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ADDITIVATION OF POLYAMIDE FIBERS BY MEANS OF MICRO- AND NANO-PARTICLES CONTAINING JOJOBA OIL

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INTRODUCTION

The textile and clothing industry, normally seen as a “traditional industry” it’s an important part of the European manufacturing industry and gives employment to over two million people.

Increased competition, specifically from Asia, and proposed abolition of all import quotas for textiles and clothing in the EU, United States, Canada and Norway in 2005, is forcing the industry to restructure and modernise. Significant restructuring has taken place over the last decade, however, there is a general recognition that producing traditional apparel products may no longer be sufficient to sustain a viable business, and the EU textile industries may have to move towards more innovative, high quality products in order to differentiate themselves and compete [1].

Innovation proliferate at every phase of the textile supply chain, from material production to final finished fabrics. The main drivers of change in textiles regard: consumer demands for comfort and performance, advanced technologies influencing product and process innovations, ecological concerns and compliance with eco-regulamentations, safety, health and aesthetics.

In the development of fibers, yarns and fabrics, functional aspects such as anti-bacterial, anti-static, UV protective, thermoregulation or biodegradable functions are playing an increasing important role.

1 INTELLIGENT TEXTILES

What exactly is “intelligence” when it comes to fabrics? The term “intelligence” is used pretty loosely – they are not talking trousers that will make you a cup of tea and then summarize Nietzsche for you!!! [2]

Du Pont refers to its Tactel and Lycra textiles as “intelligent” because of their shape-maintaining properties: you can stretch it and stretch it but it still “remembers” its form.

Intelligent textiles represent the next generation of fibers, fabrics and articles produced from them. They can be described as textile materials that think for themselves. This means that they may keep us warm in cold environments or cool in hot environments or provide us with considerable convenience and even fun in our normal day-by-day lives, for example through the incorporation of electronic devices or special colour effects.

Many intelligent textiles already feature in advanced types of clothing, principally for protection and safety and for added fashion or convenience [3].

One of the main reasons for the fast development of intelligent textiles is the importance to the military industry. This is because they are used in different projects such as extreme winter condition jackets or uniforms that change colour so as to improve camouflage effects. Nowadays the military industry has become aware of the advantage of sharing knowledge with the various industrial sectors because with joint collaboration far better results can be obtained through team-work.

Intelligent textiles provide ample evidence of the potential and enormous wealth of opportunities still to be realised in the textile industry, in the fashion and clothing sector, as well as in the technical textiles sector. Moreover, these developments will be the result of active collaboration between people from a whole variety of backgrounds and disciplines: engineering, science, design, process development, and business and marketing. Our very day-to-day lives will within the next few years be significantly regulated by intelligent devices, and many of these devices will be in textiles and clothing.

The most important intelligent materials at present in are: phase change materials, shape memory materials and conductive materials. In the following pages there is a summary of the different types of intelligent and functional textiles, explaining their main characteristics and applications.

1.1 Insulation

The required thermal insulation of clothing systems primarily depends on the physical activity and on the surrounding conditions, such as temperature and relative humidity. The quantity of heat produced by humans depends on the physical activity and can vary from 100W while resting to over 1000W during maximum physical performance. Particularly during the cooler seasons (approx. 0ºC), the recommended thermal insulation is defined in order to ensure that the body is sufficiently warm when resting. At a more intensive activity, which is often the case with winter sports, the body temperature increases with enhanced heat production. To maintain this increase within a certain limit, the body perspires in order to withdraw energy from the body by evaporative cooling. If the thermal insulation of the clothing is reduced during physical activity, a part of the produced heat can be removed by convection thus the body is not required to perspire so much.

GORE-TEX® fabric, for example, is specifically engineered to form an impenetrable barrier against wind and water while maintaining breathability. The more active one becomes, the more heat and moisture the body produces: breathable outerwear and footwear aids body's natural cooling process by allowing perspiration vapor to escape.

The quality of insulation in a garment against heat and cold is extensively governed by the thickness and density of its component fabrics. High thickness and low density improve insulation. In many practical examples, thermal insulation is provided by air gaps between the garment layers. However, the effectiveness of the insulation is also affected by the external temperature. The more extreme the temperature, be it very high or very low, the less effective the insulation becomes. Thus, a garment designed for its ability to protect against heat or cold is selected by its wearer on the expectation of the climate in which the garment is to be worn.

However, a garment made from a thick fabric will have greater weight, and the freedom of movement of the wearer will be impaired. Clearly then a garment made from an intelligent fabric whose nature can vary depending on the external temperature can provide superior protection. At the same time, such a garment must still be comfortable to wear.

As it mentioned previously, the intelligent textiles used to improve insulation are the phase change materials and the shape memory materials due to their special characteristics and properties.

1.1.1 Phase Change Materials

Every material absorbs heat during a heating process while its temperature is rising constantly. The heat stored in the material is released into the environment through a reverse cooling process. During the cooling process, the material temperature decreases continuously. A normal textile material absorbs about 1 J/g while its temperature rises by one degree Celsius.

Comparing the heat absorption during the melting process of a phase change material (PCM) with those in a normal heating process, a much higher amount of heat is absorbed if a PCM melts. A paraffin-PCM, for example, absorbs approximately 200 J/g if it undergoes a melting process. The high amount of heat absorbed by the paraffin in the melting process is released into the surrounding area in a cooling process starting at the PCM's crystallisation temperature. After comparing the heat storage capacities of textiles and PCM, it is obvious that by applying paraffin-PCM to textiles their heat storage capacities can substantially enhanced.

During the complete melting process, the temperature of the PCM as well as its surrounding area remains constant. The undesired temperature increase concomitant with the normal heating process does not occur. The same is true for the crystallisation process. During the entire crystallisation process the temperature of the PCM does not change either. The high heat transfer during the melting process as well as the crystallisation process without temperature change makes PCM promising as a source of heat storage.

In their application in textiles, the paraffins are either in solid or liquid state. In order to prevent the paraffin's dissolution while in the liquid state, it is enclosed into small plastic spheres with diameters of only a few micrometers. These microscopic spheres containing PCM are called PCM-microcapsules. The microencapsulated paraffin is either permanently locked in acrylic fibers and in polyurethane foams or coated onto the surface of a textile structure.

Active wear needs to provide a thermal balance between the heat generated by the body while engaging in a sport and the heat released into the environment. Normal active-wear garments do not always fulfil this requirement. The heat generated by the body during strenuous activity is often not released into the environment in the necessary amount thus resulting in a thermal stress situation. On the other hand, during periods of rest between activities, less heat is generated by the human body. Considering the same heat release, hypothermia is likely to occur.

In order to improve the thermal performance of active-wear garments, clothing textiles with thermoregulating properties are widely used. The thermoregulating effect provided by these textiles is based on the application of PCM. However, a suitable thermoregulating effect according to the prevailing wearing conditions can only be realised when specific design principles are applied in the development process of such active wear-garments. It is necessary, for example, to match the PCM quantity applied to the active-wear garment with the level of activity and the duration of the garment use. Furthermore, the garment construction needs to be designed in such a way as to assist the desired thermoregulation effect. For example products enhanced with Outlast® technology contain millions of microcapsules. These unbreakable microcapsules are filled with Phase Change Materials (PCMs). PCMs are very sensitive to fluctuations in temperature. Based on your skin temperature, the PCMs will seek to make you more comfortable by absorbing, storing or releasing heat back to you.

Fig.1: Distribution of human heat through the body

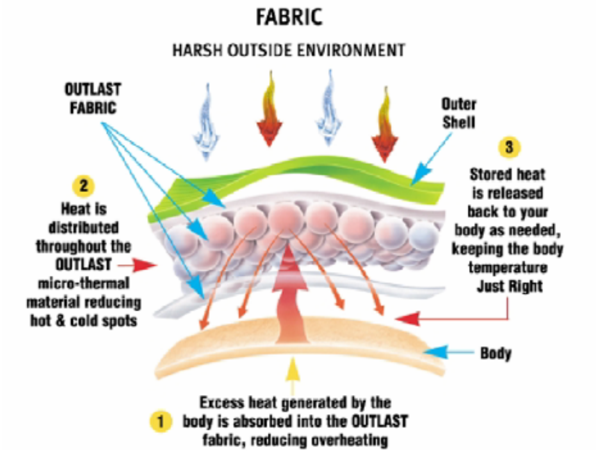


Fig.2: OUTLAST fabric assembling

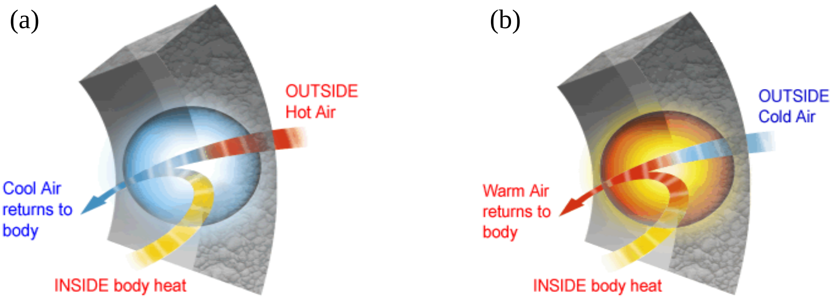


Fig.3: Heat exchange through fibers containing encapsulated PCM.
(a) cooling effect; (b) warming effect

These materials store, release and absorb heat as they oscillate between solid and liquid form, giving off heat as they change to a solid state and absorbing it as they return to a liquid state. PCMs can be incorporated within fibers or foams, or may be coated into fabrics.

1.1.2 Shape Memory Materials

These types of materials are able to revert from the current shape to a previously held shape, usually due to the action of heat. This technology has been extensively pioneered by the UK Defence Clothing and Textiles Agency. When these shape memory materials are activated in garments, the air gaps between adjacent layers of clothing are increased, in order to give better insulation. The incorporation of shape memory materials into garments thus confers greater versatility in the protection the garment provides against extremes of heat or cold.

Shape memory alloys, such as nickel-titanium, have been developed to provide increased protection against sources of heat, even extreme heat. A shape memory alloy possesses different properties below and above the temperature at which it is activated. Below this temperature, the alloy is easily deformed. At the activation temperature, the alloy exerts a force to return to a previously adopted shape and becomes much stiffer. The temperature of activation can be chosen by altering the ratio of nickel to titanium in the alloy.

In practice, a shape memory alloy is usually in the shape of a spring. The spring is flat below the activation temperature but becomes extended above it. By incorporating these alloys between the layers of a garment, the gap between the layers can be substantially increased above the activation temperature. As a consequence, considerably improved protection against external heat is provided.

Shape Memory Polymers have the same effect as the Ni Ti alloy but, being polymers, they will potentially be more compatible with textiles. The shape memory effect is observed when a plastic conforming to one shape returns, at a particular temperature, to a previously adopted shape.

For clothing applications, the desirable temperatures for the shape memory effect to be triggered will be near body temperature.

Polyurethane films have been made which can be incorporated between adjacent layers of clothing. When the temperature of the outer layer of clothing has fallen sufficiently, the polyurethane film responds so that the air gap between the layers of clothing becomes broader. This broadening is achieved if, on cooling, the film develops an out-of-plane deformation, which must be strong enough to resist the weight of the clothing and the forces induced by the movements of the wearer. The deformation must be capable of reversal if the outer layer of clothing subsequently becomes warmer.

An application of this kind of material is produced, for example, by DiAPLEX.

The intelligence of DiAPLEX lies in the unique way in which it takes advantage of Micro-Brownian motion (thermal vibration). Micro-Brownian motion occurs within the DiAPLEX membrane when the temperature rises above a predetermined activation point. As a result of this motion, micro-pores are created in the polymer membrane which allow water vapor and body heat to escape. Because permeability increases as the temperature rises, the membrane is able to respond intelligently to changes in the wearer's environment and body temperature.

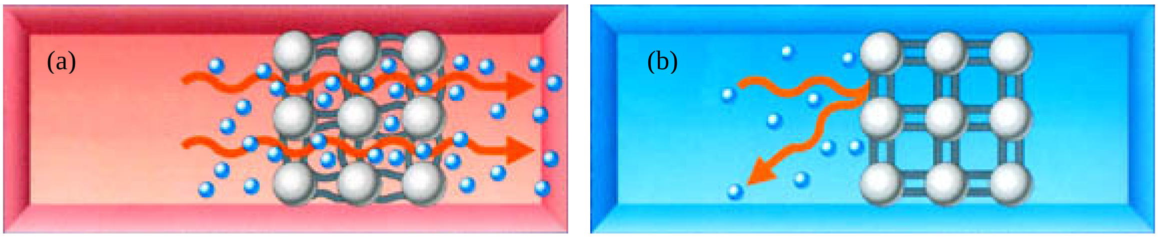


Fig.4: Ambient temperature response function of DiAPLEX fabrics.
(a) when ambient temperature is below activation point, molecular structure is rigid, so permeability is low and body heat is retained.
(b) when ambient temperature is above activation point, Micro-Brownian movement creates gaps between molecules, increasing permeability so that moisture and body heat can escape.

When the temperature within a garment is low, the DiAPLEX membrane acts to reduce permeability and prevent air and water molecules from passing through it. This helps to retain body heat. As the temperature inside the garment rises, however, the Micro-Brownian motion increases membrane permeability causing water vapor to be expelled to the outside air. This "flexible barrier function" enables the garment to intelligently adjust its insulating properties in response to temperature changes, assuring optimum comfort in any environment.

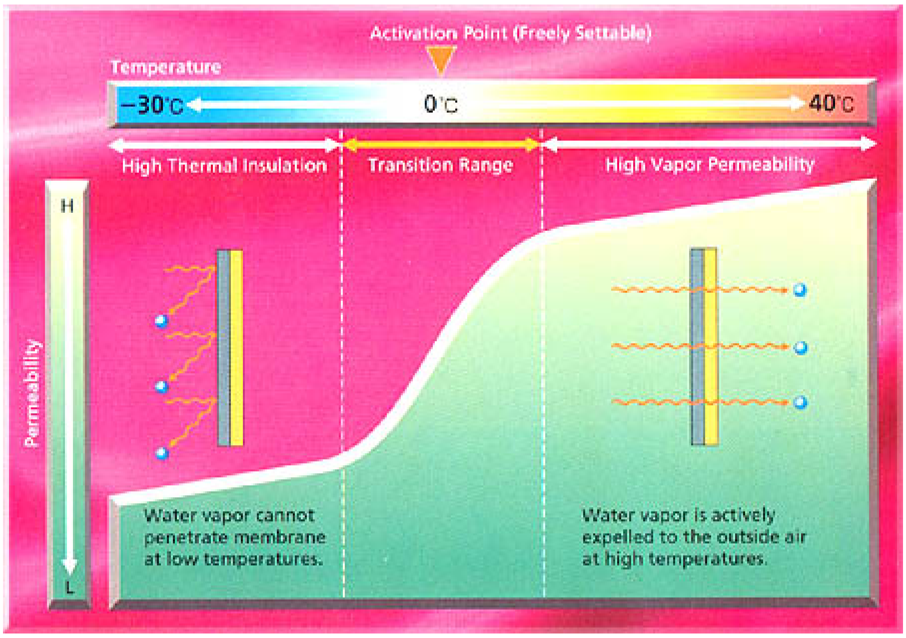


Fig.5: Flexible barrier mechanism with activation point set to 0^{o}C

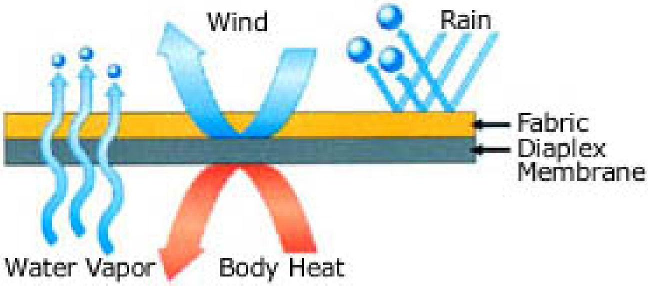


Fig.6: Cross section of DiAPLEX/fabric garment

1.2 Conductive materials

"Intelligent clothing" should put people in the position to communicate with other people and computer systems as they wish, regardless of where they are, to access global information, for example, via the Internet, and to control any activities remotely.

Clothing will combine the functions of medium, carrier and interface between humans and their environment.

Micro system technology is constantly producing increasingly smaller components enabling intelligent functions to be integrated into more and more classical products in the future without causing negative consequences on their range of use.

Everyone wears clothes in several layers one above the other in all day-to-day situations, which means that it is possible to accommodate micro system components comparatively simply and comfortably. The objective should now be to focus on integrating microchip and computer systems as invisibly as possible into clothing, thus connecting man with his environment and equipping him as a communication medium.

This is a field of innovation and a future potential of fascinating proportions which also opens up interesting possibilities in commercial terms.

Conductive fabrics combine the latest high wicking finishes with high metallic content in textiles that still retain the comfort required for clothing. With the addition of nickel, copper and silver coatings of varying thickness, these fibers provide a versatile combination of physical and electrical properties for a variety of demanding applications. For example, the thousand-fold increase in thermal conductivity of metal over conventional polymers used in clothing offers sports apparel with the minimum of thermal insulation.

Another type of fibers included in this group are carbon fibers. They are lightweight, durable, flexible and cost competitive and they are able to be crimped and soldered and subjected to textile processing without any problem.

These materials also afford designers new opportunities in developing contoured and portable products for both existing and emerging product markets. The ability to dispense with fixed casings, rigid mountings and inflexible substrates facilitates new radical possibilities in flexible, user-friendly interfacing. Exploration of human/machine interaction and wholly new types of interface sensor technology has resulted in the development of sensory fabric.

Today's switching and sensing technologies are basically rigid or semi-rigid. This results in extensive limitations on their applications and new product design becomes constrained by their physical inflexibility. Semi-rigid forms of sensing and switching interfaces such as plastic or printed membrane switches are available, but usually they need to be mounted against a rigid surface in order to function as intended. Where flexible, they tend to be impermeable and only flex in one dimension at a time.

It is hoped that the results will contribute to the possibility of developing and manufacturing smart clothes technologies in the clothing industry and the possibility of offering services which arise in conjunction with "intelligent" clothing in co-operation with other sectors.

This will provide the clothing industry with the opportunity to work together with innovative partners from other industry and consumer sectors and thus contribute to a further switch or increase in turnover towards the medical, safety, entertainment or leisure sectors. This is particularly desirable in the face of the stagnating demand for clothing from the private consumer. Constructive co-operation with the industries involved should contribute to clarifying the existing developmental questions and risks and demonstrate to the clothing industry, which is typically a small-scale industry, which technical requirements and technical demands will be made of it in the near future. The necessary prerequisites will be created to increasingly market clothing as a high-tech product and thereby also to enhance the image of the industry as a whole to the public.

1.3 Active Textile

Active textiles means clothes providing care, freshness, comfort and protection for the skin [4]. Imagine that every time we put on our favourite T-shirt it actually takes care of us. The principle is simple enough: build active ingredients into the fabric of clothing so that with the natural movement of the body, the skin is slowly freshened and revitalized. The result of bringing together fabric technology, decades of experience with health and beauty products and the power of nature itself, leads to Active Textiles offering new possibilities to fashion concepts and collections.

1.3.1 Antibacterial fibers

The inherent properties of the textile fibers provide room for the growth of micro-organisms [5]. Besides, the structure of the substrates and the chemical processes may induce the growth of microbes. Humid and warm environment still aggravate the problem. Infestation by microbes cause cross infection by pathogens and development of smell odour where the fabric is worn next to skin. In addition, the staining and loss of the performance properties of textile substrates are the results of microbial attack. Basically, with a view to protect the wearer and the textile substrate itself antimicrobial finish is applied to textile materials.

Antimicrobial treatment for textile materials is necessary to full-fill the following objectives: to avoid cross infection by pathogenic micro organisms; to control the infestation by microbes; to arrest metabolism in microbes in order to reduce the formation of odour and to safeguard the textile products from staining, discolouration and quality deterioration.

It is important to take into account the impact of stress, thermal and mechanical effects on the finished substrates. The following requirements need to be satisfied to obtain maximum benefits out of the finish: durability to washing, dry cleaning and hot pressing; selective activity to undesirable micro-organisms; should not produce harmful effects to the manufacturer, user and the environment; should comply with the statutory requirements of regulating agencies; compatibility with the chemical processes; easy method of application; no deterioration of fabric quality; resistant to body fluids; and resistant to disinfections/sterilization.

1.3.2 Antimicrobial finishing methodologies

The antimicrobial agents can be applied to the textile substrates by exhaust, pad-dry-cure, coating, spray and foam techniques. The substances can also be applied by directly adding into the fibre spinning dope. It is claimed that the commercial agents can be applied online during the dyeing and finishing operations. Various methods for improving the durability of the finish include: insolubilization of the active substances in/on the fibre; treating the fibre with resin, condensates or cross linking agents; micro encapsulation of the antimicrobial agents with the fibre matrix; coating the fibr surface at the finish stages (yarns or fabrics); chemical modification of the fiber by covalent bond formation and use of graft polymers, homo polymers and/or copolymerization on to the fibre, incorporation of the agent at the fiber spinning level.

1.3.3 Mechanism of antimicrobial activity

Negative effect on the vitality of the micro-organisms is generally referred to as antimicrobial. The degree of activity is differentiated by the term “cidal” which indicates significant destruction of microbes and the term “static” represents inhibition of microbial growth without much destruction.

The antimicrobial substances function in different ways. In the conventional leaching type of finish, the species diffuse and poison the microbes to kill. This type of finish shows poor durability and may cause health problems.

The non-leaching type or bio-static finish shows good durability and may not provoke any health problems. A large number of textiles with antimicrobial finish function by diffusion type. The rate of diffusion has a direct effect on the effectiveness of the finish. For example, in the ion exchange process, the release of the active substances is at a slower rate compared to direct diffusion and has a weaker effect.

Similarly in the case of antimicrobial modifications, when the active substances are not released from the fiber surface and so are less effective. They are active only when they come in contact with micro-organisms.

These so called new technologies have been developed by considering the medical, toxicological and ecological principles.

1.3.5 Antimicrobial substances and their effect

Many antimicrobial agents used in the textile industry are known from the food stuff and cosmetics sector. These substances are incorporated with textile substrates comparatively at lower concentrations. It must be ensured that these substances are not only permanently effective but also that they are compatible with skin and the environment.

Different antibacterial additives are available:

- organic molecules organic molecules (*Triclosan*)
- natural substances natural substances (*Chitosan*)
- inorganic complexes inorganic complexes (zeolites and transition metals Cu, Ag, Zn)

One of the most durable type of antimicrobial products is based on a diphenyl ether (bis-phenyl) derivative known as either 2, 4, 4'-trichloro-2' hydroxy diphenyl ether or 5-chloro-2-(2, 4-dichloro phenoxyl) phenol [Fig.7].

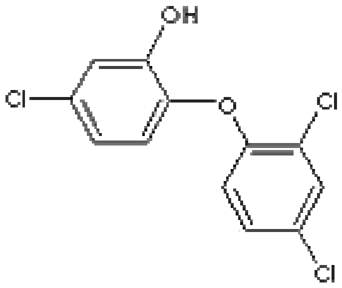


Fig.7: *Triclosan* chemical structure

Triclosan products have been used for more than 25 years in hospitals and personal care products such as antimicrobial soap, toothpaste and deodorants. *Triclosan* inhibits growth of micro-organisms by using a electro chemical mode of action to penetrate and disrupt their cell walls. When the cell walls are penetrated, leakage of metabolites occurs and other cell functions are disabled, thereby preventing the organism from functioning or reproducing. The *Triclosan* when incorporated within a polymer migrates to the surface, where it is bound. Because, it is not water-soluble, it does not leach out, and it continuously inhibits the growth of bacteria in contact with the surface using barrier or blocking action.

Chitosan is an effective natural antimicrobial agent derived from Chitin, a polysaccharide found in the exoskeleton of shellfish like shrimp or crabs. *Chitosan* is a naturally occurring substance that is chemically similar to cellulose [Fig.8]. Coatings of *Chitosan* on conventional fibers appear to be the more realistic prospect since, they do not provoke an immunological response.

Chitosan applied to textiles has been widely studied for effects such as shrink resistance, improved dye uptake, and as auxiliary or anti-static agents, etc., because of the low toxicity and good biocompatibility of this natural polymer. Usually, to bond chitosan to cotton fabrics chemically, glutaric dialdehyde is chosen as the crosslinking agent. Its performance in physics and chemistry is determined by the influence of two important structural parameters: degree of deacetylation (DD) and molecular weight (MW). which affect solubility, enrichment ions, mechanics of the chitosan membrane and flocculation.

In acidic solvents, the NH_2 group in chitosan becomes a quaternary amino group and allows the chitosan to inhibit the growth of many bacteria, including gram-negative and gram-positive ones.

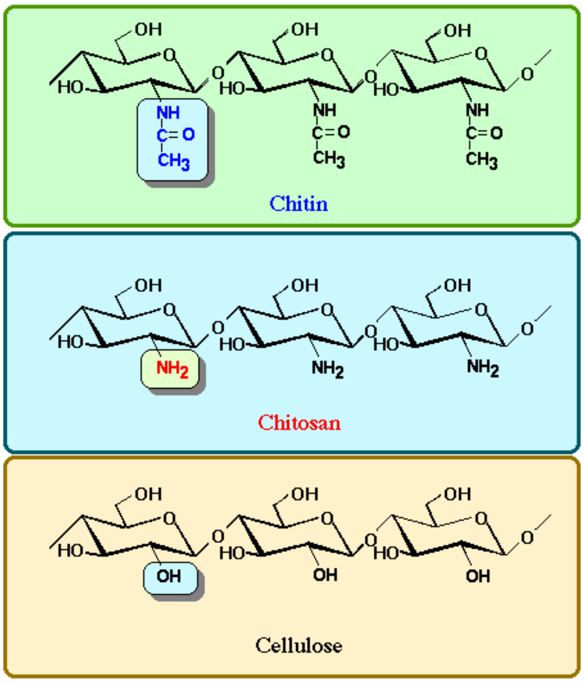


Fig.8: Chitin, *Chitosan* and cellulose chemical structure

Complexing metallic compounds based on metals like cadmium, silver, copper and mercury cause inhibition of the active enzyme centres (inhibition of metabolism). Amongst these, the silver compounds are very popular and already been used in the preparation of antimicrobial drinking water.

1.3.6 Commercial antimicrobial agents and fibers

Thomsan Research Associates markets a range of antimicrobials under the trade name “Ultrafresh” for the textile and polymer industry. Ultrafresh products were developed to be used in normal textile processes. Most Ultrafresh treatments are non-ionic and are compatible with a wide range of binders and finishes. To incorporate antibacterial into high temperature fibers like polyester and nylon, it is necessary to use an inorganic antimicrobial like Ultrafresh CA-16 or PA-42. These must be added as a special master batch to the polymer mixture before the extrusion process. For fibers such as polypropylene which are extruded at lower temperatures, it is possible to use organic antimicrobials such as Ultrafresh Nm-100, Dm-50 or XQ-32.

Nylstar active-Ag Meryl® Skinlife introduces new concepts of comfort in several applications (i.e. bodywear, female stockings, active-wear and sportswear). Today, for fiber's producers, the goal is to feed the success of microfibre, creating new evolutions.

Meryl® Skinlife is available in microfibers PA 66. It has been designed to be suitable for all technologies (i.e. Circular knitting, weaving, warp knitting, seamless, hosiery, etc.). It found the best end uses in fabrics in direct contact with the skin.

Meryl® Skinlife [Fig.9] is not bactericide: it does not decrease the bacteria level lower than the normal skin level.

Inorganic based anti bacterial agent (Ag^+ ions based) interrupts critical functions of the micro-organisms, in particular it is active against the main bacteria's groups Gram + (Staphilococcus Aureus) and Gram - (K. Pneumonia) [Fig.10].

