SCIENTIFIC BULLETIN OF ESCORENA

Volume 7

EDITURA UNIVERSITĂȚII AUREL VLAICU
ARAD

ISSN-L 2066-5687
ISSN 2069-8070

Scientific Bulletin of ESCORENA
Vol.7, Iulie 2013

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Dear Readers and Escorena Network Members!

The Scientific Bulletin of Escorena - Volume 7 is connected with the final achievements of POS-CCE project „Bast Plants – Renewable Strategic Resources for European Economy - BASTEURES" project partially financed by European Union and partially by Romanian Government by structural funds.

Bast fibrous plants: flax, hemp, jute, kenaf, ramie are so important even now in XXI century in whole world, but especially in Europe – they are natural lignocellulosic sustainable resources not only for textile fibers, fibers for reinforcing of composites, sustainable row materials for pulp and paper but also as a source for „green chemistry" and for agrofine-chemicals. They can give a high crop, like in case of hemp with 15 tones dry mass per hectare. Bast fibers are healthy fibers with positive effects on human physiology with high protection to UV radiation. They can be cultivated practically in whole Europe including rural areas and they have many uses like: textiles, fabrics, nonwoven, terpulines, rope, quality paper, friendly sophisticated

composites, healthy multifunctional use of oils, essential oils (from hemp), agrofine-chemicals like lignin, lignans, lignocyclopeptides, mucus, pectin and also for energy-shives.

The technology of cultivation, harvesting, primary processing by using sophisticated machines (used for flax and hemp) can be adapted also for jute, kenaf, ramie.

The main achievements of POS-CCE project „Bast Plants – Renewable Strategic Resources for European Economy - BASTEURES" are:

- *exploring and developing the advance biotechnology for fibers extracting;*
- *degumming and bleaching by using of polyoxometalates as modern and promising catalysts;*
- *developing of original extracting methods of oil from flax and hemp seeds for consumption (omega 3, omega 6), pharmaceutical and cosmetic purpose and also for extracting of lignans and mucous substances.*

Team of the project solves this successfully. Also the team of this project developed the technology for utilization of woody parts – shives and non spinable short fibers for valuable composites used in furniture, buildings and transport area.

Including investigation on raps (canola) through this project was obtained high quality oil for biofuels.

Working on problem of reusing of waste waters from retting the project team have developed an original method for cleaning and recycled it.

It should be noted that thanks to this project "Aurel Vlaicu" University of Arad established and developed new and modern laboratories which were equipped with modern instrumental devices like gas-chromatograph coupled with mass spectrometer, AFM-Raman microscope, FT-IR spectrometer with thermal balance for DTA/TGA analysis, UV-Vis spectrometer and others. Also, the staff working in these laboratories is well trained and has good analytical skills.

On the base of all achievements of this project we announce the pending of tree international patents and one national patent.

Also we have to mention that the results of this project were published in good rated scientific journals and were presented at international and national conferences. On base of this project it worth to add that several PhD studies were started and finished with success.

Summing up, the "Aurel Vlaicu" University of Arad and Editorial Board of Scientific Bulletin of ESCORENA is proud to have had the opportunity to take part in this project.

THE APPLICATION OF DENDRITIC MATERIAL IN TEXTILE ENGINEERING

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Abstract

During the last decade, dendritic polymers including random hyperbranched polymers, dendrigrafts, dendrons and dendrimers characterized by a highly branched structure of great regularity, a compact shape, a large number of reactive end groups, and room between the branches for taking up guest molecules have attracted considerable attention. A remarkable variety of applications for dendritic polymers has been investigated as enabling building blocks for nanotechnology. A new promising area of potential applications for dendritic polymers is the field of textiles engineering.

Therefore, this review intends to introduce a brief description of the synthesis and characteristic of dendritic polymers and new potential applications of dendritic polymers in textiles engineering. With regard to the price of dendritic polymers, the application of dendritic polymer, particularly hyperbranched polymer, will be new approach to create novel features in the field of textiles engineering.

Introduction

During these past decades, the syntheses, characterization and application of nano and bio materials have been introduced into various fields of research, especially in textile engineering [1]. Among various novel technologies, dendritic architecture have been concerned recently due to the unique properties of these materials [2 - 3]. Dendritic architecture is one of the most pervasive topologies observed in nature at dimensional length scales measured in meters (trees) to nanometers (amylopectin) [4]. Due to the unique repertoire of new properties, dendritic polymers are recognized as the fourth major class of macromolecular architecture following the linear, crosslink and branched structure [5]. Dendritic architecture consists of the four subsets that are related to degree of structural control and are listed in

ascending order: namely random hyperbranched polymers, dendrigraft polymers, dendrons and dendrimers revealed in Fig. 1 [6].

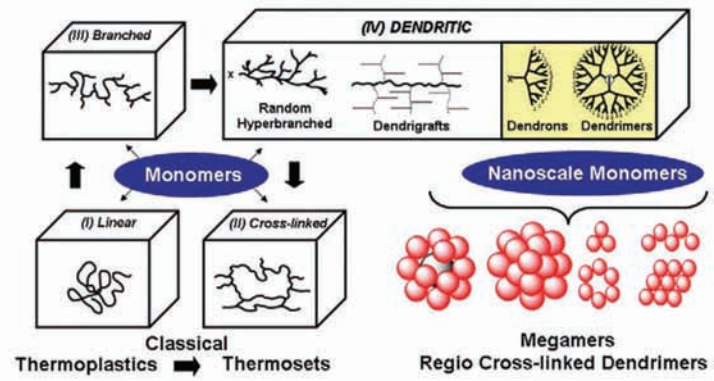

Fig. 1: Dendritic architecture consists of the four subsets: random hyperbranched polymers, dendrigraft polymers, dendrons and dendrimers *(Reprinted with permission from Ref. [6]).*

The term dendrimer refers to its characteristic appearance. It is derived from the Greek words dendron (tree branch like) and meros (part of) [7 - 8]. Synonymous terms for dendrimer include arborols and cascade molecules. However, dendrimer is currently the internationally accepted term [ ]. Generally, dendrimers consist of three basic components: a core, repeated units, and surface functional groups. The core with various multiplicities (N_c) localizes in the center of a dendrimer from which the construction of the dendrimer initiates or terminates. The repeated units or branches covalently attached to the central core are organized in a series of radially homocentric layers called "generations" (G). The branch cell also has various multiplicities abbreviated by N_b. [10]. The number of dendrimer surface groups, Z, amplifies with each subsequent generation (G) according to geometric branching laws, which are related to N_c and branch cell multiplicity N_b by the following equation 1 [11]:

$$Z=N_c N^G_b \qquad (1)$$

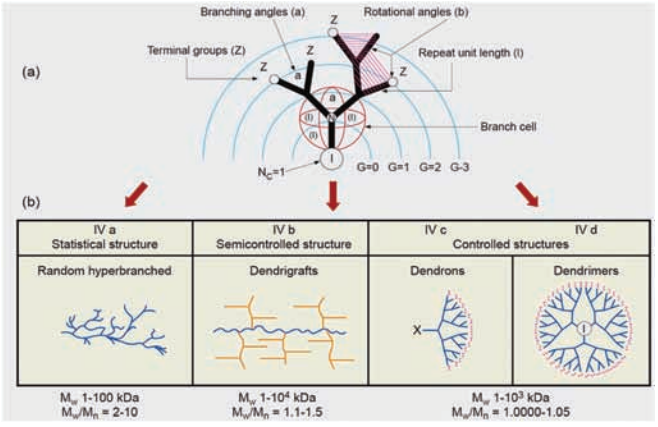

Fig. 2: All components of the dendritic structure with subclasses *(Reprinted with permission from Ref. [6]).*

Dendritic polymers may be further subdivided into four categories based on their architecture. Fig. 2 is revealed all components of the dendritic structure with subclasses [6]. As shown in Fig. 2, the dendritic polymers are open, covalent assemblies of branch cells (BCs).

The branch cells may be non-ideal with polydispersity index of Mw/Mn = 2-10 as observed for random hyperbranched polymers, or ideally organized into highly controlled core-shell-type structures as distinguished for dendrons and dendrimers (Mw/Mn = 1.0000-1.05) [1-7]. Flory was the first who apply the statistical or random hyperbranched polymers [12]. However, the first purposeful experimental confirmation of dendritic topologies did not produce random hyperbranched polymers [13]. Kim and Webster coined the popular term "hyperbranched polymers" that has been widely used to describe this type of dendritic macromolecules [14]. The other class of dendritic polymers is the dendrigraft systems, introduced simultaneously in 1991 as Comb-burst polymers by Tomalia et al. [15] and as arborescent polymers by Gauthier and Möller [16]. Dendrigraft polymers may be viewed as semi-controlled branched polymer architectures intermediate in terms of structure control between dendrimers and hyperbranched (Mw/Mn = 1.1-1.5) (Fig. 3) [17]. The multi step synthesis and slow molecular mass growth of dendrimer is often considered to be a major drawback hindering the use of these materials on a large scale. In contrast to dendrimers, dendrigrafted polymers grow faster and amplify the surface group more drastically [18].

The two most widely studied dendrimer families are the Fréchet-type polyether compositions [19] and the Tomalia-type PAMAM dendrimers [20] revealed in Fig. 3. PAMAM dendrimers constitute the first dendrimer family to be commercialized, and represent the most extensively characterized and best-understood series at this time [21]. As you can see in Fig.3, the dimension of PAMAM from 3th to 7th generation number is in the range of nano dimension. Furthermore, PAMAM dendrimer size and structure is very close to natural proteins such as insulin, cytochrome C, hemoglobin, prealbumin and hemerythrin [6].

Due to the novel characteristic of dendritic polymers, they provide a powerful tool to design hyperbranched polymers for a wide variety of applications. An area of application that, until now, has remained almost unconsidered in scientific discussions is the field of textile engineering. Therefore, this review focuses on new developments of dendritic polymers including dendrimer, dendrigraft and hyperbranched polymers in the field of textile engineering. Based on a brief description of the synthesis and characteristic of dendritic polymers, discussions of new potential textile engineering applications of dendritic polymers have been considered.

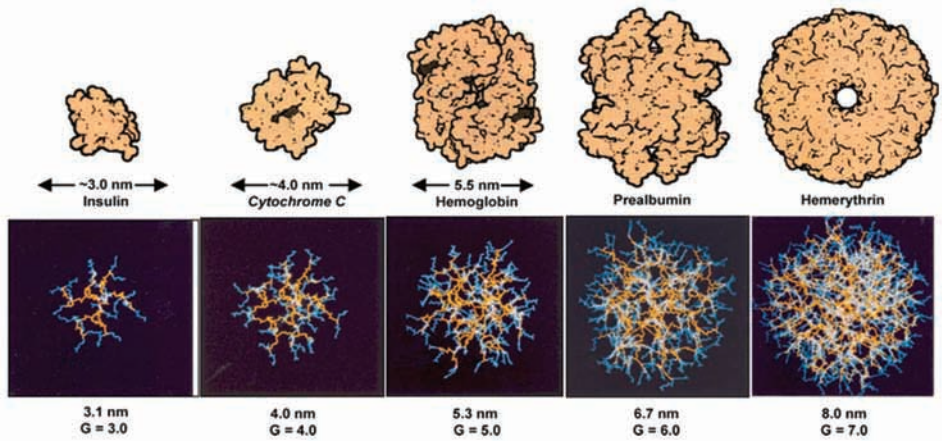

Fig. 3: The dimension of PAMAM from 3th to 7th generation number is in the range of nano dimension *(Reprinted with permission from Ref. [11]).*

Dendrimer synthesis: divergent and convergent methods

In general, synthetic methods for the preparation of branched architectures rely on two similar procedures described as divergent and convergent (Fig.4). Both procedures usually rely on mutually compatible and complementary protection and deprotection sequences [22]. In the divergent methods, dendrimer grows outwards from a multifunctional core molecule. The core molecule reacts with monomer molecules containing one reactive and two dormant groups giving the first generation; then the new periphery of the molecule is activated for reactions with more monomers. The process is repeated for several generations and a dendrimer is built layer after layer. The divergent approach is successful for the production of large quantities of dendrimers problems occur from side reactions and incomplete reactions of the end group that lead to structure defects. To prevent side reactions and to force reactions to completion large excess of reagent is required. It causes some difficulties in the purification of the final product [23]. The divergent synthetic routes first have been illustrated by Tomalia et al. [24].

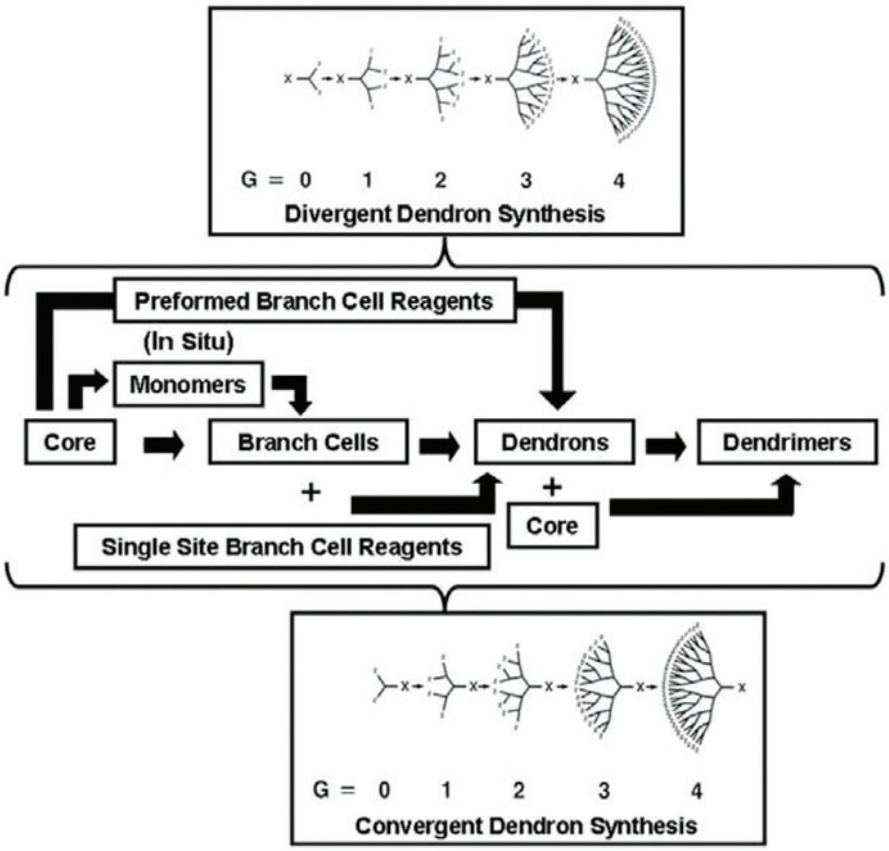

Fig. 4: Divergent and convergent synthetic strategies for dendrimer synthesis *(Reprinted with permission from Ref. [6]).*

The convergent methods were developed as a response to the weaknesses of the divergent synthesis. In the convergent approach, the dendrimers is constructed stepwise, starting from the end groups and progressing inwards. When the growing branched polymeric

arms, called dendrons, are large enough, they are attached to a multifunctional core molecule. The convergent growth method has several advantages. It is relatively easy to purify the desired product and the occurrence of defects in the final structure is minimized. It becomes possible to introduce subtle engineering into the dendritic structure by precise placement of functional groups at the periphery of the macromolecules. However, the convergent approach does not allow the formation of high generations because steric problem occur in the reactions of the dendrons and the core molecules [25]. The convergent synthetic routes first have been illustrated by Fre´chet et al. [26].

Furthermore, in contrast to the notable differences inherent in the core first (divergent) or core last (convergent) techniques, there is some similarity. The convergent protocol can be considered a "higher order" divergent method whereby "complex" monomers are attached to a central unit whether it is formally a final core or simply another self-similar monomer. However, this is where the similarity ends, as there are major differences in the outcome of using each technique. The overview of synthetic strategies for dendrimer construction annotated with discovery scientists is illustrated in Fig. 5 [6].

