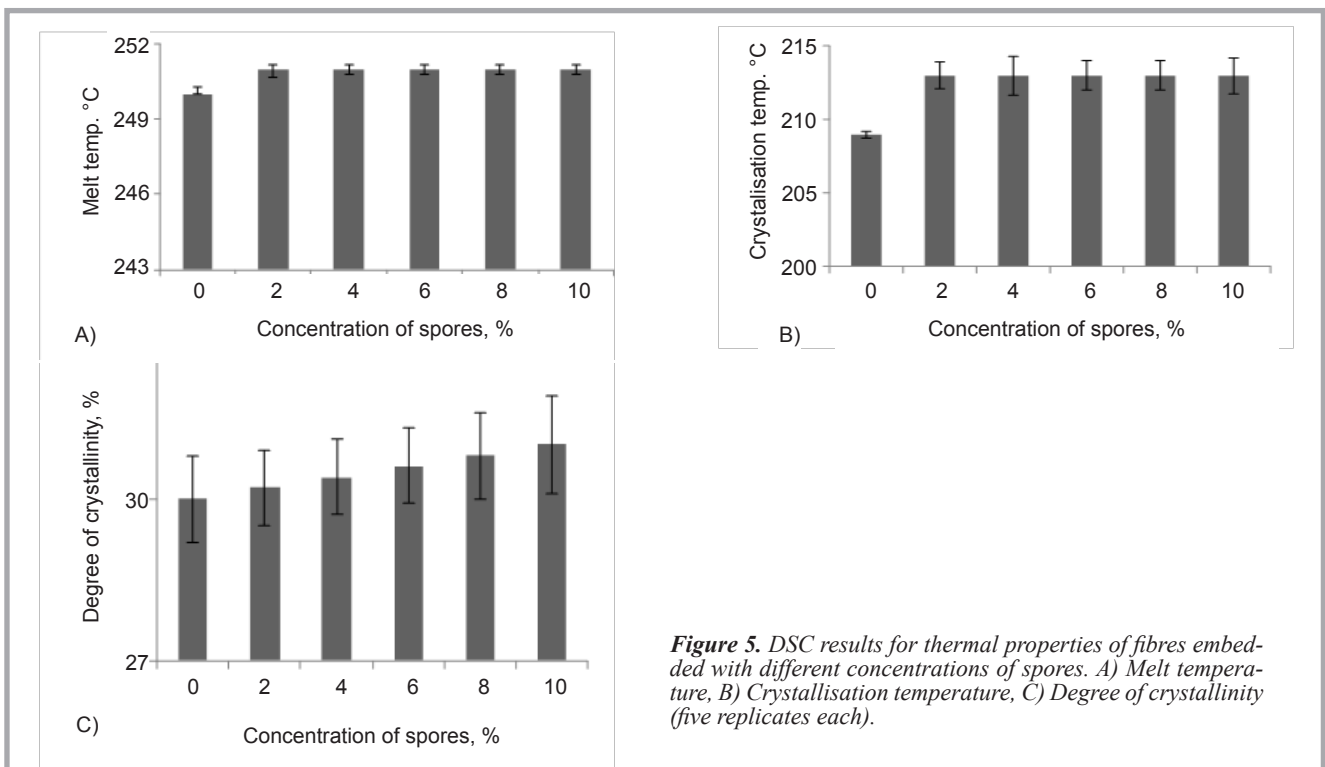

Figure 5. *DSC results for thermal properties of fibres embedded with different concentrations of spores. A) Melt temperature, B) Crystallisation temperature, C) Degree of crystallinity (five replicates each).*

have induced PET crystallisation upon cooling.

FTIR and Raman spectroscopy

Figures 6 and *7*, respectively, show FT-IR and Raman spectra for blank PET and PET fibres extruded with spores. All the samples, regardless of their spore content, have identical spectra.

The crystalline content of semi-crystalline PET can be determined from the Raman spectra in two ways [26]. The first technique determines the peak ratio of the band at approximately 1,120 cm^{-1} (ester CO–O or C–C stretching) and the Raman shift at approximately 1,100 cm^{-1} (C–O and C–C stretching or C–O–C bending). Highly crystalline samples show a large peak at 1,095 cm^{-1}, while amorphous samples show a shoulder at the 1,120 cm^{-1} peak. *Figure 8.A* shows that the sample at all concentration levels had the same Raman shift at the 1095 cm^{-1} band and an identical shoulder at 1120 cm^{-1}.