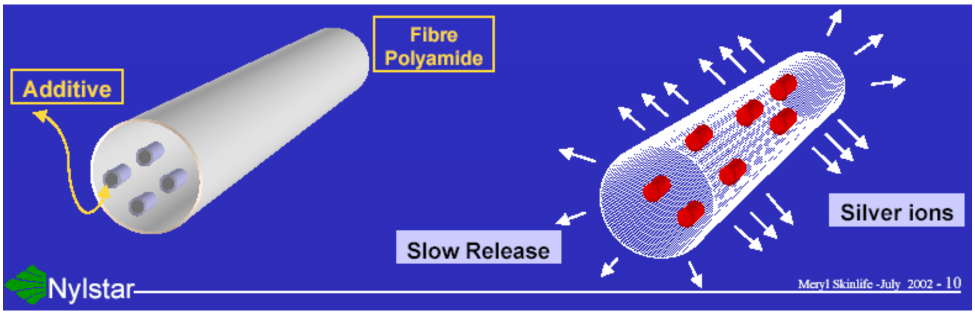


Fig.9. Silver incorporation into Meryl®Skinlife fiber

As a consequence of the presence of the exclusive bacteriostatic agent *in* the polymeric matrix (not *on* the fabric's surface), there is no migration from fabric to skin (avoiding induction of allergy).

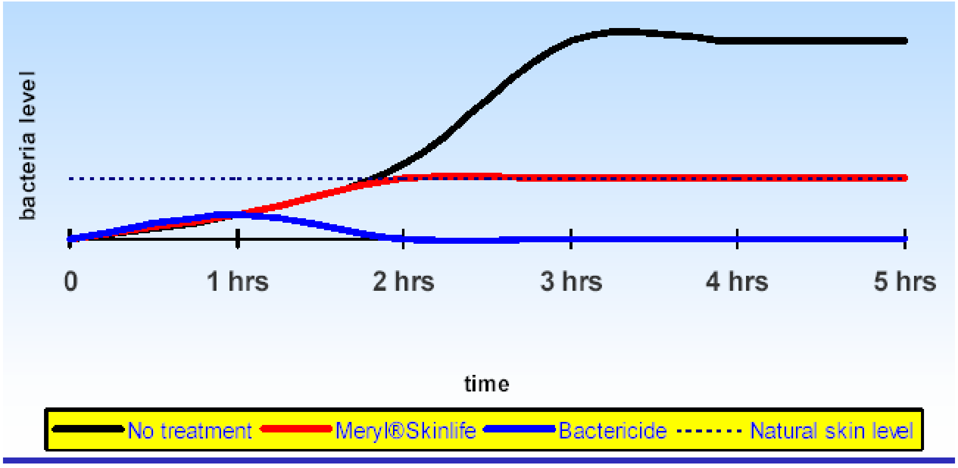


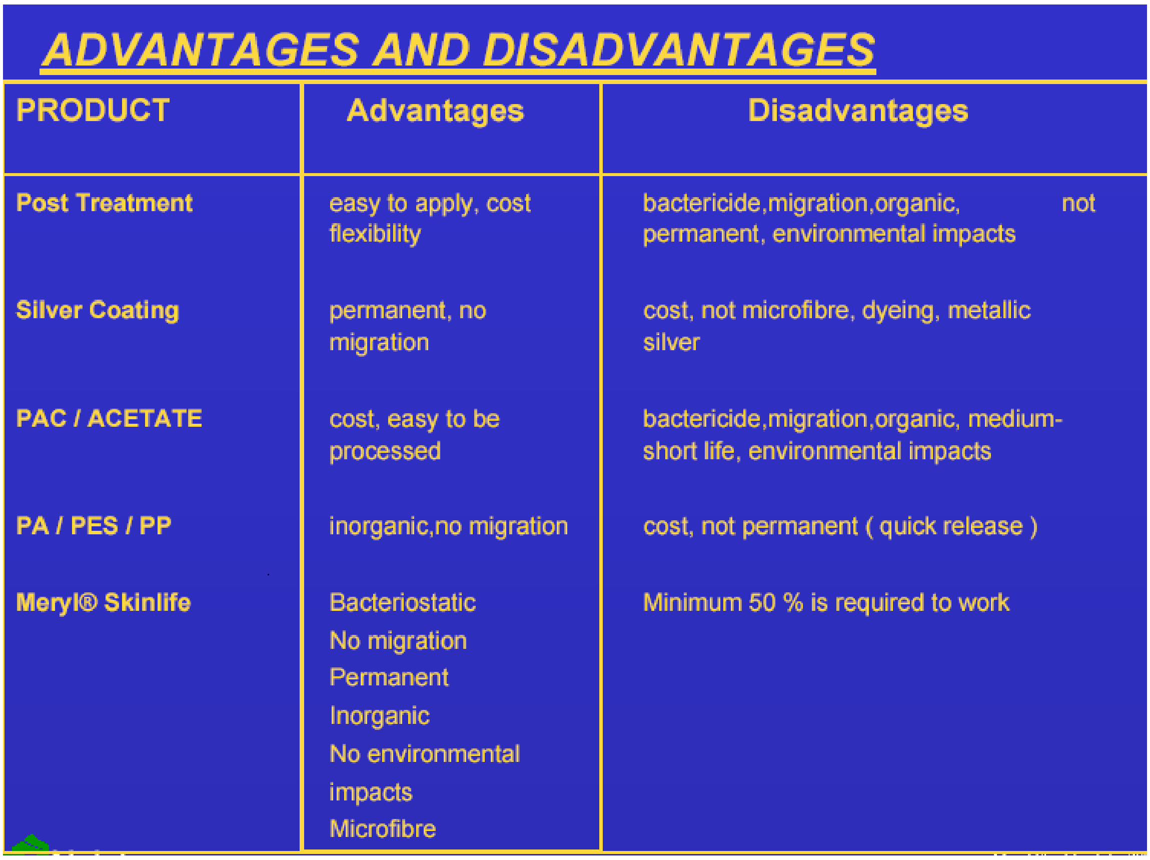
Fig.10: Bacteria population growth curves on Meryl®Skinlife fabric in skin contact

1.3.7-i Benefits of antimicrobial textiles

A wide range textile product is now available for the benefit of the consumer. Initially, the primary objective of the finish was to protect textiles from being affected by microbes particularly fungi. Uniforms, tents, defence textiles and technical textiles, such as, geo-textiles have therefore all been finished using antimicrobial agents [Table I].

Later, the home textiles, such as, curtains coverings, and bath mats came with antimicrobial finish. The application of the finish is now extended to textiles used for outdoor, healthcare sector, sports and leisure. Novel technologies in antimicrobial finishing are successfully employed in non-woven sector especially in medical textiles. Textile fibers with built-in antimicrobial properties will also serve the purpose alone or in blends with other fibers [Table II].

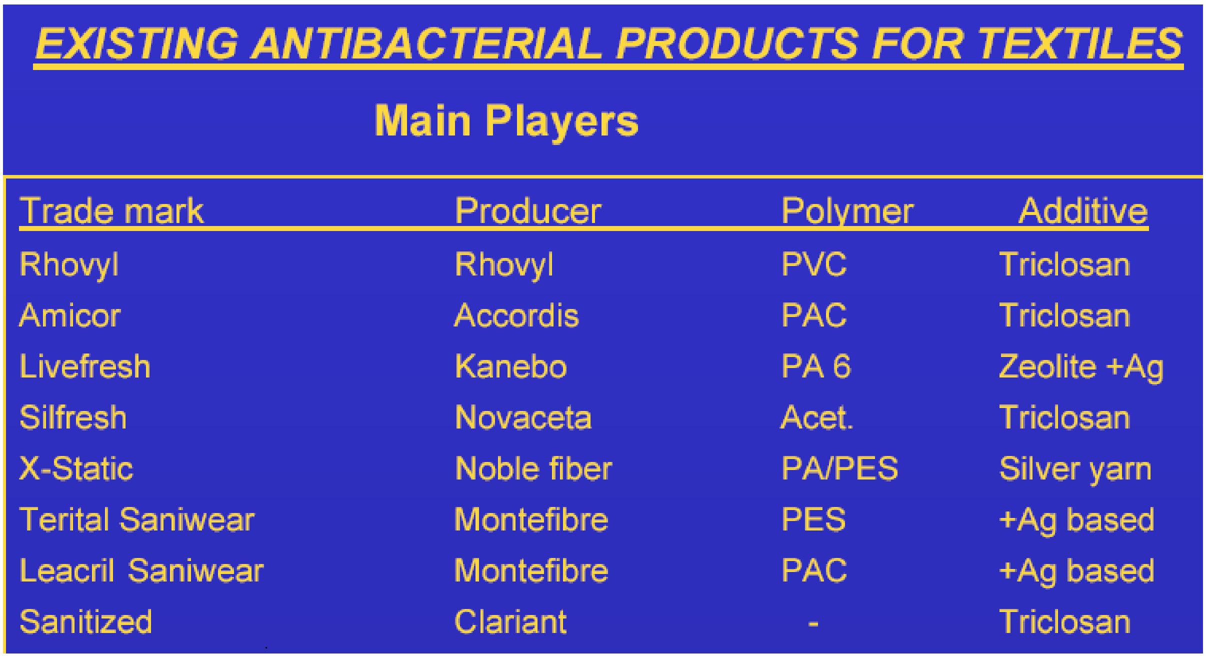
The field of application of the bioactive fibers includes sanitary materials, dressing materials, surgical threads, materials for filtration of gases and liquids, air conditioning and ventilation, constructional materials, special materials for food industry, pharmaceutical industry, footwear industry, clothing industry, automotive industry etc.



ADVANTAGES AND DISADVANTAGES

PRODUCT	Advantages	Disadvantages
Post Treatment	easy to apply, cost flexibility	bactericide,migration,organic, not permanent, environmental impacts
Silver Coating	permanent, no migration	cost, not microfibre, dyeing, metallic silver
PAC / ACETATE	cost, easy to be processed	bactericide,migration,organic, medium-short life, environmental impacts
PA / PES / PP	inorganic,no migration	cost, not permanent (quick release)
Meryl® Skinlife	Bacteriostatic No migration Permanent Inorganic No environmental impacts Microfibre	Minimum 50 % is required to work

Table I: Comparison of different antimicrobial products



EXISTING ANTIBACTERIAL PRODUCTS FOR TEXTILES

Main Players

Trade mark	Producer	Polymer	Additive
Rhovyl	Rhovyl	PVC	Triclosan
Amicor	Accordis	PAC	Triclosan
Livefresh	Kanebo	PA 6	Zeolite +Ag
Silfresh	Novaceta	Acet.	Triclosan
X-Static	Noble fiber	PA/PES	Silver yarn
Terital Saniwear	Montefibre	PES	+Ag based
Leacril Saniwear	Montefibre	PAC	+Ag based
Sanitized	Clariant	-	Triclosan

Table II: Commercial fabrics, polymers and additives

1.4 Cosmeto fibers

An example of the new, active generation of functional clothes at the centre of this innovation are some key ingredients brands from Cognis: *Skintex® and Cyclofresh™* .

1.4.1 Skintex®

Skintex® from Cognis is an innovative technology that adds extra values to clothes and tolerates several washes. Based on slow release microcapsules Skintex® uses active ingredients that have a real effect on your wellbeing.

Skintex® moisturizing works in a simple manner: the Skintex® microcapsules are embedded into the fabric. These are filled with high-grade ingredients and, over time, they are slowly released onto your skin. A protective layer of *Chitosan* – made of shell of shrimps – protects each capsule, saving its contents from warmth, drying out and the cold and giving it durability against the wear and tear of day-to-day life. At the same time, *Chitosan* has skin-caring attributes. It helps to protect the skin from dehydration and to keep a supple and velvety soft feeling. When you wear clothes fitted with Skintex®, the ingredients are released through two mechanisms. Firstly, there is the light friction you create when wearing your clothes. Secondary, the *Chitosan* layer is slowly reduced over time through your body's own enzymes – activating the ingredients and enabling them to move from the fabric onto your skin. The contents of the microcapsules include well-known skin care ingredients and aromatic fragrances. This means that as long as you are wearing your clothes, your skin will be looked after and you will feel good too. Every fabric, be it a natural or synthetic material, can be fitted with Skintex®. What's more, this can be achieved through existing manufacturing processes – so there is no need to buy additional machines to incorporate Skintex® into your fabric.

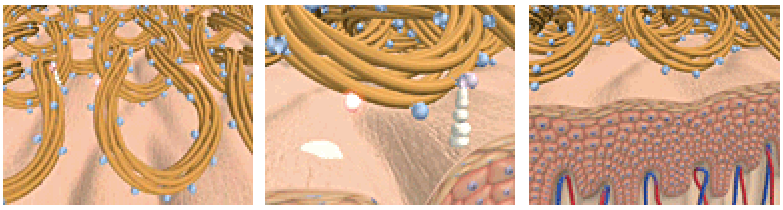


Fig.11: Skintex® microcapsules grafted on fibers

Active ingredients for Cooling

- Myritol® - Helps to protect the skin from drying out and achieves a velvety soft and supple feeling.
- Menthol - Mostly derived from peppermint oil, Menthol is well known in the food and skincare industry for its cooling and refreshing properties.

Active ingredients for Moisturizing

- Squalane - Derived from olive oil, this ingredient balances the moisture and fat content of skin.
- Vitamin E - Vitamin E protects skin from free radicals and premature ageing.
- Passion fruit Oil - A tropical fruit oil which is well known for its skin calming, relaxing and smoothing properties.

Active ingredients for Anti Heavy Legs

- Grapefruit - The oil from grapefruit peel has reviving and activating effects.
- Lemon - Lemon oil supplies freshness and vitality to tired feet.
- Menthol - Mostly derived from peppermint oil, menthol is well known in the food and skincare industry for its cooling and refreshing properties.
- Thyme - Oils from the herb thyme have antiseptic and deodorizing properties.

1.4.2 Cyclofresh™

Intelligent clothes fitted with Cyclofresh™ from Cognis recognize sweat, catch it and prevent unpleasant aromas developing within the textile. There's even a variation on Cyclofresh™ that will release fresh smells into the air as soon as you start to get sweaty and all of this is achieved through naturally based substances.

Cyclodextrins - natural, mild and efficient

Better performance and fewer additives - just what today's market demands. In fact, skin compatibility and mildness is a key issue that Cyclofresh™ tackles head on. The newest product from Cognis, Cyclofresh™ is effective on a natural basis and highly skin compatible. The most important ingredient in Cyclofresh™ is cyclodextrin, a harmless sugar molecule but with a powerful action.

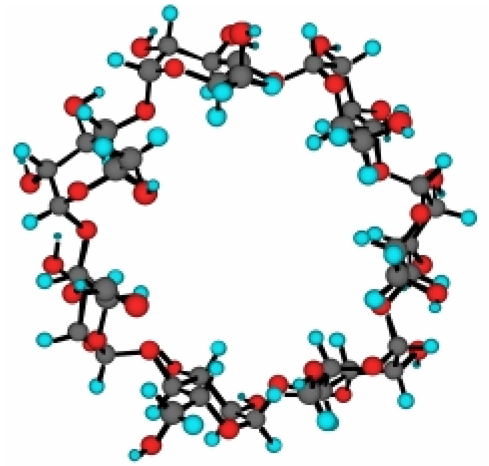


Fig.12: Cyclodextrins cage molecule

Cyclodextrin is derived from starch by adding enzymes - mainly from maize - and it has already been used for a number of years in the pharmaceutical industry. It is also valued in the cosmetics industry because of its high skin compatibility. In fact, in Germany it is now approved for use as an additive in food stuffs and can be integrated with fragrances into children's toys. Cyclofresh™ is based on this entirely renewable raw material that is readily bio-degradable.

Cyclofresh™ is an intelligent technology for garments worn next to the skin. It actually senses when it needs to become active. As soon as damp sweat reaches the garment, pleasant aromas are released which mask unpleasant bodily odours. What's more, the whole technology is based on natural raw materials such as plants which are all biodegradable.

When you sweat from sport or even just during your everyday life, Cyclofresh™ will stop bad smells from putting you in uncomfortable situations. It works by preventing the development of unpleasant body odours within the textiles in a clever way. All the sweat that gets into a fabric treated with Cyclofresh™ is absorbed and locked into the Cyclofresh™ molecules - preventing bad odors from being generated. In the next wash the sweat is quickly washed out and clothes are ready for action once more.

Technology inspired by natural laws

Cyclofresh™ battles bad smells even before they develop. This is achieved through catching the body's secretions from the skin, such as sweat, which are responsible for the development of bodily odors within the textile.

The process is based on cyclodextrins, cage sugar molecules, derived from starch, that are built like little tumblers and can absorb what are known as 'guest' molecules. Making optimal use of this storage property, Cyclofresh™ uses cyclodextrins for a dual purpose: to store fragrances to be released and to capture the organic molecules of sweat that cause unpleasant smells.

The mechanism is triggered by the moisture that develops when a person sweats. So if you wear a garment treated with Cyclofresh™ and you sweat, the cyclodextrins become active as soon as they come into contact with the moisture. The resulting chemical reaction causes the trapped fragrances to be released and, at the same time, ensures the molecules in sweat responsible for unseemly odors in the textile are locked away.

The secret lies in the properties of the sugar molecules. From the outside they are surrounded by a hydrophilic edge, but the cavity on the inside is hydrophobic and does not bind to water.

The cyclodextrins contained in Cyclofresh™ can be embedded into the fabric on a permanent basis. Even after machine washing, they remain active, every time. The number of washes cyclodextrin survives depends on the particular material being used.

The sweat particles Cyclofresh™ locks in the fabric are washed out in every machine wash. The result is that the cyclodextrins are once again ready to soak up the particles responsible for developing bad smells.

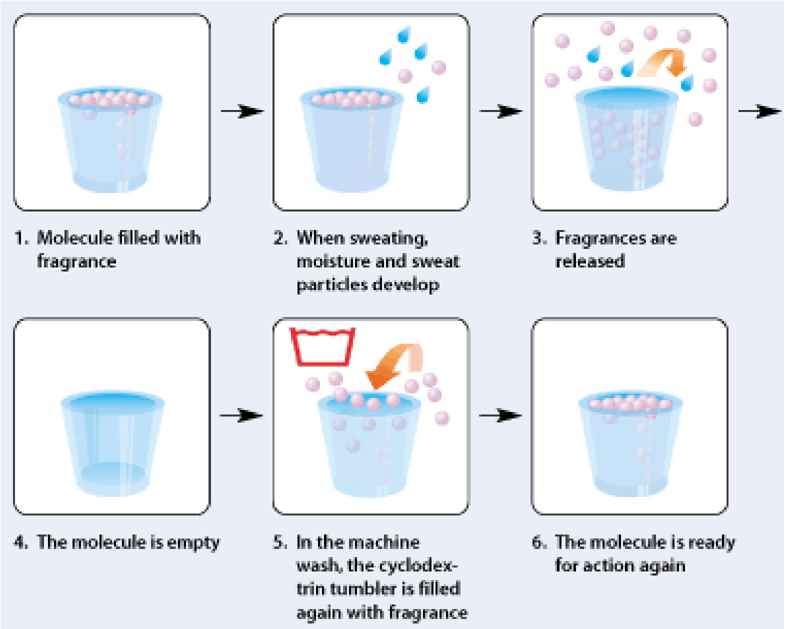


Fig.13: Cyclodextrins action mechanism

The cyclodextrins contained in Cyclofresh™ can be embedded into the fabric on a permanent basis. Even after machine washing, they remain active, every time. The number of washes cyclodextrin survives depends on the particular material being used.

The embedded fragrances are released when the garment is worn and the skin becomes moist. Even though these are eventually used up, they are replaced after washing by fragrances within your washing detergent and fabric softener. This is because cyclodextrins have a natural attraction to fragrance molecules. They very easily absorb and store fragrances from washing detergents, softeners, tumble dryer sheets and spray on perfumes. When garments are worn again, these new fragrances are gradually released and so the consumer has the opportunity to personalize the scent of their clothing.

2 - WORK OBJECTIVES

Aim of this PhD project, financed by Nylstar-Italia, is to additivate polyamide 6 fibers by means of nano and micro-particles containing a cosmetic agent to obtain products for *skin care* uses.

Three cosmetic agents were selected, among which we had to choose the best one for our applications: Myritol 312, Vitamine E and Jojoba Oil.

- Myritol 312: caprylic/capric triglyceride, is a clear, slightly yellowish, polar, odourless oil with a mean molecular weight; due to its mean spreading value, the product can be universally applied in cosmetic formulations

- Vitamin E:alpha tocopherol, a fat-soluble vitamin, protects vitamin A and essential fatty acids from oxidation in the body cells and prevents breakdown of body tissues

- Jojoba Oil: contains a 60% mixture of wax esters, including fatty acids and alcohols of chain lengths C20 to C26 (eicosenoic and docosenoic acid, eicosenol, docosenol, hexacosenol); it serves as an excellent moisturizing agent with exceptional spread and lubrication properties and leaves a rich velvety non-oily feel on the skin

2.1 Choice of the Cosmetic Agent

In order to co-extrude polyamide 6 (PA6) with the natural cosmetic agent at high process temperature (240°C) it was necessary to test thermal stability of the three components.

Thermogravimetric analysis (TGA) were performed from 25°C to 500°C under N_2 flow to point out degradation temperature when weight loss is of 5% and 50% (Fig.14); isothermal tests at 290°C under N_2 flow were performed as well to estimate total weight loss after 15 minutes heating (Fig.15). The same analysis were performed in air atmosphere (Fig.16 and Fig.17).

In table III and IV are summarized degradation temperature and weight loss in isothermal conditions of the three samples; as a result, Jojoba Oil appears to be extraordinarily stable at extreme temperatures, without displaying degradation in general composition and carbon chain length.

In addition to thermal stability and of more importance to the cosmetic chemist, jojoba also has unsurpassed oxidative stability.

Protection against free radical excesses can come from anti-oxidants that interrupt the per-oxidation or from the use of more stable materials that are resistant to oxidation, like Jojoba Oil [6].

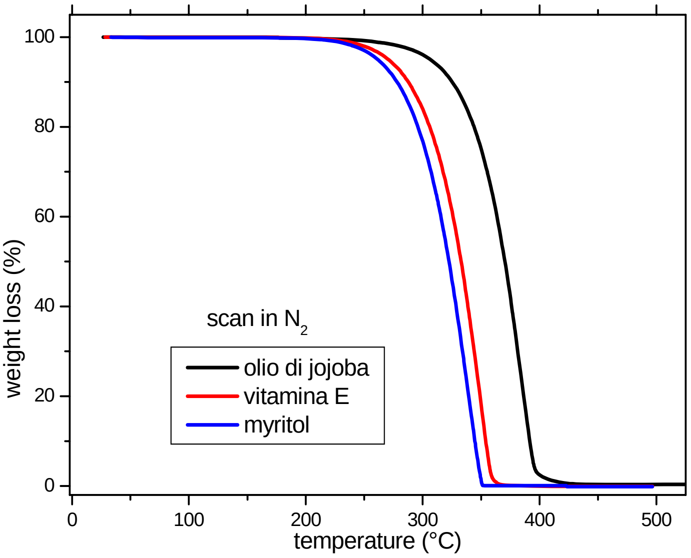


Fig.14: TGA scan in N_2

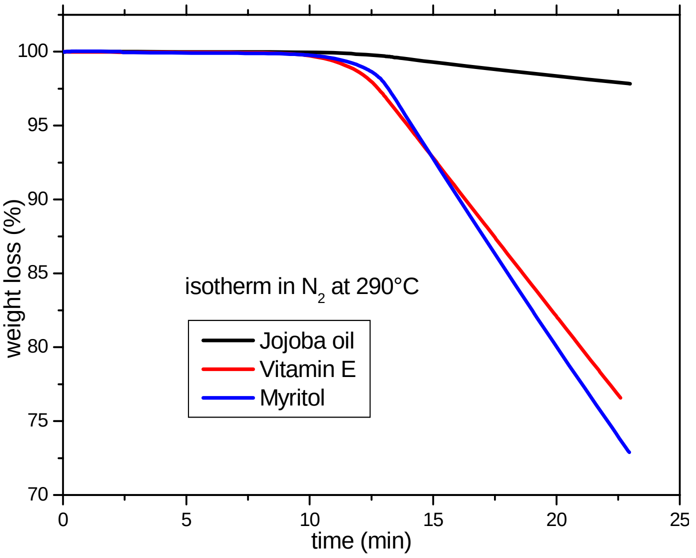


Fig.15: TGA isothermal in N_2

Sample in N_2	**Thermal degradation temperature** **weight loss 5%**	 **weight loss 50%**	**Weight loss (%) after 15 min (isotherm at 290°C)**
Jojoba Oil	**327°C**	**393°C**	**1%**
Vitamin E	**288°C**	**353°C**	**7%**
Myritol	**261°C**	**322°C**	**7%**

Table III: Comparison of thermal properties of cosmetic agents in N_2 atmosphere

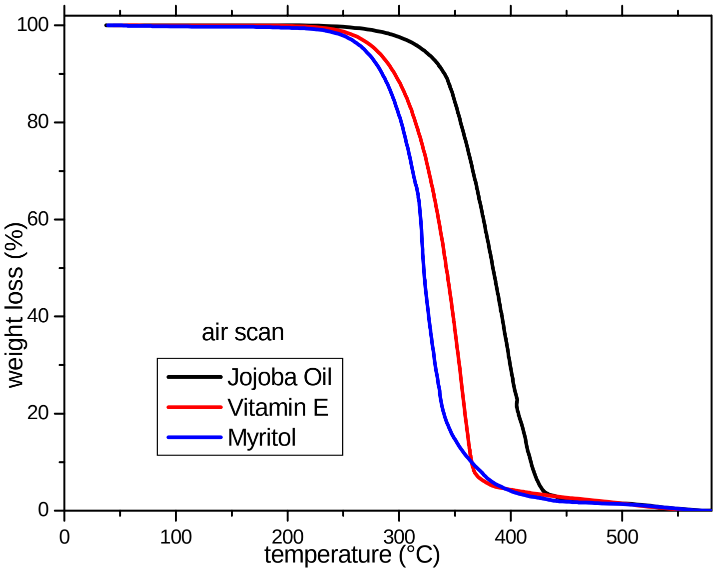


Fig.16: TGA scan in air

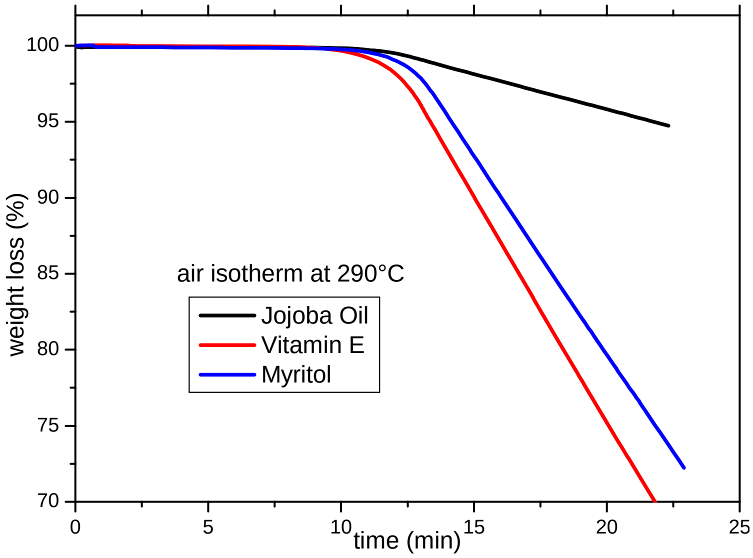


Fig.17: TGA isothermal in air

Sample in air	**Thermal degradation temperature**		**Weight loss (%) after 15 min (isotherm at 290°C)**
	weight loss 5%	**weight loss 50%**	
Jojoba Oil	**320°C**	**384°C**	**2%**
Vitamin E	**279°C**	**342°C**	**10%**
Myritol	**267°C**	**322°C**	**7%**

Table IV: Comparison of thermal properties of cosmetic agents in air atmosphere

2.2 Description of Jojoba Oil characteristics

Jojoba is one of the finest cosmetic ingredients in the world. Its excellent inherent emolliency, moisturization and oxidative stability properties rank it as one of the top cosmetic lipid materials in use today [6].