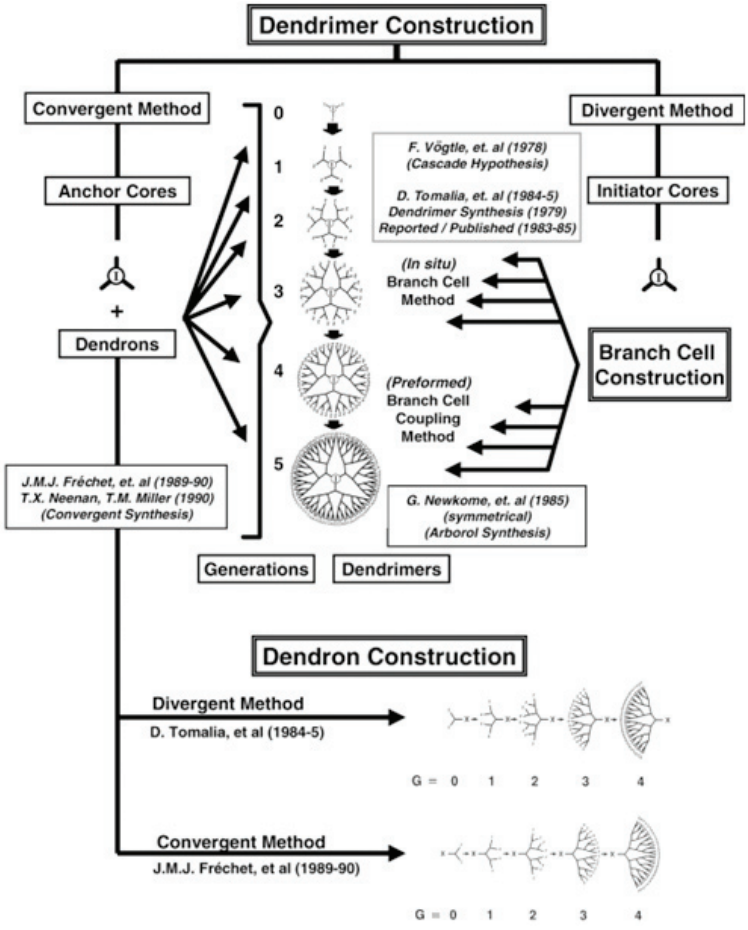

Fig. 5: Overview of synthetic strategies of dendritic polymer annotated with discovery scientists *(Reprinted with permission from Ref. [10]).*

For instance, the strategy for the first synthesized Dendrimers, polyamidoamines (PAMAMs), has been illustrated in Fig. 6 [6]. PAMAM dendrimers were synthesized by the

divergent approach. Typically, ethylenediamine (N_C=4) or ammonia (N_C=3) are used as cores and allowed to undergo reiterative two-step reaction sequences involving: (a) exhaustive alkylation of primary amines by Michael addition with methyl acrylate, and (b) amidation of amplified ester groups with a large excess of ethylenediamine to produce primary amine terminal groups. Each complete reaction sequence results in a new dendrimer generation. The half generations PAMAM dendrimers (e.g. 0.5, 1.5, and 2.5) possess anionic surfaces of carboxylic groups as illustrated in Fig. 6 [6, 10].

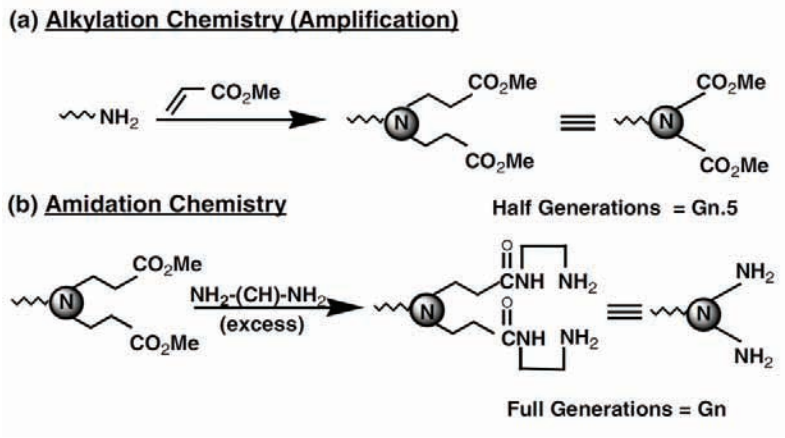

Fig. 6: The strategy for the synthesis of polyamidoamines (PAMAMs) Dendrimers *(Reprinted with permission from Ref. [6]).*

Dendrigraft synthesis:

In comparison to dendrimer synthesis, dendrigrafted structures also have been synthesized by three different strategies. The 'grafting onto' and 'grafting from' methods are both divergent techniques analogous to the core-first dendrimer syntheses. The divergent 'grafting onto' methods is based on successive coupling reactions of polymer chains with a functionalized substrate polymer, while divergent 'grafting from' methods is used cycles of polymerization initiated from functional sites located on a substrate polymer. The 'grafting through' method is a convergent approach more closely resembling the hyperbranched polymer syntheses involving coupling of preformed polymer chains in a one-pot reaction [15-17,27]. The first dendrigraft polymers reported in the literature, the Comb-burst and arborescent polymers, were prepared according to grafting onto schemes [17].

Dendritic characteristic

The properties of polymer materials can be well adjusted by changing the polymeric structure. Due to their highly branched and functionalized structures, globular shapes, well-defined molecular weights and sizes, monodispersity, multivalency, and relative nonpolar interior cavities [28], dendritic polymers show many intriguing physical and chemical properties, which is distinct from the other polymer structure. One of the most important characteristic is safety and efficacious of dendrimer particularly in biomedical applications. It is found that the toxicity of the dendrimer-based product was surface functional group, dose and generation-dependent in vitro as well as in vivo, whereas low generations (below 5^{th}) were not toxic [29-30]. In the following sections, the novel characteristics of dendritic polymers are discussed.

Rheological and Mechanical properties:

The intrinsic viscosity of polymers depends greatly on the molecular architecture. In General, the intrinsic viscosity of linear polymers, that obey the Mark—Houwink—Sakurada equation, increases steadily with increasing molecular weight, whereas a maximum appears for a dendrimers at a certain dendrimer generation [31]. For hyperbranched polymers, the intrinsic viscosity also increases with increasing molecular weight but much lower than that of linear counterpart [32-33]. The dendrigraft polymers have similar trend with the dendrimers [34]. Hammond et al. [35-36] revealed that the chemistry of the end groups and its interaction with the solvent were found to be more important at low generations, whereas at higher generations, the highly branched nature of the dendritic block was the more important factor.

As a consequence of the excluded volume associated with the core, interior and surface branch cells, steric hindrance are expected to occur due to tethered connectivity to the core. The steric congestion increases by rising generation number, Nc¬ and Nb according to de Gennes prediction as 'de Gennes' dense-packed generation [10]. Ideal dendritic growth without branch defects is possible only for those generations preceding this dense-packed state. This critical dendrimer property gives rise to self-limiting dendrimer dimensions [37].

The same behavior is also observed for the density. By increasing generation numbers, a minimum is observed in the density at the certain generation. The change of density with the generation can be explained with reference to the density distribution and fluctuations inside dendrimers, in the simplest case. Lescanec and Muthukumar [38] believed the density to be the greatest at the core and to have a monotonic decrease to the edge; Indeed, de Gennes and Hervet [39] expected the minimum density to be at the core and to increase monotonically to the outer edge. Akbari et al. [40-41] also observed a minimum density for the first generation and the monotonic increase for the additional generation in the dendrigrafted structure which are consistent with de Gennes and Hervet's prediction for dendrimers.

Fig.7 illustrated the surface area/head group (Z), refractive index, density (d) and intrinsic viscosity as a function of generation for PAMAM dendrimer from 1 to 9 generations [10]. The de Gennes dense-packed occur between generations 4 and 5 which refractive index and density revealed minimum, whereas intrinsic viscosity demonstrated maximum at the mention generation [10].

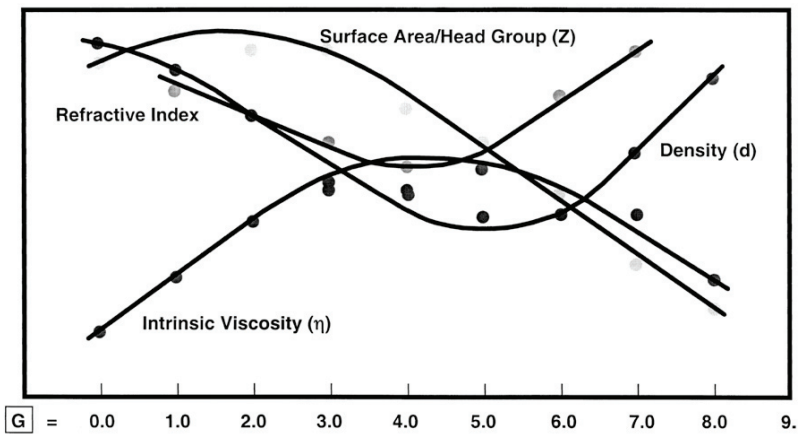

Fig. 7: Comparison of surface area/head group, refractive index, density and intrinsic viscosity as a function of generation *(Reprinted with permission from Ref. [10]).*

The very narrow polydispersity index as one of the most characteristic of dendritic structure was discussed in introduction section due to the importance of this characteristic.

Host-guest properties:

Host-guest chemistry involves the binding of a guest molecule in a receptor molecule as a host one. The design and construction of hosts that are capable of selectively binding guest molecules requires precise control over geometrical features and interacting complementarily [42]. The possibilities for encapsulating guest molecules in dendritic host as an ideal molecular containers proposed by Maciejewski in 1982 [43]. As dendritic structures possess an exterior end groups at the periphery and interior hollow branch or core, they should be able to act as a host for guest molecules. Hence, the nature of the host-guest interaction is varied by increasing generation numbers.

Poly(amidoamine) (PAMAM) dendrimers reveals the periodic properties as a function of generation (G=0-10). It demonstrates flexible scaffolding for generation beyond 4, container properties for generation between 4 to 6 and rigid surface scaffolding for generation after 7 where de Gennes dense packing is severe. These three domains have been illustrated in Fig. 8 [6]. According to Fig. 8, by increasing generation, the shape of dendrimer has been changed from flat, floppy conformations to robust spheroids. As a result, entrapment of guest molecules is difficult in earlier generation due to the low cavity, whereas the steric hindrance has limited penetration guest into the higher generation.

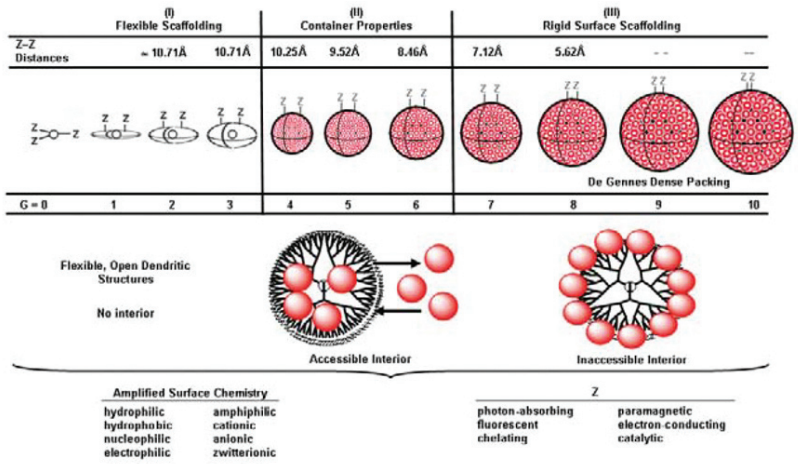

Fig. 8: Periodic properties of PAMAM dendrimers as a function of generation *(Reprinted with permission from Ref. [6]).*

On the other hand, the type of solvent, pH and ionic strength can be influence on the structure and conformation of dendrimers [44]. For instance, PAMAM dendrimers have an extended conformation at low pH resulting from repulsions between primary and tertiary positively charged amines. At neutral pH the size of the dendrimer decreases probably due to hydrogen bonding between uncharged tertiary amines and positively charged surface amines. At high pH, dendrimers contract since the global charge approaches neutrality. With decreasing solution pH, there is further increase in the size of the dendrimers [45]. Similar trend have been observed for PPI dendrimer [46-47].

The novel characteristics of dendritic polymers make them suitable to wide various

applications discussed in next section.

Applications of dendritic materials

The versatile structure of dendritic structure gives to dendrimers the capability of including a wide variety of applications such as medical [48], health care, cosmetic, catalytic agent, molecular weight and size standards, chemical / biological sensors & detectors [49], textile additive, polymer and plastics additives (e.g. for lowering viscosity, increasing stiffness, incorporating dyes, compatibilisers, etc.), creation of foams (i.e. synthetic zeolites or insulating material), building blocks for nanostructured materials, consumer goods, ink/laser-printing toners [50], dyes and paints [51], industrial adhesives, manufacture of nanoscale batteries and lubricants [52], and various healthcare/medical applications [53] such as biomedical application [54], drug delivery [55], and biomolecular binding agents [56], cellular Transport, artificial cells, diagnostics and analysis [57-58], targeted delivery supermolecular assembly [59-60], catalyst [61-62], MRI contrast agents [63-64] and other aspects of dendrimer applications [65]. As mention before, dendritic polymers provide a wide variety of applications. An area of application that, until now, has remained almost unconsidered is the field of textile engineering. As a result, this review followed by a discussion of new potential textile engineering applications of dendritic polymers.

Applications in the field of textile engineering

Novel characteristic of dendritic polymers such as highly branched structures, large number of reactive end groups and room between the branches for taking up guest molecules create these fourth classes of polymer a suitable candidate for use in the textile engineering. The only limiting factor in the widespread applications is the price of these compounds, especially dendrimers. The traditional process for creating dendrimers such as PAMAM includes an amidation step that involves thermodynamically driven, lower reaction rate, chemistry, accompanied by long reaction times. These process features require high excesses of reagent and high dilutions resulting in low production capacities per reactor and thus high costs, particularly at higher generations.

In comparison with dendrimers, hyperbranched polymers represent versatile carrier molecules with a promising price/performance ratio. They are commercially available on a ton-scale at prices ≥4 euros/kg. This opens up possibilities to meet the requirements of several challenging encapsulation and controlled-release applications [66]. As a result, for large-scale industrial use an economic alternative for dendrimers has been found in the hyperbranched polymers, which share many of the dendrimers' special properties.

In the case of dendrimer, the Priostar families of dendrimers [67] involves the use of faster, kinetically driven chemistry, combined with the use of polyfunctional branch cell reagents to rapidly and precisely build dendrimer structures in a controlled way, generation by generation. This present process yields precise structures with cleaner chemistry, requires lower excesses of reagents, and lower levels of dilution, thus offering a higher capacity method that is more easily scaled to commercial dimensions, and providing new ranges of materials at lower costs. With regard to the manufactured of dendritic polymers in high volumes at costs attractive, a wide variety of uses can be considered in the textiles engineering. Fig. 9 illustrated the various applications of dendritic polymers in the field of textiles engineering discussed in this review.

Fig. 9: The various applications of dendritic polymers in the field of textiles engineering

Dye and Dyeing fabric:

The application of dendritic materials in textiles engineering have been first utilized for the dye in a variety of purpose such as structure control and probe for dendrimer, dye combined with dendrimer for capture and transfer of photon energy, extraction and encapsulated of dye by dendrimer [68]. Specially, the interaction between dyes and dendritic polymers is especially interesting [69]. Furthermore, dendrimers have found a number of applications in inkjet printing and related techniques [49] and laser applications [70].

Dendritic polymers have been used for dyeing polypropylene fiber which usually dyed in master-bach process. Froehling [71] explained that it is possible to lock guest molecules physically within the internal cavities of a dendritic host, while the versatility of reactive end groups can be tailored to attract dyes as well as other chemical additives. Furthermore, hyperbranched polymeric additives such as Boltorn H40 have been utilized for dyeing polyethylene perephthalate (PET) fiber and sheet by disperse dye [72-73]. The thermodynamic parameters of disperse dye as well as thermal behavior of PET fiber has been investigated well by Bozorgi et al. [74-76].

The salt-free dyeing on cotton has been utilized due to contribute to environmental non-pollution an undertaken to explore promising approach to reduce cost of dye process [77]. Burkinshaw [78] applied amine terminated dendrimer, for pretreatment of cotton for reactive dyeing. The results revealed that color strength of reactive dye increased with increasing amount of dendrimer applied for pretreatment of cotton fabric in the absence of both electrolyte and alkali. The similar results were studied using direct dyeing on cotton [79]. Besides salt free dyeing, the treated fabric with an amino-terminated hyperbranched polymer revealed antibacterial properties [80].

In addition, the aggregation of other dyes such as Methylene blue [81] and azo [82] were investigated in the presence of the dendritic polymers due to the large amount of

functional end groups. Another approach to the use of the dendritic polymers is to improve the solubility of poorly soluble dyes.

Wastewater:

One of the most important applications of dendritic polymers would be their use as the removal of textile dyes and other additives from aqueous solutions as well as encapsulate water contaminants such as metal ions due to the interaction ability of their interior and functional end groups at the periphery of a dendritic structure. Fig. 10 demonstrated the recovering of metal ions from aqueous solutions by dendrimer-enhanced ultrafiltration [83]. The recovery of metal ion as well as dendrimer for repeated use which provides economically feasible processes was possible by decreasing the solution pH to 4.0 [84].