The second technique determines the peak width of Raman emission at 1,730 cm^{-1}. Highly crystalline samples give a narrow peak while the amorphous bandwidth is evidently broader. Observing the Raman spectrum in *Figure 8.B*, all samples, regardless of the spore concentration, had the same peak width, which was neither too broad nor too narrow.

■ Discussion

The selection of materials for textile and industrial applications strongly depends on their thermal, chemical and tensile properties. Because fibres are the basic units from which complicated material structures are developed, their intrinsic characteristics influence the overall properties of the resulting materials. For this reason, engineers and designers use fibre properties to develop materials of specific quality for a given application. Fibre properties are influenced by their morphology, which is determined by the polymer type, additives used, process technique and processing conditions. Among the important fibre properties are the tensile characteristics, which are determined by the tensile strength, Young's modulus and elongation at break.

From our results it was observed that incorporating spores in PET fibres resulted in a decrease in tensile strength and elongation at break with an increase in spore
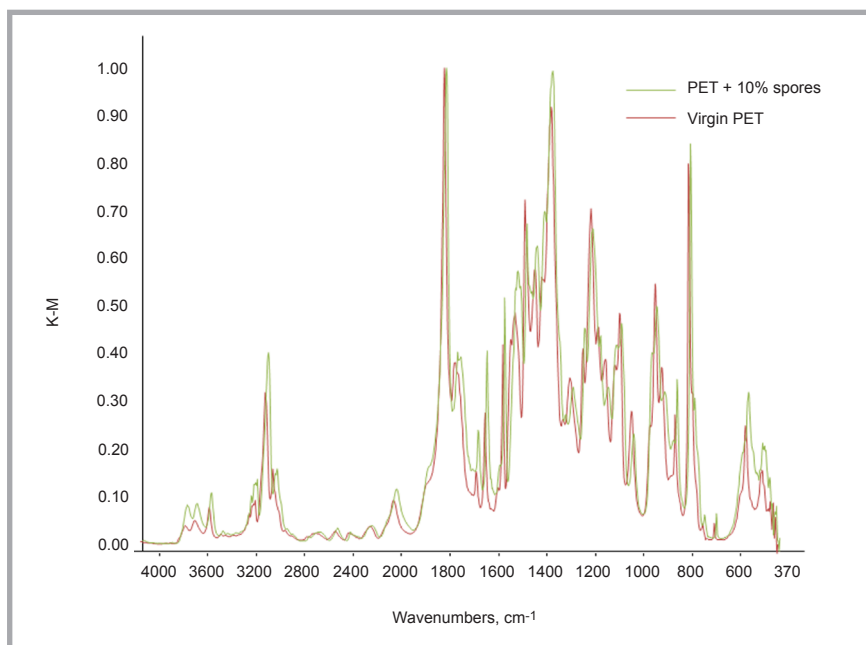

Figure 6. *FT-IR spectrum for blank PET fibres and PET fibres incorporated with 10% spores.*
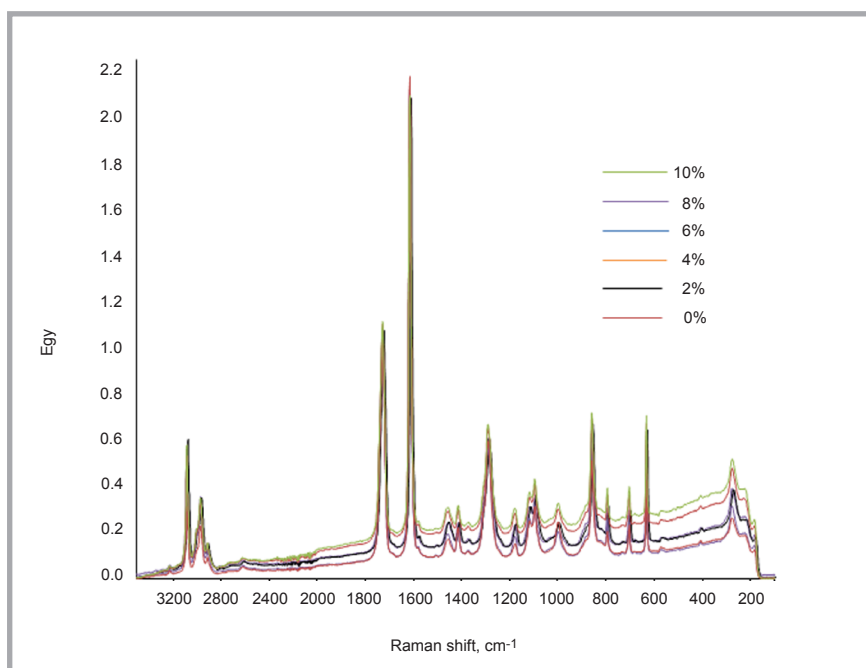