Jojoba is not a triglyceride oil. In fact it is a complex mixture of natural long-chained esters with many functional cosmetic properties that are far superior to triglycerides. Over 97% of jojoba is composed of an array of liquid wax esters, with a combination of mixed tocopherols, free sterols and other unsaponifiable material making up the balance.

All triglyceride fats and oils are easily hydrolized and oxidized for internal food metabolism. Jojoba, like other wax esters in nature, resists hydrolysis and oxidation for more effective, non-occlusive, moisture control and for photo-protection on the external surfaces of skin, hair, eyes and plant leaves.

Natural Jojoba is sourced from the seeds of *Simmondsia Chinensis*, which is a woody evergreen, desert shrub; jojoba seeds are dark, reddish-brown colour and about 1 to 1.5 centimeters long.

Approximately 50% of the weight of the seed is a mixture of long-chain liquid esters which is typically extracted by mechanical pressing.

Fig.17: Jojoba Oil

2.2.1 Physical and chemical properties of natural Jojoba

Freezing point, °C	10.0-7.0
Melting point, °C	6.8-7.0
Heat of fusion by DSC, J/g	21
Flash point, °C	295
Iodine value	82
Saponification value	92
Acid value	<2
Peroxide value	<1.0
Moisture	<300 ppm
Viscosity index	232

Table V: Physical and chemical properties of Jojoba Oil

Acid value is the most frequently determined property of Natural Jojoba. Total acid value of Jojoba is typically in the range of 0.2-0.5 (mg of KOH to neutralize acid in 1 gram of sample) and it can be reduced to less than 0.2 with refining methods.

The moisture content of Natural Jojoba is typically less than 300ppm. It typically contains between 50 and 100ppm of phosphorous in the form of hydratable and non-hydratable phospholipids. The phospholipids are considered a positive component in many cosmetic applications, but too high a level may cause turbidity and cloudiness in the jojoba.

The peroxide value of Natural Jojoba is used as a measure of its relative oxidation state at a single point time. Typically, Jojoba's peroxide value at time of packaging is less than 0.8 milliequivalents of peroxide per kg of sample.

Iodine value is a measure of unsaturation (number of double bonds). Natural Jojoba is almost exclusively composed of dienes making its iodine similar to that of oleic acid. Iodine values are typically in the range between 78 and 90.

The two most dominant factors inherent in natural lipid materials that affect their oxidative stability are molecular configuration and the presence of anti-oxidants.

In part, Jojoba's superior stability is attributed to the resonance effect along the molecule's chain. This enhances the resistance of the double bonds to oxidation. The double bonds are widely separated and are more or less equidistant from the central ester linkage. These bonds are considered "isolated" and their shared electrons are well protected against oxidation.

$$\mathbf{CH_3\text{-}(CH_2)_7\text{-}CH{=}CH\text{-}(CH_2)_m\text{-}COO\text{-}(CH_2)_n\text{-}CH{=}CH\text{-}(CH_2)_7\text{-}CH_3}$$
$$\mathbf{m=7\text{-}12;\ n=8\text{-}13}$$

Natural Jojoba, as well as, fats and oils from plants, all contain tocopherols which are known to act as free radical scavengers, like vitamin E and its isomers.

Free radicals have many damaging effects that contribute to premature aging and cancerous changes of skin. One effect is strong cross-linkage of collagene to cause thin inflexible wrinkled skin. Also, free radicals break down of hyaluronic acid diminishes the skin's water holding capacity.

2.2.2 Jojoba in skin care cosmetics

Many of the most effective ingredients for skin care formulations are those with chemical composition and physical properties similar to the skin's own surface layers. Since jojoba is completely miscible with sebum, when it is applied to the skin, a very thin, non greasy lipoid layer of Jojoba and sebum forms. This partially porous layer provides exceptional trans-epidermal respiration and moisture control. Unlike greasy occlusive materials such as petrolatum, mineral oils and some lanolin products, Jojoba provides an absolutely non-tacky and non-greasy, dry emolliency. At the same time Jojoba significantly reduces trans-epidermal water loss without totally blocking transpiration of gases and water vapour. This function is enhanced by the linking at Jojoba's cis-configuration that helps avoid tight packaging of hydrocarbon chains. Natural Jojoba serves as an excellent moisturizing agent with exceptional spread and lubricity and leaves a rich velvety non-oily feel on the skin while retarding water loss and enhancing the flexibility and suppleness of the skin.

Through continued research work, there is growing evidence that Jojoba quickly permeates the skin and exhibits softening ability from within. Pharmacodynamic studies of the penetrability of lipids have shown that there are six general factors that influence the rate of permeation into the stratum corneum:

1) Viscosity- low viscosity oils poses higher rates than high viscosity oils. Natural Jojoba has a low viscosity
2) Degree of un-saturation- unsaturated oils exhibit higher rates of permeation

3) Saponification value- the lower saponification value, the higher the rate. Natural Jojoba has a low saponification number
4) Carbon chain length- the shorter the chain length, the higher the rate
5) Lecithin content- the lesser the amount of lecithin in an oil, the greater the rate of penetration. Jojoba has no lecithin
6) Molecular configuration- straight chain and branched esters penetrate better than do triglyceride oils

Current use of Jojoba

- Hair care: shampoos, hair conditioners, hair oils, stick pomades, hair creams, hair sprays
- Skin care: facial moisturizers, facial cleaners, eye make-up remover, eye treatments, body moisturizers, hand creams, shaving lotions and after shave creams
- Scrubs and masks: foot care products, massage oils
- Sun care: after-sun creams and lotions, sun protection products, lip balm, self-tanning products
- Makeup products: cream foundations, lipsticks, eyeliner, eye-shadow/blusher
- Bath oils, soaps, baby care

MICROENCAPSULATION

“Small is better” would be an appropriate slogan for the many people studying microencapsulation, a process in which tiny particles or droplets are surrounded by a coating to give small capsules with many useful properties. The material inside the microcapsule is referred to as the core, internal phase or fill, whereas the wall is sometimes called a shell, coating or membrane. Most microcapsules have diameters of few micrometres.

The reasons for microencapsulation are countless. In some cases, the core must be separeted from its surroudings, as in isolating vitamins from the deteriorating effects of oxygen, retarding evaporation of a volatile core, improving the handling properties of a sticky material, or isolating a reactive core from chemical attack. In other cases the objective is not to separate the core completely but to control the rate at which it leaves the microcapsules as in the controlled release of drugs or pesticides [7]. Manufacturing costs are based on coating material, solvent, equipment and labor. Coating-material prices vary greatly, and as a rule, the cheapest acceptable material is used. Coatings that can be applied without solvent or water are preferred. Enviromental and safety regulations greatly increase the cost of process that use volatile organic solvents.

A classification of encapsulation processes is given below:

Category I

Liquid suspending media
Water-in-oil (W/O)   Oil-in-water (O/W)
Complex coacervation
Polymer-polymer incompatibility
Interfacial and in situ polymerization
Desolvation
Solvent evaporation from emulsion
Gelation
Pressure extrusion

Category II

Gas suspending media
Solvent Solvent-free
Spray drying and congealing
Fluidized-bed and Wurster process
Coextrusion
Vacuum coating
Gelation
Electrostatic deposition

In *Category-I*, a liquid is used as the suspending medium throughout. Emulsification or dispersion of two or more immiscible phases is a key step in these processes. In *Category-II*, a gas is the suspending medium in which the capsules are formed, and atomization of a liquid phase is the key step.

Some authors refer to *Category-I* processes as chemical processes and *Category-II* processes as physical or mechanical processes. According to this classification, processes such as solvent evaporation, gelation and polymer-polymer incompatibility are termed chemical processes even if no chemical reaction occurs.

A spray drying process in which reactive components are polymerized during the drying step to form microcapsules would be called a physical process, even though a chemical reaction clearly occurs during capsule formation.

Many *Category-I* and *Category-II* processes are similar. For example, solvent evaporation is a key step in spray-dry encapsulation and in processes involving solvent evaporation from an emulsion. The only difference is that evaporation in the former case occurs directly from the liquid phase to the gas phase. In the latter case, evaporation involves transfer of a volatile liquid to an immiscible liquid from which it is subsequently removed. Another example is gelation encapsulation. The droplets, which are gelled to form capsules, can be formed by emulsification or atomization [8].

(I)-1 APPLICATION OF MICROCAPSULES IN TEXTILES

The move by move developed consumer demands for textiles with new characteristics and added value into medical and technical fields has encouraged the industry to use microencapsulation processes as a means of imparting finishes and properties to fabrics which were not possible or cost-effective using other technology.

Textile manufacturers are demonstrating increasing interest in the application of durable fragrances to textile as well as skin softeners; other potential applications include, foe axample, insect repellents, dyes, antimicrobials, phase change materials.

(I)-1.1 Phase-change materials

Microencapsulation technology was utilised in the early 1980s by the US National Aeronautics and Space Administration (NASA) with the aim of managing the thermal barrier properties of garments, in particular for use in space suits. They encapsulated phase-change materials (PCMs) (e.g.nonadecane) with the hope of reducing the impact of extreme variations in temperature encountered by astronauts during their missions in space. Ultimately the technology was not taken up within the space programme. However, the potential was recognised and after further development the work was licensed by the inventor. Outlast Technologies has exploited the technology in textile fibers and fabric coatings [Fig.(**I)-**1].

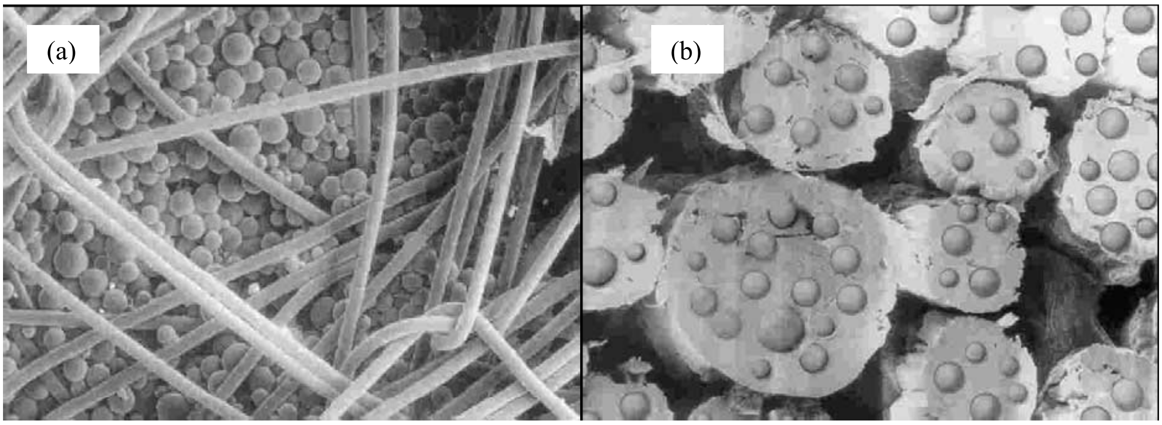


Fig.(**I**)- 1: (a) PCM microcapsules coated on the surface of fabric and (b) embedded within fibers

PCM capsules are now applied to all manner of materials [9,10], particularly outdoor wear (parkas, vests, thermals, snowsuits and trousers) and in the house in blankets, duvets, mattresses and pillowcases. As well as being designed to combat cold, textiles containing

PCMs also helps to combat overheating, so overall the effect can be described as thermoregulation.

The microcapsules have walls less than 1 μm thick and are typically 20–40 μm in diameter, with a PCM loading of 80–85%. The small capsule size provides a relatively large surface area for heat transfer. Thus the rate at which the PCM reacts to an external temperature changes is very rapid [11].

The late injection technology processes allow the in-fiber incorporation of Outlast microcapsules, loading the fiber with 5–10% of microcapsules. In this way the PCM is permanently locked within the fiber; there is no change necessary in subsequent fiber processing (spinning, knitting, dyeing, etc.) and the fiber exhibits its normal properties of drape, softness and strength.

(I)-1.2 Fragrance finishes

The addition of fragrances to textiles has been carried out for many years in the form of fabric conditioners in the wash and during tumble-drying to impart a fresh aroma.

However, no matter the quality of the technology used, the effect is relatively short-lived. Numerous attempts have been made at adding fragrances directly to fiber and fabrics but all fail to survive one or two wash cycles. Only through microencapsulation are fragrances able to remain on a garment during a significant part of its lifetime. Microencapsulation of essential oil flavours has led to many novelty applications, particularly for children's garments, but it has also allowed utilization at home and in the work place to the beneficial effects of aromatherapy.

In recent years several companies have gained much experience in the provision of microcapsules for textiles. The majority of the work has been in microencapsulated "scratch and sniff" T-shirts and in women's hosiery: it is claimed that the shirts survive washing (typically 8–20 cycles), depending on the active agent encapsulated, and the hosiery up to 10 washes. The capsules also survive drying in conventional tumble-dryers. Well-established techniques such as in situ and interfacial polymerisation are used to manufacture the capsules.

Celessence International of Hatch End, Middlesex, has been investigating and manufacturing microencapsulated fragrant-smelling compounds for a number of years.

In the early days the applications included paper handkerchiefs, gift wrapping, ornaments, greeting cards, advertising brochures, books, cartons and labels. The company has now turned its attention to textiles, using its basic technology of encapsulating fragrances in gelatin or synthetic capsules, which protects the contents from evaporation, oxidization and contamination. The capsules range in size from 1 to 20 µm.

In practice, the smaller the capsules the greater the covering of the product and the longer the fragrance will last, as it takes longer for the capsules to be ruptured by physical pressure.

Larger capsules release more fragrance when ruptured. Traditionally the “scratch and sniff” application of microcapsules used screen-printing, but now litho and web printing techniques have been adopted, initially in paper products and now in textiles.

Celessence TXT capsule systems comprise aqueous dispersions of encapsulates, which can be applied by pad, exhaustion or hydroextraction techniques to a wide variety of textile substrates. Durability to washing and handle may be further improved by incorporating suitable formaldehyde free binders and softeners. All applied products are blended from natural and synthetic materials that conform to legislative guidelines for cosmetic products [12]. For screen-printed application the encapsulates are simply mixed with water-based, solvent-free inks or binders. The capsule printing must be the last step to avoid damage of microcapsules walls, once printed, the fabric is then cured as with standard textile inks to achieve a good bond to the fibers.

The Matsui Shikiso Chemical Co of Kyoto has also developed a way of fixing aroma compounds to fabric using microcapsules. The fabric is first treated with a nitrogenous cationic compound and the microcapsule wall is manufactured to adhere to this layer. The capsules can range in size from 0.1 to 100 µm and are made using interfacial or in situ polymerisation techniques.

In Korea the Eldorado International Co of Seoul and a number of other companies offer new fabrics that emit the natural aroma of flowers, fruit, herbs and perfumes. Emulsified microcapsules containing a natural aroma or essential oil are attached to the fabric after dyeing. The capsules break on movement of the wearer, releasing the aroma.

In general the capsules continue to emit aroma for up to 25 wash cycles and on the shelf the finish will remain ready for action for between 3 and 5 years. So far the company has applied the technology to curtains, sofas, cushions and sheets, as well as some toys. Silk ties have also been produced that release fragrant oils during normal wear, and if rubbed they produce a large burst of fragrance.

Also in Korea, workers at Pusan National University were able to prepare microcapsules using melamine-formaldehyde systems containing fragrant oil [13]. When attached to cotton these capsules were able to survive over 15 wash cycles. Scanning electron microscopy indicated that the smaller of the capsules in the range survived more effectively after laundering. This phenomenon may simply be due to the relative thickness of a capsule within an adhesive film binding the capsules to the textile substrate [Fig.(**I**)-2].

Euracli, a company based in Chasse-sur-Rhone in France, has produced microcapsules containing perfumes or cosmetic moisturisers that can be padded, coated or sprayed onto a textile and held in place using an acrylic or polyurethane binder.

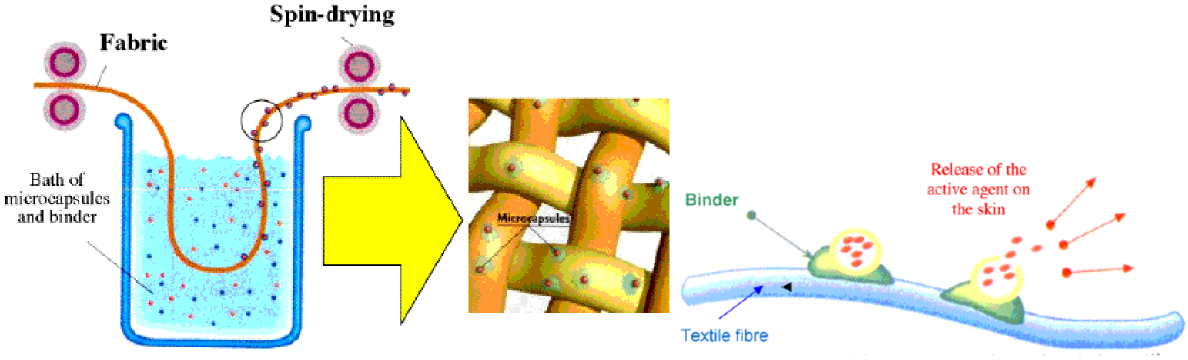


Fig.(**I**)-2 : example of microcapsules application on fabrics

(I)-1.3 Polychromic and thermochromic microcapsules

Colour-changing technology has been for a number of years generally applied to stress testers, forehead thermometers and battery testers. New applications are now beginning to be seen in textiles, such as product labelling, and medical and security flexible displays.

In addition there is continued interest in novelty textiles for purposes such as swimwear and T-shirts. There are two major types of colour-changing systems: thermochromatic which alter colour in response to temperature, and photochromatic which alter colour in response to UV light. Both forms of colour-change material are produced in an encapsulated form as microencapsulation helps to protect these sensitive chemicals from the external environment. Today manufacturers are able to make dyes that change colour at specific temperatures for a given application, e.g. colour changes can be initiated from the heat generated in response to human contact.

Physico-chemical and chemical processes such as coacervation and interfacial polymerisation have been used to microencapsulate photochromic and thermo-chromic systems. However, to obtain satisfactory shelf-life and durability on textiles, interfacial polymerisation techniques are nearly always adopted. The most widely used system for microencapsulation of thermochromic and photochromic inks involves urea or melamineformaldehyde systems [14].

(I)-1.4 Microencapsulation: the future

The ideal feature for most textile applications using microcapsules would be a system that is easy to apply, does not effect the existing textile properties and has a shelf-life on a garment that allows normal fabric-care processes to take place.

Currently, although capsules can survive 25–30 wash cycles, conventional ironing and other heat-input processes such as tumble-drying can cause a dramatic reduction in the desired effect. The microencapsulation industry must take more notice of the possibilities within the textile industry and specifically design microcapsules that overcome these problems.

For the future, the consumers desire that novel and unique effects will always be present. But more importantly, in an ever-increasing desire for convenience, the consumer will require that fabric properties are inherent in the garment, e.g. fresh odour and softness.

Consumers will expect these properties to last the lifetime of the garment, and not involve routine intervention in the form of the never-ending addition of washing aids and fabric conditioners. Microencapsulation may deliver these long-term goals.

The desire for a healthier and more productive lifestyle will continue to generate a market for textiles that promote “well-being”. Textiles that “interact” with the consumer, reducing stress, promoting comfort and relaxation, are possible through active delivery from microcapsules. In the last decade the textile industries have concentrated on developing performance fabrics with added value for sports and outdoor application, as well as novel medical textiles. Microencapsulation can play a part in this continued development, for example by allowing sensing chemicals to be attached to sports clothing and medical products; these will be able to warn of damage or hazard to the wearer. Systems can also be developed that deliver measured dosages of chemicals to combat muscle pain or other more serious injuries.

The potential applications of microencapsulation in textiles are as wide as the imagination of textile designers and manufacturers. Early success for some companies in producing microencapsulated finishes for textiles have come about from collaboration and adaptation of technology from other industrial sectors [15].

(I)-2 INTERFACIAL POLYMERIZATION

(I)-2.1 General background

There are several microencapsulation methods, however interfacial polymerization is often favoured over other techniques due to its simplicity, ability to control the microcapsule properties and the resulting membrane strength.

The basis of this method is the classical Schotten-Baumann reaction between an acid chloride and a compound containing an active hydrogen atom, such as an amine or alcohol. Polyesters, polyamide, polyurea, polyurethane, or polycarbonates may be obtained.

For polyamides, interfacial polycondensation is a bimolecular nucleophilic substitution (SN2) carried on in a biphasic medium: aqueous phase containing the hydrophilic monomer (a diamine-DA) and organic phase containing the hydrophobic monomer (an acid dichloride-DC). The volume ratio dispersed phase/ continuous phase being usually between 1/5 and 1/20 [16], the reaction is fast and can proceed at room temperature.

$$n\,(H_2N\text{-}R\text{-}NH_2) + n\,(ClO\text{-}R'\text{-}OCl) \rightarrow H(NH\text{-}R\text{-}NH\text{-}CO\text{-}R'\text{-}CO)_nCl + (2n-1)\,HCl$$

Microencapsulation by interfacial polycondensation can be carried out in two systems:

1) in direct emulsion (oil in water-O/W): organic phase dispersed in water
2) in inverted emulsion (water in oil-W/O): aqueous phase dispersed in the organic phase

If oil in water polycondensation reaction must be carried on, multifunctional acid chlorides are dissolved in the organic phase. The resulting solution is emulsified in an aqueous suspending medium. A polyfunctional amine is added to the aqueous phase and diffuses to the organic phase-water interface, where it reacts with acid chloride dissolved in the organic solvent [Fig.(**I**)-3].

Emulsion formation and stabilization is facilitated by adding little amount of a polymeric emulsifier, eg, partially hydrolized (88%) poly(vinyl alcohol) and using an efficient stirring system. The stabilizer play two important roles:

1) it reduces interfacial tension between the two phases, assuring the dispersed phase stabilization at droplets level
2) it creates an electrostatic (or steric) barrier at the interface, preventing droplets breaking or coalescence to obtain a narrower size distribution

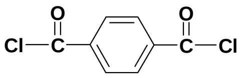
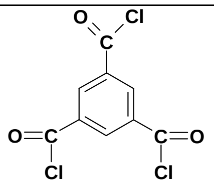
The emulsifier choice depends on the emulsion to prepare: it’s better to use an hydrophilic surfactant for direct emulsion, while a lipophilic surfactant is good for an inverted emulsion.

The use of a strong alkali (NaOH or $NaHCO_3$) is necessary as well since it diffuses easily toward the polycondensation site to neutralize the HCl produced; in this way, diamine protonation and reduction of its reactivity is avoided [17].

Acid chlorides employed include sebacoyl chloride [SBC], adipoyl chloride [ADP] and terephthaloyl dichloride [TDC]. These acid chlorides hydrolyze slowly at solvent-water interfaces, so solvent solutions of them can be emulsified in an aqueous phase without loss functionality.

After emulsification is complete, amines such as diethylenetriamine [DETA] and hexamethylenediamine (HMDA) are added to the aqueous phase.

The reaction produces the polymer capsule wall. Under right conditions, thin flexible walls form rapidly at the interface. A cross linking agent can be used to obtain microcapsule with good mechanical properties: a trichloride in the organic phase (trimesoyl chloride or benzentricarbonil choride [BTC]) or a triamine in the aqueous phase (trisaminoethylenamine [TAEA]).

HMDA	$NH_2\text{-}(CH_2)_6\text{-}NH_2$
DETA	$NH_2\text{-}(CH_2)_2\text{-}NH\text{-}(CH_2)_2\text{-}NH_2$
TAEA	$NH\text{-}(CH\text{-}CH\text{-}NH_2)_3$
SBC	$ClOC\text{-}(CH_2)_8\text{-}COCl$
ADP	$ClOC\text{-}(CH_2)_4\text{-}COCl$
TDC	
BTC	

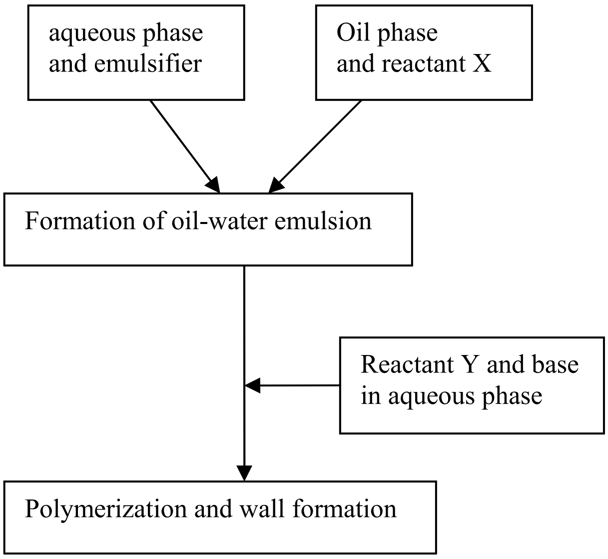


Fig.(**I**)-3: Scheme of interfacial oil in water polymerization reaction

In principle, water could be encapsulated by the same process if a water in oil emulsion was used. This technology is not designed for solids, although it can be used to encapsulate solids dispersed in a liquid. Problems with this process involve reaction of the active agent with the reagents used to form the capsule wall, as well as limitations caused by solubility behavior of the active agent.

The properties of microcapsules obtained by interfacial polymerization may be controlled by a number of factors: the chemical nature of monomer(s) and the conditions under which the polycondensation reaction is performed determine the chemical composition and the porosity of the microcapsule membrane and the degree of polymer cross-linking. The microcapsule size distribution can also be controlled by appropriate modifications of the process conditions (surfactant type and concentration, stirring rate, etc.) [18].

(I)-2.1.1 Effect of stirring rate

The dispersion grade obtained by stirring the two immiscible phases is determined by droplets breaking and droplets coalescence. It has been demonstrated that increasing stirring rate, it can be possible to obtain smaller mean diameters and narrower size distribution [19,20] .

(I)-2.1.2 Effect of emulsifier concentration

The emulsifier agent influences not only microcapsules stability and dispersion but also their size. In general, for a given stirring rate, mean diameter of microcapsules decreases when emulsifier concentration increases and size distribution curve becomes narrower.

(I)-2.1.3 Effect of monomers dilution

Monomers dilution enlarges size distribution curve and increases mean diameter. In fact, monomers fraction which actually react influences the shape of microcapsules size distribution curve: higher this fraction, narrower will be the curve since it will be bigger quantity of formed polymer at the microcapsules interface. Microcapsules will be more resistant and so less involved in coalescence.