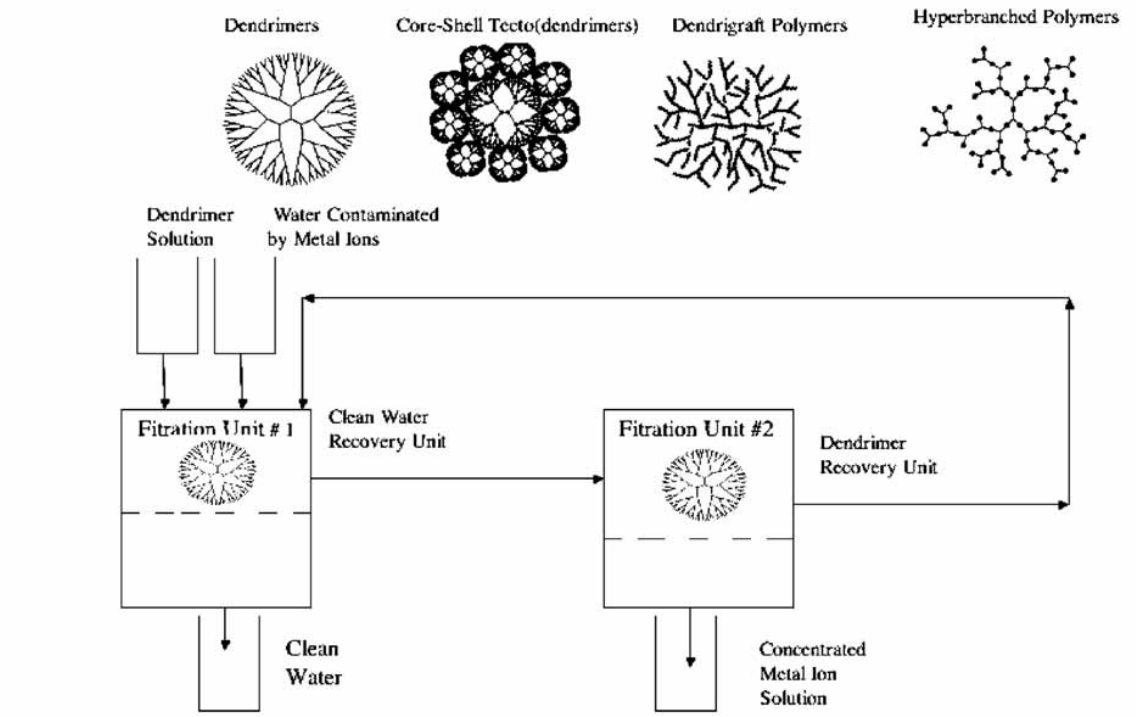

Fig. 10: Recovery of metal ions from aqueous solutions by dendrimer enhanced ultrafiltration *(Reprinted with permission from Ref. [85]).*

Dye removal from colored textile wastewater by poly(propylene imine) dendrimer was studied by Hayati et al. [85]. In addition, surface modification [86] and production of a composite nanofiltration membrane using dendritic polymers is a utilizing feature in wastewater application [87].

Drug delivery using fabric:

Besides, widespread application of various dendrimers in drug delivery or biological application, drug delivery through textiles is a novel promising feature of application of dendritic materials. Among various characteristic of dendritic properties, host-guest properties of dendritic molecules has developed significantly and now occupies a unique position within the area of supramolecular chemistry [88]. Due to the presence of functional end group at the periphery as well as the hallow interior in dendritic boxes [89], control of drug release

through fibers is possible. Therefore, they exhibit great potential application especially on the nanometric scale as a nanoscale container and scaffold such as fiber [90]. These unimolecular container and scaffolding behaviors appears to be a periodic property that is specific to each dendrimer family or series. Similar cyclodextrin, dendritic polymer can be utilized for this purpose [91].

Novel finishing:

In these days, incorporation of novel finishing processes on fabric using nanotechnology has been receiving considerable attention. Among various nano and bio materials, applications of dendritic polymers have been concerned recently in textile industries due to the unique properties of these materials. The versatile structure of dendritic polymers give them to capability of including a wide variety of nonpolar or charged guest molecules into their hydrophobic pockets by hydrophobic/hydrogen-bond interactions, or on the surface by electrostatic interactions, forming different types of inclusions or ion-pairs in aqueous solutions [92]. These characteristic makes dendritic polymers suitable candidate in various finishing agent on the textiles, particularly for the carriers in host-guest systems. A variety of finishing process can be applied on textiles in the presence of dendritic polymers such as flame retardant, super hydrophobic, antistatic, super hydrophilic, perfumery, antibacterial, and water/oil repellency properties which discussed in this section.

The application of permanent fragrant worsted fabric utilizing dendritic material as one of the nano size materials was concerned by Akbari et al. [93]. It seems that fragrance can be stuck into the internal branch cells and the functional end groups of dendritic materials can be attached to the fabric. Consequently, these binding on the fabrics make almost permanent fragrant into the worsted fabric without any effect on physical properties such as breaking strength, bending length, air permeability, fabric weight and wrinkle recovery angles.

Physical properties, salt-free dyeability, antimicrobial activity, and antiultraviolet property of the treated cotton samples were tested by Zhang et al. [94]. Their investigation revealed that the treated cotton fibers by dendritic polymer had no effect on the mechanical properties. Besides, the application of amino-terminated hyperbranched polymer can enhance the substantivity of the cotton fabric, reduce the electrolyte dosage, and potentially lead to salt-free dyeing as well as improvement of the thermal stability and the moisture regain. Furthermore, the treated cotton fabric can be dyed with acid dyes effectively, reduced UV transmission and increased UPF.

Furthermore, it seems that the antimicrobial property of textile fabric treated with amine terminated hyper branched polymer as well as dendrimer consider more attention due to the presence of huge cationic end groups [95-96]. For instance, the excellent antimicrobial property of cotton cellulose fabric grafted with poly(propylene imine) dendrimer have been recently studied [97-98]. Ghosh etal. [99] revealed that modified dendrimers with ammonium functionalities and silver-dendrimers complexes exhibited antibacterial efficacy against S. aureus when applied onto the Nylon/Cotton blend fabric.

In addition, the effects of water repellency of cotton/polyester blended fabric on the physical properties as well as color assessment of blended fabric were investigated in the presence of fluorocarbon , nanoparticle and dendrimer by Colleoni et al. [100]. It has been showed the dyestuffs do not interact with finishing products after modification of the surface roughness. Furthermore, mechanical characteristics of the fabric are not significantly altered

by finishing treatments.

Surface modification:

The use of dendritic polymers as surface modification on the fiber, film and fabric is fairly unexplored and their application is still to be optimized; in this section, their influence on novel characteristic is worthy of investigation, particulary the dendrigrat formation on the surface. For instance, chemical modification of chitosan with cationic hyperbranched dendritic polyamidoamine on cotton fabric has been investigated to improve dye uptake as well as antimicrobial activity [101]. Surface modifications of cotton fiber for apparel use also have been considered by dendrimer [102]. Acrylic copolymers film has been modified via dendrigrafted with citric acid illustrated in Fig. 11 [103]. This modification has been improved the characteristics of the fibers such as swelling/de-swelling in basic and acidic media as pH actuators, nanocarbon fiber precursors, or as active particles for loading with guest molecules [104].

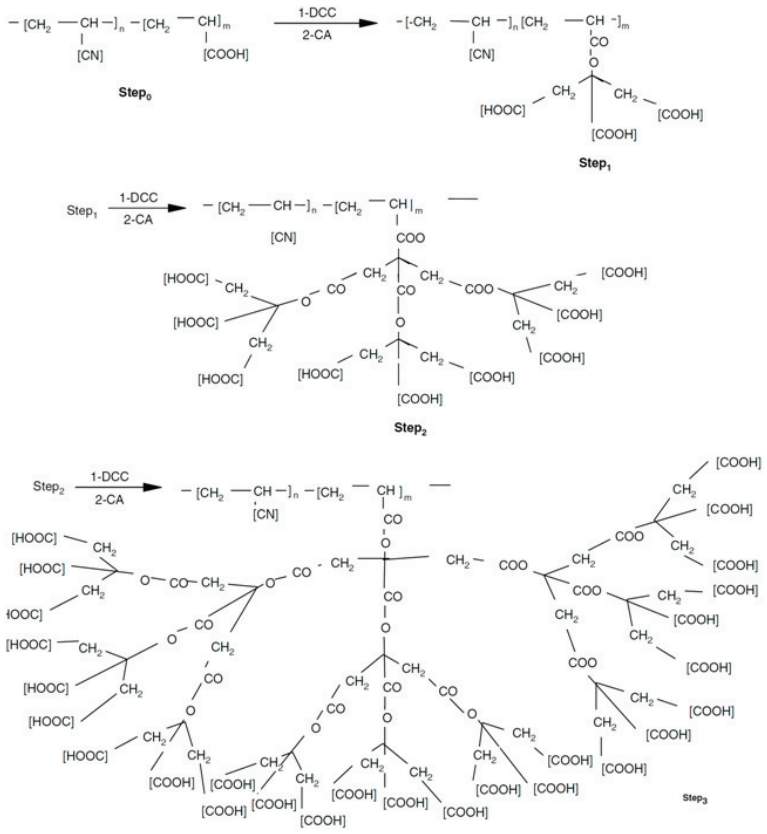

Fig. 11: Theoretical preparation routes of citric acid dendrigraft from zero to four generation with 100% conversion as surface modification of acrylic copolymer. *(Reprinted with permission from Ref. [103]).*

Conclusion

During the 21st century, dendritic polymers reveal a key role as enabling building blocks for nanotechnology. Dendritic polymers are recognized as the fourth major class of macromolecular architecture consisting of four subclasses including random hyperbranched polymers, dendrigrafts, dendrons and dendrimers. They characterized by a highly branched

structure of great regularity, a compact shape, a large number of reactive end groups, and room between the branches for taking up guest molecules have attracted considerable attention. Therefore, they exhibit great potential application especially on the nanometric scale as a nanoscale container and scaffold. These properties are determined by the size, shape, and multiplicity of the construction components that are used for the core, interior, and surface of the dendrimer. As a result, a remarkable variety of applications for dendritic polymers has been investigated in the field of textiles engineering.

This review covers the synthesis, characteristic and new potential applications of dendritic polymers in textiles engineering in the variety of applications including wastewater, permanent fragrant fabric, water repellency, improvement of dye ability, dyeing PP fabric, drug delivery using fabric, novel finishing, surface modification, antibacterial properties. With regard to the price of dendritic polymers due to complex multistep synthesis of dendrimers, the application of dendritic polymer, particularly hyperbranched polymer, will be new approach to create novel features in the field of textiles engineering.

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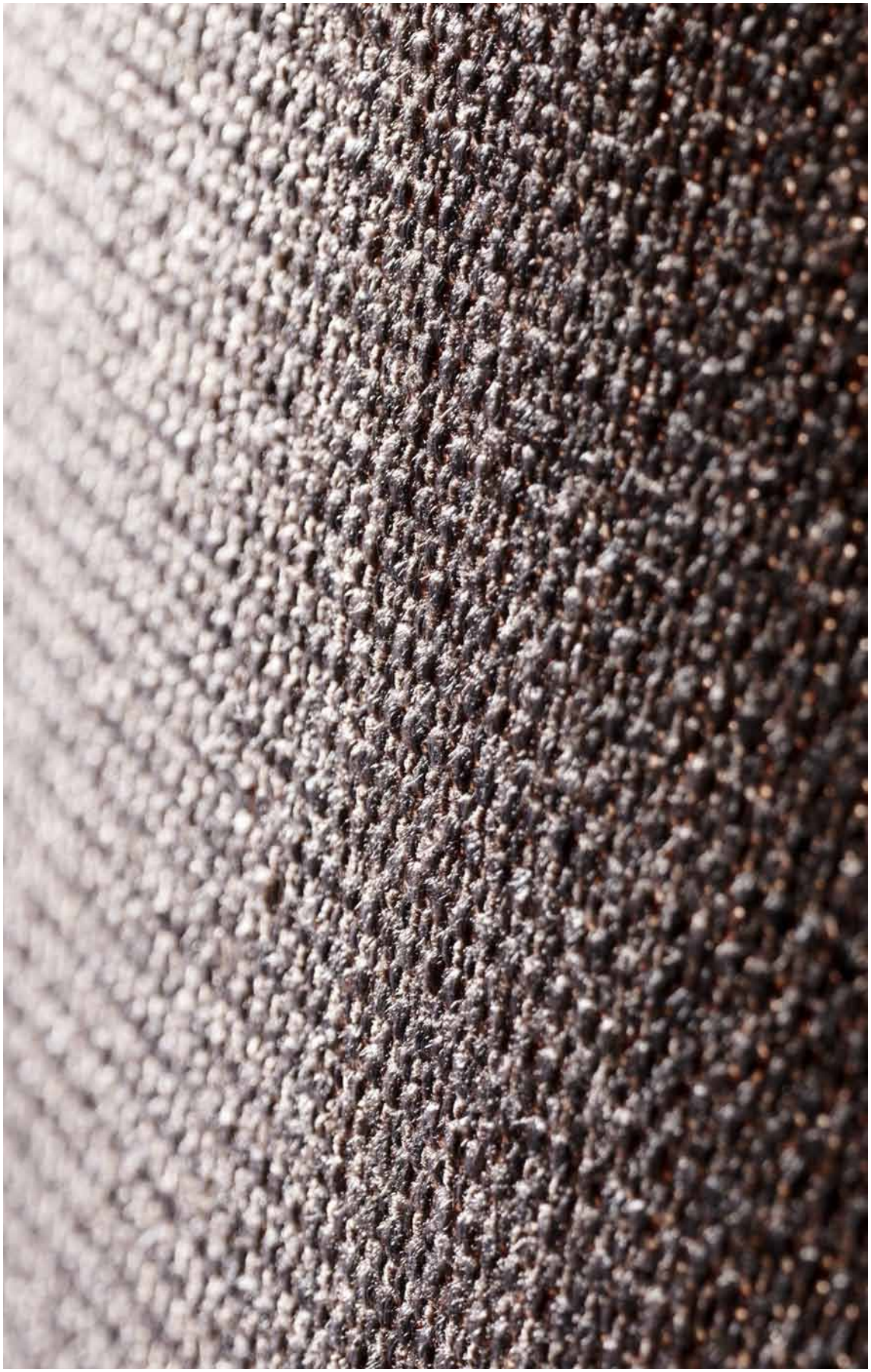

ATOMIC FORCE MICROSCOPY: DIFFERENT APPROACH TO DISCOVER THE PAPER

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Abstract

Natural fibers were used as material in paper industry for centuries and then their use decayed. Currently, it is considered a new normal course to include natural fibres in the technology of production of paper as resource with high potential to be available in many countries, especially where the wood is not available. Paper sheets containing pulp from second category fibers, SCF, consisting of a mixture of bleached pulp of very short cotton fibers and chemical degumming hemp tow and respectively, from long wooden kraft, were attained. In the bleaching procedure of SCF was used peroxide delignification procedure, in the presence of a polyoxometalate ($Na_2H_3PMo_{10}V_2O_{40}$) as oxidative reagent, in aqueous solution. Paper sheets containing bleached long wooden kraft were also obtained. Mechanical, optical, and surface characteristics (atomic force microscopy) analyses of these two types of paper sheets were determined to evaluate the possible application of the SCF to be used in paper industry.

Keywords

Atomic force microscopy, hemp, paper, peroxide bleaching, polyoxometalate

1. Introduction

Natural fibers used for paper and packaging production are very diverse due to ample resources available world-wide. As the prices for obtaining paper and packaging from wooden plants are high, and the wood resources are modest in some regions of the world,

new alternatives are examined in order to use annual plant fibers (e.g. cotton, flax, sisal, hemp). Another resource represent the textile wastes, which arise during manufacturing of yarn and textile fabrics, that could be used to obtain high quality paper, bacterial cellulose [1], chemically modified cellulose [2-4], and also for low grade applications (car insulation, seat stuffing, fibres for upholstery, and even building materials). The wood and non-wooden plant (e.g. flax, hemp, cotton, etc.) pulps contain residual lignin that is responsible for the yellow and even brown color of the pulp. Usually the lignin has to be removed from the pulp by delignification and this process should be selective and not harmful for the physico-chemical properties of the bleached pulp. Ecologic-friendly technologies, such as hydrogen peroxide, oxygen, ozone bleaching are alternatives to conventional chlorine-based bleaching technologies of the pulps[5]. Polyoxometalates (POMs) were reported to be used in both anaerobic and aerobic conditions of delignification of the lignocellulosic pulps of wooden plants [6]. In the anaerobic conditions the reoxidation of POM reagents is demanded in order to be reused in a secondary stage. In the application of POM as catalyst, in aerobic conditions, POM oxidizes the lignin from pulp and the reduced form of POM is reoxidized by molecular oxygen in the same phase. The Keggin type polyoxometalates were reported to be the most suitable POMs for the delignification process [6]. POMs used in delignification process are: $[PV_2Mo_{10}O_{40}]^{5-}$, $[SiW_{11}O_{40}]$ [7], $Na_{5(+2)}[Si_{1(-0.1)}MoW_{10(+0.1)}O_{40}]$ [8], $[SiW_{11}VO_{40}]_{5-9}$, $[SiW_{10}V_2O_{40}]^{6-}$, $[AlVW_{11}O_{40}]^{6-}$ [10], $[SiW_{11}Mn(H_2O)O_{39}]^{6-}$ [11], $[PMo_{12}\text{-}nVnO_{40}]^{(3+n)-}$ (n = 1-6) [12,7].

