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TRENDS IN THE BIO-FIBERS APPLICATION

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ABSTRACT: Bio-fibers represent an emerging and innovative component of the textile value chain.The strong expansion of the bio-fiber applications is expected to take place in the next few years. The article will review major issues related to bio-fibers application and the technological substitution of old fiber production technology by the new technology. The Fisher-Pry description and its variants have been widely used in the study of technology substitution. Although the model was introduced using empirical arguments, it is now a well-known fact that the model considers a special ease of logistic growth and can be obtained from the Lotka-Volterra competition equations. The MATLAB program for utilization of Fisher Pry and generalized model will be described.Estimates of the innovation diffusion process will be examined for the case of replacement of polyester fibers by PLA fibers.

1. INTRODUCTION

The bio-fiber industry is still in its infancy trying to identify and explore market niches that add value to this approach. This systemic and integrated "from the cradle to the cradle" concept is equally concerned with the carbon's complete cycle and with the promotion of the replacement petrochemical derived fibers with equivalent bio-fibers from renewable sources. Current production volume in fibers is estimated to be between 50.000 and 100.000 tons per year. However, the long term prospects indicating if it is becoming a mainstream fiber with mass application (e.g. a volume of 3-5 MM Tons) or a niche for specific end-uses and target groups, remain undefined and uncertain. Hence understandings of the unfolding technological change that accompany a new introduction are critical. This is necessary to help the major constituencies with a strong vested stake – industry, R&D community and policy makers.

The information will guide decision makers regarding resources to invest and nurture those directions which indicate the greatest potential. Furthermore, it will help define strategies for a successful outcome. The course of innovation may be measured by a number of factors ranging from R&D investments, process technology advances, total consumption in terms of annual sales or inventory on hand etc – just to mention a few. Innovation diffusion is best described by the characteristic S-shaped curve based on the "bandwagon" effect assumption. Hence, a firm's decision to adopt a new technique is dependent on the number of firms already using it. Bio-fibers were launched by existing players (e.g. DuPont for PTT) as well as newcomers (e.g. NatureWorks – Cargill for PLA, Metabolix for PHA, Clereplast for nanoadditives etc). However it also requires setting up vertical alliances in aligning investments and marketing.

The main aspect of the innovation process are that it can be both internal or external to the company and is directed by simultaneous emergence/substitution of both old and new techniques involving changes in characteristics driven by market place.

2. CONCEPTUALIZATION OF BIO MATERIALS

In terms of understanding the terminology, there are three distinct concepts:
Bio-based: Materials produced using carbon that comes from contemporary (non-fossil) biological sources and may or may not be biodegradable. Carbon 14 signature quantifies bio-based content.
Biodegradable: Biodegradable materials are limited to materials that convert to carbon-di-oxide, water and biomass through the microbial digestion. They may or may not be bio-based. The American Society of Testing and Materials (ASTM) has standards for bio-based and biodegradability.
Biopolymers: Biopolymer is a term that includes bio-based and some biodegradable plastics, as well as non-plastic materials, such as proteins, lipids and DNA. Hence, according to ASTM D6866-06, a biopolymer is a special polymer that involves living organisms in its synthesis process. It therefore has a partial or total biochemical origin whereby it can be partially or totally produced from natural, renewable materials (biomass) and can be biodegradable, thus satisfying ASTM D6400-04, or not. Biopolymers can be grouped into three classes as given below [1, 2]:

1. Polymers extracted directly from biomasses, with or without modification. For example starch modified polymers and polymers derived from cellulose.
2. Polymers produced directly from microorganisms in their natural or genetically modified state. The typical example is polyhydroxyalcanoates (PHAs).
3. Polymers obtained with the participation of bio-intermediaries, produced with renewable raw materials. Examples are: polylactic acid (PLA); bio-polyethylene (BPE) obtained from polymerization of ethylene produced from bio-ethanol; bio-nylon via diacids from biomasses; and bio-polyurethanes which incorporate polyols of vegetable origin.