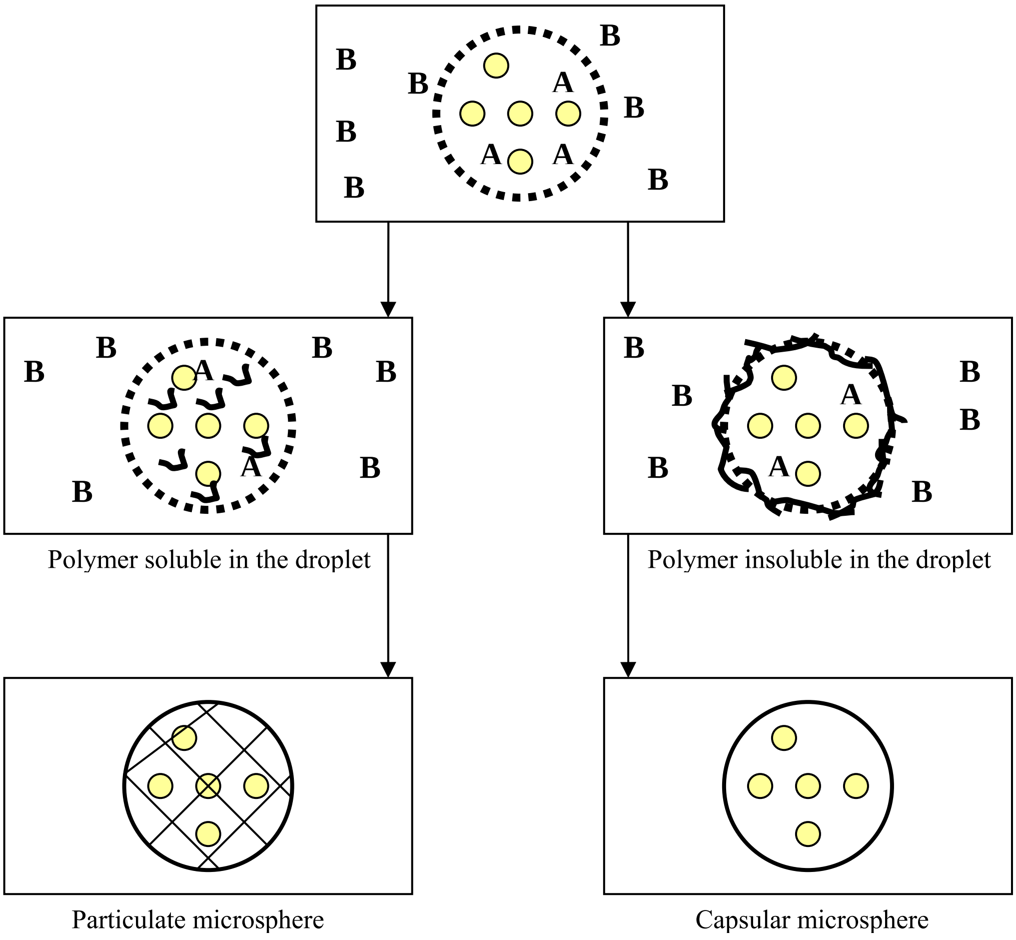
(I)-2.1.4 Temperature effect

In general, microcapsules size decreases if temperature increases and polycondensation reaction is favoured as well, since longer polymer chains are formed.

(I)-2.2 Mechanism of particle/capsule formation

In a two phase interfacial polycondensation process, the initially formed droplets can be appropriately described as “moulds” or “templates” for the formation of final microspheres/microcapsules. The manner in which the particles are formed and their final morphology is determined largely by the solubility of the polycondensate molecules in the droplet phase. Two extreme situations are considered below:

1) the oligomer molecules formed during the early stages of the polycondensation process are highly soluble in the droplets. Thus, irrespective of where they are formed, the oligomers become trapped (and grow larger) inside the droplets. Under these conditions, the particles become gradually solvent swollen microspheres (or monolithic microcapsules) with an homogeneous matrix structure, and hence the term particle-forming interfacial polycondensation.
2) the initially-formed oligomer molecules are highly insoluble in the droplet phase. Thus, the oligomer grow in the initial loci of their formation until they become insoluble. At this point they collapse and precipitate at the interface. The precipitated oligomer/polymer chains are deposited on the droplets surface, and thus form a primary membrane around the droplets. Further polycondensation of the monomers (usually on one side) increases the thickness of the membrane and produces the final capsule wall. Preparation of nylon microcapsules provides the most typical example of capsule-forming interfacial polycondensation.



Polymer soluble in the droplet

Polymer insoluble in the droplet

Particulate microsphere

Capsular microsphere

Fig.**(I)**-4: Idealized mechanism of particle capsule formation by interfacial polycondensation.
A and B complementary monomers, ○ the core material to be encapsulated.

Particles formed under these conditions are slightly or highly porous, depending on the degree of polymer precipitation inside the droplets/particles.

The mechanism of capsule formation proceeds in three consecutive stages: (1) an initial period of polycondensation, (2) the formation of a primary membrane around the droplets, ad (3) subsequent growth of this membrane to the final capsule shell or wall.

All three steps are controlled by a number of interrelated parameters, such:

- concentration and partition coefficients of the monomers,
- volume ratio of the two phases,

- type and concentration of additives, e.g. stabilizer, buffer, the core substance to be encapsulated
- type of stirrer and rate of stirring
- rate of polymerization and polymer molecular weights
- temperature of the polymerization mixture
- chemical structure and cristallinity of the polymer
- solvency of both phases for the polymer

Among these parameters, partition coefficients of the monomers in the two phase system determine the initial loci of polycondensation.

(I)-2.3 Membrane formation

The site of membrane growth is determined by respective values of partition coefficients of the monomers in the two solvent used. The polycondensation reaction begins where the product of the concentrations of the monomers has the highest value. For polyamide, the polycondensation site is the organic phase. In fact, the dichloride solubility in the aqueous phase is negligible while the diamine is partitioned between the two phases, mainly in the aqueous phase.

The process of polycondensate precipitation and the formation of primary membranes around the droplets is controlled largely by the solvency (swelling power) of the medium, i.e. both the aqueous and the organic phase. The higher the solvency of the medium for the polymer, the ticker and less porous the membrane is expected to be.

Another factor likely to influence the morphology of the membrane around the droplets is the rate of precipitation of the polymer chains during the initial polycondensation period. In general, the higher the rate of polymer precipitation, the less uniform (the more porous, the more permeable) the membrane. Polymer precipitation during the initial polycondensation period is proportional to the rate of polycondensation. It is, therefore, basically possible to control the morphology (i. e. permeability) of the membrane by factors which affect the rate of polycondensation such as monomer concentration and the rate of the addition of DA to the suspension mixture.

In the case of direct emulsion, thickness depends tightly by the DC quantity in the droplet [17] (which determines the maximum quantity of polyamide that can be produced), on the other hand for an inverted emulsion thickness is proportional to the DA quantity in the aqueous phase. Actually, just neuter molecules of DA can pass through the organic phase.

(I)-2.3.1 Co-effects of organic solvent and DA partition coefficient on thickness

The partition coefficient K of neuter DA changes with DA solubility in the organic solvent and its nature.

For example, if n increases for a linear DA (NH_2-$(CH_2)_n$-NH_2), K decreases [21]. Thickness is therefore a compromise between DA chemical nature (its neuter fraction) and its partition coefficient. It is worth noting that K changes not only with the organic solvent, but also depends on the emulsifier nature and concentration.

(I)-2.3.2 Temperature effect on thickness

Thickness is strongly influenced [21] by temperature since most of constants are temperature depending. If we take into account just the effect of the temperature on acid-base DA dissociation (k_a), this aspect affects DA neuter fraction and subsequently final thickness. As well, temperature affects the DA diffusion across the membrane or the partition coefficient.

It is worth noting that the membrane thickness is strongly related to polymer swellability operated by each phase, rather than by maturation time [16].

(I)-2.4 Membrane growth and wall formation

Two steps of growth are individuated [16]:

- instantaneous formation of a primary thin and dense membrane around the droplets
- membrane grows till to obtain the final microcapsule shell characterized by a second porous layer forming the 90% of global thickness [Fig.(**I**)-5]

Following the formation of a primary membrane around the droplets, the two complementary monomers are separated from each other by the membrane. From this moment on, the

polycondensation reaction can proceed only if the membrane is permeable to at least one monomers. In other words, one of the monomers must cross the membrane from one side to the other. The passage of HMDA across the nylon membrane, is probably mediated by reversible hydrogen bonding between the diamine and the amide groups on the film. The permeability of the films for the respective monomers decreases with increasing film thickness. This also means that in most capsule-forming interfacial polycondensation procedures, the final capsule shell is in effect the primary membrane formed as a result of polymer precipitation.

Fig.(**I**)-5 shows that the process does actually involve the formation of a relatively thin film (primary membrane) at first, and that this primary membrane is formed on the organic side of the interface, involving oligomers formation growing up on the organic side till they precipitate and forming an high molecular weight layer.

A plausible explanation for the alveolus layer observed could be as follows: when the external layer begins to grow, small droplets of aqueous phase appear on the organic side of the membrane and coalescent till causing polymer precipitation at the interface water/oil of these droplets which stops coalescence phenomenon.

Growing rate of polymeric chains is equal to the diffusion rate of the diamine toward the reaction site. Growing rate is inversely proportional to membrane thickness: when thickness grows with maturation time, chains take more time to build up and precipitation time is longer.

For this reason, droplets need more and more time to coalescence before polymer precipitation at the interface, involving alveolus creation or pores, which are larger at higher distance from the primary layer (following membrane section).

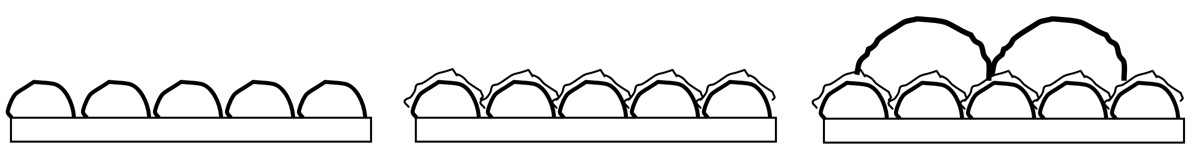


Fig.(**I**)-5: Nylon primary membrane formation and subsequent growth on the organic side

It is, therefore, reasonable to speculate that the thickness of the final capsule wall maybe largely related to the swelling power of the suspension mixture for the polymer, rather than the time that microcapsules remain in the polymerization mixture following the formation of the membrane [16].

(I)-3 EXPERIMENTAL

We prepared microcapsules of a series of polyamides from aliphatic and aromatic chlorides with a series of polyamines, and investigated their external morphology which might influences permeabilities. Linear aliphatic polyamides are permeable to low molecular weight materials, and their physical properties deteriorate above relatively low temperatures (~150°C); polyamides from aromatic chlorides with aromatic amines are very intractable, we therefore used only one aromatic monomer component and found chlorides convenient for this purpose. The yield and quality of the membrane of the microcapsules obtained by interfacial polymerization may be controlled by a number of factors [22]. Specifically, in our system the chemical natures of the chloride and amine components and of the solvent, and the conditions under which the polycondensation reaction is performed, will determine the nature and the molecular weight of the polymer as well as its degree of cross-linking and crystallinity, and whether or not the membrane is porous.

Experimental parameters which are likely to be of importance are the concentrations of the monomers, the temperature, the rate of mixing and the reaction time. In connection with the effective concentrations of the monomers during formation of microcapsules by interfacial polymerization, there is much evidence in literature that after the formation of the “pre-membrane” the polymerization proceeds via diffusion of the amine through the membrane, and reaction with the chloride at the inner face of the microcapsule wall [23].

The effective amine concentration at the reaction site will then be very much less than in the bulk aqueous solution.

The time required for maturation we consider to be determined by the diffusion of the amine from the bulk aqueous solution through the membrane to the organic phase. The rate of this diffusion, which is low compared with the rate of reaction of the monomers in solution, will be determined by the permeability of the membrane, which in turn depends on factors such as the molecular weight of the polymer and the extent of its cross-linking.

The results suggest that throughout the membranes of linear polymers the diffusion of amine is of uniform rate. For the cross-linked polymers, however, there appear to be channels through which diffusion is more rapid than through the bulk. These channels could be void or contain a high portion of polymer which is not cross-linked.

In general, membranes of linear polymers are quite porous, while increasing the cross-linking results in more non-porous membranes [23].

(I)-3.1 Materials

The following materials were employed: 1,6-hexamethylenediamine [HMDA (Aldrich)], diethylenetriamine [DETA (Aldrich)], terephthaloyl dichloride [TDC (Aldrich)], sebacoyl dichloride [SBC (Fluka)], adipoyl dichloride [ADP (Aldrich)].

Trisaminoethylamine [TAEA (Aldrich)], 1,3,5-benzentricarbonyl chloride [BTC (Aldrich)] were used as tri-functional cross-linking agents, respectively in aqueous and organic phase.

Polyvinyl acetate with an average molecular weight of 90 000 and a degree of hydrolysis of 88 mol % [Mowiol® 18-88 (Hoechst)] was used as stabilizer.

De-ionized water, containing Tween® 20 [50gL^{-1} (Aldrich)] was used to slow down the polycondensation reaction.

Jojoba Oil [JOJ (MCY products)] was of commercial grade and consisted of a complex mixture of liquid wax linear esters. It has a density of approximately 0.863gcm^{-3} and a viscosity of 33cP at 25°C.

Sodium hydroxide [NaOH (Aldrich)] and sodium sulphate [Na_2SO_4 (Aldrich)] were used respectively as acid captor and storage agent.

Toluene [TOL (SDS)] and cyclohexane (SDS) were distilled over calcium hydride to remove water and so to reduce acid polychloride hydrolysis. Terephthaloyl dichloride was crystallized from cyclohexane.

(I)-3.2 Three steps of synthesis

Three solutions were prepared separately:

Sol.I -- aqueous solution containing ~10gL^{-1} of the stabilizer,

Sol.II -- aqueous solution containing the stabilizer (~10gL^{-1}), the amine and sodium hydroxide (group amine/group hydroxide = 1:1), Sol.III -- organic phase containing the acid dichloride and tri-chloride monomers (molar ratio acid dichloride/acid tri-chloride = 3:1).

Polyamide microcapsules were prepared by interfacial polycondensation, keeping constant the molar ratio of amine groups and acid chloride groups at 2:1 (except for experiments nº1, 2 and 5).

The experimental procedure consisted of the following steps: a rotor-stator homogenizer [Ultra-Turrax® T25 basic, IKA®, Fig.(**I**)-6] was employed at 24 000rpm for 5min to obtain the dispersion of sol. III in sol. I (oil in water). Then ultrasonic irradiations were used to finally get smaller size droplets: an immersion system (Bandelin Sonoplus HD 2200) with the possibility of controlling time, irradiations cycles and the power of frequence was employed.

The emulsion thus formed was transferred into a reactor vessel [Fig.(**I**)-7] equipped with mechanical stirrer. Sol. II was added dropwise for the polycondensation. Two types of reactor vessel were used: a jacketed reactor of 1L at constant temperature of 15°C for large amounts of organic phase (100mL) and a reactor vessel of 250mL plunged in a thermostatic bath at 15°C for small amounts of organic phase (25mL). All polycondensations were conducted at stirring rate of 200rpm.

After 1h30 the reaction was stopped by dilution with water containing Tween® 20, the microcapsules were withdrawn from the reactor and washed at room temperature to remove the amine excess.

Model microcapsules containing toluene were prepared before each synthesis of Jojoba Oil microcapsules to select the appropriate experimental conditions.

Fig.(**I**)-6: Ultra-Turrax® homogenizer

Fig.(**I**)-7: Sovirel reactor

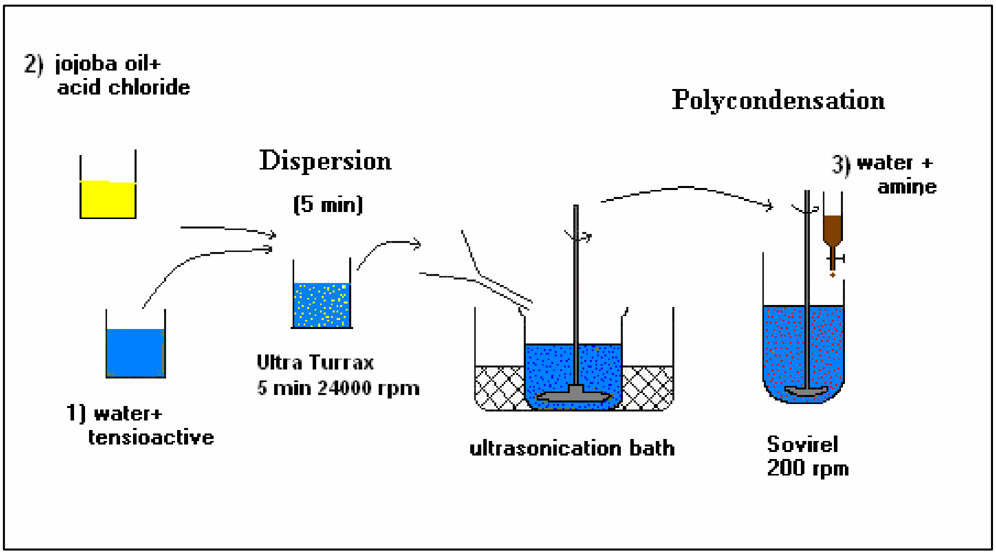


Fig.(**I**)-8: Three steps of interfacial polymerization reaction

(I)-3.3 Washing of microcapsules

The centrifugation-decantation procedure was followed: the microcapsules were separated from the reaction medium by centrifugation for 5min at 2000rpm (SIGMA 4K10, Bioblock). They were successively re-dispersed and centrifuged two times in de-ionized water and finally stored in de-ionized water containing Na_2SO_4 (3%w/v), to avoid the coalescence of microcapsules.

(I)-3.4 Microcapsules observations

The size and surface morphology of microcapsules were characterized by scanning electron microscope. For this purpose, a drop of solution containing microcapsules were left to dry on a thin glass at room temperature and then coated under vacuum with a gold layer before examination.

(I)-3.5 Results and discussion

Very small microcapsules (in the submicron range) have been already synthesized by using ionic and non-ionic co-surfactants in addition to the main stabilizer [24].

In the present investigation the aim was to obtain polyamide microcapsules Jojoba Oil containing with mean diameter of ~5μm by means of ultrasonic irradiations. The following synthesis parameters were investigated: the polyamine and acid poly-chloride chemical nature, the influence of oil-soluble or water soluble tri-functional cross-linking agent, and the ultrasonic irradiations parameters during the dispersion step.

(I)-3.5.1 Effect of polyamine type

It is well known that the diffusion of a substance through a polymer membrane takes place, in general, only in the non-crystalline regions. To promote Jojoba Oil diffusion through the microcapsule membrane a triamine (DETA) was tested which leads to a high crosslink density contributing to the reduction of the volume fraction of crystalline regions [17,25]

On the other hand, in order to obtain microcapsules having improved mechanical stability, a diamine (HMDA) was used providing to membranes characterized by high crystallinity and low porosity [26].

Synthesis conditions of microcapsules prepared by changing the polyamine type are listed in Table (**I**)-I.

Exp. nº	**C_{DETA} ($molL^{-1}$)**	**C_{HMDA} ($molL^{-1}$)**	**Ratio $NH_2/COCl$**	**V_{TOL} (mL)**	**V_{JOJ} (mL)**	**Photo SEM**
1	0.086	-	3:1	100	-	Fig.(**I**)-9a
2	0.086	-	3:1	-	100	Fig.(**I**)-9b
3	-	0.086	2:1	100	-	Fig.(**I**)-10a
4	-	0.086	2:1	-	100	Fig.(**I**)-10b

Table (**I**)-I: Experimental conditions of model and oil containing microcapsules by changing the polyamine type.

Vessel reactor of 1L at 15°C C_{TDC}= 0.03$molL^{-1}$ C_{BTC}= 0.01$molL^{-1}$

When DETA was used, it is not possible to distinguish isolated microcapsules, neither with TOL [Fig.(**I**)-9a] nor with JOJ [Fig.(**I**)-9b]. It was found [24] that microcapsules produced by equimolar concentration of DETA and TDC resulted in a highly porous membrane caused by the high cross-linking density which increases the polymer permeability.

In our case, microcapsule membranes seem to be not able to retain the organic phase. Toluene as well as Jojoba Oil cross the membrane and the polycondensation reaction continues at the oil/water interface in the solution bulk.

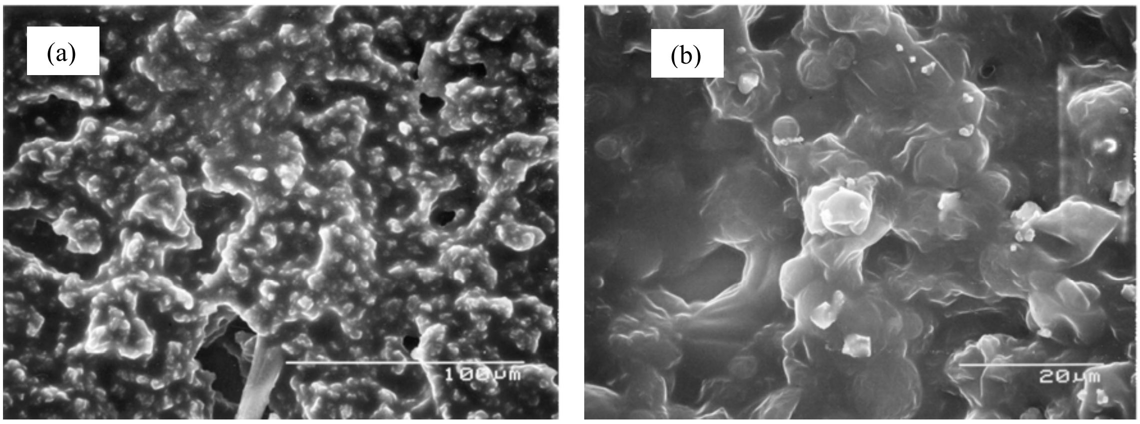


Figure (**I**)-9. SEM photomicrographs of microcapsules.
Effect of polyamine type: (a) DETA/TDC/TOL, magnification 500x; (b) DETA/TDC/JOJ, magnification 1500x

On the other hand it has been demonstrated [26] that in presence of HMDA the polyamide membrane overall porosity is reduced because of the formation of linear polymer chains, resulting in a more packed chain arrangement.

Model microcapsules [Fig.(**I**)-10a] appear collapsed under SEM for the presence of toluene in their core. Toluene, a highly volatile solvent, evaporates during samples preparation for SEM investigation.

Particles size, measured by SEM observations, is of ~15µm for microcapsules prepared by HMDA/TDC/TOL [Fig.(**I**)-10a] and by HMDA/TDC/JOJ [Fig.(**I**)-10b].

Moreover, it has been demonstrated [26] that the growth rate of the membrane sub-layer into the organic phase as well as its morphology is controlled by the relative permeabilities of the skin to the reacting monomers and the respective solubilities in the two phases. The diffusion rates of the reacting amines through a polyamide membrane increase as the amine solubility in the organic phase increases.

The partition coefficients of DETA, TAEA and HMDA in water/cyclohexane (50mL /450mL) solution were measured in our laboratory, their values increase in the order: HMDA<TAEA<DETA, that means DETA is not very soluble in the organic phase so, for identical time reaction (1h30), the capsule wall membranes are thin and not strong enough to prevent the exit of the active agent.

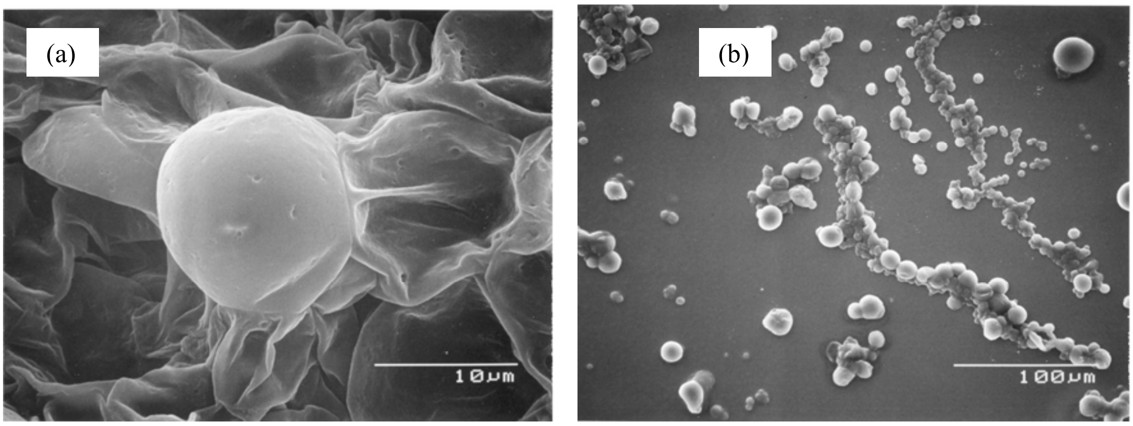


Figure (**I**)-10. SEM photomicrographs of microcapsules.

Effect of polyamine type: (a) HMDA/TDC/TOL, magnification 3000x; (b) HMDA/TDC/JOJ, magnification 300x

(I)-3.5.2 Influence of the cross-linking agent

In order to compare the effect related to the presence of the tri-functional cross-linking agent, BTC is dissolved in the organic phase or TAEA in the aqueous phase.

The following syntheses, listed in Table (**I**)-II, were carried out:

Exp. n°	**C_{HMDA} ($molL^{-1}$)**	**C_{TAEA} ($molL^{-1}$)**	**C_{BTC} ($molL^{-1}$)**	**TDC ($molL^{-1}$)**	**Ratio $NH_2/COCl$**	**V_{TOL} (mL)**	**Reactor vessel at 15°C**	**Photo SEM**
3	**0.086**	**-**	**0.01**	**0.030**	**2:1**	**100**	**1L**	Fig.(**I**)-10a
5	**0.015**	**0.005**	**-**	**0.007**	**3:1**	**25**	**250 mL**	Fig.(**I**)-11a
6	**0.066**	**0.022**	**0.01**	**0.030**	**2:1**	**100**	**1 L**	Fig.(**I**)-11b

Table (**I**)-II: Influence of cross-linking agent

SEM analyses show that when the tri-functional cross-linking agent is in the organic phase [Fig.(**I**)-10a], microcapsules keep the compactness of the membrane; when TAEA was used as tri-functional cross-linking agent in the aqueous phase, soft membranes are obtained. In fact, under SEM conditions, microcapsules are not visible any more [Fig.(**I**)-11a].

By using both BTC and TAEA, no significantly changes are observed on the morphological characteristics of the synthesized membranes [Fig.(**I**)-11b].

The presence of BTC seems to be necessary in our case to obtain stable microcapsules whereas the TAEA presence has no influence if BTC is used.

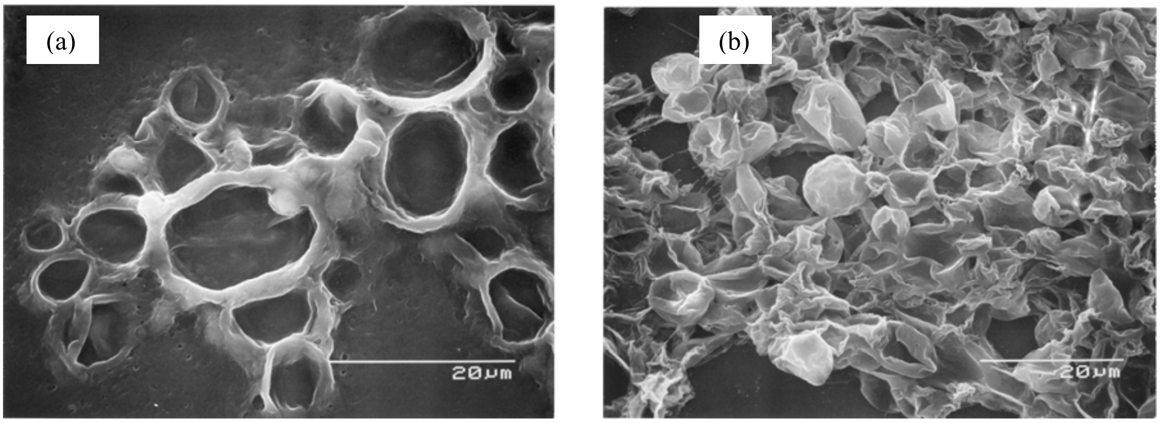


Figure (**I**)-11. SEM photomicrographs of microcapsules. Effect of cross-linking agent:
(a) HMDA/TAEA/TOL; magnification 2000x; (b) HMDA/TAEA+BTC/TOL, magnification 1500x

(I)-3.5.3 Effect of ultrasonic irradiations

The microcapsules size distribution can be controlled by appropriate modifications of the process conditions during the dispersion step. Usually both stabilizer concentration and stirring rate are efficient in producing smaller and more homogeneous samples of microcapsules. In order to a further reduction of microcapsules size, different time, cycles and frequence of ultrasonic irradiations were tested.