Usually, the main physical characteristics of the paper samples (tensile strength and stiffness, breaking length, bursting strength, opacity, etc.) are evaluated using common methods and commercially available devices.

Advances in morphological characterization in cellulose research use the application of atomic force microscopy (AFM). AFM was previously used to determine the surface topography of conducting and non-conducting samples at macro- and nano-scale and also to measure surface forces and nano-mechanical properties [13]. AFM was used to determine the nanoscale structures of paper and/or cellulose, respectively, such as microfibrils [14,15], cellulose model surfaces [16] or to evaluate the structural changes of cellulose caused by process or morphology changes caused by different treatments [17-19]. Chemically modified hemp fibers suitable for thermoplastics or concrete composites [20], hardwood and softwood nanofibrillar model films [21] were also evaluated by AFM.

In the present study we have used pulp obtained from second category fibers (SCF) which contain a mixture of very short cotton fibers and chemical degumming hemp tow (Cannabis sativa L.) to attained specialty paper. Another aim of the present work was the bleaching of the SCF, accomplished by the removal of the lignin in a selective manner by using hydrogen peroxide and a polyoxometalate ($Na_2H_3PMo_{10}V_2O_{40}$) as oxidation reagent.

Materials and methods

Materials and reagents

A commercial bleached long wooden kraft pulp with the following features: burst index 6.9 kPa m^2/g; tear index 10.3 mN m^2/g; breaking length 10,500 m; opacity 88 % (Pols, Heintzel AG, Austria) has been used. The long wooden pulp has been refined to 30º SR according to ISO 5267. These data were obtained from the pulp suppliers. Second category fibers, SCF, contained 60 % very short cotton fibers (1-1.5 cm) and 40 % chemical degumming hemp tow (up to 2 cm in length). Hemp was obtained from Faltin S.A. (Falticeni, Romania). Chemicals

and reagents (V_2O_5, MoO_3, H_3PO_4, Na_2CO_3, H_2O_2) used to obtain $Na_2H_3PMo_{10}V_2O_{40}$ had synthesis grade (Sigma-Aldrich).

Sample preparation

The mixture of natural fibers (cotton and chemical degumming hemp tow), 130 g, was bleached with hydrogen peroxide in the presence of polyoxometalate (POM), dried, and subjected to cutting and shredding processes up to 0.5 cm. The chemical degumming of the hemp tow has been done in FI-RI VIGONIA S.A. (Timisoara, Romania), accordingly to the method described in 22.

$Na_2H_3PMo_{10}V_2O_{40}$ was synthesized and directly used in solution (0.6 % POM reported to the mixture of fibers, w/w) in the first step of bleaching of the SCF at pH 5 and temperature 80 °C, for one hour. The fibers were let to cool down at room temperature, filtered and washed with water. In the second step, was performed the alkaline oxidation (0.1 N NaOH) with 1.5 % H_2O_2 and 2-3 % Na_2SiO_3 by using methods described and adapted from literature 23-25. Then the fibers were let to cool down, filtered and washed with water (pH neutral). Thereafter, the pulp was formed using laboratory scale devices and typical composition for paper manufacture was applied. Paper sheets of 20 cm in diameter were made by using second category fibers, SCF, and long wooden kraft, respectively, in a HAAGE Rapid-Koethen sheet former apparatus (Emst-Haage Apparatebeau GmbH&Co., Germany, STAS 6095/3).

Mechanical characteristics

The mechanical properties of paper samples were determined by using the following devices: L&W Tensile Tester (Lorentzen&Wettre, Sweden): SR EN ISO 1924-2; for bursting test: BS20T (Tecnolab, Italy): SR EN ISO 2758; L&W Tearing Tester used Elmendorf method (Lorentzen&Wettre, Sweden): SR EN 21974; opacity and brightness: Elrepho (Lorentzen&Wettre, Sweden): ISO 2469; all properties were measured in standard conditions: SR EN 20187.

AFM

NTEGRA Probe NanoLaboratory AFM (NT-MDT, Moskow, Russia), Software Nova_1644, equipped with an M Plan Apo 100x magnification objective that has the numerical aperture of 0.70 (Mitutoyo, Kawasaki, Japan) and a RPC-TVPCI camera which helps to locate the sample position were used. For storing the optical information a CCD camera was utilized. Paper samples were added to two-sided tape on sapphire support and the measurements were carried out under ambient conditions (temperature: 22 ± 1 °C, relative humidity: 40 ± 10). Noncontact 'Golden' silicon cantilevers (NSG30 from NT-MDT, Moskow, Russia) with a resonance frequency of 320 ± 80 kHz, were used. All samples were measured in semicontact mode ("tapping" mode) to capture simultaneously topography and phase images. Area of the paper samples has been investigated at 30 x 30 μm^2 and 15 x 15 μm^2 (with a scan velocity of 10.12 $\mu m \cdot s^{-1}$), respectively. Average roughness, Ra; Root Mean Square, RMS; Surface skewness, Ssk; and Coefficient of kurtosis, Ska were determined using ISO 4287/1 (Nova_1644).

Results and discussion

Sample preparation

The delignification and bleaching of wooden and non-wooden fibers by alternative method to chlorination bleaching and alkaline extraction is an attractive and actual challenge

for the industrial application in paper industry. The use of second category fibers, SCF (very short cotton fibers and chemical degumming hemp tow), which can not be recycled for yarn and textile production, in the manufacture of paper, was applied in this work. This mixture of fibers was bleached to remove the residual lignin by using peroxide method and a polyoxometalate as oxidation reagent, in two stages, with a yield of 80 %. The pulp obtained from this bleached mixture of fibers was used to obtain paper sheets. There was also obtained paper sheets from long wooden kraft pupl commercially available in order to use as control.

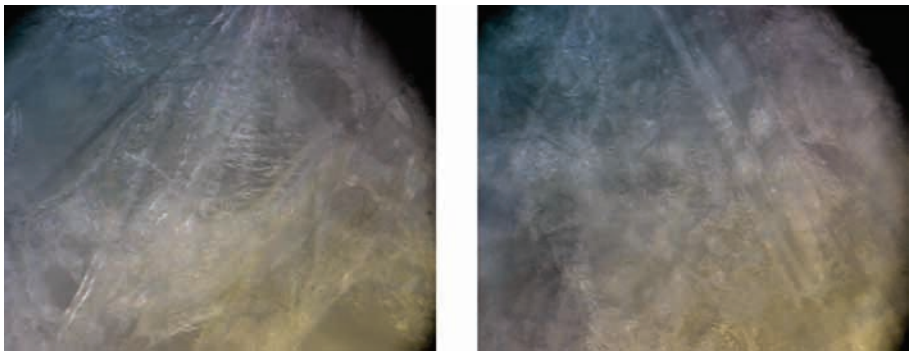
Mechanical and optical characteristics

The main mechanical and optical properties of the new paper samples obtained are exhibited in Tabel. 1. The values of mechanical properties (breaking length, burst index, tear index, etc.) of the new paper samples significantly decrease for paper containing SCF, compared to the paper obtained from long wooden kraft pulp. It is worth to mention that by using pulp containing SCF bleached by peroxide and POM, in two stages, the brightness of paper samples containing SCF decrease with maximum 19% compared with paper obtained from long wooden kraft, which is a good achievement for the final quality of the paper (Tabel 1).

Tabel 1. Mechanical and optical properties of the new obtained paper sheets.

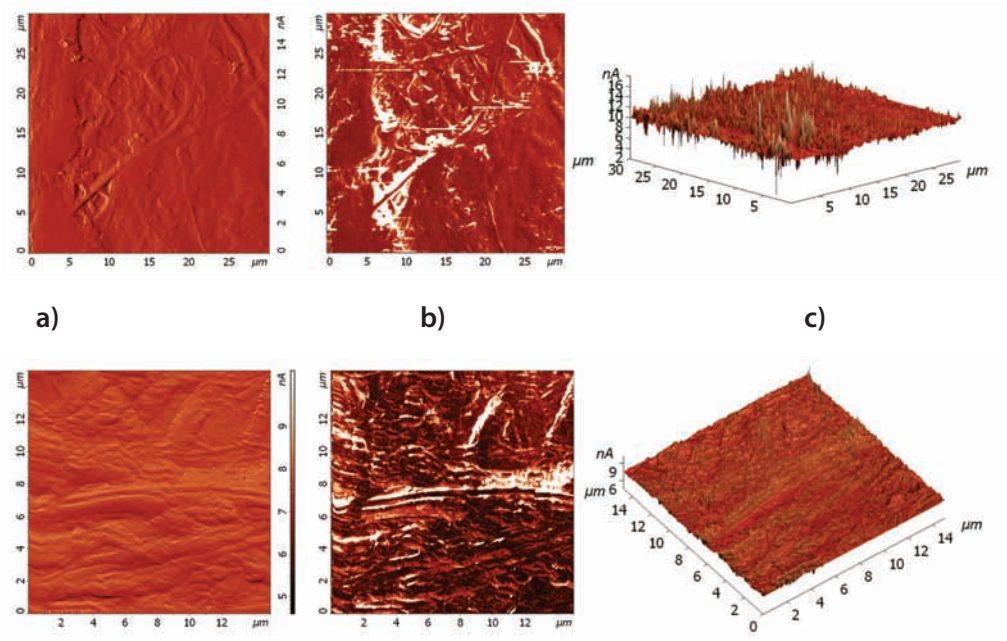
Parameter	Paper obtained from long wooden kraft	Paper obtained from pulp containing second category fibers
°SR	47	65
Weight (g/m^2)	66.2	62.0
Burst index (Nm/g)	94.96	61.9
Breaking length (m)	9500	6310
Tear index ($mN\ m^2/g$)	10.5	7.8
Tear resistance (kN/m)	6.28	3.84
Tensile strength (kPa)	324	211
Elongation (%)	1.94	2.19
Brightness (%)	85.1	69.1

a)



b) c)

Figure 1. Atomic Force Microscope installed at ICDISTN of "Aurel Vlaicu" University and microscopic images of paper sheets obtained from: a) long wooden kraft and b) pulp containing second category fibers (magnification 100x).



a) b) c)

d) e) f)

Figure 2. AFM images of paper samples obtained from long wooden kraft: a) 2D, b) phase, c) 3D, and from pulp containing SCF: d) 2D, e) phase, f) 3D.

Tabel 2. Characteristic parameters calculated from AFM images for the paper samples.

Sample	Average Roughness, Sa	Root Mean Square, Sq	Surface skewness, Ssk	Coefficient of kurtosis, Ska
Paper obtained from long wooden kraft	413.657 nm	503.672 nm	-0.0340474	-0.57691
Paper obtained from second category fiber	483.895 nm	574.534 nm	-0.280389	-0.812995

AFM imaging

Microscopic methods are suitable tools to determine the end-use properties of paper such as opacity, linting, absorbency, printability. Therefore, by measuring the distribution of porosity, mass and smoothness of the paper sheets at micro- and nano-scale it is possible to assess their relationship with paper properties. Atomic force microscopy was used to receive information about the roughness of the paper samples obtained from pulp containing SCF and from long wooden kraft pulp. In Fig. 1 are exhibited microscopic images of the paper sheets performed with a 100x magnification. Thereafter, was used AFM semicontact topography (tapping) mode of imaging and we performed a substraction of third order curve to obtain the final images presented in Fig. 2. As expected, the AFM phase contrast images gave little information due to the roughness and inhomogeneous properties of the paper samples (data not shown). Moreover, the simultaneous registered AFM images unveiled the less orientated fibrillar structure of fibrils in the images of paper samples obtained from second category fibers due to the inconsistent length of these fibers. This result is, probably a consequence of the manual cutting of the natural fibers. Because the samples were exposed to humid conditions during recording the AFM images, a thin contamination layer, major component being water, is presented in all the surfaces. The light parts that appears in the images most probably occurs due to the presence of more hydrophilic cellulose which is contained in the second category fibers that could present a water film of contamination and by the used paper additives on the surfaces. In Table 2 are presented the values of the Average roughness, Ra; Root Mean Square, RMS; Surface skewness, Ssk; and Coefficient of kurtosis, Ska. These parameters exhibited higher values for the paper samples containing SCF in comparison with paper obtained from long wooden kraft with 12-15%, except for the value of Coefficient of kurtosis, Ska, which increase with 29%.

Conclusions

In the present study, paper sheets were obtained from pulp containing bleached mixture of second category fibers (containing very short cotton fibers and chemical degumming hemp tow) and from long wooden kraft pulp. An eco-friendly approach, in which H_2O_2 and a polyoxometalate compound, $Na_2H_3PMo_{10}V_2O_{40}$, as oxidation reagent of lignin in the bleaching process, in a rapid two-steps procedure of SCF, was employed. Physical and mechanical properties of the obtained samples were measured and the topography of the surface of the paper samples was evaluated. Bleached second category fibers may be used as starting material to obtain specialty paper (e.g. paperboard, banknote, etc.) and which demonstrated, in contrast with the paper obtained from long wooden fibers, to exhibit more modest values for the physical and mechanical properties, except the elongation.

Acknowledgements

This work was supported by project co-funded by European Union through European Regional Development Fund Structural Operational Program "Increasing of Economic Competitiveness" Priority axis 2, operation 2.1.2. ID project 679, cod SMIS CNSR 12638: "Bast plants – Renewable Strategic Resources for European Economy". - „BASTEURES". No. 210/2010 POS-CCE. We thank Prof. Dr. Eng. Alexandru Botar for providing the polyoxometalate and for fruitful discussion. We also thank Chem. Anca Falup and Dr. Eng. Gheorghe Dutuc from Somes S.A., Dej, for performing some of the analyses.

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NEW POSSIBILITIES OF USING MULBERRY SILKWORM FEED

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In the countries where the silk industry is developed, white mulberry is one of the most important plants. Its leaves are the best food for the caterpillars of mulberry silkworm (Bombyx Mori L.). It is still not fully investigated why the silkworms prefer mulberry. However, it is certain that the protein substances produced in silkworm bodies in 70% come from mulberry leaves. These substances constitute one of the finest fibers - natural silk. Currently, mulberry is cultivated mainly in Asia, where sericulture maintains its high position. The fact that mulberry contributes not only to the formation on the silk but also can be used for other purposes has drawn attention of scientists to this plant. The exploitation of mulberry tree in Poland is limited to the life of silk in summers therefore new potential applications of this raw material are sought after. Literature reports confirm very rich composition of mulberry leaves in terms of bioactive substances. These compounds can be used in prevention of lifestyle diseases,. The paper presents the studies on the content of bioactive substances in the leaves of white mulberry and the potential of using the silkworm feedstock for humans.

Keywords: silk industry, silk fiber, mulberry silkworm (Bombyx Mori L.), white mulberry (Morus alba L.), bioactive compounds, lifestyle diseases

Introduction

Silk is one of the most ancient and valuable fibers in the world. Back in the antiquity it

was a valued commodity imported to Europe along the Silk Route from China and the process of its manufacturing was kept secret. This thin glossy and very strong natural fiber is apart from wool one of the natural fibers of animal origin. It is derived from cocoons of mulberry silkworms. The fisrt stage of development of mulberry silkworm is a caterpillar, which eats enormous amounts of white mulberry leaves and in its 4th week starts producing cocoons made of silk fiber. There are numerous races of silkworms and several other animals capable of producing fibers with similar properties, yet not as good as silk produced specifically by mulberry silkworm (Bombyx Mori L.). Other silkworm varieties have been labeled as wild silkworms. Nowadays, the mulberry silkworm is a completely domesticated monophagy and feeds only on the mulberry. The quality of mulberry leaves has direct effect on the quality of produced silk. The formation of silk in the silkworm organism is a result of absorption of the nutritional substances found in mulberry leaves. Thus the caterpillar is the link between the leaf and the fibber. Silk fiber is composed from two main ingredients i.e. fibroin and sericin, with small amounts of pigments, waxes and minerals. Fibroin is the actual fiber and sericin is a gluing substance that covers the fiber, which is dissolved during boiling of silk. One may say that mulberry leave is the raw material for production of silk and silkworm caterpillar is the element that processes it into the fiber. The exquisite properties of silk result directly from the leaves of white mulberry [Frentzel 1986, Kopański 1955, Krasnodębski 1953, Pieprzyk-Kokocha 2005].

What makes mulberry leaves so special that the fiber derived from them is of highest quality among all natural fibers?

White mulberry (Morus alba L.) is a large long-living tree with light grey bark, which gets darker with age. The leaves are light green soft and shiny in various shapes. The tree does not have special soil requirements and grows in almost whole Europe. However the area of growing does not overlap with the area of mulberry cultivation for silkworm breeding. Despite the fact that mulberry is tolerant to frost the length of vegetation period plays an important role, thus north European countries do not have suitable climate for mulberry. In order to obtain as much good quality leaves as possible, mulberry requires special treatments [Butt 2008, Litwińczuk 1993, Pieprzyk-Kokocha 2005]. Fresh and well insolated leaves contain about: 73% water, 7,5 % protein, 1,1 % lipids, 10,6 % carbohydrates, 2,6 % mineral substances, 5,2 % ciał bezazotowych, and small amounts of vitamins (B, C and D) and enzymes [Kopański 1955, Krasnodębski 1953].