Figure 7. *Raman spectrum for PET fibres embedded with different concentrations of spores.*

concentration. This trend can be attributed to the spore agglomerates observed in the polymer matrix. Spore agglomerates induced cracks on the fibre surface, obstructing stress transfer between the spores and polymer matrix, which created weak points in the fibres, resulting in earlier failure [21, 27- 29].

Two main factors may have contributed to the agglomeration of spores in the polymer matrix. The first factor to consider is the extrusion process conditions,

specifically the high temperature and shear stress. Spores are known to form agglomerates in suspensions during heat treatment due to increased surface hydrophobicity caused by the denaturing of the protein coats [18, 30, 31]. Therefore the force originating from the shear stress possibly imparted a higher energy on the spores, which overcame the spores' electrostatic repulsive force, leading to the formation of agglomerates. The second factor is the poor dispersion of spores in the polymer matrix, influenced by spore
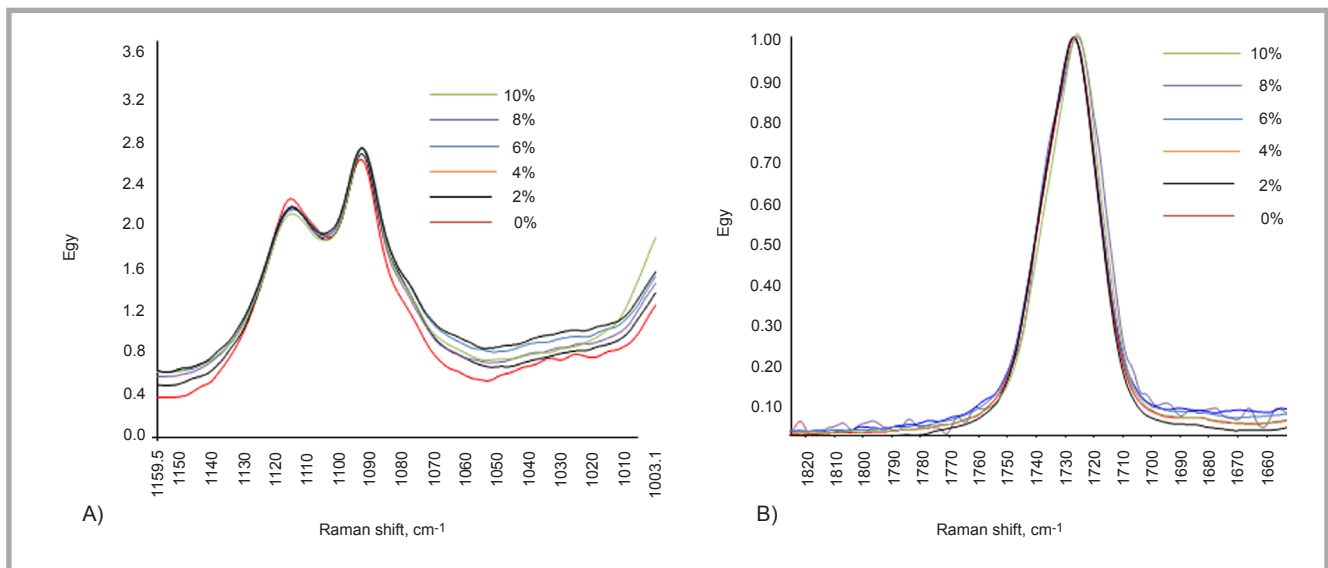
***Figure 8.** Raman spectra of PET fibres extruded with different concentrations of spores; A) at 1095 cm^{-1} and 1120 cm^{-1} band, B) at 1730 cm^{-1} band.*

size and loading. Normally, small sized particles tend to agglomerate more than larger ones, while chances of forming agglomerates increases with loading [4, 15, 16, 32, 33]. As was seen with the TEM microscopy, there was no preferential orientation of spores in the polymer matrix, which suggests heterogeneous and poor dispersion of spores; hence the resulting agglomerates.