The polycondensation conditions applied during the preparation of the various types of microcapsules are summarized in Table (**I**)-III.

Exp.nº	V_{TOL} (mL)	V_{JOJ} (mL)	Ultrasonic irradiations				Photo SEM
			time (min)	cycle	pow (W)	T(°C) final	
7	25	-	5	5*10%	55	42	Fig.(**I**)-12a-b
8	25	-	2:30	5*10%	100	50	Fig.(**I**)-13
9	-	25	5	5*10%	55	41	Fig.(**I**)-14a-b
10	-	25	3:30	-	80	43	Fig.(**I**)-15
11	25	-	10	5*10%	10	70	Fig.(**I**)-16

Table (**I**)-III: Experimental conditions for ultrasonic irradiations.

Reactor vessel = 250mL at 15°C; HMDA = 0.021molL^{-1}, TDC = 0.007molL $^{-1}$, BTC = 0.002molL^{-1}

Ultrasonic irradiations cause the increase of dispersion final temperature; the presence of irregularities on the surface of model microcapsules [Fig.(**I**)-12 and Fig.(**I**)-13] is partially assigned to the heating of toluene during the dispersion step which probably influences the initial skin membrane equilibrium formation. In 15min the temperature lowered from 40°C to constant 15°C. During this time the aggregation of the unstable colloidal polyamide particles leads to a less regular skin structure. In fact, when the dispersion step takes place at 25°C (experiment nº 3), no so many voids are observed.

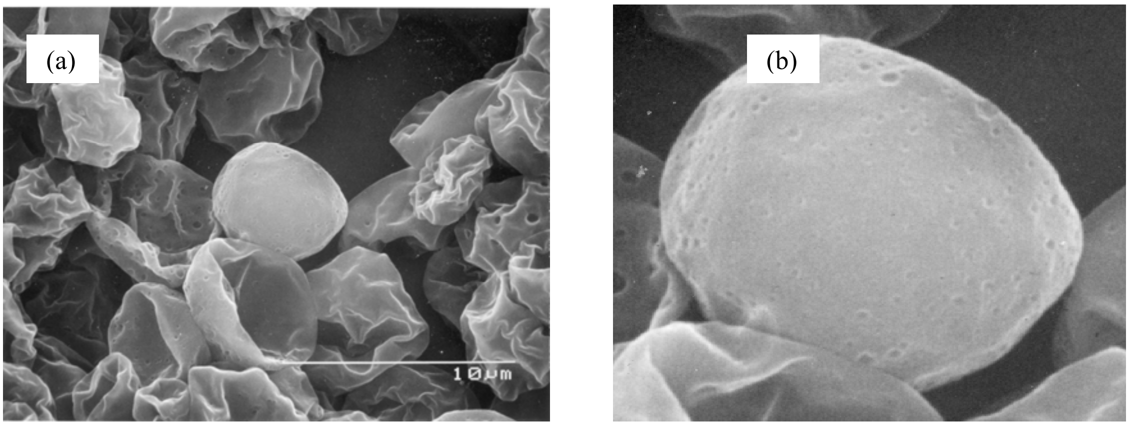


Figure (**I**)-12. SEM photomicrographs of microcapsules.

Effect of ultrasonic irradiations: 5min, 5*10%cycle, 55W, (a) magnification 5000x, (b) enlarged detail

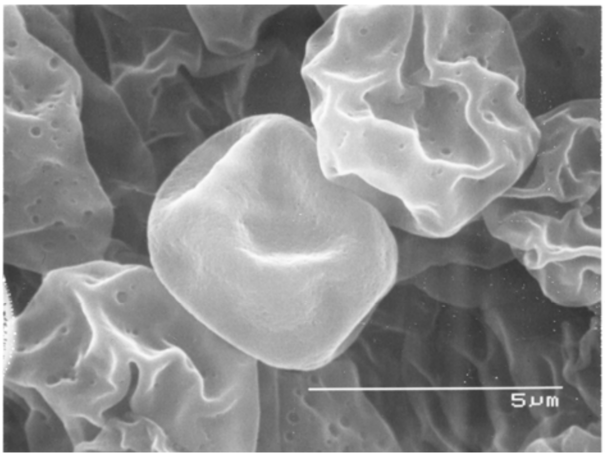


Figure (**I**)-13. SEM photomicrographs of microcapsules.
Effect of ultrasonic irradiations: 2:30min, 5*10%cycle, 100W, magnification 10 000x

When experiments were carried out in presence of Jojoba Oil [Figs.(**I**)-14a-b and Fig.(**I**)-15] microcapsules are spherical and have a continuous and smooth surface. A plausible explanation [27] may be found in the low degree of polymer swelling and the low volatility of Jojoba Oil.

SEM pictures demonstrate that particles have mean diameter of ~5µm after ultrasonic irradiations; the photos [Fig.(**I**)-14a and Fig.(**I**)-15] show also the reproducibility of results in terms of microcapsule size and membrane aspect for two different experimental synthesis conditions.

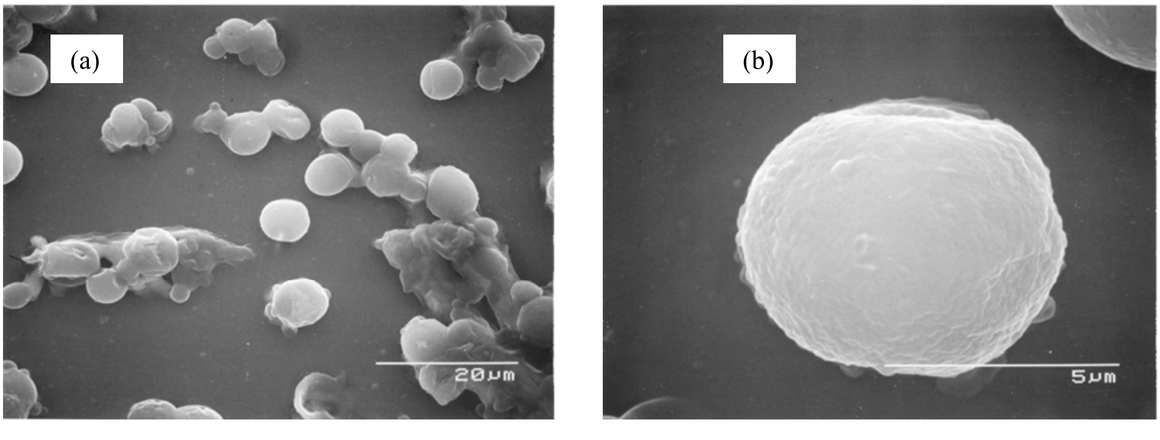


Figure (**I**)-14. SEM photomicrographs of microcapsules.
Effect of ultrasonic irradiations: 5min, 5*10%cycle, 55W, (a) magnification 1500x, (b) magnification 10 000x

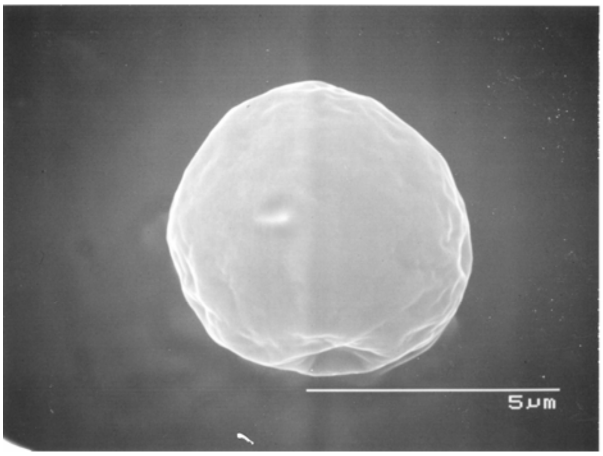


Figure (**I**)-15. SEM photomicrographs of microcapsules.
Effect of ultrasonic irradiations: 3:30min, no cycle, 80W, magnification 10 000x

If time of ultrasonication was longer (10min), temperature raised 70°C and SEM picture [Fig.(**I**)-16] shows polymer residues mixed with some small collapsed microcapsules. This may be attributed to microcapsules destruction, caused by both the high vapour pressure of toluene after the heating (which tends to break the membrane) and the collapse by evaporation (during the vacuum step of sample preparation for SEM examination).

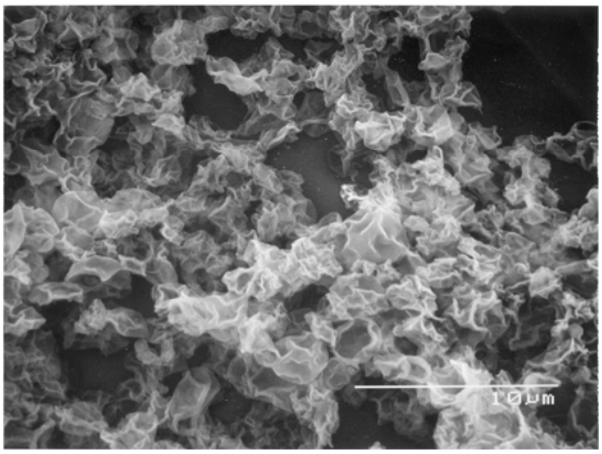


Figure (**I**)-16. SEM photomicrographs of microcapsules.
Effect of ultrasonic irradiations: 10min, 5*10%cycle, 10W, magnification 4000x

(I)-3.5.4 Effect of acid polychloride type

Since aliphatic and aromatic polyamides are characterized by several different properties (e.g. mechanical stability, thermal behaviour, chemical reactivity), aliphatic acids dichloride (SBC and ADP) were used to synthesize microcapsule wall membranes.

Experimental conditions are listed in Table (**I**)-IV.

Exp. n°	C_{TDC} (molL^{-1})	C_{SBC} (molL^{-1})	C_{ADP} (molL^{-1})	V_{TOL} (mL)	V_{JOJ} (mL)	Ultrasonic irradiations (no cycle)			Photo SEM
						time (min)	pow (W)	T(°C) final	
10	0.007	-	-	-	25	3:30	80	43	Fig.(I)-15
12	-	0.007	-	25	-	3:30	80	40	Fig.(I)-17
13	-	0.007	-	25	-	1:30	40	19	Fig.(I)-18
14	-	0.007	-	-	25	3:30	80	41	*
15	-	0.007	-	-	25	2:30	60	36	Fig.(I)-21
16	-	-	0.007	25	-	3:30	80	42	Fig.(I)-19
17	-	-	0.007	25	-	1:30	80	29	Fig.(I)-20
18	-	-	0.007	-	25	1:30	80	29	*

Table (**I**)-IV. Effect of acid poly-chloride type.

Reactor vessel 250mL at 15°C, HMDA = 0.021molL $^{-1}$, BTC=0.002molL^{-1}

*Photos of SEM observations are not exploitable

Model microcapsules prepared by SBC and ADP containing toluene [Fig.(**I**)-17, Fig.(**I**)-18, Fig.(**I**)-19 and Fig.(**I**)-20] have good size and morphological characteristics; no irregularities are detected on their surface probably because aliphatic acids dichloride lead to a less rigid and more crystalline wall membranes.

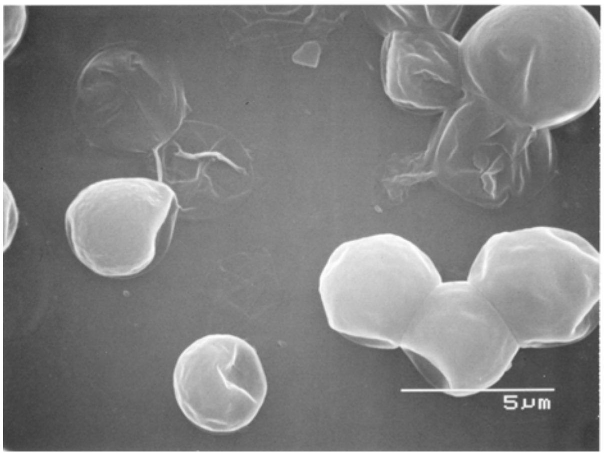


Figure (**I**)-17. SEM photomicrographs of microcapsules.
Effect of acid poly-chloride type: 3:30min, no cycle, 80W, HMDA/SBC/TOL, magnification 6000x

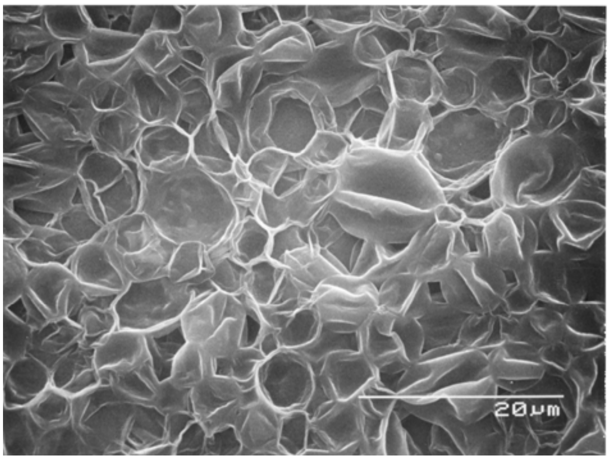


Figure (**I**)-18. SEM photomicrographs of microcapsules.

Effect of acid poly-chloride type: 1:30min, no cycle, 40W, HMDA/SBC/TOL, magnification 2000x

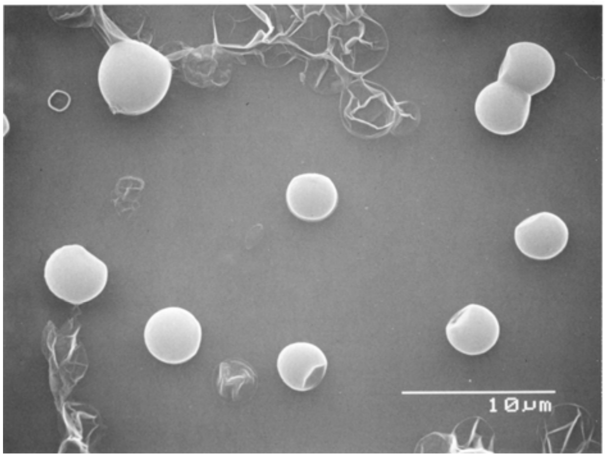


Figure (**I**)-19. SEM photomicrographs of microcapsules.

Effect of acid polychloride type: 3:30min, no cycle, 80W, HMDA/ADP/TOL, magnification 3000x

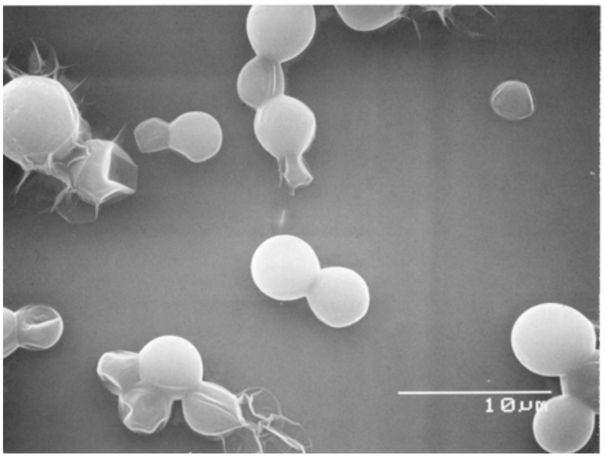


Figure (**I**)-20. SEM photomicrographs of microcapsules.
Effect of acid polychloride type: 1:30min, no cycle, 80W, HMDA/ADP/TOL, magnification 3000x

When Jojoba Oil was used as organic phase it is not possible, for the same reaction time (1h30), to point out the presence of microcapsules, even varying preparation conditions (experiments nº 14, 15 and 18). Just for experiment nº15 one SEM photo is exploitable. This picture [Fig.(**I**)-21] shows a continuous oily layer in which microcapsules are dispersed.

The partition coefficient of the amines varies with the type of organic solvent, influencing the degree of polymerization and consequently the thickness and morphology of the polymer membrane [27].

With toluene as organic phase, even changing the acid dichloride type (aromatic or aliphatic) model microcapsules have good aspect. With Jojoba Oil as organic phase, even if the partition coefficient of HMDA is different, polyterephthalamide microcapsules are still good.

On the other hand, when Jojoba Oil is the organic phase and the reacting acid dichloride monomer is aliphatic, no good microcapsules can be observed. So, it is reasonable to think that something related to the chemical nature of the acid dichloride in the oil phase (e.g. diffusion rate toward oil/water interface, rate of hydrolysis of COCl groups, etc.) influence the membrane formation mechanism. However, since interrelated parameters are involved, a full understanding of the problem requires a further investigation.

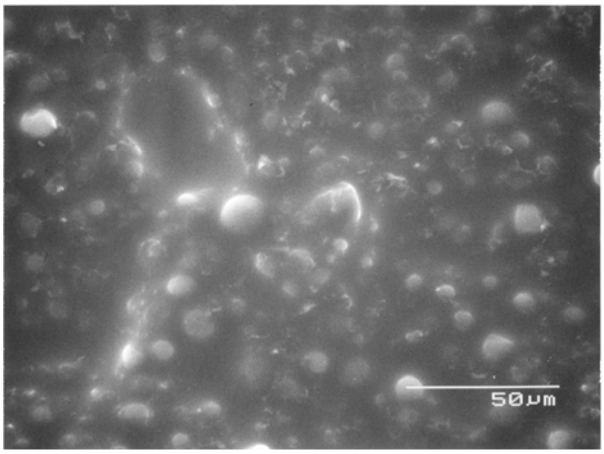


Figure (**I**)-21. SEM photomicrographs of microcapsules.

Effect of acid polychloride type: 2:30min, no cycle, 60W, HMDA/SBC/JOJ, magnification 600x

(I)-3.6 Thermal characterization

Differential scanning calorimeter (DSC) analysis was performed on HMDA-DCT microcapsules from -30°C to 250°C [Fig.(**I**)-22]: only Jojoba Oil solid-liquid transition at 15°C is present.

TGAs of microcapsules sample show [Fig.(**I**)-23] their thermal stability, in fact degradation at 5% weight loss takes place at 306°C in N_2 and 237°C in air. These temperatures are lower compared to that of pure Jojoba Oil but still compatible with process temperature of nylon 6.

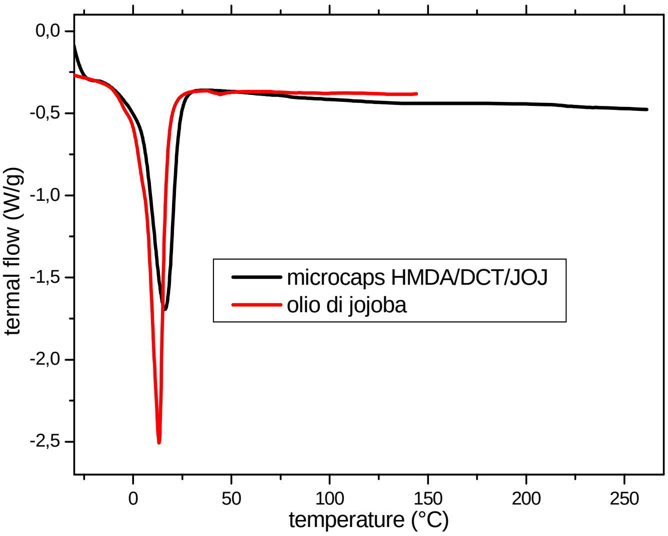


Figure (**I**)-22. DSC of HMDA/DCT/JOJ microcaps and Jojoba Oil.

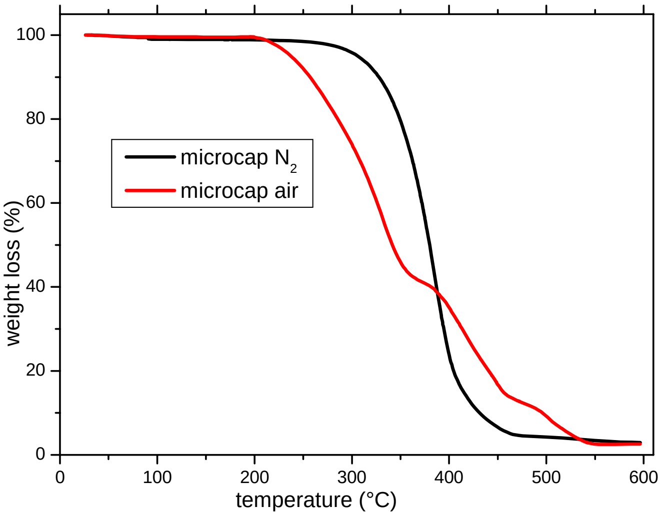


Figure (**I**)-23. TGA of HMDA/DCT/JOJ microcaps in air and N_2

(I)-3.7 Addition of Jojoba microcapsules in polyamide 6 matrix

Obtained Jojoba Oil microcapsules based on HMDA-DCT were added to nylon 6 matrix by melt extrusion.

Two blends were prepared containing 5 wt% and 10 wt% microcapsules by means of a laboratory mini-mixer (Haake Rheomix CTW5). Process was carried on at 240°C, with a screw speed of 100 rpm for 5 min.

(I)-3.7.1 Morphological observation

Polyamide 6 additivated samples were fractured in liquid N_2 and then observed by SEM.

As it can be seen in Fig.(**I**)-24, pure polyamide 6 surface is smooth and compact, while blends surfaces [Fig.(**I**)-25 and Fig.(**I**)-26] show voids left by microcapsules which do not strongly adhere at the matrix.

Since isolated microcapsules have mean diameter lower than 15µm, larger pores visible in both cases in SEM photomicrographs could be attributed to microcapsules aggregation.

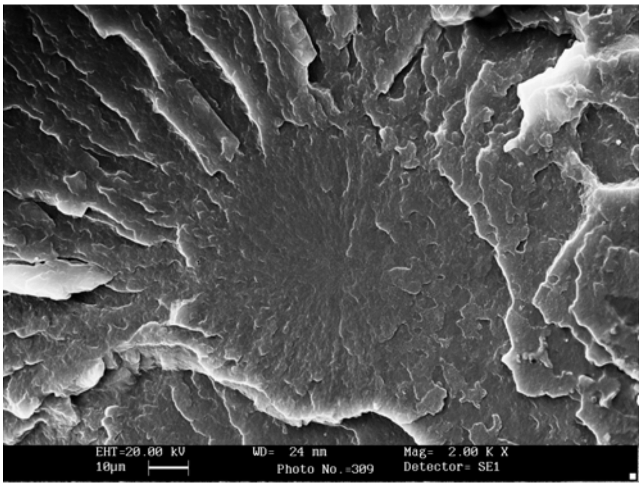


Figure (**I**)-24. SEM photomicrograph of PA6 matrix.

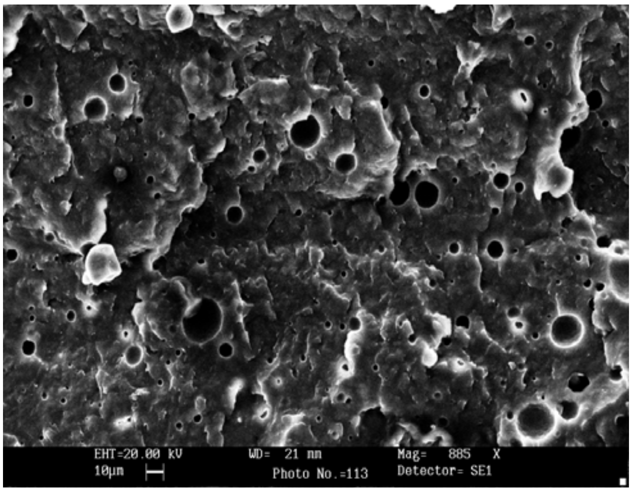


Figure (**I**)-25. SEM photomicrograph of PA6 matrix containing 5wt% microcapsules

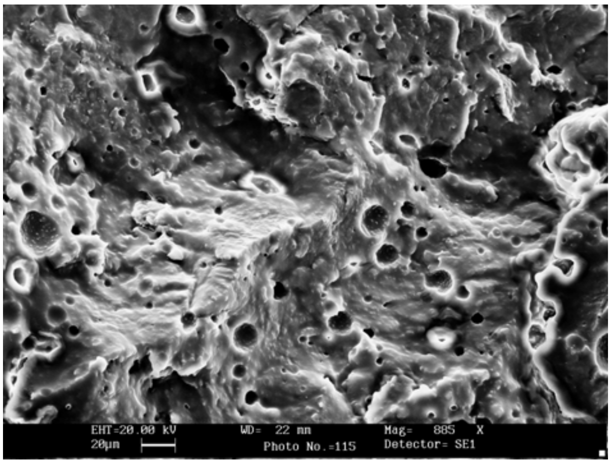


Figure (**I**)-26. SEM photomicrograph of PA6 matrix containing 10wt% microcapsules

(I)-3.7.2 Thermal characterization

Polyamide samples containing 5 wt% and 10 wt% microcapsules were characterized by DSC analysis from -20°C to 260°C: thermogram in Fig.(**I**)-27 shows the first endothermic peak related to Jojoba Oil melting transition at 13°C and the second endothermic peak at 226°C corresponding to the fusion of the crystalline portion of polyamide 6. The heat of fusion of sample containing 10 wt% microcapsules is 7.9 J/g, nearly 2 fold the heat of fusion of sample containing 5 wt% microcapsules (3.4 J/g); this means that during the extrusion process politerephthalamide shell is able to protect Jojoba Oil inside the capsule.

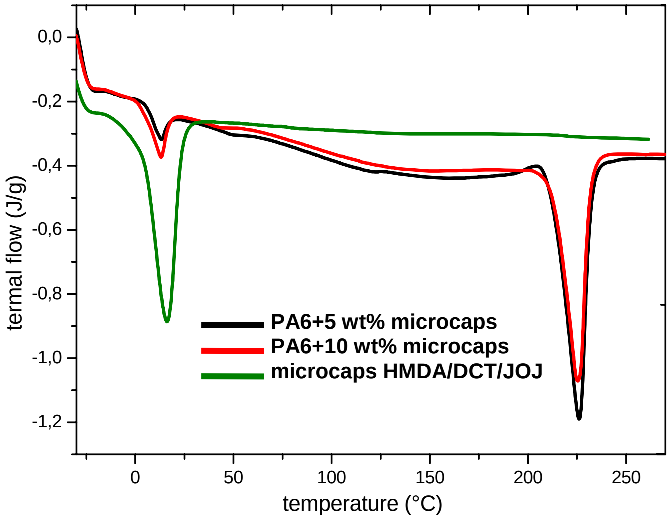


Figure (**I**)-27. DSC of HMDA/DCT/JOJ microcapsules and PA6 matrix containing 5 and 10 wt% microcapsules

(I)-4 FINAL REMARKS

Polyamide microcapsules Jojoba Oil containing having mean diameter of ~5µm were synthesized by means of ultrasonic irradiations.

A qualitative description of microcapsules characteristics in terms of dependence upon both the formulation and the process conditions has been reported.

In summary, the combination of HMDA with TDC and BTC produces the best microcapsule membranes with smooth and dense surfaces and low porosity. The efficiency of using the cross-linking agent in the organic phase instead of in the aqueous phase is also demonstrated by SEM observations.

By using aliphatic acid dichloride, even if model microcapsules containing toluene have good aspect, no Jojoba Oil microcapsules can be formed in the same experimental conditions. It means that the system behaviour is strictly dependent on the type of the organic phase.

An interesting outcome of SEM study shows the possibility to reduce microcapsules size from ~15µm diameter to ~5µm diameter by using ultrasonic irradiations during the dispersion step.