More and more information is available on the mulberry leaves as a good source of bioactive substances i.e. the substances that stimulate desired course of metabolic processes in humans. Functional food, which shows beneficial and well documented effect on human health, is a potential source of these substances. The bioactive ingredients that have already been tested for their beneficial effect are for example dietary fiber, poly-unsaturated fatty acids, vitamins, mineral elements and phyto-chemical substances such as flavonoids and phenolic acids [Charunuch 2008, Mazza 1998, Srivastava 2003, Świderski 2003]. The bioactive substances play an important role in prevention of the so called lifestyle diseases, which prevalence depends on the civilization development of a society. These diseases include mainly diabetes, hypertension, coronary disease and obesity. Health burden linked to lifestyle, air pollution, and UV radiation is additionally increased as a result of high amounts of free radicals in human organisms. The radicals may cause damage to the lipids in cell walls, proteins, enzymes and to DNA, what results in changes of functioning of body cells. Human organism is equipped with a

defense mechanism in the form of endogenic anti-oxidants. However, anti-oxidants from food (e.g. phyto-chemical poly phenolic compounds) can have an important role in decreasing the oxidative damage [Dudek-Makuch 2007, Betlejewski 2007].

Materials and methodes

The studies were conducted on water and water-ethanol extracts of white mulberry leaves that were analyzed with HPLC.

The materials for the study were the leaves of white mulberry (Morus alba L.) of Wielkolistna Żółwińska variety, collected at the experimental Farm of the Institute of Natural Fibers and Medicinal Plants in Petkowo (Poland). This variety has been bred specially for use in sericulture.

Water and 70% ethanol (V/V) were used for the extraction of biologically active substances, and then the extract was filtered. In case of alcohol, the extraction was complemented with distillation under low pressure. The extracts were frozen and lyophilized.

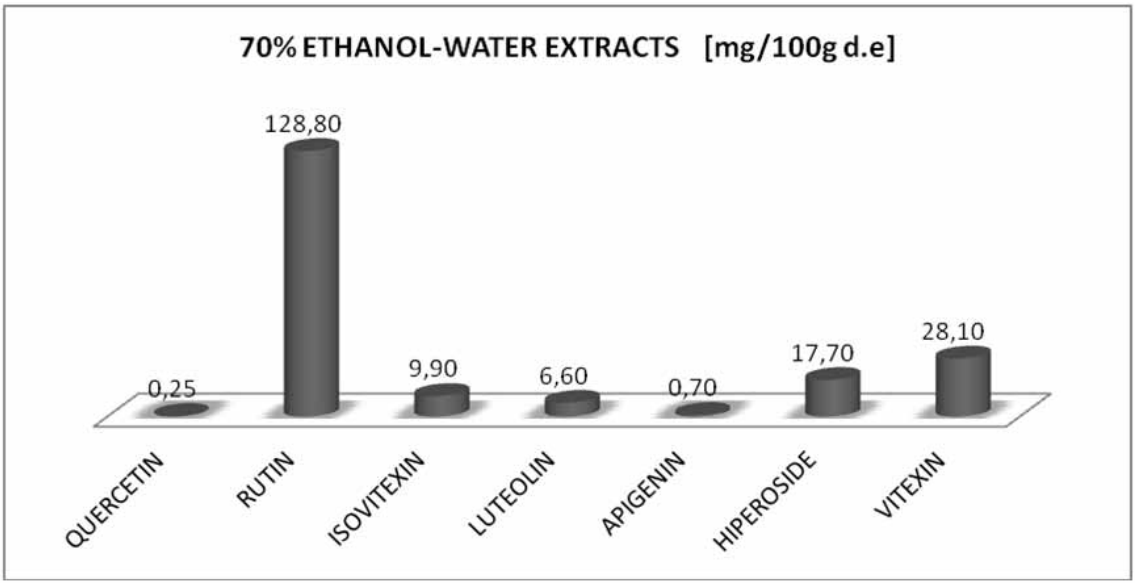
he poly phenolic profile was determined with the use of HPLC with DAD detection. Methanol was added to the dry extract. The solution was heated with reverse cooler, and then it was cooled and infiltrated. The methanol extraction was run twice, then the infiltrate was evaporated until dry under low pressure and finally water was added. The extract was centrifuged three times with methylene chloride. The water layer was evaporated until dry under low pressure. The remaining matter was dissolved in methanol and determined with the use of HPLC.

Results and discussion

The content of bioactive substances in ethanol-water and water extracts of white mulberry leaves is presented in Figures 1 and 2. The following poly phenolic compounds have been identified in the studied extracts: quercetin, rutin, hyperozide, vitexin, apigenin, isovitexin, and phenolic acids i.e. chlorogenic and rosemary acids. Quercetin is a flavonol that reduces the risks of stomach ulcers; it is an anti-alergic, anti-inflammatory and immune modulating compounds. It is aslo found to be one of the factors reducing the occurrence of pathogenic lesions in diabetes. Rutin is a flavonol with anti-cancer, anti-inflammatory and anti-thrombotic properties. It has chelating capabilities towards several metals e.g. iron and copper. Another flavonol found in mulberry leaves, hyperozide, has vasoprotective , hypotensive (lowers blood pressure), diuretic, anti-inflammatory, anti-sclerotic activity. It also improves blood circulation and prevents clotting of veins. Luteolin is also a flavonoid compound with diuretic, anti-inflammatory and anti-alergic properties. Anther flavonoid determined in the mulberry leaves is vitexin which is a compound of high medical importance as it improves coronary circulation and is regarded as mild cardiac medicine. Due to its low toxicity it can be used over long periods. Apigenin shows strong anti-oxidant and anti-inflammatory properties – it has radical scavenging activity, inhibits the lipid peroxidase activity what prevents oxidation of LDL fractions to their oxy-LDL fraction that causes sclerosis. Apigenin also has certain anti-cancer properties. Isovitexin is found to be a strong anti-oxidant. Within phenolic acids detected in mulberry leaf extracts was rosemary acid, a substance used in treatment and prevention of numerous diseases e.g. in stabilizing biological tissues, protection against UV radiation and reactive oxygen species including free radicals. Rosemary acid is characterized with anti-oxidant, anti-inflammatory, anti-viral anti-hormonal activity. The other phenolic acid found

in mulberry was chlorogenic acid, whcih lowers carbohydrate absorption in alimentary tract, what forces the organism to use its reserves of sugars. This acid improves the sensitivity of cells to insulin and acts as a strong anti-oxidant [Charunuch 2008, Dudek-Makuch 2007, Dugo 2009, Gawlik 2004, Grajek 2011, Jeszka 2009, Kopacz 2008, Naowaboot 2009].

FIGURE 1. The content of bioactive compounds in ethanol-water extracts from the leaves of the white mulberry [mg/100 g s.e.]



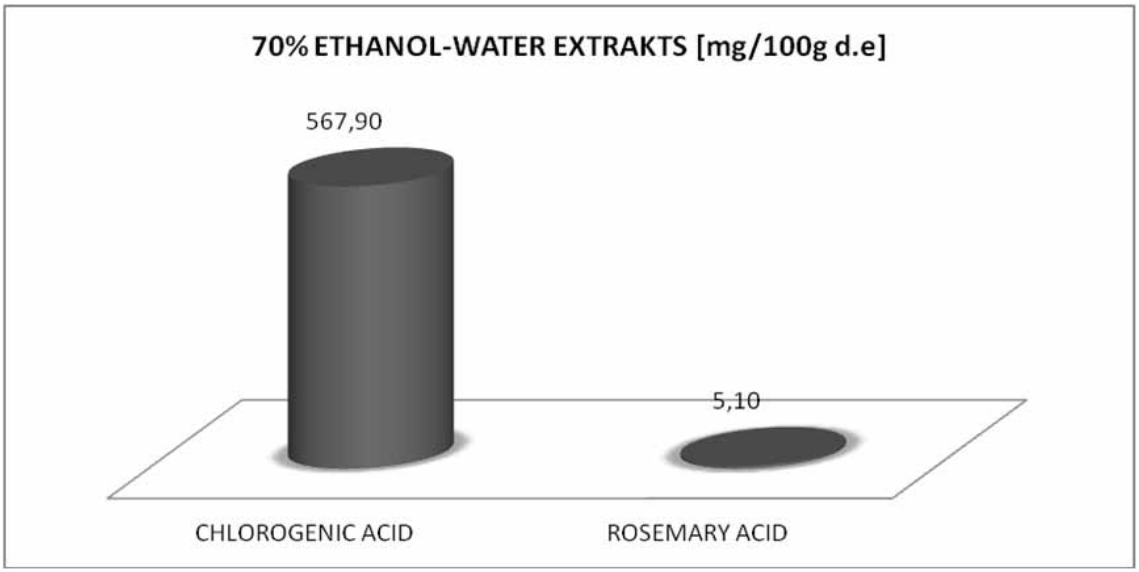
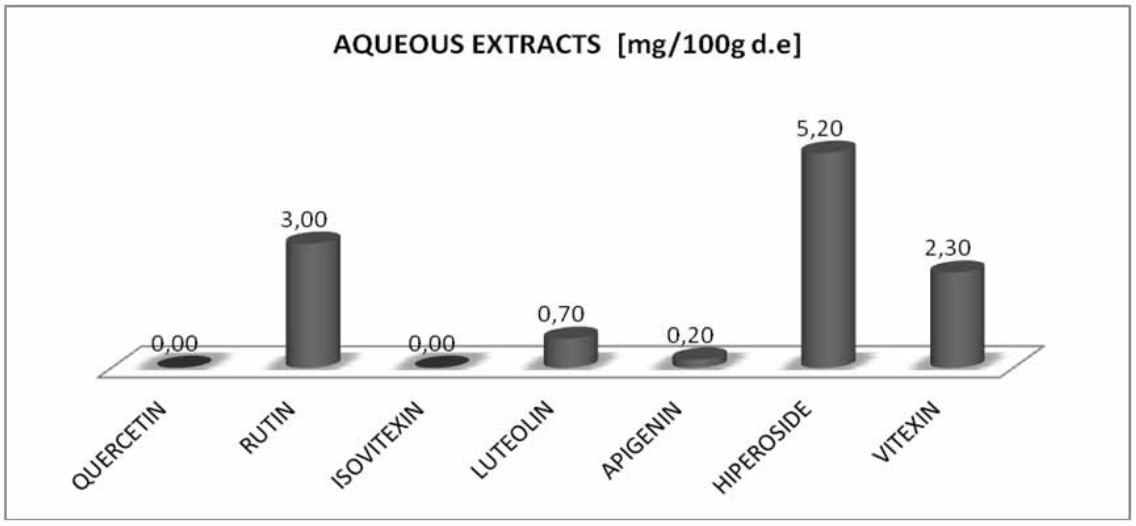
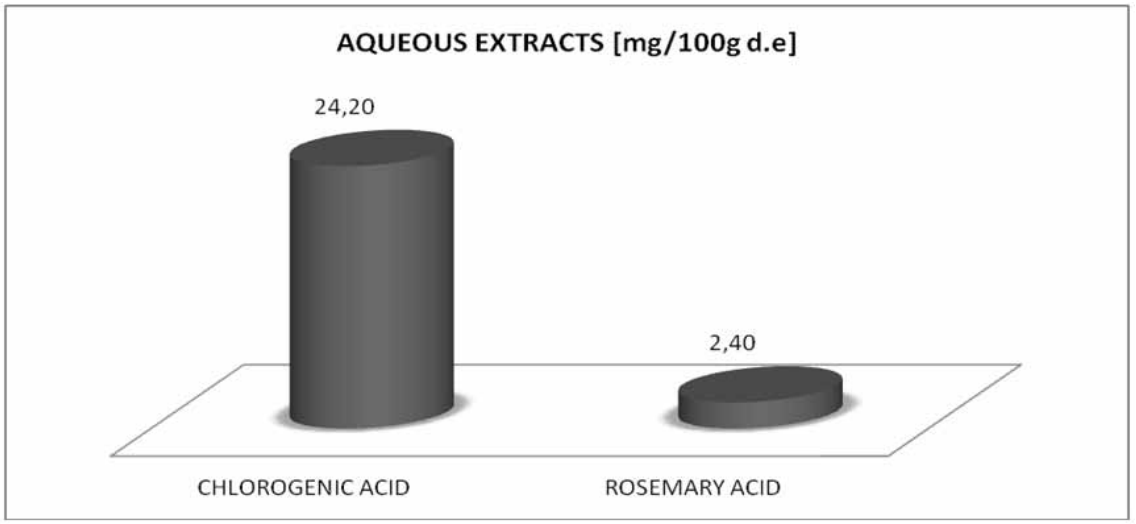


FIGURE 2. The content of bioactive compounds in aqueous extracts from the leaves of the white mulberry [mg/100 g s.e.]





The results obtained in the study allow to state that both types f extracts contained phenolic compounds, whereas the content of these substances in ethanol-water extracts was much higher than in aqueous extracts. In both types of extracts (ethanol-water and water) the highest amounts were observed for chlorogenic acid (567,90 mg/100g d.e and 24,20 mg/100g s.e respectively). In ethanol-water extracts significant amounts of rutin were determined (128,80 mg/100g s.e), and then vitexin, hiperozide, isovitexin, lueolin, rosemary acid, apigenin and quercetin (see Figure 1). However, water extracts were characterized with high content of hyperozide (5,20 mg/100g s.e), and smaller amounts of rutin, rosemary acid, vitexin, luteoiln

and apigenin. In case of water extracts two compounds were not detected i.e. quercetin and isovitexin (Figure 2).

Phenolic compounds that are natural anti-oxidants, acting as oxygen scavengers, chelating metals and protecting cells and reducing the oxidative damage are of high importance to human organism. Therefore, the slogan „mulberry not only for silkworms" seems more and more justified by scientific data [Cieślik 2005, Grajek 2011, Kolanowski 1999].

Conclusion

The leaves of white mulberry, apart from being an important element of sericulture, are also a source of bioactive substances beneficial for human health. Thus it is worthwhile to introduce them as a permanent element of human diet for prevention of lifestyle diseases. Although there are several products with the addition of mulberry leaves such as tea made of dried and powdered leaves and rice snacks with the leaf extracts, the studies on new food applications of mulberry and its nutritional components should e continued.

The work is part of the project titled "New bioactive food with healthy properties" – PO IG 01/01/02 - 00-061/09.

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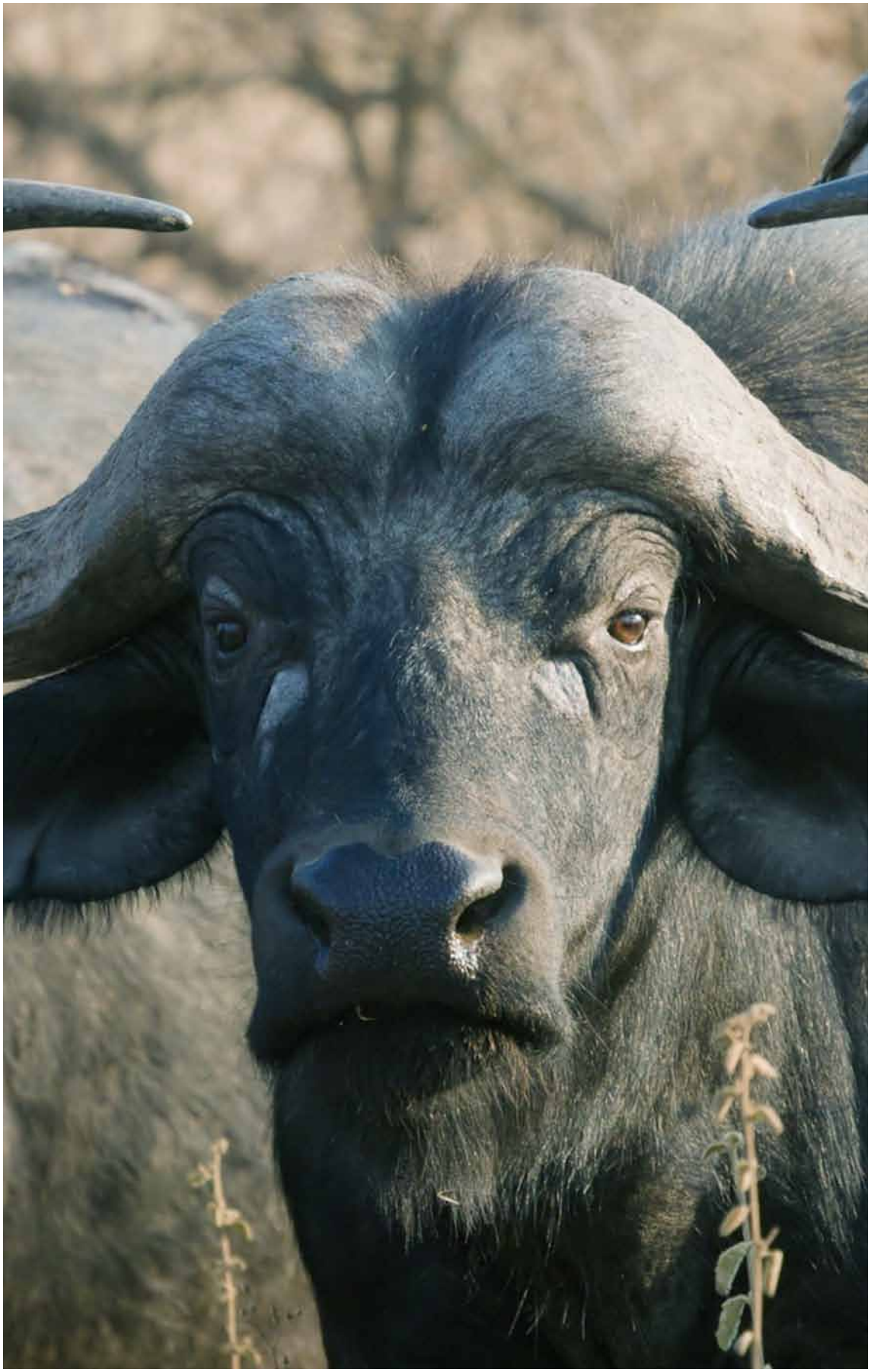

BUFFALO LIVESTOCK AND PRODUCTS IN EUROPE

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Abstract

Buffalo livestock and strategies are reported for all the countries in Europe, where buffalo specie is reared and used for food production, as Italy, Romania, Bulgaria, Germany, Macedonia, United Kingdome, Greece, Serbia, Albania, Ukraine, and Hungary.
Particularly Italy situation is discussed as in this country selection, milk recording and production, management, nutrition and reproduction techniques, quality food and marketing are really developed at top level.