Moreover the optical micrograph of PET fibres extruded with spores was characterised with cracks parallel to the fibre axis (***Figure 2.B***).These cracks can be associated with a decrease in the macromolecule arrangement of PET along the fibre axis possibly caused by adding spores to the structure [34, 35]. This suggests poor a dispersion of spores in the polymer matrix and poor spore-matrix interface adhesion bonding [35, 36]. The poor dispersion of spores influenced by spore size and loading may have led to the formation of agglomerates which possibly induced the cracks observed generated by de-bonding between the spores and PET polymer [37 - 39].

The DSC results showed a slight increase in the crystallinity of PET fibres incorporated with spores, confirming the Young's modulus results in tensile testing, which suggest that spores may have worked as a crosslinking point of PET molecular chains, making them more complete, hence restricting the motions of the molecular segments and resulting in a brittle fibre that has low elongation at break and high Young's modulus. This implies that because PET is a semi-crystalline

polymer, any foreign material interacting with the polymer at the amorphous phase will result in an increased crystallinity; a phenomenon previously reported by [3] in their work on Polyethyleneterephthalate/Clay nanocomposites. Moreover crystallinity also influences the thermal properties, including the melting and crystallisation temperatures. These thermal properties determine how a material reacts to heat applications. The slight increase in crystallinity could be the reason behind the increase in melt and crystallinity temperatures observed, possibly due to changes in the polymer's degree of polymerisation. However, FT-IR and Raman characterisation showed that all samples, regardless of their spore content, had an identical degree of crystallinity. The difference between the DSC and spectroscopy results may be explained by the fact that spectroscopy tests analyse behaviour changes at a specific point on the surface of the sample, while DSC analyses the bulk of a relatively bigger sample. Therefore the FT-IR and Raman results suggest the absence of spores on the surface of the fibres, which may be attributed to poor dispersion and inhomogeneous distribution of spores in the polymer matrix.

Generally the most optimal conditions for producing spores/PET fibres would be to have the highest concentration of spores integrated in the PET fibres, as this would result in a higher functionality. However, many papers have shown that incorporating foreign additives into the polymer matrix can influence the fibres' tensile properties, resulting in poor qual-

ity fibres with a high load of additives. Thus the optimal conditions in this paper represent a fair compromise between the concentration of spores and corresponding tensile properties.

The concentration of spores successfully incorporated into PET fibres ranged from 0 to 10% (w/w). Concentrations higher than 10% (w/w) blocked the spinnerets and therefore could not be extruded. An increase in spore concentration resulted in a decrease in tensile properties with 10% (w/w) spores, giving the lowest properties (***Figure 1***). In order to select an optimal spore concentration, it is important to have a fair trade-off between the tensile properties and concentration of spores. Therefore 6% (w/w) spores was selected as the optimal concentration because its tensile properties fall within the acceptable range giving the narrowest standard deviation for the tensile strength (± 0.2), elongation at break (± 3.8) and Young's modulus (± 3.5) (***Table 1***).

Hence the best process parameters for extruding *B. amyloliquefaciens* spores in PET fibres are:
- A spore concentration of 6% (w/w) of *B. amyloliquefaciens* spores
- Barrel section 1 heated at 280 °C for the feed stock
- Barrel section 2 heated at 290 °C for plasticising
- Barrel section 3 heated at 295 °C for pumping
- The die heated at 295 °C
- Pressure of 6.0 ± 0.2 MPa
- Residence time of 5 ± 0.5 minutes.