TGA and DSC analysis and SEM observations of polymer blends confirmed the high thermal and mechanical resistance of polyamide cross-linked shell microcapsules, preventing Jojoba Oil degradation and promoting its combination with nylon 6.

The restriction for this research line was the difficulty to get well dry and isolated microcapsules without breaking their shell during the separation step from bulk solution and the availability of injection technology for direct spinning of microcapsules in fibers.

NANOTECHNOLOGY IN TEXTILE FIELD

Nanotechnology is an emerging interdisciplinary technology that has been booming in many areas during the recent decade. Nanotechnology endeavours are aimed at manipulating atoms, molecules and nano-size particles in a precise and controlled manner in order to build materials with fundamentally new organization and novel properties. Nanotechnology is called a “bottom up” technology by which bulk materials can be built precisely in tiny building blocks, different from traditional manufacture “top down” technology. Therefore, resultant materials have fewer defects and higher quality.

The fundamentals of nanotechnology lie in the fact that properties of substances dramatically change when their size is reduced to the nanometre range. When a bulk material is divided into small size particles with one or more dimension (length, width or thickness) in the nanometre range or even smaller, the individual particles exhibit unexpected properties, different from those of the bulk material. It is known that atoms and molecules possess totally different behaviours than those of bulk materials; while the properties of the former are described by quantum mechanics, the properties of the latter are governed by classic mechanism.

With only a reduction of size and no change in substance, fundamental characteristics such as electrical conductivity, colour, strength and melting point can all change. Therefore nanomaterials show promising application potentials in a variety of industrial branches such as chemistry, electronics, medicine, automotive, cosmetics or the food sector.

For example, ceramics, which normally are brittle, can easily be made deformable when their grain size is reduced to the low nanometre range. Moreover, a small amount of nano-size species can interfere with matrix polymer bringing up the performance of resultant system to an unprecedented level. These are the reasons why nanotechnology has attracted large amounts of research activity and media attention.

Advantages of nano-sized additions

The Nanocomposites 2000 conference has revealed clearly the property advantages that nano-material additives can provide in comparison to both their conventional filler counterparts and base polymer. Properties which have been shown to undergo substantial improvements include:

- Mechanical properties e.g. strength, modulus and dimensional stability
- Decreased permeability to gases, water and hydrocarbons
- Thermal stability and heat distortion temperature
- Flame retardancy and reduced smoke emissions
- Chemical resistance
- Surface appearance
- Electrical conductivity
- Optical clarity in comparison to conventionally filled polymers

Application fields

The following table [Table(**II**)-I] gives an overview on potential markets and products based on nanoparticulate materials [29].

Automotive industry • Lightweight construction • Painting (fillers, base coat, clear coat) • Catalysts • Sensors	**Chemical industry** • Coating system based on nanocomposites • Impregnation of papers • Switchable adhesives • Magnetic fluids	**Engineering** • Wear protection for tools and machines (anti-blocking coatings, scratch resistant coatings on plastic parts) • Lubricant-free bearings
Electronic industry • Data memory (MRAM, GMR-HD) • Displays (OLED,FED) • Laser diodes • Glass fibers • Optical switch • Filters (IR-blocking) • Conductive, antistatic coatings	**Construction** • Thermal insulation • Flame retardants • Surface-functoinalized building materials for wood, floors, stone, roof tiles • Facade coatings	**Medicine** • Drug delivery systems • Active agents • Contrast medium • Medical rapid tests • Prostheses and implants • Antimicrobial agents and coatings • Agents in cancer therapy
Textile/fabrics/non-woven • Surface-processed textiles • Smart clothes	**Energy** • Fuel cells • Solar cells • Batteries • Capacitors	**Cosmetics** • Sun protection • Lipstick • Skin creams • Tooth paste
Food and drinks • Package materials • Storage life sensors • Additives • Clarification of fruit juice	**Household** • Ceramic coatings for irons • Odors catalyst • Cleaner for glass, ceramic, floor, windows	**Sports/outdoor** • Skin wax • Antifogging of glasses/goggles • Antifouling coatings for ship/boats • Reinforced tennis rackets and balls

Table (**II**)-I: Overview on applications of nanomaterial based products in different areas

(II)-1 APPLICATION OF NANOTECHNOLOGY IN TEXTILE MANUFACTURING

The textile industry has already impacted by nanotechnology. Research involving nanotechnology to improve performances or to create unprecedented functions of textile materials are flourishing. These research endeavours is mainly focused on using nano-size substances and generating nanostructures during manufacturing and finishing processes.

Nano-structured composite fibers are the area where we see the early blooming of nanotechnology: those composite fibers employ nano-size fillers such as nanoparticles (clay, metal oxides, carbon black), graphite nanofibers (GNF) and carbon nanotubes (CNT). Besides, nano-structured composite fibers can be generated through foam-forming process.

The main function of nano-size fillers is to increase the mechanical strength and improve the physical properties such as conductivity and antistatic behaviours. Due to their large surface area, these nanofillers have a better interaction with polymer matrices. Being in the nanometre range, the fillers might interfere with polymer chain movement and thus reduce the chain mobility. Being evenly distributed in polymer matrices, nanoparticles can carry load and increase the toughness and abrasion resistance; nanofibers can transfer stress away from polymer matrices and enhance tensile strength of composite fibers.

(II)-1.1 Classification of nanomaterials

Additional physical and chemical performances imparted to composite fibers vary with specific properties of the nanofillers used. Distribution of nanofillers in polymer matrices through mechanical and chemical approaches is one of the important aspects leading to high quality of nanostructured composite fibers. Although some of the filler particles such as clay, metal oxides, carbon black have previously been used as microfillers in composite materials for decades, reduction of their size into nanometre range have resulted in higher performances and generated new market interest.

(II)-1.1.1 Clays and clay modification

Common clays are naturally occurring minerals and are thus subject to natural variability in their constitution. The purity of the clay can affect final nanocomposite properties.

Many clays are aluminosilicates, which have a sheet-like (layered) structure, and consist of silica SiO_4 tetrahedra bonded to alumina AlO_6 octahedra in a variety of ways. A 2:1 ratio of the tetrahedra to the octahedra results in smectite clays, the most common of which is montmorillonite [Fig.(**II**)-1].

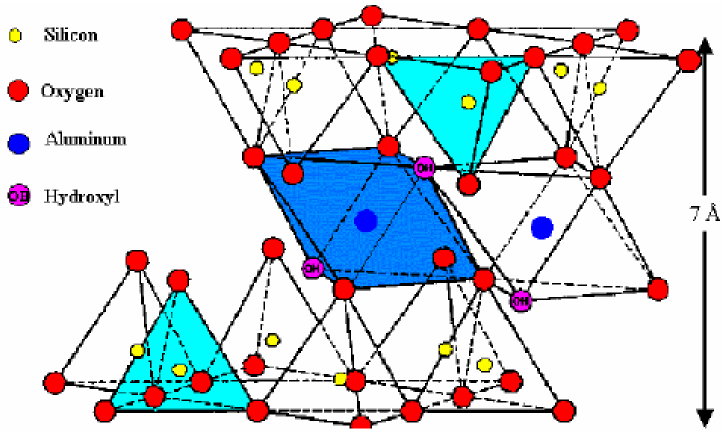


Figure (**II**)-1: Montmorillonite structure

Other metals such as magnesium may replace the aluminium in the crystal structure. Depending on the precise chemical composition of the clay, the sheets bear a charge on the surface and edges, this charge being balanced by counter-ions, which reside in part in the inter-layer spacing of the clay. The thickness of the layers (platelets) is of the order of 1 nm and they are not totally rigid, but have a degree of flexibility.

The clays often have very high surface areas, up to hundreds of m^2 per gram. The clays are also characterised by their ion (e.g. cation) exchange capacities, which can vary widely. One important consequence of the charged nature of the clays is that they are generally highly hydrophilic species and therefore naturally incompatible with a wide range of polymer types.

A necessary prerequisite for successful formation of polymer-clay nanocomposites is therefore alteration of the clay polarity to make the clay ‘organophilic’. An organophilic clay can be produced from a normally hydrophilic clay by ion exchange with an organic cation such as an alkyl ammonium ion [Fig.(**II**)-2].

For example, in montmorillonite, the sodium ions in the clay can be exchanged for an amino acid such as 12-aminododecanoic acid (ADA):

Na^+-CLAY + HOOC-R-NH_3 + Cl^- . HOOC-R-NH_3 +-CLAY + NaCl

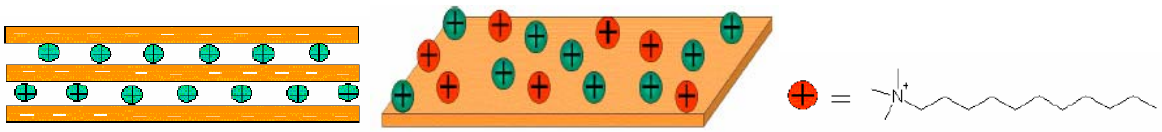
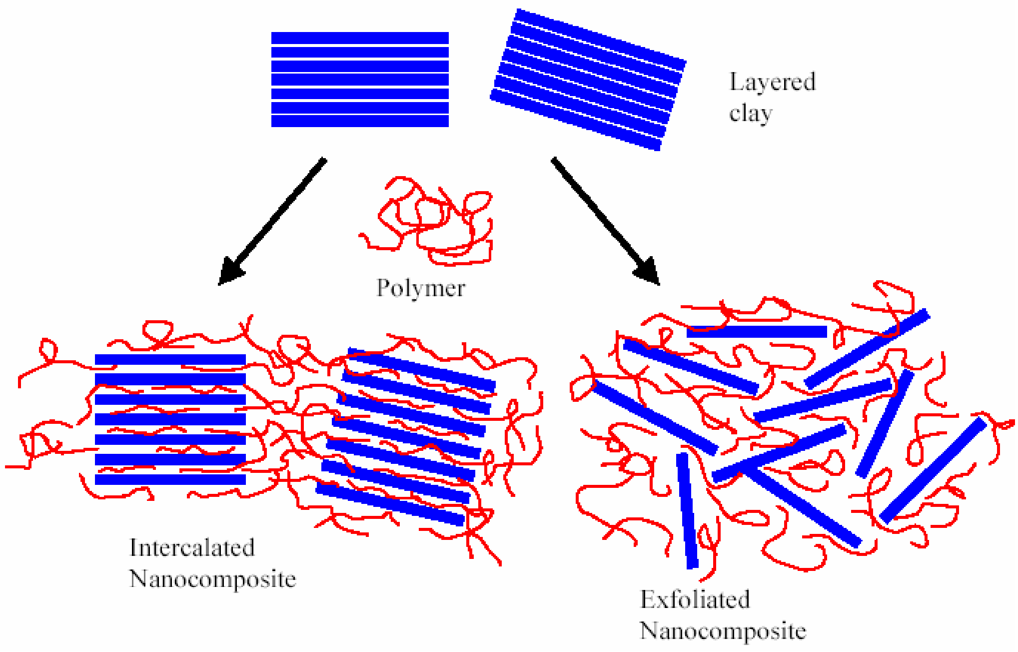


Figure (**II**)-2: Ion exchange with alkyl ammonium

Although the organic pre-treatment adds to the cost of the clay, the clays are nonetheless relatively cheap feedstocks with minimal limitation on supply. Montmorillonite is the most common type of clay used for nanocomposite formation; however, other types of clay can also be used depending on the precise properties required from the product. These clays include hectorites (magnesiosilicates), which contain very small platelets, and synthetic clays (e.g. hydrotalcite), which can be produced in a very pure form and can carry a positive charge on the platelets, in contrast to the negative charge found in montmorillonites.

Polymer incorporation

The correct selection of modified clay is essential to ensure effective penetration of the polymer or its precursor into the interlayer spacing of the clay and result in the desired exfoliated or intercalated product [Fig.(**II**)-3]. Indeed, further development of compatibiliser chemistry is undoubtedly the key to expand this nanocomposite technology beyond the systems where success has been achieved to date.



Figure(**II**)-3**:** Formation of intercalated and exfoliated nanocomposites from layered silicate and polymer

In recent years, there has been extensive study of the factors which control whether a particular organo-clay hybrid can be synthesised as an intercalated or exfoliated structure. Since clay nanocomposites can produce dramatic improvements in a variety of properties, it is important to understand the factors which affect delamination of the clay. These factors include the exchange capacity of the clay, the polarity of the reaction medium and the chemical nature of the interlayer cations (e.g. ammonium ions). By modifying the surface polarity of the clay, ammonium ions allow thermodynamically favourable penetration of polymer precursors into the interlayer region. The ability of the ammonium ion to assist in delamination of the clay depends on its chemical nature such as its polarity. The loading of the ammonium ion on the clay is also crucial for success and it should be take into account that a commercial organoclay may not have the optimum loading for a particular application. For positively charged clays such as hydrotalcite, the ammonium salt modification is replaced by use of a cheaper anionic surfactant. Other types of clay modification can be used depending on the choice of polymer, including ion-dipole interactions, use of silane coupling agents and use of block copolymers. Each type differs in chemical composition and crystal structure.

Polymer can be incorporated either as the polymeric species itself or *via* the monomer, which is polymerised *in situ* to give the corresponding polymer-clay nanocomposite. The second of these is the most successful approach to date, although it probably limits the ultimate applicability of these systems.

Polymers can be introduced either by melt blending, for example extrusion, or by solution blending. Melt blending (compounding) depends on shear to help delaminate the clay and can be less effective than *in situ* polymerisation in producing an exfoliated nanocomposite.

Both thermosets and thermoplastics have been incorporated into nanocomposites, including:

- nylons
- polyolefins, e.g. polypropylene
- polystyrene
- ethylene-vinyl acetate (EVA) copolymer
- epoxy resins
- polyurethanes
- polyimides
- poly(ethylene terephthalate) (PET)

The earliest example of the *in situ* polymerisation method was work by Toyota on synthesis of clay-nylon nanocomposites and this remains probably the most studied system. In a typical synthesis ADA-modified clay is dispersed in the monomer caprolactam, which is polymerised to form the nylon-6-clay hybrid as an exfoliated composite. Complete exfoliation may be preceded by intercalation of the monomer in the clay. Generally, low concentration of clay (a few %) are incorporated in these nanocomposites, partly because this is often sufficient to modify the desired properties significantly, but also because higher levels of clay can adversely increase the system viscosity leading to poor processability, although the viscosity increase is shear rate dependent. Other nylons and copolyamides (*e.g.* nylon-6/6,6) have also been incorporated in clay nanocomposites. Functionality such as hydroxyl groups can be introduced into the ammonium salt modifiers to improve compatibility with the nylon *via* hydrogen bonding, this can lead to an enhancement of desirable nanocomposite properties.

Although the incorporation of particulate material into polymers generally results in an increased melt viscosity, nanocomposite formulations exhibit a greater fall in viscosity with shear rate than their unfilled counterparts. This results in insignificant differences in viscosity at the shear rates frequently encountered in commercial melt fabrication processes. In addition, due to the substantially lower loading levels required to achieve the same property levels obtainable via conventional filler materials, the viscosity increases with nanoclay formulations are obviously low in comparison to their more conventionally filled counterparts. Furthermore, the lower loading levels will also be advantageous in minimising abrasive effects on processing equipment.

Clay nanoparticles posses electrical, heat and chemical resistance and an ability of blocking UV light. Therefore, composite fibers reinforced with clay nanoparticles exhibit flame retardant, anti-UV and anti-corrosive behaviours. For example, nanoparticles of montmorillonite, one of the most commomnly used clay, have been applied as UV blocker in nylon composite fiber. The mechanical properties with a clay mass fraction of only 5 wt% exhibits a 40% higher tensile strength, 68% greater tensile modulus, 60% higher flexural strength and a 126% increased flexural modulus [30, 31].

Another function of clay nanoparticles is to introduce dye-attracting sites and creating dye-holding space in polypropylene fibers, known as non-dyeable fiber due to its structural compactness and lack of dye-attracting sites. Nanoparticles of montmorillonite are modified with quaternary ammonium salt and then mixed into polypropylene before it is extruded as a result, polypropylene with clay nanoparticles by weight percentage of 5% can be coloured by acid dyes and disperse dyes [32, 33].

(II)-1.1.2 Metal oxide nanoparticles

Nano-size particles of TiO_2, Al_2O_3, ZnO and MgO are a group of metal oxides that possess photo-catalytic ability, electrical conductivity, UV absorption and photo-oxidizing capacity against chemical and biological species. Intensive researches involving the nanoparticles of metal oxides have been focusing on anti-microbial, self-decontaminating and UV blocking functions for both military protection gears and civilization health products. Nylon fibers filled with ZnO nanoparticles can provide UV shielding function and reducing static electricity of nylon fiber. A composite fiber with nanoparticle of TiO_2/MgO can provide self-sterilizing function [34, 35].

(II)-1.1.3 Carbon nanofibers and carbon nanoparticles

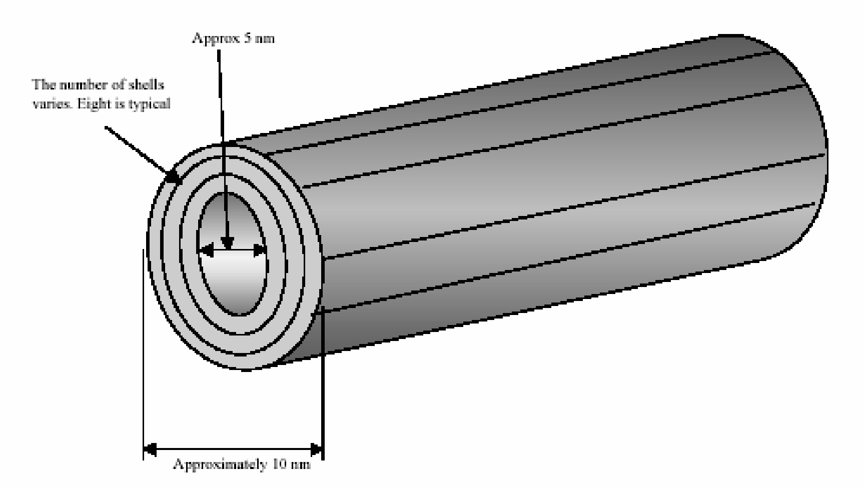
Carbon nanofibers and carbon black nanoparticles are among the most commonly used nano-size filling materials. Carbon nanofiber can effectively increase the tensile strength of composite fibers due to its high aspect ratio, while carbon black nanoparticles can improve their abrasion resistance and toughness. Both of them have high chemical resistance and electric conductivity.

Much publicity has surrounded the development of single wall carbon nanotubes (SWNT), the so-called Buckytubes, but while these are still some way off large-scale commercial production, the corresponding multi-layer carbon nanotubes (MWNT) have been known for some time and, furthermore, are available in practical commercial quantities.

CNT consists of tiny shell(s) of graphite rolled up into a cylinder(s) with 100 times the tensile strength of steel at one-sixth weight, thermal conductivity similar to copper, but with the ability to carry much higher currents, CNT seems to be a wonder material. They are usually made by carbon-arc discharge, laser ablation of carbon, or chemical vapour deposition.

The layers consist of graphitic carbon and the tubes typically have an internal diameter of *ca.* 5 nm and external diameter of *ca.* 10 nm [Fig.(**II**)-4].

The proportion of graphitic structures in the nanotubes and fibers can vary over a fairly wide range, with a concomitant variation in surface energies. The nanotubes tend to be of high purity and produce low out-gassing during processing and, in comparison with carbon fiber and carbon black reinforced composites, the resultant nanocomposites have a much reduced tendency to shed particulates in use. Because of the electrical conductivity of the carbon nanotubes and nanofibers, the nanocomposites have much reduced surface resistivity in comparison to the unfilled polymer. These properties impact on the potential applications of the composites.



Figure(**II**)-4: Carbon nanotube

The nanotubes have been used in composites with a variety of matrix resins, including polyamides, polyesters, polycarbonates and their blends, polystyrene and high performance polymers such as polyphenylene sulphide (PPS), PEI and polyetheretherketone (PEEK). Extension to polyolefin systems is anticipated in the near future. Effective dispersion of the nanotubes into the polymer is essential to achieve the required properties. Addition of nanotubes to a polymer system leads to an increase in viscosity during processing and this effect can vary from small to significant; however. The composite mechanical properties reported tend to be comparable to those found for composites based on conventional fillers and fibres, including a reduction in impact strength in some cases. Although the modulus of carbon nanotubes is very high, this has not yet been translated into big improvements in composite modulus, for reasons which are not fully understood.

A number of application areas are being pursued for the nanocomposites, particularly where the purity and electrical conductivity characteristics noted above are important. The potential applications of CNTs include conductive and high-strength composite fibers, energy storage and energy conversion devices, sensors, and field emission displays [36, 37].

PEEK, PEI and polycarbonate composites are all being actively investigated. The nanofibers have also been used to reinforce cement, where only a few % can have a significant effect on increasing compressive strength and reducing crack propagation.

(II)-1.1.4 Nanocellular foam structures

Using nano-size fillers is one of the most common approaches to create nano-structured composite fibers. Another approach is to generate nano-size cellular structures in polymer matrices [38].

A certain amount of nano-size porosity in material results in attributes such as lightweight, good thermal insulation, high cracking resistance without sacrificing in mechanical strength. A potential application of cellular structure is to encapsulate functional components inside of nano-size cells.

One of the approaches is to make use of thermodynamic instability to produce nano-cellular materials. Controlled dosing of supercritical CO_2 is used to tailor the viscosity of a polymer melt. The domains of CO_2 embedded in the polymer melt expand in volume when the pressure applied to the system is suddenly reduced. These nano-bubbles are then permanently entrapped in the polymer when the temperature falls below the solidifying temperature of the polymer matrix. The porosity of the final composite can be in the range of 10-20 nm. In order to keep the pore size within nanometre range, a great effort is made in controlling the thermodynamics of the foam- forming process. The resultant nano-cellular fibers can be used as high-performance composite fibers as well as for sporting and aerospace materials.

(II)-1.2 Nanotechnology in textile finishing

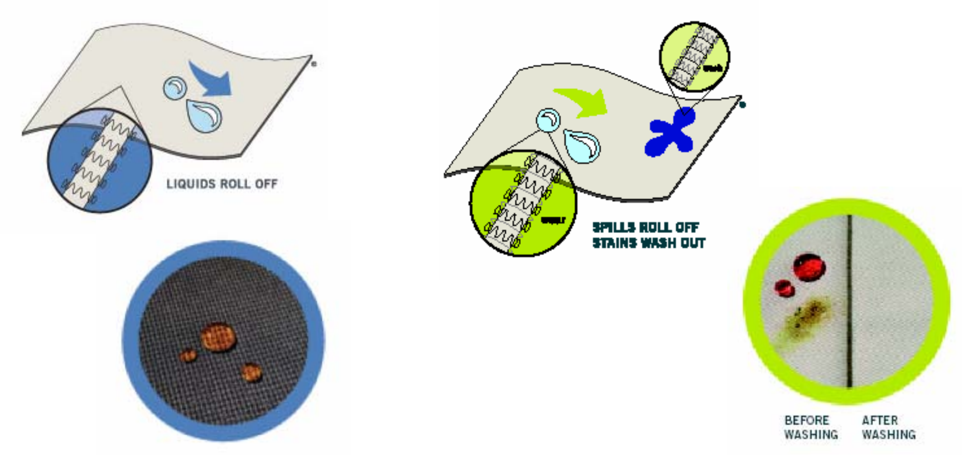
The impact of nanotechnology in textile finishing area has brought up innovative finishes as well as new application technique. Particular attention has been paid in making chemical finishing more controllable. Ideally, discrete molecules or nanoparticles of finishes can be brought individually to designated sites on textile materials in a specific orientation and trajectory through thermodynamic, electrostatic or other technical approaches.

Highly durable water-and-oil repellent finishing

Nano-Tex [Fig.(**II**)-5] uses nanotechnology to transform the molecular structures of fibers and create fabrics that offer unsurpassed performance and comfort. Each fiber has been fundamentally transformed through nanotechnology, and the result is a fabric that:

- draws moisture away from skin

- balances body temperature
- retains its natural softness
- allows fabric to breathe naturally
- maximizes performance over time



Figure(**II**)-5: NanoTex fabric

(II)-1.2.1 Upgrade of chemical finishes and resultant functions

Nanotechnology not only has exerted its influence in making versatile fiber composites but also has had impact in making upgraded chemical finishes. One of the trends in synthesis process is to pursue a nanoscale emulsification, through which finishes can be applied to textile material in a more through, even and precise manner.

Finishes can be emulsified into nano-micelles, made into nanosols or wrapped in nanocapsules that can adhere to textile substrates more evenly. These advanced finishes set up an unprecedented level of textile performances of stain-resistant, hydrophilic, anti-static, wrinkle resistant and shrink proof abilities [39].

(II)-1.2.2 Nanoparticles in finishing

Nanoparticles such as metal oxides and ceramics are also used in textile finishing to alter surface properties and impart textile functions [40].

As an example, the fabric treated with nanoparticles TiO_2 and MgO replaces fabrics with active carbon, previously used as chemical and biological protective materials. The photocatalytic activity of TiO_2 and MgO nanoparticles can break harmful and toxic chemicals and biological agents. These nanoparticles can be pre-engineered to adhere to textile substrates by using spray coating or electrostatic methods. Finishing with nanoparticles can convert fabrics into sensor-based materials. If nano-crystalline piezoceramic particles are incorporated into fabrics, the finished fabric can convert exerted mechanical forces into electrical signals enabling the monitoring of bodily functions such as heart rhythm and pulse if they are worn next to skin [41, 42].

(II)-1.2.3 Self assembled nanolayers

Self-assembled nano-layer (SAN) coating is a challenge to traditional textile coating. Research in this area is still in embryo stage. In self-assembled nano-layer coating, target chemical molecules form a layer of thickness less than nanometre on the surface of textile materials. Additional layers can be added on the top of the existing ones creating a nano-layered structure. Different SAN approaches are being explored to confer special functions to textile materials. One of the technical approaches is to use electrostatic attraction to self-assemble nano-layer coatings on textile materials for protective and self-healing function. The electrostatic approach is particularly appealing as the thickness, homogeneity and sequence of these nano-layers can be precisely controlled by control of molecular architecture, self-assembly and electrostatic interactions [43].

In addition, the self-healing capability makes this technique particularly tolerant to defects [44].

The self-assembly process begins by exposing a charged surface to a solution of an oppositely charged polyelectrolyte. The amount of adsorbed material is self-limiting by the charge density substrate. Surplus polymer solution adhering to the support is removed by simply washing it in a neutral solution. Under the proper conditions, the polyion is adsorbed with more than the stochiometric number of charges relative to the substrate, reversing the sign of the surface charge. In consequence, when the substrate is exposed to a second solution containing a polyion of opposite charge, an additional polyion layer is adsorbed reversing in this way the sign of the surface once again. Consecutive cycles with alternating adsorption of polyanions and polycations result in stepwise growth in total thickness of polymer films [45].

The fundamentals of the electrostatic self-assembly are more complicated than they appeared to be. Although this technique is based on the electrostatic attraction between positively and negatively charged species, the interaction between these charged species is specific to the nature of the substrate and that of the polyelectrolytes. Polyelectrolyte adsorption is nearly irreversible, so the built-up films do not represent equilibrium structures. This behaviour adds to the versatility of the method, but implies that a close kinetic control of the adsorption process is required in order to control film thickness and growth. The electrostatic self-assembly may depend on factors controlling the entropy of the polymer chains, such as molar mass, flexibility of the chains, ion exchange capacity as well as the hydrophobic interactions, charge transfer interactions, π-π stacking forces, and hydrogen bonding. No single theory is available that can provide a complete description of the self-assembly process; moreover, deeper understanding of the specificity of ion-ion and ion-substrate interactions on surface of textile materials with complicated contour remains a challenge [46-49].