Bio-fibers from biomaterials are therefore defined as materials that contain biopolymers in various percentages and can be extruded/molded under thermal-mechanical (heat & pressure) stress. They are thus potential alternatives to conventional thermoplastic synthetic fibers of petrochemical origin, such as polyolefines and polyester.
The redesign of polymers is already happening, and biopolymers are already on the market. However, the use of biopolymer is small (0.1 to 0.2 per cent of total EU plastics). The technology to produce them on a large scale is still in its infancy and so is the research on their impacts.
Environmental considerations: Although significant research and product development has been done with biodegradable plastics, there is debate as to whether they actually degrade in natural habitats rather than under experimental conditions, particularly if they are present in large amounts.
Biodegradation may also influence the types and concentrations of soil micro flora in disposal areas. Enrichment of soil with certain micro flora which could have unanticipated risks, such as an outbreak of a new microbial disease
Bio-based plastics require biological f**eedstock**, which can be corn, Soya, wheat or sugarcane, for example. This raises questions around sufficient farming land to cultivate the feedstock and possible conflicts with food production.
One solution could be the use of alternative feed-stocks and industry is investigating algae for the production of bio-based polymers. The use of algae as a feedstock may have less

impact because it has a high yield, can grow in a range of environments and does not compete with land-based food crops.
Although bio-based polymers are renewably sourced, this does not mean that they will reduce waste. Instead, they produce a different form of plastic waste that may require different waste management systems.
However, it must be ensured that any changes in the product do not have "side-effects" further down the line during the products use or disposal. For example, if redesign actually makes a product less durable, then it will be discarded and replaced more often, which could increase plastic waste.
There is **disagreement about the life cycle impact of biopolymers**and some research indicates biopolymers may have a more **negative impact** on the environment than conventional polymers due to their weight and production methods. Some biopolymers have less impact on fossil fuel use and global warming potential than traditional polymers; they could have greater environmental impacts in terms of eutrophication and eco-toxicity. These would be caused by fertilizer use, pesticide use and land use change required for agriculture production as well as from the fermentation and other chemical processing steps.
However, European Bio-plastics (the trade association for manufacturers of bio-plastics in Europe) suggests that it may not be appropriate to directly compare bio-plastics (which are at a very early development stage) to older materials as the latter have optimized their life cycle over time.
The environmental assessment of man-made cellulose fibers, cotton, novel bio-based fibers (PLA fibers), and fossil fuel-based fibers (PET and PP) based on some indicators as non-renewable energy use (NREU), renewable energy use (REU) and cumulative energy demand (CED) are given in fig. 1.