In Italy 50,000 buffaloes are recorded every month during the lactation, showing a milk yield of 2,220 kg in 270 days of lactation with 8.4% fat and 4.6% protein, as many champions produce more than 5,000 kg for lactation. Artificial insemination is largely applied.

The National Association of Italian Buffalo breeders was instituted on 1979, the Buffalo Genealogical Book for the Mediterranean Italian Buffalo Breed on 1980, the famous mozzarella cheese obtained the Denomination Origin Protected on 1993, with Decree of Agricultural Ministry, approved by European Union, where milk and mozzarella characteristics are defined for consumer guarantee.

In Italy 400,000 buffaloes are managed and fed in intensive system: the females are kept loose in paddock and mechanically milked twice a day; the males are managed in feed-lots or on slatted floor stables for fattening and are slaughtered at 15 months, achieving more than 400 kg live weight. Even if many products are appreciated coming from milk, as ricotta, provola, scamorza, treccia and other cheeses, or coming from meat, as steaks, roast, ham, bresaola, salami, the most important product in the Italian and international market is mozzarella, of which 36,000 tons are produced every year, with a value of 500 million euros. The consumption is 82% in Italy, 18% for export, particularly for Germany, France, USA, UK.

Keywords: buffalo livestock, management, products, Mediterranean Italian breed.

Introduction:

The buffalo population and economy in Europe shows two different trends: an increasing trend in Italy, where population, genetics, technologies, high quality products from both milk and meat lines and market are in progressing, and a decreasing trend in the most of other countries, where a draught animal disappeared as mechanization was introduced, without a selection of a dairy buffalo breed. Other countries more, where in the past buffalo species was not known, introduced dairy buffaloes, particularly from Italy, to create a new buffalo market, as U.K. and Germany.

1. ITALY

1.1. Selection, milk recording and production

Buffalo Genealogical Book was instituted by Italian Ministerial Decree on June, 23, 1980 and was held by A.I.A.(Italian Association of Breeders).

The A.N.A.S.B. (National Association of Buffalo Species Breeders) had been instituted on 1979 and recognized on the 1994 by Agricultural Ministry.

The Ministry, with Ministerial Decree n° 20154 has entrusted the management of the Book to A.N.A.S.B. on year 2000. In the same year other decree (D.M. 201992 on July,5, 2000) recognized buffalo enrolled in Genealogical Book pertaining to the only own race: "Mediterranean Italian" (figure 1).

The animals rose in Campania and in Lazio Regions of Italy give the milk used for the production of the famous "Mozzarella di Bufala Campana D.O.P. " (figure 2). The D.O.P. (Denomination Origin Protected) Mozzarella di Bufala Campana was recognized with the Ministerial Decree on May 10, 1993, published on the G.U. n.219 on 17/9/1993, and after from European Union; that means that this cheese mozzarella has to be produced in defined areas of the Provinces of Caserta, Salerno, Benevento, Napoli, Frosinone, Latina, Rome,(Foggia was added after), coming only from fresh milk of buffalo cows of Mediterranean Italian breed, registered in the Buffalo Genealogical Book. The Decree establishes the milk characteristics (fresh within 16 hours from milking, raw, minimum fat 7%,), processing techniques (acidification, coagulation, stretching, moulding) and mozzarella characteristics. The logo is represented in figure 3. The control and guardianship is effected by "Consorzio per la tutela del formaggio Mozzarella di Bufala Campana", so the European consumer is guarantee that the logo means a quality product of the made in Italy, according the best standard of animal management, welfare and health, according also the best characteristics of mozzarella, as sanity, freshness, flavour and juiciness.

The main factors that have contributed to the development of buffalo in Italy in the past few years have been the following: no regimen of milk quotas; increase of the consumption of mozzarella in Italy and export in many countries in the world; the high price of buffalo milk (about 1.20 euro/ kg) in comparison with cattle milk (about 0.40 euro/kg), the high technology of farmers, high level of management and breeding, high genetic value of the herd, obtained by performance and progeny testing, animal recording and selection, artificial insemination applying, starting with an organization born more than 50 years ago.

Several cycles of progeny tests, with the publication on 1997 in the first time, of the genetic indexes of breeders of buffalo species, both males and females, are effected by ANASB.

The execution of the milk recording in buffalo is applied according ICAR (International Committee for Animal Recording, Moioli, 2005), according to the Regulations of the Buffalo Species and to the norms emanated in the Central Technical Committee of the milk recording

of the bovines and the buffaloes. For being able to be subordinate to the control, as a result of completely voluntary adhesion, the farms must fulfil to some prescriptions: they must be subordinate to the inspection from an expert of race of A.N.A.S.B. ; they must possess the sanitary certificate from National Sanitary System that attests its indemnity and must have the bulls with genealogical certificate in order to admit they to service.

For Mediterranean Italian Buffalo, the productive controls regard: the quantity of milk in kg, the determination of the percentage of fat and of proteins (kg and %) and the somatic cells.

The beginning of the official lactation starts at calving; the first control cannot be carried before the five days from calving and not beyond 75 days. The duration of the reference lactation is 270 days; in any case the duration of the effective lactation must be indicated.

Every milk control must be made on all the milking ordinarily practiced by the breeder in the 24 hours, annotating also the hour in which the same control is carried out, the quantity of milk found must be indicated in kilograms, the milk must be weighed with the balance or be determined with lactometers.

For every subject are reported the following data: number of current lactation, daily production expressed in kg milk, % fat, % proteins and number of somatic cells, the effective production from the calving for: kg milk, kg fat and proteins and the daily medium production, the milk production in comparison to the reference lactation of 270 days, "equivalente bufala matura" (E.B.M.) expressed in kg of milk, fat and proteins (Coletta and Caso, 2008).

E.B.M is a hypothetical production for a buffalo that started his lactation in January at five years old; the productive ability is the ratio between E.B.M. of the single buffalo and the mean I.B.M. of the farm.

All data are collected by ANASB, which decides on the selection goals which are presently to increase not only the milk quantities but specifically the mozzarella cheese production according to the mozzarella index:

Mozzarella (kg)= Milk (kg) x (3.5 x % proteins + 1.23 x % fat – 0.88) / 100

Figura 1. Mediterranean Italian breed, Tor Mancina farm, Rome (Borghese photo 2006).

Figure 2. Mozzarella and the colours of Italian flag: green, white, red.

Figure 3. Logo of Mozzarella di Bufala Campana DOP

In Italy there are 370 000 buffaloes and the mean milk production is over 2200 kg for lactation, in confront of other Mediterranean countries where the maximum production is less than 1900 kg. In Italy the milk production in 46,799 recorded buffaloes (ANASB, 2009) was 2 221 kg (8.24 % fat and 4.66 % protein) in 270 days of lactation (Table 1). Recorded buffaloes are raised in 290 herds with an average of 161.3 head per farm.

Table 1. Italian Buffaloes (ANASB 2009)

N° Head	370 000
N° Dairy buffaloes	180 000
N° Recorded buffaloes	46 799
% Recorded Buffaloes	26.0
N° Recorded farms	290
N° Head/farm	161.3
kg milk production (in 270 d)	2 221
% Fat	8.24
% Protein	4.66

In the year 2010 milk production in 270 days of lactation was 2180 kg with 8.47% fat, 4.59% protein. The recorded buffaloes were 50,240 with an increasing of 7.35% (ANASB, 2011).). In the year 2011 the milk production was 2134 kg with 8.4% fat and 4.7% protein on 54,548 recorded buffaloes, with a further increasing of 8.57% on recording extension.

In other countries the buffalo productivity is lower, due to the fact that only Italy has undertaken a great deal of work on recording, on selection, on reproductive and genetic improvement, on health, on feeding and livestock systems, as is shown in the following analysis.

The recorded buffalos on year 2006 were 40.425, with an increase of 1,2% regarding 2005.

In figure 4 is clearly evinced how the buffalo head number increased in the period 1981 – 2006 and this is the basis for the genetic development and the milk capacity improvement.

On the basis of 26,462 considered lactations, we found on 2006 an average production of kg 2.178 with fat average of 8,09 % and a proteins average of 4.67%. (Coletta and Caso, 2008).

In the reported period, the average production expressed in kg, has been increased slowly but constantly from 1990 with 1893 kg for lactation until 2004 with 2184 kg for lactation, until 2009 with 2221 kg for lactation.

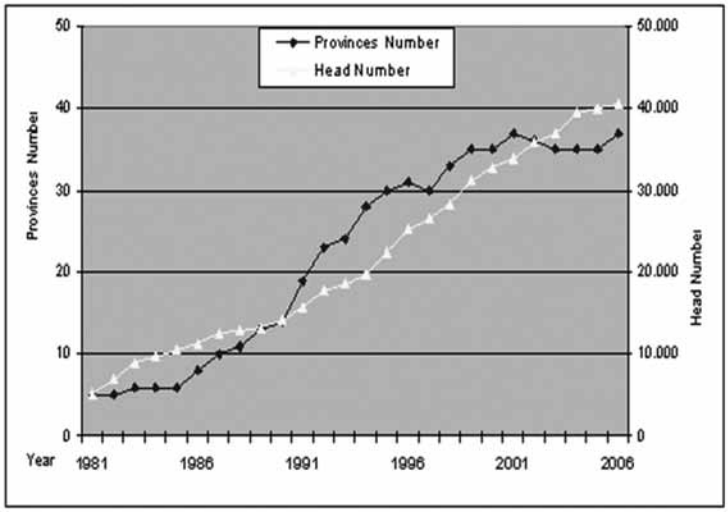

Figure 4. Recorded Buffaloes in the years 1981-2006 (Coletta and Caso, 2008).

In the last few years, in Italy, milk composition has been improved: the average protein content has raised from 4.4% in 2002 to 4.6% in 2010 while the average fat content raised from 7.3% in 2002, to 8.5% in 2010, without operating any selection for the character of protein and fat content. Moreover the possibilities for genetic improvement for milk quantity and quality will be higher, if the selection pressure will be increased reducing the number of bred females, discarding the low productive females. At the present time there are many females in Italy producing more than 5,000 kg milk/270 days of lactation) until the maximum production of 5600 kg with 8.32% fat and 4.63% protein.

There are in Italy two Bull Buffalo Centres for semen production: the COFA (Cooperativa Fecondazione Artificiale) in Cremona Province, Lombardia Region, in North of Italy, where there are many bulls with genetic potential to produce more than 4000 kg milk/ lactation as Malandrino Bull and O-B-One Bull lines. The Chiacchierini Bull Centre in Perugia Province, Umbria Region, in Middle Italy: this one started a genetic selection programme with CIPAB consortium and actually produces semen from 16 tested bulls from different bloodlines, coming from mothers over 3100 kg milk yield per lactation with more than 4.5% protein: there are Ciripicchio Bull with 4494 kg milk/lactation and Jesce Sole Bull with 4157 kg milk/ lactation, as recorded in the best daughters, and Brillante, the best bull for pedigree index of 2010-2011 progeny test. This stud is one of the few European A.I. studs authorized as insect-proof quarantine barn, located away from the semen production zone. It is authorized for worldwide export for the excellent sanitary level. Chiacchierini Bull Centre produces sexed semen too, available from a lot of bulls.

Hereafter the selection will be directed at the improvement of the yield of mozzarella cheese, not simply for milk production, since the farm income is based firstly on mozzarella cheese, secondly on the sale of pregnant heifers, lastly on beef sales and finally on the sale of semen and embryos of high genetic value.

The largest proportion of the buffalo population can be found in Provinces of Caserta and Salerno (Campania region), and the next localities for size of population are the Provinces of Frosinone and Latina (Lazio region), which are in the Denomination of Protected Origin (D.O.P.) area.

The control and monitoring of pathologies is affected by the local veterinary services and by the "Istituto Zooprofilattico Sperimentale" (Animal Prophylaxis Research Institute), one for the Lazio region and another for the Campania region. The hygienic control of the milk production and of the milk products in the industry is of a particularly high standard.

Research on the buffalo species is carried out by the Animal Production Research Institute, Monterotondo, Rome, where are the General Secretary of the International Buffalo Federation (IBF) and the FAO Inter-Regional Cooperative research Network on Buffalo that publish the Buffalo Newsletter, and by the Federico II University, Naples.

1.2. Management and nutrition

Italian buffalo management is today exclusively intensive, as in the past it was extensive too with calves milking from cows in the open air (figure 5) separately or together with milking man by hands. This figure is disappeared, now existing only intensive system: dairy buffaloes are kept loose in paddocks close to the milking room, where the cows are submitted to udder control and mechanically milked twice a day. The females are normally artificially inseminated in the paddock, using high genealogy semen, preferably in February-March after oestrus induction, to obtain calving before spring (about 50% fertility), as the milk is paid more in spring and summer according the consumer demand. After one month from

artificial insemination the empty females are naturally mated (figure 6), obtaining another 30% fertility with a total mean fertility rate of 80%.

The buffalo cows are selected too for udder and teat conformation and adaptability to milking machine (figure 7).

Milk production is sustained by diets with a high energy (from 0.85 to 0.95 MFU/kg dry matter-DM) and a high protein concentration (14-16 % crude protein on DM), based on maize and other silages, cereal grains, soya, alfalfa or "graminaceae" hay and by-products. The feeding stuffs movement and distribution is effected by mixing trucks along the feeding line in paddock or in feed-lots (figure 8); the movement and stocking of dung is also mechanized; therefore there are no smallholders in Italy, but only farmers with an average herd size of 161.3 head per herd. Heifers are also fed intensively in order to achieve puberty before 20 months (Borghese et al., 1997, Borghese, 2005). The heifers are housed loose in paddocks all year long, utilizing the same modern systems used for dairy cows.

In intensive systems the buffalo cows normally receive unifeed composed of maize silage, concentrates, hay, straw and sometimes by-products. For example, a 600 kg live weight buffalo cow producing 10 kg milk, would be fed 15.3 kg DM (33 % maize silage, 42 % alfalfa hay, 8 % maize grain and 17 % concentrate with 38 % proteins,) with 12.7 Milk Feed Units (FU), 2.1 kg crude proteins and 3.5 kg crude fibre. Maize silage can be highly increased: some rations foresee until 60% maize silage, 26% concentrates, 14% hay and straw, sometimes by products (tomato peel, brewer grain residuals, sugar beet pulp) (Borghese, 2010).

Experimental diets (Barile et al., 2010) were carried out with maize or sorghum silages (16% on DM): in the first diet maize silage was 71.2%, alfalfa hay 9.3, concentrate 19%; in the second diet sorghum silage was 60.9%, alfalfa hay 10.1%, concentrate 28.5%. In both groups milk FU/kg were 0.9, crude protein 15.6%, crude fibre 21.2% on DM. Both diets produced more than 8 kg milk/head/day (8.03-8.78 respectively with maize or sorghum) with 8.74-8.47% fat and 4.98-4.78% protein respectively during lactation 270 days long.