Our preceding work on the resistance of *Bacillus amyloliquefaciens* spores to melt extrusion process parameters [3] clearly showed that spores can be successfully incorporated in PET fibres during extrusion. Additionally the present study shows that incorporating spores into PET fibres can result in decreased material properties. Nevertheless PET fibres normally have a tensile strength of 3 - 7 cN/dtex, an elongation of 20 - 50%, modulus of 77 - 87 cN/dtex and a melting temperature of around 250 °C [34, 40]. By comparing the results of this study, it can be seen that the properties reported fall within the acceptable range and therefore the fibres produced are as good as normal PET fibres but with the additional advantage that they can have an additional function.

Nevertheless the results of this work suggest cracks observed in the polymer matrix, caused by spore agglomerates and inhomogeneous dispersion of spores, as possible reasons for the slight decrease in tensile properties. In the case of a need to further optimise the properties of these fibres, the problem of spore dispersion and formation of agglomerates should be solved. Hence the critical challenge would be to identify the best technique to promote homogeneous dispersion of spores and find ways to prevent them from forming agglomerates in the polymer matrix.

■ Conclusions

There was a good adhesion bond between the spores and polymer matrix, while the tensile strength, modulus and elongation at break were dependent on the spore concentration. Additionally a slight increase in the degree of crystallinity and melting and crystallization temperatures was observed, which remained constant at all spore concentration levels. However, the properties of the fibres produced were within the acceptable range and are therefore as good as normal PET fibres.