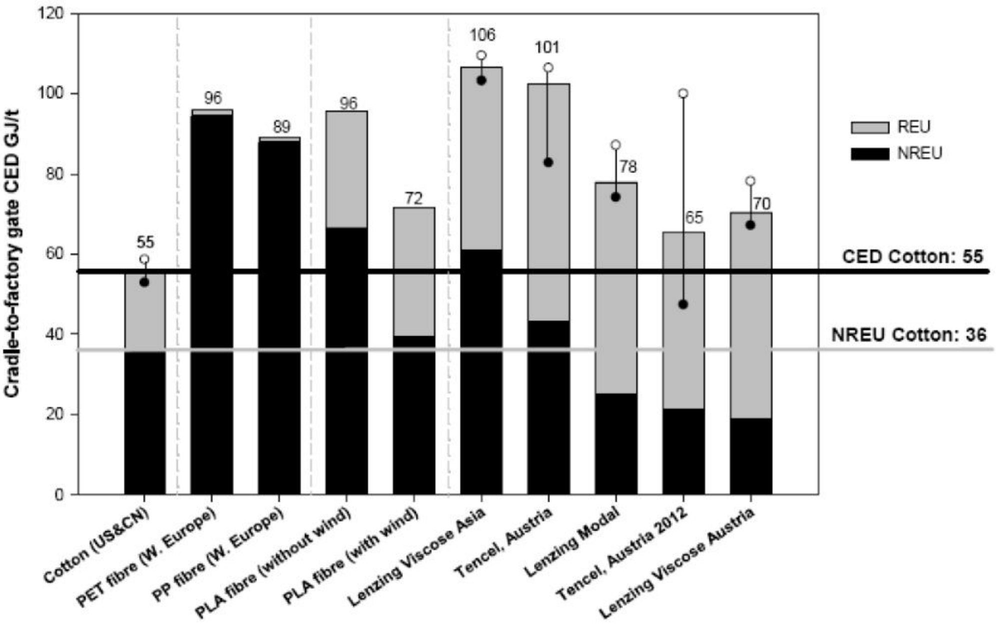

Figure 1:*Comparing one tone staple fiber, cradle-to-factory gate[8].*

The numbers above each column in fig. 1 represent CED. The uncertainty ranges represent the uncertainty of CED. For man-made cellulose fibers, the uncertainty ranges are caused by using different pulp mix and different allocation methods; for cotton, the lower value represents Chinese cotton and the higher value is for US cotton. Lenzing Viscose Asia is viscose fiberbased on Eucalyptus as wood source and Asia Local electricity, coal, gas, oil. Lenzing Viscose Austria is viscose fiber based on Beech as wood source. Tencel Austria is

Lyocell fiber based on Eucalyptus and Beech as wood source. Tencel Austria 2012 is Lyocell fiber processed by 100% recovered energy.PLA with wind purchases wind energy (via renewable energy certificate) to offset process electricity [7].
In terms of cumulative energy demand (CED), cotton is the most favorable choice. Man-made bio-based fibers, including cellulose fibers and PLA fibers, require relatively large REU compared to cotton, PET and PP. This is caused not only by the feedstock energy requirements, but also by the large amount of biomass energy used in the production.
The comparison of cradle-to-factory gate global warming potential (GWP) divided into the impact of released fossil CO_2andembodied biogenic $CO_2$is shown in fig. 2.Indicator GWP is based on a number of factors, including the radiative forcing of each greenhouse gas relative to that of CO_2, as well as the decay rate of each gas (the amount removed from the atmosphere over a 100 years) relative to CO_2[9].

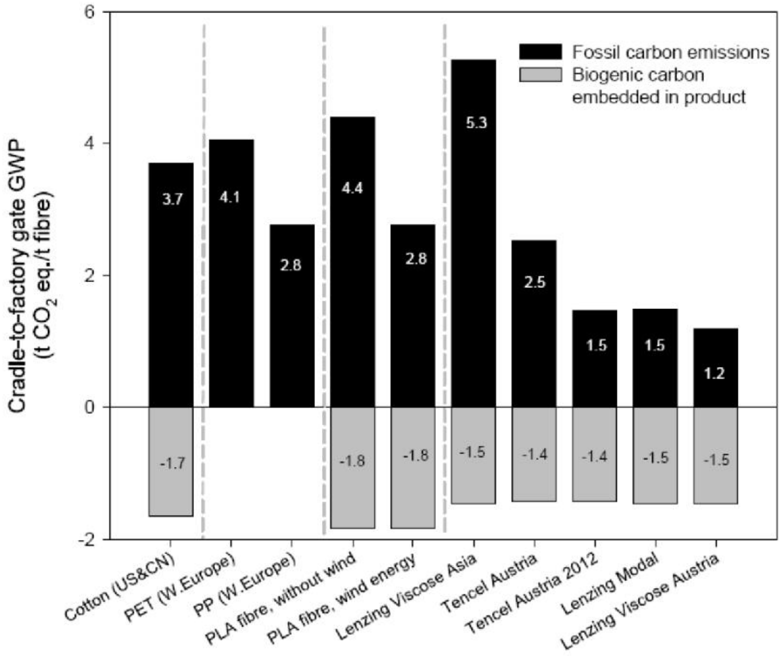

Figure 2:*Comparing one tone staple fiber, cradle-to-factory gate. Breakdown into the impact of released fossil* CO_2 *and embodied biogenic* CO_2 *(default allocation method for byproducts).*