The calves are normally taken off the mothers, they receive colostrum in the biberon (particular bottle) and after reconstituted milk, in single cage 1 or 2 months after birth, to avoid infections and to control the consumption, after in multiple boxes (figure 9), where the calves receive milk replacers, starter concentrates and good hay until the weaning (about 3 months for males, 3-5 months for females). The males follow the meat line and they are managed in feed-lots or in slatted floor stables for fattening (figure 10), as the females are preferably managed in open air, especially if pasture is available.

Figura 5. Extensive system: calf with cows. Tor Mancina farm, Rome (Borghese photo 2006).

Figure 6. Intensive system with mating. Tor Mancina farm, Rome (Moioli photo 1994).

Figure 7. Beautiful Mediterranean Italian Buffalo cow in intensive system. Tor Mancina farm, Rome (Borghese photo 2006).

Figure 8. Intensive system: feed-lot. Tor Mancina farm, Rome (Borghese photo 2006).

Figure 9. Calves managed in box.

Figure 10. Intensive system for fattening. Tor Mancina farm, Rome (Borghese photo 2006).

1.3. Buffalo food and market

The largest proportion of the buffalo population is localized in Provinces of Caserta and Salerno (Campania Region), and the next localities for size of population are the Provinces of Frosinone and Latina (Lazio region), which are in the Denomination of Protected Origin (D.O.P.) area .

The hygienic control of the milk and milk products in the industry is of a particularly high standard.

The market is mainly based on mozzarella cheese, very famous one, not only for the local consumption according the traditional Italian cooking style, but also in many foreign countries. There are different types of mozzarella, the best one is produced in D.O.P. area (figure 12) according the regulations: it is hand made by raw buffalo milk, soft, juicy and tasty, rich of live ferments, natural yeasts and microbes, it is coming from a difficult processing schedule, particularly for stretching phase (figure 11), it changes taste during time, not preserving in fridge but in mozzarella water and the shelf life is about 5 days. The industrial mozzarella, even if produced in D.O.P. area according the regulations, is made by machines and microbes die during pasteurization, with the advantage of a longer shelf life, preserving in fridge (until

more than 2 weeks) but the material is too compact and the taste is hard and anonymous; this product is distributed in supermarket and for export. After that there is a lot of false mozzarella, produced by mixing buffalo and cow milk or out of D.O.P. regulations. The basic price of mozzarella at cheese industry is 10 euro/kg, with a good profit, utilizing 4 litres of milk/kg mozzarella and starting from the milk price as 1.20 €/litre that is more than 3 times the price of cattle milk. The price in the shop increases as more as the quality of mozzarella and the distance from the site of production until 20-30 €/kg. The market is richer in Campania and Lazio Regions, where is easy to find shop with a lot of products coming from milk and meat industry. The mozzarella D.O.P. consumption is about 82% for the Italian market, 18% for the export, particularly for Germany (20% of the export), France (20%), USA (18%), U.K. (12%) (Borghese, 2005, 2010).

In the year 2010, 36000 tons of mozzarella was produced, with an increase of 12.5% respect to the 2009, with a sales volume of € 300 million at the production, € 500 million at the consumption (Borghese, 2011).

Another very appreciated product is the ricotta (figure 13), that is not really cheese because it is produced boiling the serum proteins remaining after the produced curd.

After mozzarella market, now meat market is rapidly increasing: now there are some fattening centres for the production of excellent buffalo carcasses. Calve carcasses are appreciated for clear and tender meat (figure 14) but normally the live weight at slaughter is 400-440 kg obtained at 15-16 months of age with 800-1000 g/d of daily gain, managed on slatted floor (figure 10) to avoid bad smell of urine and faeces: young bulls without defect or pathologies, beautiful carcasses with conformation R (good), medium fattening (figure 15) according Italian market requirements are obtained, 52% dressing percentage, 57% net dressing percentage, 62% meat on carcass, meat with low fat (less than 3%), very clear, tender and juicy, with good dietetic qualities: <50mg cholesterol /100 g, unsaturated fatty acid/ saturated fatty acid >1, iron >1.5mg/100g.

The first quality cuts are well represented with good muscular growth and are sold at 14-25 €/kg for typical restaurants and many products, as bresaola, salami, cacciatorini are sold in typical shop together with buffalo cheese, as meat also obtained I.G.P. (Indication Geographic Protected) "Carne di Bufalo Campana".

Very appreciated and common products are: mozzarella, treccia, scamorza, crescenza, robiola, caciocavallo and other cheeses, ricotta, yogurt; meat and meat industry products: bresaola, salami, sausages, caciorollo, cacciatorini (little salami) (figure 16).

Finally Italy is a reference point as buffalo importance in human food sustainability for high quality products.

Figure 11. Milk processing and mozzarella production.

Figure 12. Typical Italian Mozzarella di Bufala Campana DOP "Aversana type".

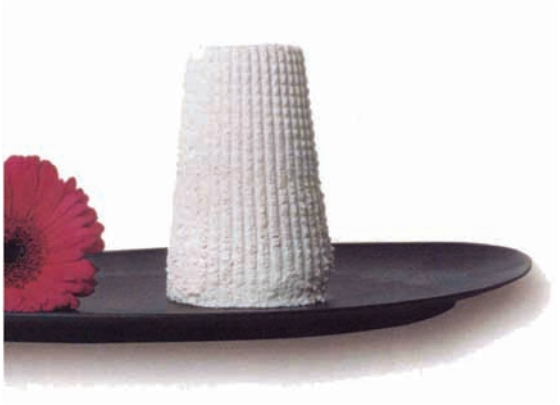

Figure 13. Typical Italian ricotta.

Figure 14. Calves buffalo carcasses.

Figure 15. Rump of young bull with conformation R and fatness 2+ .

Figure 16. Scamorze, bresaola and salami from buffalo.

2. ROMANIA

Despite the fact that the origins of buffalo in the area are unclear, it is sure that they were introduced about 1000 years ago - by perhaps the Crusaders or the Islamic invaders. The buffalo found in the north in the Carpathians were, possibly, introduced 500 years earlier by the Avars (SAVE, 2011). But this theory is not real, because buffaloes coming from Mongolian

countries have to be Swamp subspecies; on the contrary Romania buffaloes are typical Mediterranean, River subspecies and therefore coming from Near East (Borghese, 2012). Even though the origins are not yet clear, it is possible to see that the buffalo have adapted to their local environments: the Carpathian and Transylvanian types have hard hooves for moving over stones and have a thick winter coat. Wherever the buffalo live, this Riverine type loves to swim.

Various traditional products were made with their milk, meat and skins. Their muscle power was used on the farm as traction. Buffalo were valued for their frugality, longevity and triple-use.

The negative side of the buffalo is, perhaps, part of the key to its downfall: the cows often only let down their milk for one person – usually the man of the family - they can also be aggressive and are extremely wilful and stubborn. These factors, along with the increased use in tractors and the promotion of high-yield cows led to the buffalo being replaced. Numbers in the last 20 years have decreased from tens of thousands down to, in some countries; too few to make breeding viable without import of new stock (SAVE, 2011).

The buffalo population in Romania was more than 200 000 head in 1996 (Borghese, 2005). Actually it is about 25,000 head, located particularly in Transylvania, classified as Mediterranean Carpathian breed. The SAVE Foundation (SAVE, 2011) organized an International Workshop on Conservation of Autochthonous Buffalo on 6-7 May 2011 in Sighisoara (Romania), as the real risk for Carpathian buffalo is the extinction. The conservation strategy is based only on subsidies, so the population is rapidly decreasing as family farmers don't need more animals for draught and carry as in the past.

The average milk production, but only in few recorded animals, in 2008 was 1,800 kg per lactation (274 days) with some champion producing until 3290 kg per lactation (Vidu, 2010) with fat percentage moving from 5.2 to 6.2% and protein from 3.5 to 3.9%. The animal recording is at good level (669 recorded animals in 2009) and artificial insemination too with 2041 effected A.I. in 2008 (Vidu, 2010). The mean age at the first calving is 36 months, calving interval is 485 days.

Buffaloes are still used today on small private farms for draught and the goal of the selection process is to create a dual-purpose type of animal (milk and meat), realizing good daily gains (600-800 g), in order to slaughter the males at 22 months with 460 kg of live weight. At present the calves are also fattened to be slaughtered at four months (100 kg of live weight).

The animals are housed and tied during the winter due to the unfavourable weather conditions and fed with hay, bran, concentrates, silage, grazing on pasture in the warm season (figure17, 18, 19).

As Romania buffaloes can have these performances, but only if correctly managed, they need soon a project to increase rapidly the milk production capacity in all the population, even applying artificial insemination with Italian semen, to create a milk-cheese market and justify a buffalo economy in the country.

Subsidies are not a long-term, sustainable solution for conservation of the species, one or two animals for family. Policy changes can lead to immediate decrease in numbers as subsidies are cut or the focus of them merely changes.

Connecting with nature conservation in protected areas by grazing provides a cost-effective eco-management system whereby buffalo can obtain a monetary value without requiring a commercial activity. This, in turn, can be coupled with agri-tourism activities, use within extensive production systems and linked to local traditions and ethnic minorities.
In many of the countries concerned, availability of land and land ownership has been negatively

affected by historical processes. Land has changed hands, been collectivised or, in some places, national borders have changed. Often it is impossible to find out who really owns a piece of land, this is compounded by the fact that many traditional farms are so small-scale that, to buy a land parcel large enough for a commercially viable buffalo herd would mean tracking down many previous owners and their relations in order to negotiate a purchase (SAVE, 2011).

Markets for buffalo products (dairy products and meat) exist but could be improved upon. Common dairy products are yogurt, butter, soft cheese and typical cheese as Vladeasa and Braila (Borghese, 2005).

Figure 17, 18, 19. Buffaloes on Transylvania pastures in Meschendorf (Borghese photo 2011)

3. BULGARIA

The mechanization entered in the agriculture and led to a decrease in the buffalo population. For this reason it was necessary to change the genetics of the native buffalo from draft type to milk type. 20 pregnant buffalo cows and 10 bulls from the Indian Murrah breed from India, 50 buffalo cows and 4 bulls from Nili Ravi from Pakistan were imported in Bulgaria in 1962 and 1974 respectively. This activity was effected systematically under the scientific management of the Buffalo Research Institute in Shumen and the National Animal Selection Centre (Alexiev, 1998). This was the beginning of creating a new milk breed, the Bulgarian Murrah (figure 20,21) with genetic potential 2000 kg milk yield, 7.5% fat content and 550-600 kg body weight of adult buffalo cows.

For the purpose of optimizing genetic improvement of the buffalo population in respect of milk ability, a selection program based on genetic level of the population and on the artificial insemination was developed by Alexiev (1979) and improved by Peeva (2000). In the program an estimation of the most important traits was made, as well as of fixed and variable parameters. A model, including four pathways of genetic transmission and inbreeding depression was developed (Alexiev et al., 1991). According to the programs of the authors an annual genetic gain of 1.06% and 1, 89% for milk yield was realized, respectively.

The number of buffaloes in Bulgaria at 01.11.2008 was 8968, including 5153 dairy buffaloes (Peeva, 2009).

On the private farms, where the population is concentrated the reduction is 36,0%, whereas on the state and cooperative farms this reduction is 98,8% compare to 1990. The interest in buffaloes increased during the last years which led to building buffalo farms with capacity from 10 to 100 dairy buffalo cows. From the total number of the buffaloes, 43,8 % are rearing in farms with capacity up to 20 buffaloes and 56,3% with more than 20 (Peeva, 2009).

As a result of the crossing up to now the buffalo population is more than 80 % of Bulgarian Murrah breed. As the results of the crossing of Bulgarian Local buffalo with Murrah breed during the last decades came substantial transformations on its type and body

conformation. The cows from Bulgarian Murrah breed are characterize as animals with deep and wide thorax and body compact in comparison with Bulgarian buffalo cows.

Another evidence of the presence of genetic capacity for high milk newly population is the fact that many buffalo cows have a milk yield above 2500-3000 kg and some of them – more than 4500 kg.

The champion of the population is crossbred F2 from which is obtain 5349 kg with 6,64 % fat for 305 days (Peeva, 2009).

During 2009 from Italy was imported semen of Mediterranean buffaloes to cross with Bulgarian Murrah. The main purpose of the crossing is to increase genetic diversity in buffalo population, to decrease inbreeding and improve the body conformation of the animals.

The mean values of the lifetime traits in the Bulgarian Murrah are as follow: productive life is 1451.18, which is equal to 3 years and 4 months (Ilieva and Peeva, 2007), longevity is 2646 days (7 year, 3 months) as for culled cows at first, second and third lactation is respectively 1254, 1708, 2435 days (Peeva and Ilieva, 2007); lifetime milk yield – 5851 kg; milk yield per day of life time – 1.97 kg; lifetime lactation period – 858 days; milk yield per day of lactation period – 6.64 kg; lifetime lactations number – 3.67; lifetime calving interval – 1288 days; milk yield per day of productive life – 4.43 kg (Peeva, 2009).

The percentage of culled cows for low productivity is 19%, including buffalo cows having milk yield below 200 kg per lactation of 120 days; the prolapses takes 11% of the total culled cows, including vaginal and uterine prolapses; the proportion of culled cows with short lactation is 7%; the culled cows for old age (over 8 lactations) are 9% of total: this shows that the longevity of buffaloes is longer than in cattle (Peeva and Ilieva, 2007).

Main source for meat are male calves. Investigations regarding the fattening abilities of buffalo calves show considerable differences by comparison with beef calves (Dimov and Peeva, 1994). The average daily gain of buffalo calves is between 650 and 1083 g.

The most effective slaughter body weight is 400 kg (Dimov and Peeva, 1994).

The buffalo has lower dressing percentage compare to cattle. For suckling calves it is about 56 %; to 4 months of age it is 59.4 %; from 6 to 12 months it is 45 %; from 12 to 18 months it is 47 % and over 24 months 45.3 % (Peeva, 2009).

The average age at first calving is within the range from 32 to 40 months on different farms in the country and different breeds (Peeva, 2000).

The calving interval range from 436 to 505 days according breed, nutrition and management of the farms (Peeva, 2000).

Buffaloes were raised on the State farms, kept tied in closed sheds, machine milked and fed maize silage, alfalfa or grass hay, straw and concentrates.

The animals were manage in separate groups according to physiological conditions: suckling calves, females four to twelve months, heifers, pregnant heifers, dry cows and milking cows.

After the changes in the political and social-economic system in 1989, buffaloes were transferred to the new private farms, where scientific and genetic activities were limited and the animal numbers have drastically declined.

Actually, there are only 9 200 head, of which 5 880 are cows of Bulgarian Murrah in Bulgaria (Borghese, 2011). These animals are submitted for milk recording and to artificial insemination.

Milk recording, selection, artificial insemination and progeny testing are coordinated by the Buffalo Research Institute in Shumen.

Products: White brine cheese, typical yoghurt, salami, sausages, Pastarma. The most of the market is link to the typical buffalo yogurt, very appreciated and to meat by products.

Figure 20. Bulgarian Murrah bull (Alexiev photo, 1998).

Figure 21. Bulgarian Murrah herd (Alexiev photo, 1998).

4. GERMANY

In Germany there are now 2111 buffaloes, in 14 different Regions, but particularly in Sachsen (434), in Baden-Wurttemberg (389) and in Brandenburg (287) (Thiele, 2009, Borghese, 2010). The Germany is an example of adaptation capacity of buffaloes to cold climates; they

can stay on the snow without problem (figure 22). Normally the animals are managed in the stables during winter and on the pasture during spring and summer (figure 23). The population started with 625 head imported by Italy and Bulgaria in 2001, showing now typical characteristics of Mediterranean or European breed, much more similar to Balkan type (figure 24, 25) than to Bulgarian Murrah. The population had a quick increasing linked to a rich market of high quality products, coming from milk and meat processing as mozzarella and other cheeses, cream, yogurt, sausages, meat boxes, and also beauty products (figure 26).
Germany is another example of a new and rich market, invented by the buffalo farmers.

All buffalos are recorded in the German livestock controlling system.

According the report related to the 2 biggest buffalo herds of Sachsen (Saxony), Dr. Golze reported the level for traits of fertility, milk and growth performance relating to the years 2004/2005 (Guglielmetti, 2007):

Weight at birth was found to be 44.7 kg for male buffalo calves and 39.5 kg for female buffalo calves respectively. Weight at 3 months was 147.0 kg for male calves and 132.4 kg for female calves. Weight at 9 months was 351.2 kg for male calves and 305.7 kg for female calves.

Males were used for breeding from the age of two years (Guglielmetti, 2007).

Figure 22. Mediterranean buffalo on the snow in Sachsen (Guglielmetti photo 2007).

Figure 23. Buffalo on the pasture in Sachsen (Guglielmetti photo 2007).

Figure 24. Mediterranean buffalo young bull, Chursdorf, Germany, *(Manfred Thiele photo 2008).*

Figure 25. Mediterranean buffalo cow, Chursdorf, *Germany, (Manfred Thiele photo 2008).*

Buffalo heifers were first mated at the age of 18 to 24 months. Age at first calving was 35 months on average. Calving interval was on average 633.5 days. The buffalo bulls were commonly slaughtered at a weight between 540 and 760 kg (Guglielmetti, 2007).