(II)-1.3 Future prospect

Future developments of nanotechnologies in textiles will have a two fold focus: 1) upgrading existing functions and performances of textile materials; 2) developing smart and intelligent textiles with unprecedented functions. The latter is more urgent from the stand point of homeland security and advancement of technology. The new functions with textiles to be developed include 1) wearable solar cell and energy storage; 2) sensors and information acquisition and transfer; 3) multiple and sophisticated protection and detection; 4) health-care and wound healing functions; 5) self-cleaning and repairing functions.

Undoubtedly, nanotechnology holds an enormously promising future for textiles. It is estimated that nanotechnology will bring about hundreds of billions dollars of market impact on new materials within a decade; textile certainly has an important share in this material market [50].

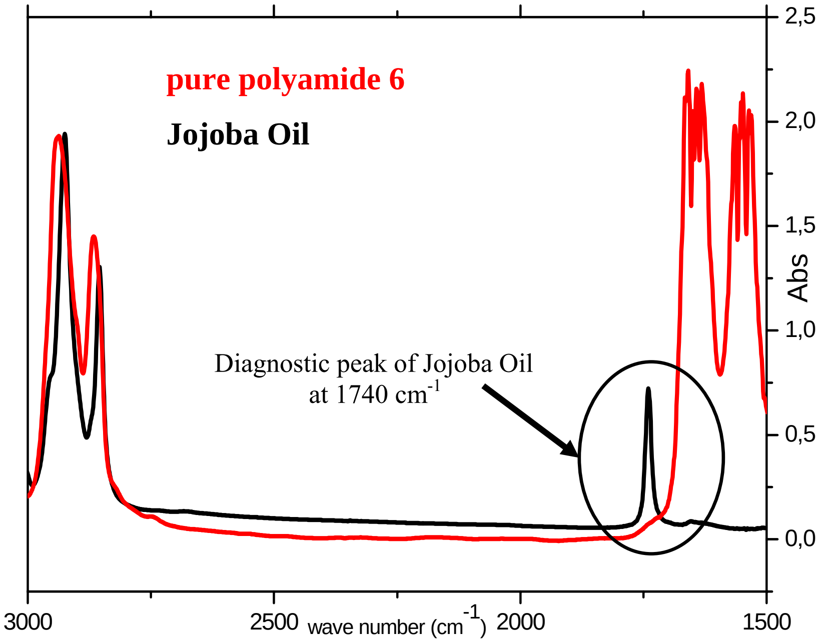
(II)-2 EXPERIMENTAL

(II)-2.1 Nanocomposite fibers for cosmetotextile applications

Aim of the PhD project is to incorporate Jojoba Oil into nylon fibers in order to obtain active skin care textiles.

Since the polyamide matrix and the cosmetic oily agent have no chemical and physical compatibility, two types of nano-sized filler were used to promote their blending: organically modified clay Nanomer®I.28 (montmorillonite containing 25 wt% trimethyl stearyl ammonium groups supplied by NANOCOR Inc.) and nanosized $CaCO_3$ (supplied by Solvay). The filler has the rule of powder vector which adsorbs and facilitates the dispersion of the cosmetic oil throughout the polymer matrix.

A series of nylon 6 nanocomposites with different filler/Jojoba Oil contents have been prepared by direct melt compounding. FTIR microscope analysis was choosen as investigation technique to check Jojoba Oil concentration and its time desorption through the polyamide, since esteric characteristic group of Jojoba Oil at 1740 cm^{-1} does not appear in polyamide 6 spectrum [Fig.(**II**)-6]. Polymer blends nanoscale morphology, thermal and mechanical properties of fibers have been studied as well.



Figure(**II**)-6: Spectra overlap of pure polyamide 6 and Jojoba Oil

(II)-2.2 Polyamide 6/organoclay-Jojoba Oil nanocomposite fibers

(II)-2.2.1 Preparation of polyamide 6/organoclay-Jojoba Oil hybrid nanocomposites

Melt blended nanocomposites were formed using a Haake Rheocord Rheomix 600 co-rotating twin mixer with a screw speed of 30rpm at 240°C for 2 minutes to avoid cosmetic oil degradation. The organoclay and Jojoba Oil were mixed in weight ratio 1:1 (nanjoj) and a wide range of polyamide 6/organoclay-Jojoba Oil nanocomposites containing 1.5, 3.5, 5, 7 and 8.5 wt% organoclay-Jojoba Oil paste were prepared.

(II)-2.2.2 Preparation of polyamide 6/organoclay-Jojoba Oil nanocomposite fibers

Nanocomposite blends (nanjoj) were reduced in pellets and dried at 100°C for 24h and then extruded through the die of a Bohlin Instruments Inc mod.RH7 capillary rheometer at 240°C to form fibers [Fig.(**II**)-7] having mean diameter of ~200µ.

Standard die diameter was 1mm, velocity of extrusion was 5mm/min, the take up speed was manual so it was not possible to calculate the draw ratio.

Figure(**II**)-7: Sample of nanocomposite fibers

(II)-2.2.3 X-ray diffraction and transmission electron microscopy

Wide-angle X-ray Scattering (WAXS) measurements of the as-mixed samples were performed at room temperature using a PW 1830/00 Philips diffractometer (Cu Kα Ni-filtered radiation) equipped with Philips (PW 3020model) powder goniometer and a sample holder for sample spinner.

The high voltage was 40 kV and the tube current was 30 mA. A standard sample was employed to determine the instrumental broadening.

The scanning rate was conducted over a range of 2θ= 1-10°.

Ultrathin sections (with thickness of ca.50nm) for transmission electron microscopy (TEM) observations were cut from as-extruded nanocomposite pellets under cryogenic conditions using a Leica EM FCS ultramicrotome with a diamond knife. The TEM microghraps were taken using ZEISS EM 900 transmission electron microscope under an accelerated voltage of 50 kV.

(II)-2.2.4 TGA measurements

Thermal properties of polyamide 6/organoclay-Jojoba Oil nanocomposites were analysed by TGA performed at a heating rate of 10°C/min from room temperature up to 550°C under N_2 flow by using a Hi-Res TGA 2950 from TA Instruments. The inorganic content of each composite was calculated from the residue left at 500°C. The actual percentage of organoclay, closely related to the amount of Jojoba Oil, was determined by 25% correction of organic content in Nanomer®I.28.

(II)-2.2.5 Mechanical tests

The tensile properties of the fibers were determined using an Instron mechanical tester (Model 4204) at a crosshead speed of 8.4mm/min at room temperature. Property values reported here represent an average of the results for tests run on at least 20 specimens.

(II)-2.2.6 FTIR analysis

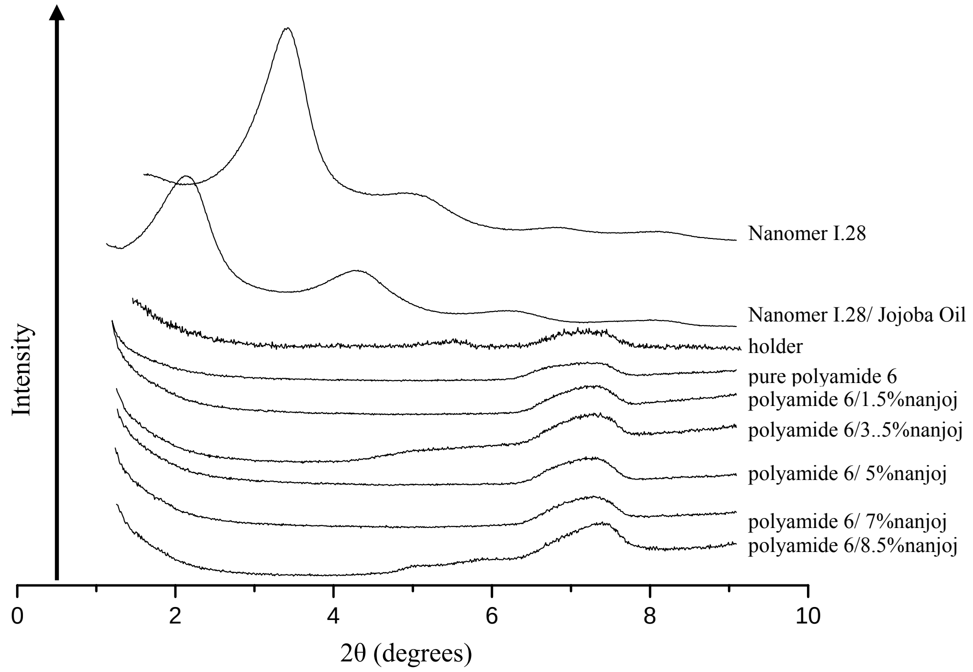
Thin sections of c.a. 20 micron were cut using a Reichert-Jung 1150/Autocat microtome at room temperature. Sections were compressed at 100 atm to further reduce thickness and then observed by FTIR Perkin Elmer System 2000 equipped with optic microscope IR Autoimage.

(II)-2.3 Results and discussion

(II)-2.3.1 Nanostructure and morphology

The clay dispersion within polyamide 6 matrix has been characterised by WAXS.

WAXS results for pure polyamide 6 and its organoclay-Jojoba Oil nanocomposites with different clay concentrations are shown in [Fig.(**II**)-8].



Figure(**II**)-8: WAXS spectra for pure polyamide 6 and its organoclay-Jojoba Oil nanocomposites with different clay concentrations.

The first reflection for the surface-modified clay, Nanomer$^{®}$I.28, was found at $2\theta = 3.39°$ which corresponds to an interlayer distance of 26Å.

The WAXS peak for organoclay-Jojoba Oil mixture was found at $2\theta = 2.14°$ that can be related to an interlayer distance of 41Å.

Probably Jojoba Oil alkyl chains have great physical affinity with the organo-modifier in Nanomer$^{®}$I.28, such a resulted increasing of the interlayer spacing causes a big shift of the diffraction peak toward lower values of 2θ [51].

In general, one might expect that larger spacing may allow to easier exfoliation since platelet-platelet attraction is reduced. It is implied that diffusion of polymer chains inside clay galleries is less hindered due to increased spacing and ultimately leads to improved exfoliation [52] resulting in hybrids with better dispersion of clay and Jojoba Oil.

Actually after melt compounding with polyamide 6, the basal plane of organoclay disappears in the WAXS patterns for the obtained nanocomposites with different organoclay-Jojoba Oil loading levels up to 8.5 wt%.

The absence of basal plane peak indicates the delamination and dispersion of clay nanolayers within the polyamide 6 matrix, i. e., the formation of an exfoliated nanostructure.

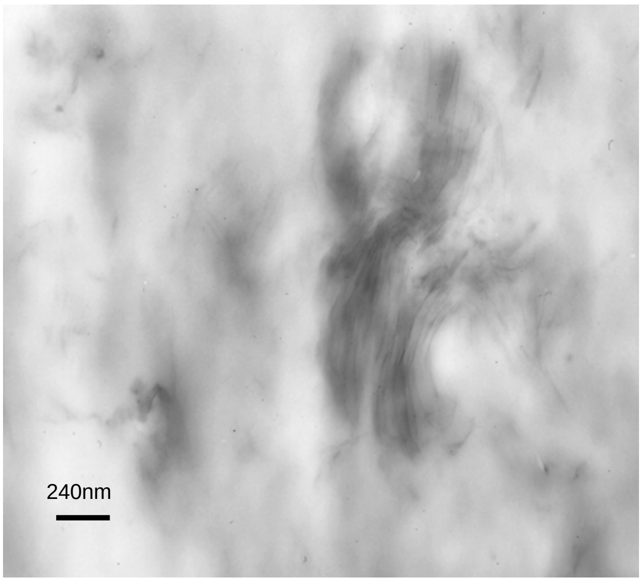
It is worth noting that in spite of the absence of the basal plane, a broad shoulder in the small angle region is usually observed in WAXS patterns for the obtained nanocomposites with high clay loading (e. g. 8.5 wt%), probably indicating the formation of partially exfoliated/ partially intercalated nanostructures [52].

There is a quite small peak in the 3.5 wt% scan occurring around $2\theta = 5.5°$ corresponding to a basal spacing of 16Å. This spacing is less than that of repeat spacing of the modified organoclay, this may be due to the collapse of a small fraction of the organoclay galleries caused by ammonium ion degradation [53].

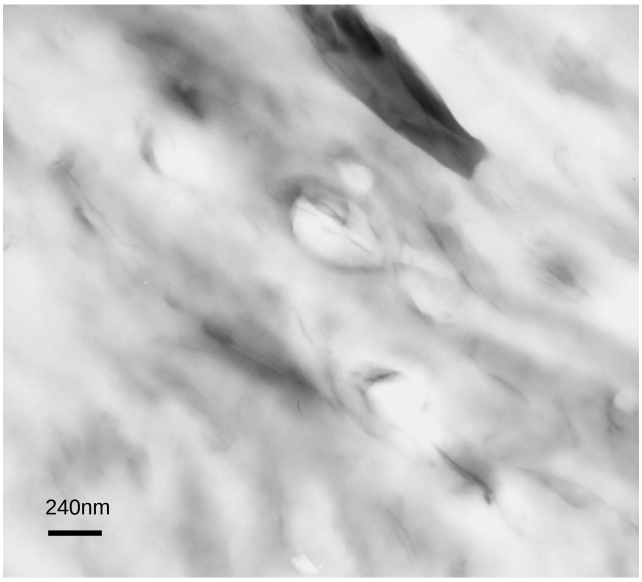
It is well known that WAXS information alone is not sufficient to characterize a nanocomposite. Consequently, the organoclay dispersion in polyamide was further analyzed by TEM.

TEM studies were conducted to examine the precise disperion of the clay layers within the polyamide nanocomposite blends. Typical TEM photographs for blends containing 1.5, 3.5, 5 and 7 wt% of organoclay-Jojoba Oil are shown in Figs.(**II**)-9,10,11,12,13.

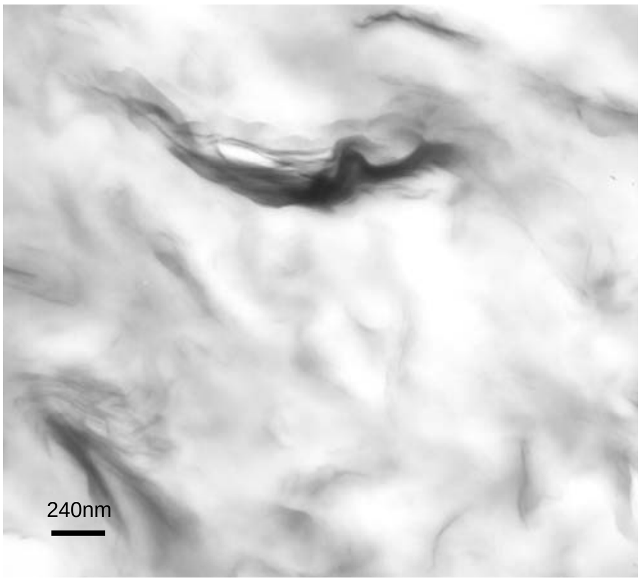
The dark lines are the intersections of clay layers (1 nm thick) and white or light gray regions are polymer [51]. It is worth noting that all the photos show bright holes probably formed by sublimation of oil drops trapped into the matrix as a consequence of high local temperatures generated by incident electron beam. Higher is Jojoba Oil content, many are voids.



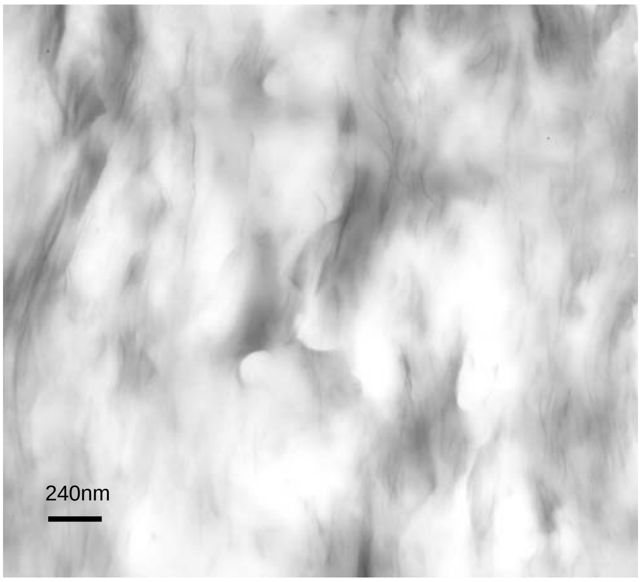
Figure(**II**)-9: TEM photo of polyamide 6/1.5 wt% nanjoj



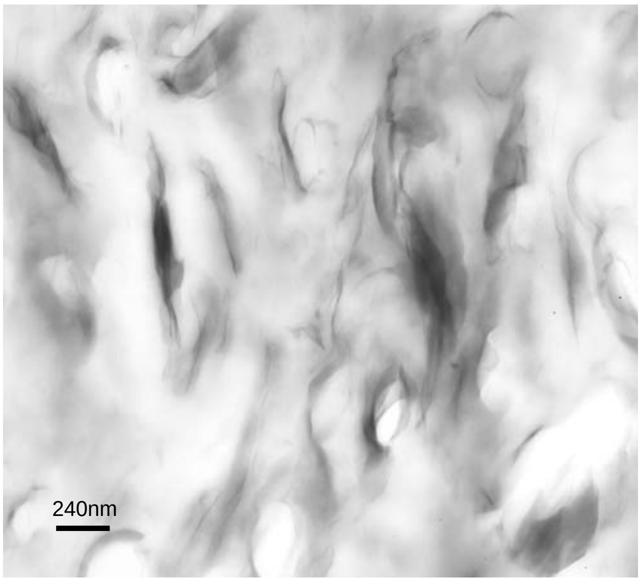
Figure(**II**)-10: TEM photo of polyamide 6/3.5 wt% nanjoj



Figure(**II**)-11: TEM photo of polyamide 6/5 wt% nanjoj



Figure(**II**)-12: TEM photo of polyamide 6/7 wt% nanjoj



Figure(**II**)-13: TEM photo of polyamide 6/8.5 wt% nanjoj

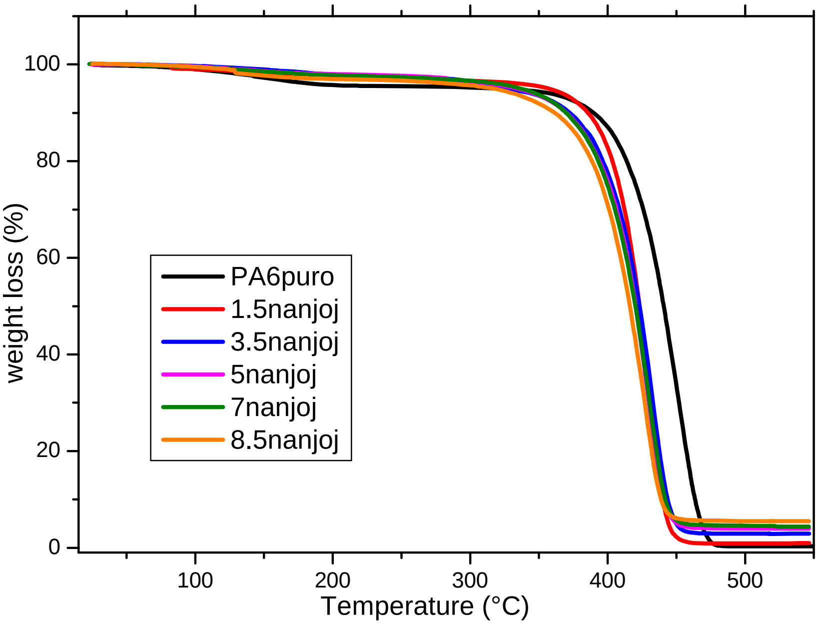
Some of the clay layers show individual dispersion of delaminated sheets in the matrix, as well as regions where the regular stacking arrangement is maintained with a layer of polymer between the sheets. Although a face to face layer morphology is retained, the layers are irregularly separated by the polymer; some stacks appear parallel to the plane of observation (large dark regions). For all the samples some of the clay is well dispersed in polyamide matrix and some of it is agglomerated.

It is well accepted that the state of the clay particles affected the thermal behaviour and the tensile mechanical properties of each polymer/clay hybrid.

(II)-2.3.2 Thermal properties

The thermal stability of pure polyamide 6 and its nanocomposites has been investigated [Fig.(**II**)-14].

The improved thermal stability for polymer/clay nanocomposites is mainly due to the formation of char which hinders the out-diffusion of the volatile decomposition products, as a direct result of the decrease in permeability, usually observed in exfoliated nanocomposites [54].



Figure(**II**)-14: Weight loss as funcion of temperatureof pure polyamide 6 and its nanocomposites.

In this case, despite exfoliation occurs (as evidenced by WAXS and TEM), the decomposition temperature is not improved by the presence of organoclay, excepted at nanofiller concentration of 1.5 wt%.

Since Jojoba Oil degradation temperature under N_2 flow is 393°C at 50% weight loss and for pure polyamide 6 is 441°C, Jojoba Oil decomposition process is faster than that of polyamide and its dispersion through polymer matrix promotes in advance the degradation mechanism. This feature is valid for every sample loading.

Decomposition temperatures at 5% and 50% weight loss are listed in Table (**II**)-II.

Samples	Degradation temperature (5% weight loss)	Degradation temperature (50% weight loss)
Pure polyamide 6	322°C	441°C
PA6/1.5 wt% nanjoj	357°C	424°C
PA6/3.5 wt% nanjoj	322°C	423°C
PA6/5 wt% nanjoj	335°C	420°C
PA6/7 wt% nanjoj	335°C	420°C
PA6/8.5 wt% nanjoj	316°C	416°C

Table (**II**)-II. Degradation temperatures by TGA under N_2 flow at 5% and 50%

The weight of the final residue at 500°C was found to increase by between 0.90 and 5.34 wt% in accordance with the increase in organoclay loadings (from 1.5 up to 8.5 wt%).

The actual percentage of Jojoba Oil in the final nanocomposite was calculated by:

$$\%\ \text{Jojoba Oil} = \%\ \text{organoclay} = \%\ \text{MMT}_{ash} / (100 - \text{OC})$$

where % MMT_{ash} is the mass after incineration relative to the original nanocomposite mass; OC is the % organic content in the organoclay as reported by suppler.

The experimental nanofiller contents and the relative corrections are listed in Table (**II**)-III.

Sample	Experimental filler content (wt% by TGA)	Actual organoclay content (wt% by correction)
PA 6	0	0
PA 6/1.5wt%nanjoj	0.90	1.20
PA 6/3.5wt%nanjoj	2.48	3.31
PA 6/5 wt%nanjoj	3.06	4.08
PA 6/7 wt%nanjoj	4.14	5.52
PA 6/8.5wt%nanjoj	5.34	7.12

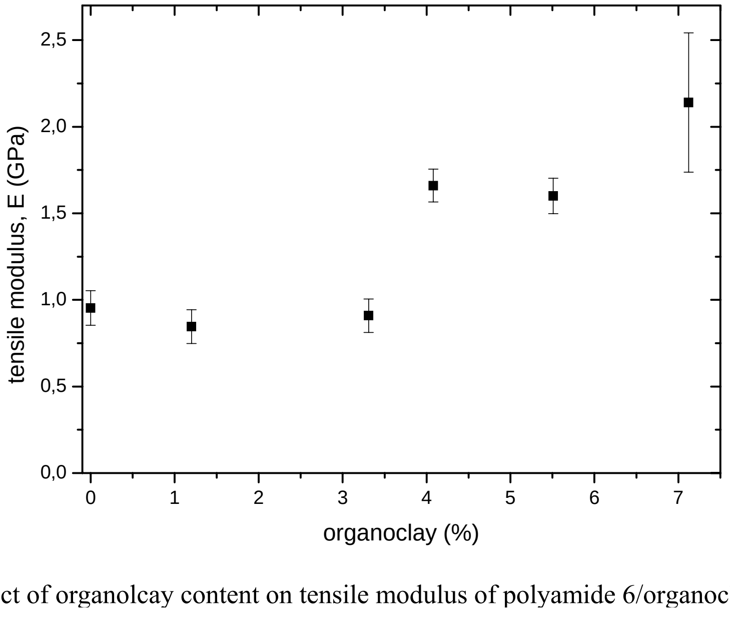
Table(**II**)-III: Experimental nanofiller contents by TGA and relative corrections

(II)-2.3.3 Mechanical properties

The effect of clay content on the tensile properties of polyamide 6 nanocomposites compared to pure polyamide 6 has been investigated. Table (**II**)-IV summarizes the moduli and the other mechanical properties of the hybrid fibers. Fig.(**II**)-15 shows the effect of organoclay concentration on the modulus of nanocomposites.

Samples	Actual filler content (wt%)	Young's modulus (GPa)	Yield strength (MPa)	Strain at yield point (%)	Elongation at break (%)	Ultimate strength (MPa)
PA 6	0	0.953±0.100	0.041±0.003	0.0943±0.0023	-	-
PA 6/ 1.5%nanjoj	1.20	0.846±0.097	0.045±0.002	0.0832±0.0037	-	-
PA 6/ 3.5%nanjoj	3.31	0.909±0.097	0.050±0.003	0.0666±0.0058	2.34±0.19	50±3
PA 6/ 5%nanjoj	4.08	1.66±0.095	0.062±0.002	0.0465±0.0027	2.37±0.25	54±4
PA 6/ 7%nanjoj	5.51	1.60±0.102	0.060±0.002	0.0460±0.0033	2.23±0.31	53±5
PA 6/ 8.5%nanjoj	7.12	2.14±0.402.	0.072±0.007	0.0433±0.0036	2.36±0.09	66±8

Table(**II**)-IV. Mechanical properties of polyamide 6/organoclay-Jojoba fibers

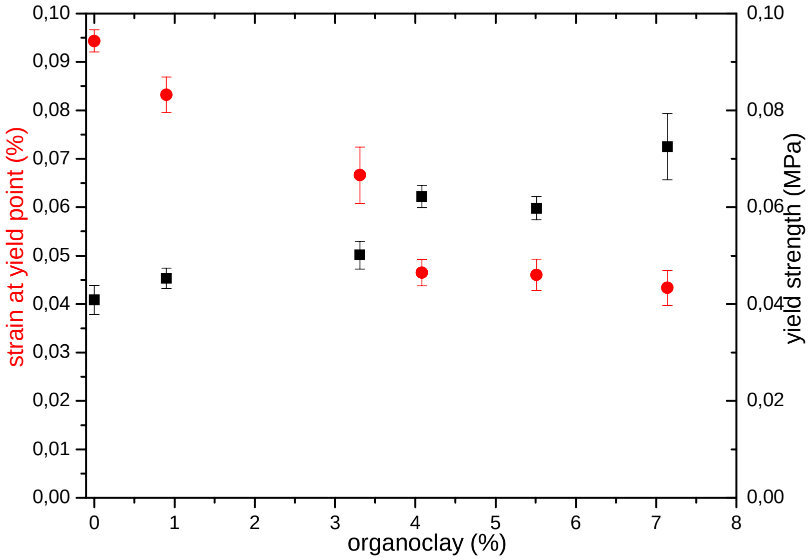


Figure(**II**)-15:Effect of organolcay content on tensile modulus of polyamide 6/organoclay Jojoba fibers

The tensile modulus of the hybrid fiber containing theoretical 5 wt% of organoclay (experimental 4.1 wt%) was 1.7 times greater than that for pure polyamide 6. When the organoclay content in polyamide 6 reached 8.5 wt% (experimental 7.1 wt%), the modulus increased about 2.2 fold over that of pure polyamide 6. This was consistent with the general observation that the introduction of an organoclay into a polymer matrix is found to improve its mechanical modulus, although there isn’t a linear correlation between the organoclay loading and modulus growth.

It is worth noting that for hybrid fibers containing 1.5 wt% and 3.5 wt% of organoclay the tensile modulus was nearly identical to that of pure polyamide 6. This seems to be the result of debonding between organoclay and polyamide 6; debonding could be also the explanation of tensile modulus declination when the theoretical amount of organoclay in polyamide was 7 wt% [51].