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It can be seen that all man-made cellulose fibers have lower GWP than PET fibers; all man-made cellulosefibers except for Lenzing Viscose Asia have lower GWP than PET, PP, PLA without wind and cotton; Lenzing Modal and Tencel Austria 2012 have nearly zero carbon emissions; and Lenzing Viscose Austria has a negative GWP, which means that it sequestrates more carbon in the product than it emits.

3. PLA FIBER SUBSTITUTION

PET is aromatic polyester, incorporating a benzene ring in each repeat unit and PLA is aliphatic polyester, with only relatively small pendant methyl groups to hinder rotation and to prevent easy access to the oxygen atoms in the ester linkage (see Fig.3).

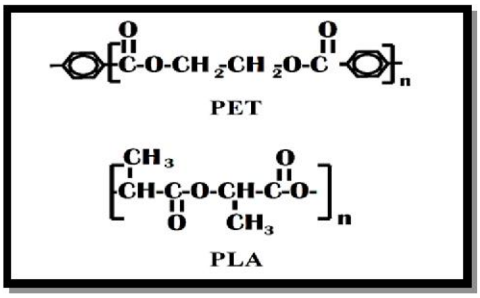

Figure3:*Structure of PET and PLA*

The PET chain is nominally linear, while the PLA molecule tends to assume a helical structure. These differences allow purer grades of PLA to crystallize much more readily and to a greater extent, than PET, resulting in dramatically different processing requirements for the fiber manufacturer. These differences sometimes present obstacles, but more often provide a greater degree of control over final fiber properties such as strength, shrinkage, and bulk.

Unique polymer characteristics also arise from the fact that the lactide dimer occurs in three forms: the L form, which rotates polarized light in a clockwise direction, the D form, which rotates polarized light in a counter-clockwise direction, and the Meso form, which is optically inactive. During polymerization, the relative proportions of these forms can be controlled, resulting in relatively broad control over important polymer properties.

So with a thermoplastic "natural" fiber polymer, unique polymer morphologies, and control over the isomer content in the polymer, a relatively broad spectrum of properties is available to the fiber manufacturer.

The comparison of some thermal and mechanical properties of PLA fibers with other fibers are shown in the figs. 4 – 5[3]. In fig. 4 the scans of DSCare shown. The differences between melting points are clearly visible.

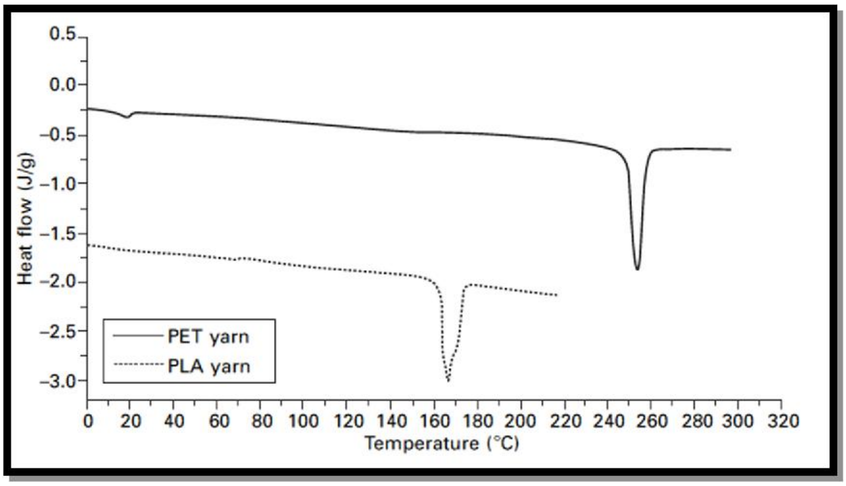

Figure4*:DSC scans of PET and PLA*

The tensile stress strain curves are shown in the fig. 5.