Regarding milk performance Dr. Golze reported (Guglielmetti, 2007) that in the Chursdorf herd over a 305-day lactation period, milk yield was on average 2232 kg in the first lactation and 2577 kg in the second lactation. Fat yield was 193.7 kg in the first lactation and

237.7 kg in the second lactation. Protein yield was on average 101.0 kg and 123.7 kg for the first and second lactation respectively. There was found a big variation for these traits.

A recent study (Guglielmetti and Golze, 2009), conducted by the Saxon Regional Office for Environment, Agriculture and Geology, required male and female young buffalos to be slaughtered at an age of 647 days (561 to 757 days, n = 12). Weight at slaughter was 549 kg on average. The dressing percentage was 56.7%, whereas the weight of the two halves was 307.1 kg. The percentage of valuable parts was found to be 62.5% on average. The meat taken off the M. longissimus dorsi contained 21.4% raw protein, 2.5% raw fat, 75.0% water and 1.1% ash. At 48 hours after slaughter pH was at 5.5. The drip loss was 3.5%, loss after grilling 32.6% and loss after cooking 47.3%. Shrinkage on chilling was 3.6% after 14 days and 4.2% after 21 days. According to Minolta CR300 the meat colour was 33.3. Tenderness was measured: 5.2 kg at 48 hours post mortem, 3.4 kg after 14 days and 2.8 kg after 21 days.

Figure 26. Typical buffalo products from Germany.

5. MACEDONIA

The buffalo farms in Macedonia are very few, 4 or 5 at all perhaps, and the total population is very reduced, probably 175 animals (SAVE, 2011), but nobody from many people knows exactly the reality; there is a farm in Debreshte village (near Ropotovo), with some local dairy cows and 12 buffaloes of Mediterranean breed, but small and compact, that were bred on natural pasture (figure 27, 28). The first problem of the farmer is that they have no male and very high consanguinity. The proposed solution is the introduction of artificial insemination by Italian semen to increase the milk production, actually very low, and to introduce different and better genetic basis (Borghese, 2010).

In Mojanci village (near Kocani), there is a family farm with 8 buffaloes in the farmyard close their house, of the same Mediterranean breed (figure 29), but the animals were bigger than in the previous farm. The farmer produces simple cheese that is sold in local market (figure 30).

The reality is that a programme to save and develop buffaloes in Macedonia is a priority to maintain biodiversity, to conserve buffalo genetic that was introduced 5 centuries ago with

Turkish invasion, to develop animal farms and typical products for local market and as a basis for tourist economy. The project presented by the Animal Science Institute to the Agricultural Ministry, will be carried out with the cooperation of Italy (Borghese, 2011).

Figure 27. Mediterranean Macedonia breed, Ropotovo, Macedonia. *(Borghese photo, 2008).*

Figure 28. Buffaloes on pasture, Ropotovo, Macedonia. *(Borghese photo, 2008).*

Figure 29. Family management in Mojanci village, Kocani, Macedonia. *(Borghese photo, 2008).*

Figure 30. Simple cheese in Mojanci village, Kocani, Macedonia. *(Borghese photo, 2008).*

6. UNITED KINGDOM

There are a maximum of 2500 breeding females in the UK and probably a maximum of 1200 milking animals and maybe less (Borghese, 2010).

As for milk yields, the average is 1500 kg per year. This was due to poor quality buffalo imported from Romania and also some mis-information through ignorance of the nutrition of buffalo.

An imported way of bulls too has been from the North of Romania. The best animals are without doubt those that show signs of Bulgarian Murrah ancestry, and indeed the sires of over half of foundation animals were Bulgarian (from AI).

Lactation length is about 300 days in the best (with perseverance) but considerably less in some, particularly in the first lactation. Calving interval is usually a bit over 365 days (Wood, 2009).

7. GREECE

In Greece, due to the rapidly changing socio-economic conditions, including the mechanisation of the agricultural sector and the substitution of buffalo milk by milk produced by imported dairy cattle, the number of buffaloes has declined dramatically over the last decades. As a result, from the 75 000 animals counted at the end of the 50s, today only few head remain. There are 2503 buffaloes in Greece (Ligda, 2009). Currently the population has increased, reaching 3137 animals by the end of 2010 (SAVE, 2011) with 28 herds distributed in 21 localities in western, central and northern Greece; most animals are found in the area of Lake Kerkini National Park where they are considered an integral part of the protected area. All herds are monitored by the Centre for Livestock Genetic Improvement (CLGI) in the framework for the conservation of genetic resources in the livestock breeding sector run by the Ministry of Rural Development and Food. Herd books and records are kept by CLGI in collaboration with the Association of Buffalo Breeders of Greece (Kazoglou et al., 2011).

Lactation length varies from 210 to 280 days with an average lactation milk of 700-1000 kg while the age at first calving is 36-48 months (Borghese, 2010).

The age at slaughter for young stock is 15-17 months and the weight at slaughter is 350-400 kg.

The cows are milked twice a day at the farm by hand.

Buffaloes are not used for draught, but only for milk and meat production. The dairy products obtained from buffaloes are yogurt, white cheese in brain, butter, kaimaki and cream.

Each farmer has his own bulls available for natural service in fields and used in proportion 1 to 8-15 cows. Artificial insemination is not applied. Efforts for buffalo production are made by researchers of Greek Focal Point for the Preservation and Conservation of the Animal Genetic Resources, at the Aristotle University of Thessaloniki, with the support of the Ministry of Agriculture to rehabilitate buffalo production and to let buffalo farming, at present under protection, to become an economic viable activity. Really the buffalo market is much reduced.

7. SERBIA

There are 1200 buffaloes in Serbia (SAVE, 2011) of Mediterranean breed, Balkan type (figure 31, 32). They are kept in extensive low input production system (figure 31, 32). The number of buffaloes and trend of population is stable, in the last ten years. Activity on

conservation is supported by the Ministry of Agriculture, through the subsidies and program for crossbreeding in pure breed (Stojanovic, 2011).

Buffaloes could have an important role for high quality food (production of health and safety food, organic production, particularly appreciated are local fresh cheeses, figure 33) , ecological production and integral development of rural areas, anticipating combination of agriculture and rural tourism (Stojanovic, 2011).

Figure 31. Mediterranean Serbian cow. (Srdjan Stojanovic photo, 2011)

Figure 32. Mediterranean Serbian cow (Srdjan Stojanovic photo, 2011).

Figure 33. Fresh cheese. (Srdjan Stojanovic photo, 2011).

8. ALBANIA

Albanian buffalo is an authochtonous breed, classified in the group of Mediterranean breed.

The mantel is black or dark grey and rarely with white spots. Horns arched back and side inward bent. Buffalo population is 321 Albania head (SAVE, 2011). They has been used mainly as draught power; however Albanian farmers and consumers have been interested for their milk and meat products: milk yield is around 450-600 kg in the first lactation going up to 850- 980 kg in the third one; its fat and protein content are respectively 3-10.2% and 5.3-6.8% (Papa and Kume, 2011). Fertility rate is round 80-85% and days open 120-150 days.

During 2010 more than 21 farmers, in four regions of Albania, have received subsidies for buffaloes: as result the size of buffalo population is increasing; the breeding nucleus in four farms has been established. Until now 13 male lines are selected. Nevertheless there is the need to control inbreeding level and provide breeders for an exchange of the breeding stock (Papa and Kume).

9. UKRAINE

There are 115 buffaloes in Ukraine (SAVE, 2011). The percent of crossbreds with Murrah is very high. The Mediterranean Carpathian breed is present too. Some animals were imported by Armenia on 1984. The Ukrainian buffalo population has the real risk of extinction.

In 2004 private initiatives collected rare and unique animals for tourist attraction: one part stays spread over Western Ukraine and the other is located in Kiev region (Jacobi, 2011).

The "Saving of Agro-biodiversity of Carpathian mountains" is working to stop decline of buffalo population, to create nucleus herd farms, to support contact among the owners, to

regulate problem of inbreeding, to search private people who are ready to create small buffalo farms and village communities working in cooperation production (Jacobi, 2011).

As buffalo cannot survive as zoo animal only for tourist attraction, but need to become milk and meat producer.

10. HUNGARY

A small but tenacious population is living in Hungary for many years (Cockrill, 1974). They were introduced by the Turks in 16th century and the population is named Carpathian or Mediterranean Hungarian Breed (figure 34, 35). There has occurred a decline of population due to loss in economic value of working buffaloes (Karpati, 1997). According SAVE (2011) there is 200 buffalo head in Hungary. According direct information by the Ministry of Agriculture and Rural Development, there are 2000 buffaloes, most of them living in National Parks, as gene reserves.

Now, according a new project, some new modern farm are going to be created, introducing Mediterranean Italian head of high genetic value from Italy, with the purpose to originate a market of milk and meat quality products.

Figure 34, 35. Mediterranean Hungarian buffalo.

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Extract from the:
"The Essential Flax"
N. Lee Pengilly, 2005, Saskatchewan Flax Development Commission, Saskatoon, Canada
pp. 80-81 "The Impact of Flax on the Liver or Liver Disease"
Dr. Susan Hemmings

The liver diseases are major killers. Linseed was used for many years by people as a healthy food. The liver is the largest internal organ in our body and is essential to life and performs an important function in the metabolic breakdown and detoxification of chemicals to eliminate them from our body. Damage of this organ plays a critical role in the development of liver disease with a common outcome, the development of liver cirrhosis, and eventually consequence liver cancer. In the western society death caused by liver diseases it happens very often. Cirrhosis is associated with a great morbidity and high mortality. Liver cancer, which develops from cirrhotic state, is one of the fastest moving and lethal forms of cancer known.

The author studied the impact of flax products on liver damage, using "Fischer 344 rats". This study shown that long term flax consumption is safe, non toxic and does not harm the liver, but it's beneficial for the liver thanks to activity of SDG (secoisolariciresinol diglucoside). Consumption of flax has the ability to protect the liver from acute injuring and against the development of liver cancer.

SOME PRACTICAL USES OF FLAX SEEDS AND OIL

Dr. Agnieszka Kręgielczak, Prof.dr. Ryszard Kozlowski, Dr.Eng. Dana Radu

Flaxseed grits

Content: flaxseed

Flaxseed grits is abundance of valuable nutritional ingredients. It contains easily digestible gelating dietary fiber, valuable protein, lecithin, phytohormones, anti-oxidants and micro- and macro-elements. Soluble flaxseed fiber swells during preparation and forms a delicate gel.

Nutritional flaxseed grits is easily digestible and ensure better slide of food.

Use: for preparing gruels, as additive to soup, especially from milk, yoghurt, and cereals.

Preparation: put the grits to cold, hot or boiling water, milk or soup – at best 1 small teaspoonful per glass of the liquid. Stir a few times and set aside until the grits swell.

Nutritional value per 100 g of product:

Protein	40 g
Fat	9 g
Digestible carbohydrates	3 g
Dietary fibre	36 g
Sodium	0.04 g
Energetic value	253 kcal (1064 kJ)

Flax cake

Composition: flax seed defited flour (grounded) – ½ glass (125 cm)
Butter – 125 g

Wheat flour – ½ glass
Brown sugar – 2 spoons
Eggs – 1
½ spoon of disintegrated almonds or nuts.

Mix the butter with sugar, add the egg and yogurt with yeast and mix. Add partially the wheat flour and almonds or nuts. Put the dough to freeze for 30 minutes and after this time start to form the cake and put it for 10-12 minutes to oven at 180 oC.

Salad souse with linseed oil

Composition: cold pressed flax oil – ¼ glass
Garlic – 2 cloves
Juice from 1 lemon
Water – ¼ glass
Salt
Pepper
Fresh basil

Ground garlic with salt, add lemon juice and partially slowly add flax oil and water. Add chopped lives of basil and pepper. It's good for salads from tomatoes, cucumbers, lettuce and also for mixed vegetable or others.

Flax tea

Grounded defited flax seeds – 2 spoons
Boiling water ½ liters (500 ml)
2-4 slices of lemon
Honey – according to wish

Put the grounded defited flaxseed in the tea pot and pour boiling water, keep 15 minutes. Add slices of lemon and honey according to taste.

This tea is especially for pregnant women.

Project co-funded by EUROPEAN UNION trough the European Regional Development Fund
Sectorial Operational Programme "Increase of Economic Competitiveness"

"Investing for your future"

PRIORITY AXIS 2 – Research, Technological Development and Innovation for Competitiveness
Operation 2.1.2: "Complex research projects fostering the participation of high-level international experts"
"Bast Plants - Renewable Strategic Resources for European Economy"
Contract No 210/2010
Project value: 6.842.915 RON
Completion date: 20th July 2013
Contribution of European Union: 4.979.998, 34 RON
Romanian Government contribution value: 1.019.999, 66 RON
Project beneficiary: "AUREL VLAICU" UNIVERSITY – Arad, Romania
TECHNICAL AND NATURAL SCIENCES
RESEARCH-DEVELOPMENT-INNOVATION INSTITUTE of UAV

BASTEURES

The project objectives

The **main objective** of the project is the complete capitalization of the bast plants (flax, hemp) and rape in order to obtain advanced materials, auxiliary raw materials and energetic products by developing and applying new and competitive processing/extraction technologies for both, primary and secondary products of these plants, in a sustainable economical development context.

These renewable raw materials resources are studied by researchers for their huge potential to offer valuable economical solutions in many sectors.

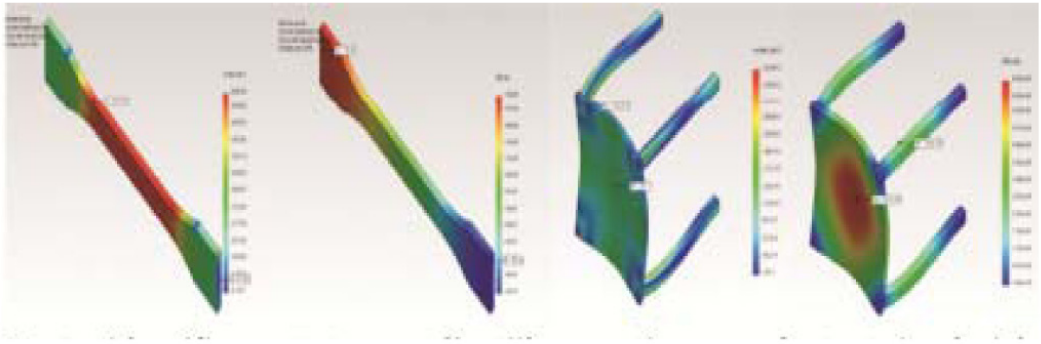
For transforming the bast plants (flax, hemp) and rape - **in advanced materials** (advanced textiles fabrics, paper, bio-composites), **auxiliary raw materials** for food industry and pharmacy (oils for functional food, agro-fine-chemical are natural sources for extracts with anticancer, antibacterial, immunoglobulin level controlling, nutritive, etc. properties included in production of drugs, cosmetics, bioremediation agents etc.) **and energetic products** (bio-fuel) performed technologies based on the novel achievements from different fields (chemistry, biotechnology, applied physics, materials, textiles, textiles chemistry, wood chemistry, paper industry, etc.) are developed in this project for the complete capitalization of these resources in a closed circle.

In order to attend the major objective of the programme – "to enhance the Romanian enterprises' productivity and to reduce the gaps to the average productivity at the EU level" as well as increasing and diversifying the Romanian products and innovative services, the team will offer different solutions. Some of the technological solutions developed in this project are:

➢ **Technical solution for composite materials using bast plants**

Thermosetting composites

Matrix (polymers, resins) Fibers (short fibers, shives)



In order to identify all practical applications, behavior simulations of the composite material were carried out, for different resistance structures

➢ Technical solution to obtain paper from bast fibers

Bleaching of cellulose from ligno-cellulosic fiber wastes was performed with ODPM without chlorine

Paper obtained from bleached and unbleached cellulose derived from short fiber wastes (resulting by the spinning of flax-cotton and hemp-cotton mixtures –based on cotton spinning technology)

➢ New technical solutions for retting of bast plants

The physical and mechanical characteristics of hemp fibers using the 6 new retting solutions.

Variants	1	2	2 bis	3	4	5	6
SR (N)	330	230	310	300	290	280	250
Flexibility (mm)	41	23	29	43	40	36	32
Nm	74	35	61	53	30	31	23

Group	**T**					**F**				Test analysis methods
Quality	Superior	I	II	III	IV	I	II	III	IV	
Base color	light yellow or greenish yellow									According to standard samples
Other colors	E	E	LG	GG	GG	LG or LGr	LG or LGr	GG		
Blackened, underretted fibres, ligneous parts, peewees % maximum	E	E	2	3	5	1	3	4	6	
Retting strand force Nmin	320	280	220	170	150	270	210	200	180	Ro STAS 6183/2-69
length density Nm (tex)										Ro STAS 8468-69
Flexibility mm (minimum)										-
Legend: E – Excluded; LG - light green; GG - greenish gray; LGr - light gray										