Fig.(**II**)-16 show the dependence of yield strength and strain at yield point on organoclay content: as expected yield strength slightly increased with the concentration of montmorillonite, on the contrary the strain at yield point decreased with clay loading.



Figure(**II**)-16: Effect of organoclay content on strain at yield point (●) and yield strength (■) of polyamide 6/organoclay-Jojoba fibers.

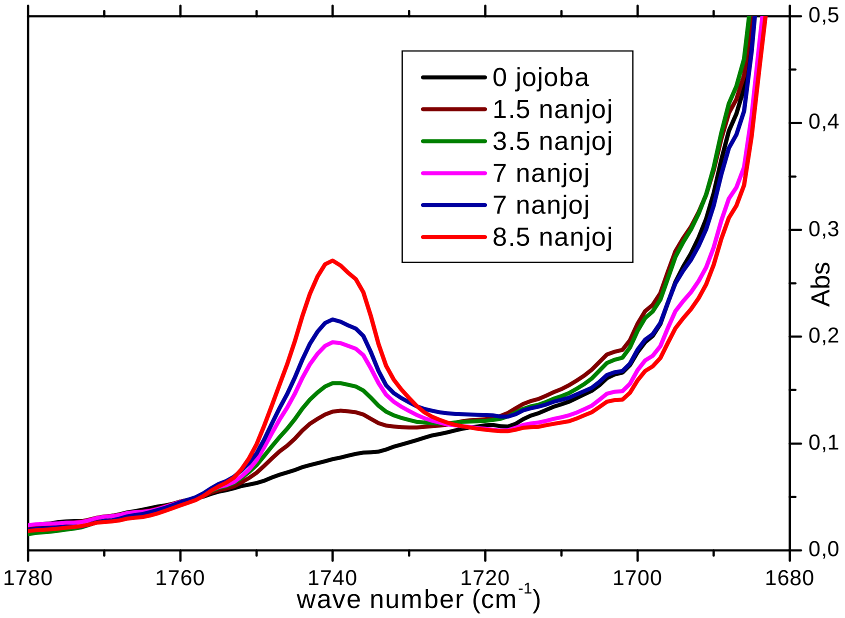
In general virgin polyamides are very ductile at low test rates. Increasing the clay content leads to a sacrifice in ductility compared to pure polyamide 6, in this case elongation at break values are quite similar up to 3.5 wt% organoclay concentration, such a behaviour is consistent with results found by Fornes et al. [55] for low molecular weight polymer matrix.

(II)-2.3.4 FTIR analysis

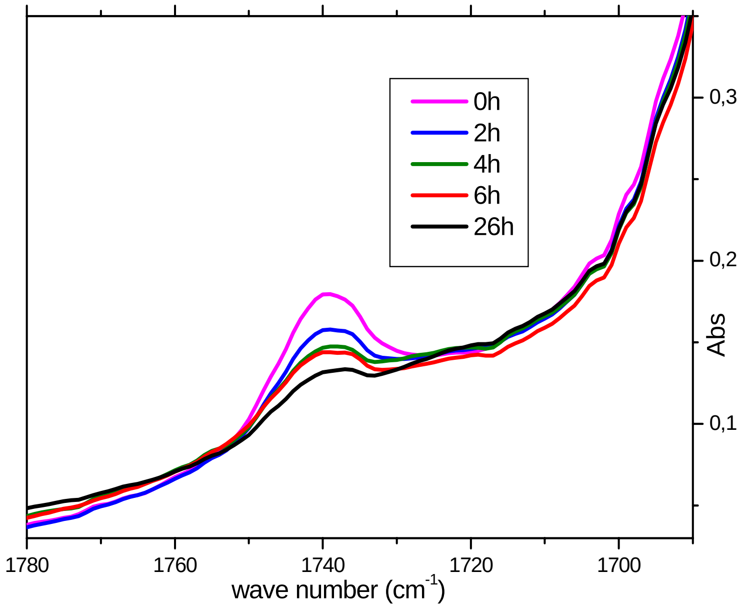
It was possible to check Jojoba Oil content in nanocomposite blends observing the characteristic peak signal of Jojoba Oil at 1740 cm^{-1}, which appears in spectra of polyamide 6 nanocomposites containing Jojoba Oil and does not appear in polyamide 6 nanocomposite without it [Fig.(**II**)-17].

Polymer blend thin sections were dipped in isopropanol for increasing time (2 to 26 h) to study Jojoba Oil desorption through the polyamide matrix: the decrease of peak intensity at 1740 cm^{-1} corresponded to a Jojoba Oil release. For every sample a progressive content reduction of the cosmetic agent was observed [Figs.(**II**)-18,19,20,21].

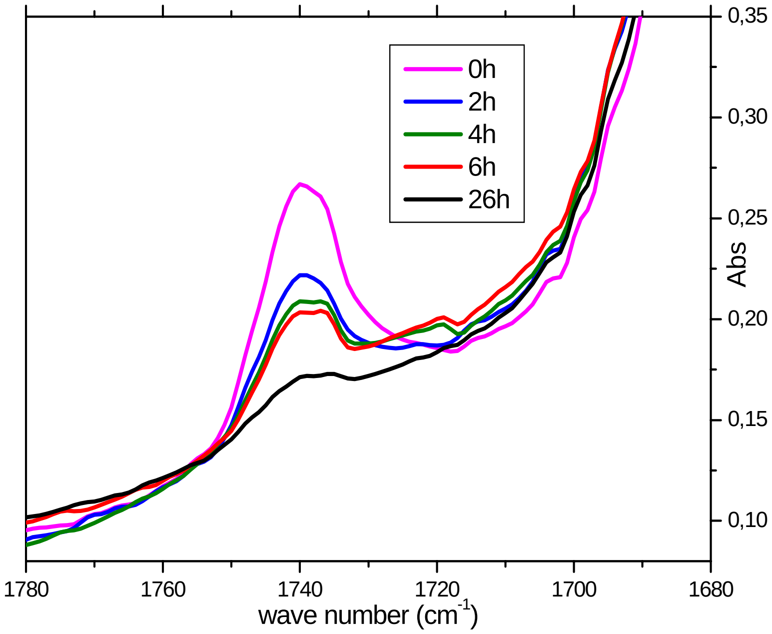
A normalization procedure is necessary to cancel thickness differences among samples and on the same sample at different site of observation. Effective Jojoba Oil contribute (peak height) was isolated from polyamide 6 spectrum carrying out a spectra subtraction: Abs vs time is the ratio between CO peak height and polyamide 6 internal standard peak height at 3080 cm^{-1} [Fig.(**II**)-22].



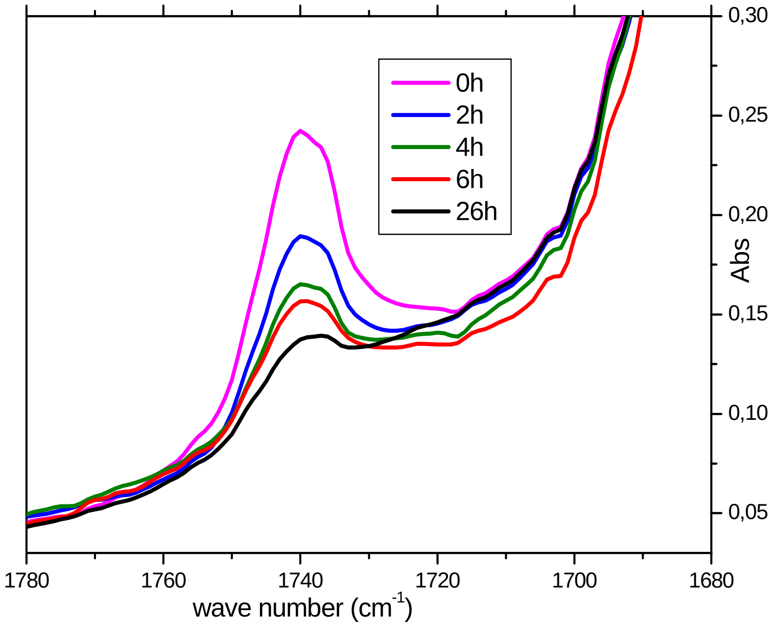
Figure(**II**)-17: FTIR spectra before contact with solvent of polyamide 6/organoclay-Jojoba sections



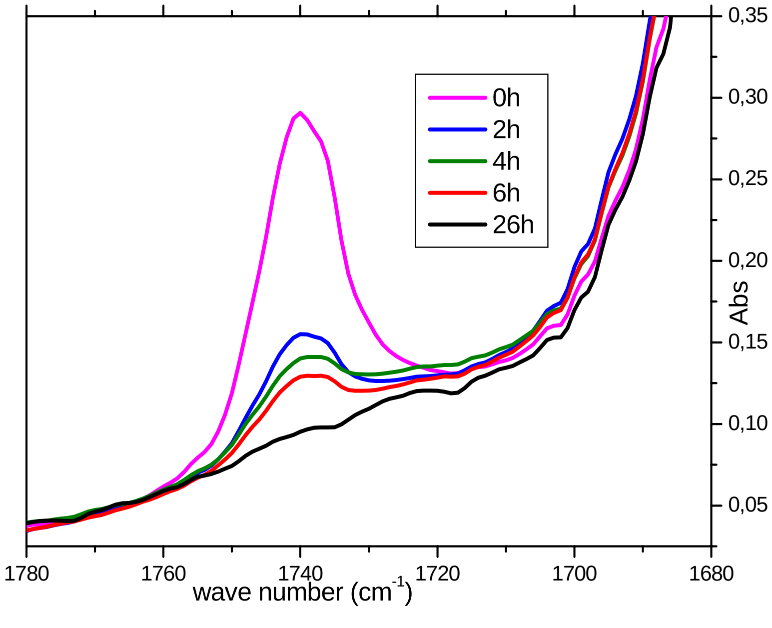
Figure(**II**)-18: Release of Jojoba Oil through polyamide matrix for polyamide 6/3.5 wt% nanjoj.



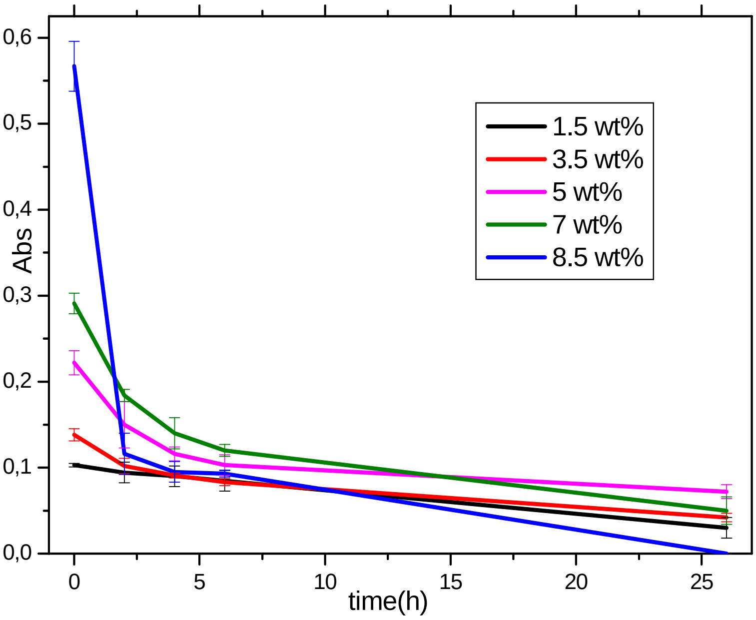
Figure(**II**)-19: Release of Jojoba Oil through polyamide matrix for polyamide 6/5 wt% nanjoj.



Figure(**II**)-20: Release of Jojoba Oil through polyamide matrix for polyamide 6/7 wt% nanjoj.



Figure(**II**)-21: Release of Jojoba Oil through polyamide matrix for polyamide 6/8.5 wt% nanjoj.



Figure(**II**)-22: Time release of Jojoba Oil through polyamide 6/organoclay-Jojoba sections

It is interesting to note that Jojoba Oil is released slowly at low organoclay concentration (1.5 wt%, 3.5 wt%, 5 wt%) and faster when organoclay concentration is higher (7 wt% and 8.5 wt%).

It seems that the polyamide 6 has a maximum capacity, related to the hydrophobic nature of the matrix, to hold back the lypoid agent; going beyond this physico-chemical limit the release mechanism cannot be controlled.

(II)-2.4 Polyamide 6/$CaCO_3$-Jojoba Oil nanocomposite fibers

In order to compare the effect of nanofiller type as blending agent, nanosized $CaCO_3$ was used as well to obtain nanocomposite fibers. The experimental preparation procedure was the same as for polyamide 6/organoclay blends; mechanical tests and FTIR analysis were performed to charactherize and reveale differences between the two systems.

(II)-2.4.1 Mechanical tests and FTIR analysis

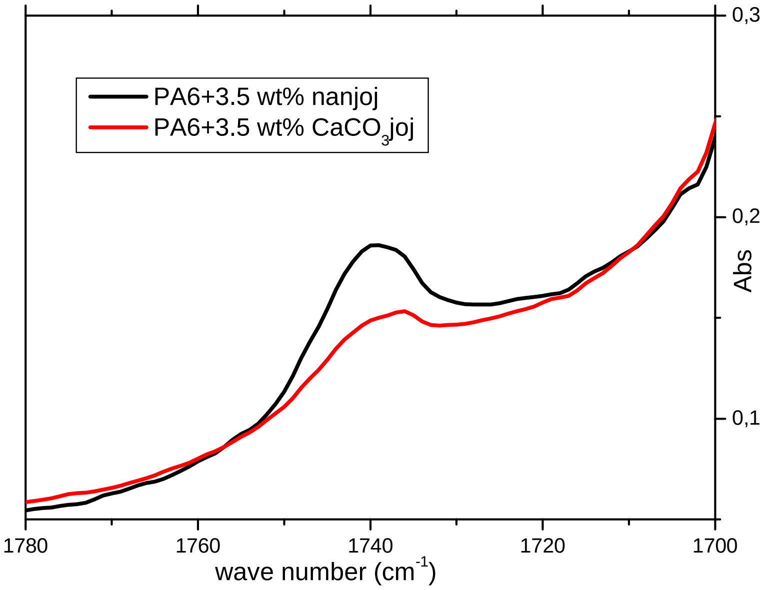
As an example, mechanical properties of 1.5, 3.5 and 8.5 wt% $CaCO_3$-Jojoba Oil are reported in Table(**II**)-V.

Sample	Young Modulus (GPa)	Yield strength (MPa)	Strain at yield point (%)
PA 6	0.953±0.100	0.041±0.003	0.0943±0.00231
PA 6/1.5%$CaCO_3$-Joj	0.813±0.150	0.036±0.003	0.0858±0.00871
PA 6/3.5%$CaCO_3$-Joj	0.566±0.063	0.029±0.002	0.0927±0.00798
PA 6/8.5%$CaCO_3$-Joj	0.792±0.064	0.030±0.004	0.0751±0.00820

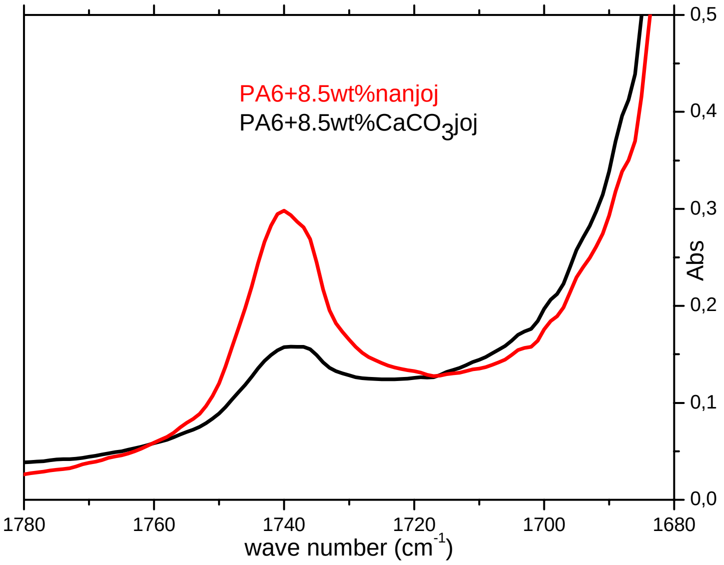
Table (**II**)-V: Mechanical properties of polyamide 6/$CaCO_3$-Jojoba fibers

It is worth noting that Young Modulus does not increase incresing nanofiller loading and values of yield strength and strain at yield point are nearly similar to that of pure polyamide 6. One might think that this nanosized filler could be better compared to the organoclay since it doesn't vary significantly nylon 6 mechanical properties but FTIR analysis showed that the characteristic esteric Jojoba Oil peak had not equal intensity in $CaCO_3$ and organoclay systems at the same experimental content [Figs.(**II**)-23,24].

This meansthat degradation occurs since the filler structure does not exert oil and polymer protection. For this reason, any desorption experiment in isopropanol was carried out.



Figure(**II**)-23: Polyamide 6/organoclay-Jojoba and polyamide 6/CaCO$_3$-Jojoba sections at the same filler content



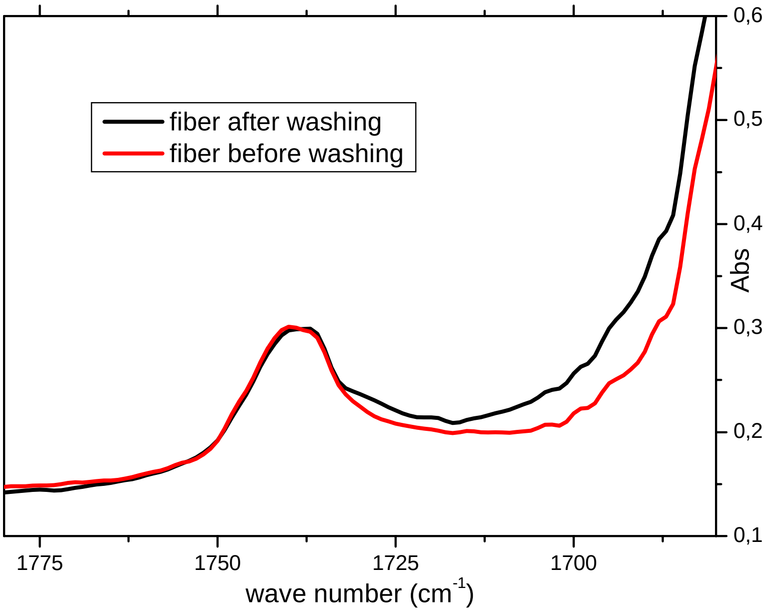
Figure(**II**)-24: Polyamide 6/organoclay-Jojoba and polyamide 6/CaCO$_3$-Jojoba sections at the same filler content

(II)-2.5 Fibers washing and skin contact simulation

The last step on nanofibers study has been to test their behaviuor in conditions simulating the practical application.

For this purpose samples of 8.5 wt% nanjoj fiber were pressed under 150 atm and observed by FTIR microscope after 2 hours contact with water and soap (2g of DASH-commercial laundry detergent-in 100ml water) at 50°C.

As it can be seen in Fig.(**II**)-25 CO signal at 1740cm^{-1} does not change its intensity.



Figure(**II**)-25: Simulation of washing laundry at 50°C for 2 hours

To simulate human skin surface condition, sebum formulation was prepared according approximately to literature. [56]

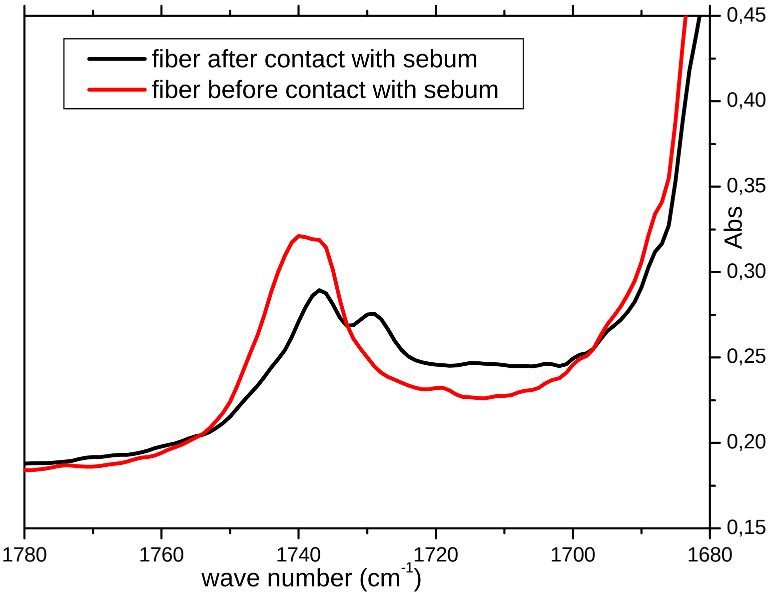
Human sebum is a mixture of triglycerides, fatty acids, wax esters, squalene, cholesterol, and cholesterol esters.

The following percentage quantity of components was used:

Squalane (16%-$C_{30}H_{50}$), Tripalmityne (8%- $C_{51}H_{98}O_6$), Oleyc acid (10%- $C_{18}H_{34}O_2$), Palmitic acid (7%- $C_{16}H_{32}O_2$), Myristic acid (5%- $C_{14}H_{28}O_2$), Cholesterol (3%-$C_{27}H_{46}O$), Glycerol (50%- $C_3H_8O_3$).

At normal skin temperature (skin surface temperature is 32°C), sebum contains both a solid and a liquid phase; into sebum formulation was dipped the 8.5 wt% organoclay/Jojoba pressed fiber for 48h at 37°C.

To be sure that any solid sebum residue was on the sample fiber, before FTIR observation the fiber was kept in isopropanol for 5 minutes. Recorded spectra showed that CO signal of Jojoba Oil changed in shape and position: two shoulders are present at 1737 cm^{-1} and 1730 cm^{-1}, probably due to different rates of release of Jojoba components in contact with long alkyl chains of sebum formulation [Fig.(**II**)-26].



Figure(**II**)-26: Simulation of skin contact at 37°C for 48 hours

(II)-3 FINAL REMARKS

To compare the effect of nanofiller type on the mechanical, thermal and release properties of polyamide 6/Jojoba Oil systems, both commercial organoclay and nanosized $CaCO_3$ were used to prepare polymer blends.

A serie of polyamide 6/nanofiller-Jojoba Oil nanocomposites with different filler-Jojoba Oil contents have been prepared by melt compounding and then extruded from a capillary rheometer to obtain fibers useful in cosmetic field.

WAXS and TEM analyses show that nanocomposite blends have exfoliated and partially intercalated morphologies.

TGAs show that thermal stability of nanofibers is improved by about 30°C when clay loading is 1.5 wt%; higher concentrations lead to a less significant improvement, probably due to the presence of Jojoba Oil which is characterized by a faster degradation mechanism.

Tensile tests indicate that mechanical properties of polyamide 6/organoclay-Jojoba Oil nanofibers at high clay loadings are enhanced compared with neat polyamide 6; on the other hand, when clay concentration is low (less than 5 wt%) the behaviour of cosmeto-nanofibers is overall similar to that of polyamide 6 neat fibers. Such a result seems to be promising for our purpose, since these new cosmeto-nanofibers designed to applications in cosmetic field should have the same range of utilization of traditional nylons.

FTIR observations allow to check Jojoba Oil presence in every polymer blend: cosmetic agent degradation is prevented by layers structure of the organoclay and time desorption in solvent of Jojoba Oil was studied by variation of peak intensity at 1740 cm^{-1}. It was found that time release of the cosmetic agent through polyamide 6/organoclay-Jojoba nanocomposites (containing less than 7 wt% clay concentration) is slow and controlled due to the finer dispersion of organoclay within polymer matrix.

Concerning systems containing $CaCO_3$, mechanical tests confirmed that these nanoparticles did not vary significantly tensile properties of nylon fibers, even at high nanofiller loading. Nevertheless FTIR analysis show that Jojoba Oil is not protected by degradation during extrusion processes.

Simulations of application conditions were carried out and qualitative considerations are as follows:

1) the cosmetic oil content did not vary after nylon fibers washing, allowing regular textile laundery treatments,
2) when nanofibers are in contact with sebum at body temperature, Jojoba Oil characteristic peak is split in two signals indicative of different rates of components release.

These results encourage further investigation on release mechanism of the cosmetic agent through the polymer matrix, promoting the interest on potential applications of such nanofibers in cosmetotextile field.

CONCLUSIONS

The textile and clothing industry, normally seen as a traditional industry, needs nowadays to fight increased competition specically from Asia.

There is a general recognition that traditional apparel products may be no longer sufficient to sustain a viable business and the EU textile industries have to move towards more innovative and high quality products.

New materials and technologies promote development of high-tech textiles, characterized by unprecedented functions and effects.

An example of the new way to combine tradition and innovation is represented by fibers having skin care activity, which are able to release on the wearer cosmetics and perfumes agents.

Widely spreaded are microcapsules containing active substances grafted on the textile or spinned into the fibers, which can release thei content as a consequence of body heat and friction.

Otherwise, the active agent embebbed into the fabric can be transferred thanks to humidity exchange between skin and fibers surface.

Specific purpose of this PhD work has been to estimate the possibility of making products having *skin care* effects by means of Jojoba Oil additivation to nylon fibers.

Since polyamide 6 and Jojoba Oil have different physico-chemical nature, the additivation was carried on by means of two different strategies: synthesis of politerephthalamide microcapsules containing Jojoba Oil and direct dispersion of Jojoba Oil into the polyamide matrix using a nanosized filler acting as additive carrier.

In this study polyamide microcapsules Jojoba Oil containing having mean diameter of ~5μm were synthesized by means of ultrasonic irradiations.

A qualitative description of microcapsules characteristics in terms of dependence upon both the formulation and the process conditions has been reported.

In summary, the combination of HMDA with TDC and BTC produces the best microcapsule membranes with smooth and dense surfaces and low porosity. The efficiency of using the cross-linking agent in the organic phase instead of in the aqueous phase is also demonstrated by SEM observations.

By using aliphatic acid dichloride, even if model microcapsules containing toluene have good aspect, no Jojoba Oil microcapsules can be formed in the same experimental conditions. It means that the system behaviour is strictly dependent on the type of the organic phase: it is reasonable to think that something related to the chemical nature of the acid dichloride in the Jojoba Oil phase (e.g. diffusion rate toward oil/water interface, rate of hydrolysis of COCl groups, etc.) influence the membrane formation mechanism.

An interesting outcome of SEM study shows the possibility to reduce microcapsules size from ~15μm diameter to ~5μm diameter by using ultrasonic irradiations during the dispersion step.

Obtained microcapsules were melt extruded with polyamide 6; TGA and DSC analysis and SEM observations of polymer blends confirmed the high thermal and mechanical resistance of polyamide cross-linked shell microcapsules, preventing Jojoba Oil degradation and promoting its combination with nylon 6.

The restriction for this research line was the difficulty to get well dry and isolated microcapsules without breaking their shell during the separation step from bulk solution and the availability of injection technology for direct spinning of microcapsules in fibers.

On the other side, promising potential applications offered by new nanomaterials led to verify the possibility of using nanofibers in cosmeto textile field.

To compare the effect of nanofiller type on the mechanical, thermal and release properties of polyamide 6/Jojoba Oil systems, both commercial organoclay and nanosized $CaCO_3$ were used to prepare polymer blends.

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Tensile tests indicate that mechanical properties of polyamide 6/organoclay-Jojoba Oil nanofibers at high clay loadings are enhanced compared with neat polyamide 6; on the other hand, when clay concentration is low (less than 5 wt%) the behaviour of cosmeto-nanofibers is overall similar to that of polyamide 6 neat fibers. Such a result seems to be promising for our purpose, since these new cosmeto-nanofibers should have the same range of utilization of traditional nylons.

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