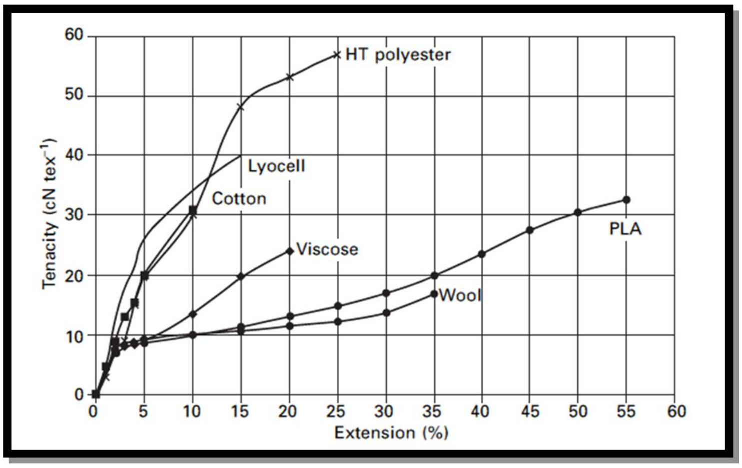

Figure5:*Stress strain curves for PLA and other common textile fibers*

The comparison of flammability properties of PLA and PET are summarized in the table 1[3].

Table 1*: Comparison of PLA and PET flammability properties*

Property	PLA	PET
Flammability	Continues to burn for two minutes after flame removed	Continues to burn for six minutes after flame is removed
Smoke generation	63 m^2kg^{-1}	394 $m^2 kg^{-1}$
LOI	26%	22%

PLA fibers are most likely to find a foothold in the substitution of PET fibers in hygiene and medical applications as pointed out by Gupta et al [3]. To understand this phenomena Fisher - Pry model (logistic S curve) can be used [5]. Their model allows a forecast of technological substitution with only the limited amount of data that is available in the early stages of a substitution. The Fisher-Pry substitution theory states that as a new technology begins to replace an existing technology without a major change in function, the substitution will tend to go to completion at a constant rate of substitution. The method is accurate especially after 20% substitution.The theory was empirically derived, so there is no theoretical proof that the method is valid; but it works in about 95% of the substitutions to which it has been applied.
Conditions necessary for application of Fisher Pry theory:

- New technology must satisfy some basic need or function
- Substitution must have started
- New technology must be capable of completely substituting the old technology in the market segment being analyzed

Fisher Pry is not applicable if the invention has only been demonstrated or there is no technological advance, such as a substitution based solely on fads or styles.If the substitution is 20% complete then the forecast by Fisher Pry is very accurate. In the early stages with less than 5% substitution the forecast is likely to be optimistic towards the new technology.

Actual time for 50% substitution may be 40% longer. When 20% substitution is achieved, it is often too late for old technology company to switch to new technology.
In a growing market "old technology" company may not even realize it is losing market share until substitution is 40% complete.
Generally leader in old technology cannot become leader in new technology due to:

1. Different raw materials used for the two technologies.
2. Fear of competing with themselves doesn't allow old technologies to do research in new technology.

Important considerations for applying Fisher Pry model:

- Specify exactly what function is being substituted
- Units must be same.
- Common density must be used.
- Identify what market is available for substitution. Upper limit must be used in the equation if some substitution is not possible.