References

1. Oerlikon. The fiber year 2009/10. A world survey on textile and nonwovens industry. Volume 9, Remscheid, Oerlikon textile GmbH & CO. KG., 2010.
2. Broda J, Gawlowski A, Fabia J, Slusarczyk C. Super-molecular Structure of Polypropylene Fibers Modified by Additives. *Fibers and Textiles in Eastern Europe* 2007; 15, 5-6: 30 - 33.
3. Gashti M, Moradian S. Effect of Nanoclay Type on Dye-ability of Polyethylene Terephthalate/Clay Nanocomposites. *Journal of Applied Polymer Science* 2012; 125: 4109 - 4120.
4. Zeng X, Lin D, Cai X, Zhang X, Tan S, Xu Y. Morphology and Thermal and Mechanical Properties of Phosphonium Vermiculite Filled Poly(ethylene terephthalate) Composites. *Journal of Applied Polymer Science* 2012; 126: 601 - 607.
5. Gao Y, Cranston R. Recent Advances in Antimicrobial Treatments of Textiles. *Text Res J* 2008; 78: 60 - 72.
6. Ristić T, Zemljič L, Novak M, Kunčič M, Sonjak S, Cimerman N, Strnad S. Antimicrobial efficiency of functionalized cellulose fibers as potential medical textiles. *Science against microbial pathogens: communicating current research and technological advances* 2011; 6: 36 - 51.
7. Bang H, Kim H, Jin F, Woo J, Park S. Conjugate Spun of Polyethylene Terephthalate Resin Modified with 1,4-Cyclohexanedimethanol. *Bulletin of the Korean Chemical Society* 2011; 32: 542 - 546.
8. Park S, Kim H, Jin F, Park S. Particle Dispensability Improvement of Polyester Fibers with a New Line Injection. *Bulletin of the Korean Chemical Society* 2010; 31: 2637 - 2643.
9. Leskovšek M, Jedrinović G, Stankovič Elesini U. Properties of polypropylene fibers with incorporated microcapsules. *Acta Chimica Slovenica* 2004; 51: 699 - 715.
10. Vihodceva S, Kukle S, Barloti J. Nanolevel Functionalization of Natural Fiber Textiles. *IOP Conf. Series: Materials Science and Engineering* 2011; 23: 012037.
11. Son W, Youk J, Park W. Antimicrobial Cellulose Acetate Nanofibers Containing Silver Nanoparticles, Carbohydr. *Polymer* 2006; 65: 430–434.
12. Kusuktham B. Spinning of poly (ethylene terephthalate) fibers incorporated with modified calcium silicate. *Journal of applied polymer science* 2012; 124: 699 - 705.
13. Hong K, Park J, Sul I, Youk J, Kang T. Preparation of Antimicrobial Poly(vinyl alcohol) Nanofibers Containing Silver Nanoparticles. *Journal of Polymer Science Part B: Polymer Physics* 2006; 44: 2468 - 2474.
14. Williams J, HaloSource V, Cho U. Antimicrobial Functions for Synthetic Fibers: Recent Developments. *American Association of Textiles Chemists and Colorists Review* 2005; 5: 17 - 21.
15. Deshmukh S, Rao A, Gaval V, Seena J, Mahanwar P. Effect of Particle Size and Concentration on Mechanical and Electrical Properties of the Mica Filled PVC. *Journal of Minerals & Materials Characterization & Engineering* 2010; 9: 831 - 844.
16. Šupova M. Problem of hydroxyapatite dispersion in polymer matrices: a review. *Journal of Materials Science: Materials in Medicine* 2009; 20: 1201 - 1213.
17. Onuegbu G, Igwe I. The effects of filler contents and particle sizes on the mechanical and end-use properties of Snail shell powder filled Polypropylene. *Materials science and Application* 2011; 2: 811 - 817.
18. Bhowmik R, Katti K, Katti D. Influence of Mineral on the Load Deformation Behavior of Polymer in Hydroxyapatite-Polyacrylic Acid. *Journal of Nanoscience and Nanotechnology* 2008; 8: 2075 - 2084.
19. Arencón D, Velasco J. Fracture Toughness of Polypropylene-Based Particulate Composites. *Materials* 2009; 2: 2046 - 2094.
20. Dubnikov I, Berezina S, Antonov A. Effects of rigid particle size on the toughness of filled polypropylene. *Journal of Applied Polymer Science* 2004; 94: 1917 - 1926.
21. Shao-Yun F, Xi-Qiao F, Bernd L, Yiu-Wing M. Effects of particle size, particle/matrix interface adhesion and particle loading on mechanical properties of particulate–polymer composites. *Composites: Part B*. 2008; 39: 933 - 961.
22. Shumigin D, Tarasova E, krumme A, Meier P. Rheological and Mechanical Properties of Poly(lactic) Acid/Cellulose and LDPE/Cellulose Composites. *Materials Science (Medžiagotyra)* 2011; 17: 32 - 37.
23. Juhee A, Balasubramaniam V. Physiological Responses of Bacillus amyloliquefaciens Spores to High Pressure. *Journal of Microbiology and Biotechnology* 2007; 17: 524 - 529.
24. Margosch D, Gänzle M, Ehrmann M, Vogel R. Pressure inactivation of Bacillus endospores. *Applied and Environmental Microbiology* 2004; 70: 7321 - 7328.
25. Ciera L, Beladjal L, Almeras X, Mertens J, Gheysens T, Nierstrasz V, Langenhove L. Resistance of Bacillus amyloliquefaciens spores as a function of melt extrusion process parameters. Textile & Fibers in Eastern Europe 2014; 22, 2, 104: 102-107.
26. Litchfield D, Baird D. The role of nanoclay in the generation of poly(ethylene terephthalate) fibers with improved modulus and tenacity. Polymer 2008; 49: 5027 - 5036.
27. Zi-Kang Z, Yong Y, Jie Y, Zong-Neng Q. Preparation and Properties of Organ soluble Polyimide/Silica Hybrid Materials by Sol–Gel Process. *Journal of Applied Polymer Science* 1999; 73: 2977 - 2984.

28. Li G, Helms J, Pang S, Schulz K. Analytical modeling of tensile strength of particulate filled composites. *Polymer Composites* 2001; 22: 593 - 603.

29. Reynaud E, Jouen T, Gauthier C, Vigier G, Varlet J. Nanofillers in polymeric matrix: a study on silica reinforced PA6. *Polymer* 2001; 42: 8759 - 68.

30. Wiencek K, Klapes N, Forgrding P. Hydrophobicity of Bacillus and Clostridium spores. *Applied Environmental Microbiology* 1990; 56: 2600 - 2605.

31. Furukawa S, Narisawa N, Watanabe T, Kawarai T, Myozen K, Okazaki S, Ogihara H, Yamasaki M. Formation of the spore clumps during heat treatment increases the heat resistances of bacterial spores. *International Journal Food Science and Technology* 2005; 102: 107 - 111.

32. Boesel L, Reis R. A review on the polymer properties of Hydrophilic, partially Degradable and Bioactive acrylic Cements (HDBC). *Progress in Polymer Science* 2008; 33: 180 - 190.