If a new technology begins to replace an existing technology without a major change in function, it will tend to go to completion usually at a constant rate of substitution. Diffusion theory predicts that the yearly relative capacity increase of the new technology decreases with an increasing market share. Thus the volume increase *dV* depends on the market share of the new technology f and there is a correlation between the two variables. The rate of new technology market share *df/dt* can be expressed by rate function (logistic grow) [6].

$$\frac{df}{dt} = \frac{k}{L} f\left(L - f\right) \qquad (1)$$

where L is upper limit of market share. The solution of this differential equation has the form

$$f = \frac{L}{1 + \exp\left(-k(t - t_h)\right)} \qquad (2)$$

where f is market share for new technology at time t, t_h is time for 50% takeover (i.e. for $f = L/2$) and k is constant (proportional to the growth rate). This function can be simply return to the straight line by rewriting

$$\ln\left(\frac{f}{L - f}\right) = k\left(t - t_h\right) \qquad (3)$$

For the case when new product at limit time fully substitute old one is $L = 1$ (original Fisher - Pry model [5]).

4. PLA GLOBAL PRODUCTION AND PENETRATION ANALYSIS

PLA global production has been 74, 151 and 229 KT/Annum in 2003, 2007 and 2009 respectively. It is expected to grow to 473 and 833 KT/Annum in 2013 and 2020 (Forecast by Nature Works). The fraction of the production utilized for fibers was 20%, 30% and 30% during the early years and expected to account for 50 % in fibers by 2020.
Parameters of Fisher-Pry model (2) were estimated by nonlinear regression. The program FPA in MATLAB language was created. In this program is standard option to compute all three parameters L, k and t_h. In the case of few points it is possible to fix L and compute the

parameters k and t_h only. This second option was used here. The parameter estimates calculated by FPA program for saturation L = 0.8, 0.85, 09, 0.95, 1 are given in the tab. 2.

Table 2:*Parameter estimates for PLA penetration analysis*

saturation L [-]	rate k [year^{-1}]	time of half saturation t_h[year]	2013 penetration f_{2013} [-]
0.80	0.309	2005.23	0.734
0.85	0.286	2005.70	0.756
0.90	0.269	2006.16	0.776
0.95	0.254	2006.61	0.794
1.00	0.243	2007.05	0.809

Corresponding model shapes (lines) and data (stars) are presented in the fig. 6.
It is possible to compute that for L =1 the 98% of the target market of PET in hygiene and medical application would be accomplished by 2024. The rate of penetration as measured by the increase in relative share of PLA/PET is 0.243. Finally, the market forecast indicated by Nature Works seems to indicate PLA saturation (total penetration) of approx. 90%.

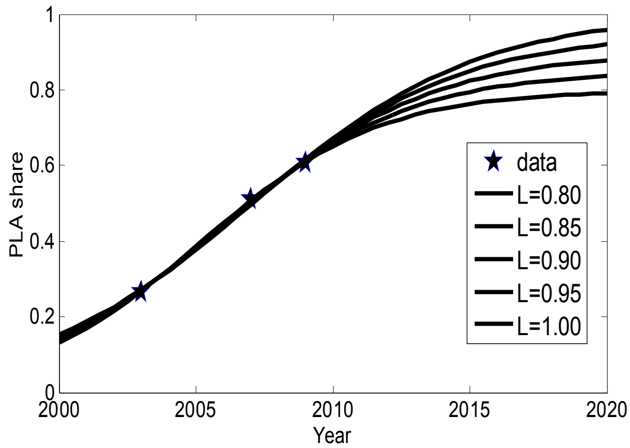

Figure 6:*PLA Fiber Substitution Characteristics (Fisher-Pry model)*

5. CONCLUSION

The current bio-fiber applications represent a niche segment of the textile value chain. In order to grow, new products must be developed which are not only biodegradable but also favorable to the environment, demand less energy than synthetic fibers during processing, release only carbon dioxide and water on degradation, fertilize the soil during composting, and obtained exclusively from renewable raw materials.Clearly, bio-fibers are not an environmental panacea, but rather another avenue to explore products with new properties and for living in a sustainable way.

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