33. Espigares I, Elvira C, Mano J, Vazquez B, San Roman J, Reis R. New partially degradable and bioactive acrylic bone cements based on starch blends and ceramic fillers. *Biomaterials* 2003; 23: 1883 - 1895.

34. Zupin Z, Dimitrovski K. *Mechanical Properties of Fabrics Made from Cotton and Biodegradable Yarns Bamboo, SPF, PLA in Weft*. ISBN: 978-953-307-194-7, 2010. http://cdn.intechweb.org/pdfs/12238.pdf

35. Lee J, Yeea A. Fracture of glass bead/epoxy composites: on micro-mechanical Deformations. *Polymer* 2000; 41: 8363–8373.

36. Dubnikova I, Berezina S, Antonov A. Effect of Rigid Particle Size on the Toughness of Filled Polypropylene. *Journal of Applied Polymer Science* 2004; 94: 1917–1926.

37. Mangesh D, Ravindra D. Polyester Nanocomposite fibers with Antibacterial Properties. *Advances in Applied Science Research* 2011; 2: 491-502.

38. Chen X, Yu J, Guo S. Structure and Properties of Polypropylene Composites Filled with Magnesium Hy-drixide. *Applied Polymer science* 2006; 102: 4943-4951.

39. Yi W, Fei Z, Guan W, Feng C. Preparation and Properties of Polypropylene Filled with Or-gano-Montmorillonite Nanocomposites. *Journal of Applied Polymer Science* 2006; 100, 4: 2875- 2880.

40. Fan Y, Lou J. Shinozaki D. Microstructure Dependent Properties of Polypropylene-Clay Nanocomposites. *Applied Polymer science* 2007; 103: 204-210.

INSTITUTE OF BIOPOLYMERS AND CHEMICAL FIBRES

LABORATORY OF PAPER QUALITY

Since 02.07.1996 the **Laboratory has had the accreditation certificate of the Polish Centre for Accreditation No AB 065**.

The accreditation includes tests of more than 70 properties and factors carried out for:
- pulps
- tissue, paper & board,
- cores,
- transport packaging,
- auxiliary agents, waste, wastewater and process water in the pulp and paper industry.

The Laboratory offers services within the scope of testing the following: raw -materials, intermediate and final paper products, as well as training activities.

Properties tested:
- general (dimensions, squareness, grammage, thickness, fibre furnish analysis, etc.),
- chemical (pH, ash content, formaldehyde, metals, kappa number, etc.),
- surface (smoothness, roughness, degree of dusting, sizing and picking of a surface),
- absorption, permeability (air permeability, grease permeability, water absorption, oil absorption) and deformation,
- optical (brightness ISO, whitness CIE, opacity, colour),
- tensile, bursting, tearing, and bending strength, etc.,
- compression strength of corrugated containers, vertical impact testing by dropping, horizontal impact testing, vibration testing, testing corrugated containers for signs „B" and „UN".

The equipment consists:
- micrometers (thickness), tensile testing machines (Alwetron), Mullens (bursting strength), Elmendorf (tearing resistance), Bekk, Bendtsen, PPS (smoothness/roughness), Gurley, Bendtsen, Schopper (air permeance), Cobb (water absorptiveness), etc.,
- crush tester (RCT, CMT, CCT, ECT, FCT), SCT, Taber and Lorentzen&Wettre (bending 2-point method) Lorentzen&Wettre (bending 4-point metod and stiffness rezonanse method), Scott-Bond (internal bond strength), etc.,
- IGT (printing properties) and L&W Elrepho (optical properties), ect.,
- power-driven press, fall apparatus, incline plane tester, vibration table (specialized equipment for testing strength transport packages),
- atomic absorption spectrmeter for the determination of trace element content, pH-meter, spectrophotometer UV-Vis.

Contact:

INSTITUTE OF BIOPOLYMERS AND CHEMICAL FIBRES
ul. M. Skłodowskiej-Curie 19/27, 90-570 Łódź, Poland
Elżbieta Baranek Dr eng. mech.,
tel. (+48 42) 638 03 31, e-mail: elabaranek@ibwch.lodz.pl