Università di Napoli "Federico II"
Dipartimento di Scienze Fisiche

Tesi di Dottorato
in
Tecnologie Innovative
per Materiali Sensori ed Imaging
XIX CICLO
2003-2006

POLYMER BASED MICROPARTICLES FOR ADVANCED COMPOSITE MATERIALS APPLICATIONS

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This thesis reports on the preparation and characterization of polymer based micro-sized beads to be used as fillers for advanced composite materials.

In the Part I physical properties of urea-formaldehyde microcapsules containing an epoxy resin are presented and discussed. Microcapsules were prepared by *in situ* polymerization of monomers in an oil-in-water emulsion.

Differential scanning calorimetry (DSC), thermo-gravimetric analysis (TGA) and scanning electronic microscopy (SEM) were applied to investigate thermal and morphological microcapsule properties. Microencapsulation was detected by means of FT-IR and Raman techniques.

It was found that the amount of encapsulated epoxy resin as well as the extent of urea-formaldehyde polymerization depends on the reaction temperature and the stirring speed.

In the Part II the influence of thermosetting microspheres on the properties of an epoxy resin was investigated. For this purpose, the preparation and the morphological characterization of two types of epoxy-based microparticles was carried out. The microspheres were then added to an EPON828-3,3'DDS matrix to study their influence on the rheological and thermo-mechanical behaviour. Two epoxy systems were used to prepare microspheres: a Bisphenol A-type resin (EPON825) cured with 2,4-diaminotoluene (DAT), and a Bisphenol F-based epoxy resin (PY306) crosslinked with diethyltoluenediamine (DETDA). Both systems of microspheres were synthesized through dispersion polymerization and differed to each other in the size, as evidenced by morphological analysis. These microparticles were blended, in different weight percents (10 and 20wt. %), with a matrix consisting of diglycidyl ether of Bisphenol A (EPON828) and 3,3'-diaminodiphenylsulphone (3,3'DDS). Rheological behaviour of the prepared blends was preliminarily studied. After cure, the dynamic-mechanical properties of the composites were also investigated. Results indicated that the reactivity of the uncured blends, as well as the viscoelastic properties of crosslinked systems are influenced not only by the nature and the amount of the microparticles introduced, but also, in a significant way, by their size.

Dedicated to my daughters
Roberta e Francesca

Acknowledgement

It has been a great learning experience and opportunity to work with Professor Carfagna. I would like to thank him for giving me the opportunity to do a variety of different things in these years.

I have learned a lot from these unique experiences, I am very thankful to him for that.

I am also very thankful for having Veronica Ambrogi as friend, collaborator and colleague in this Ph.D. endeavor. I would not have made so much progress thus far without her help, support, enthusiasm, guidance and encouragement. Her ability to constantly challenge my knowledge and push to come up with new chemistry and explain the same has been a very enriching experience which very few people experience in their graduate careers, I thank her very much for that. She will always be my best friend for the rest of my life.

Microencapsulation is like the work of a clothing designer. He select the pattern, cuts the cloth, and sews the garment in due consideration of the desires and age of his customer plus the locale and climate where the garment s to be worn.

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A.Kondo

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The Art of Microencapsulation

What do scratch-and-sniff perfume advertisements, laundry detergent, baking mixes, and aspirin have in common? Each product relies on microencapsulation to provide its unique attributes. Microencapsulation is a process by which tiny particles of liquid, solid or gas active ingredient are packaged within a second material for the purpose of shielding the active ingredient from the surrounding environment. These capsules, which range in size from one micron to seven millimeters, release their contents at a later time by means appropriate to the application.

The preparation of a microencapsulated product involves a number of steps. First, the need for microencapsulation, whether it is to enhance the quality of an existing product or to develop an entirely new product, must be identified. Next, a shell material that provides the desired release characteristics must be chosen. Finally, a process to prepare the microcapsules mst be selected.

This procedure is something an art, as Asajo Kondo assert in *Microcapsule Processing and Technology:*

"Microencapsulation is like the work of a clothing designer. He select the pattern, cuts the cloth, and sews the garment in due consideration of the desires and age of his customer plus the locale and climate where the garment s to be worn. By analogy, in microencapsulation, capsules are designed and prepared to meet al the requirements in due consideration of the properties of the core material, intended use of the product, and the environment of storage...."(A. Kondo, *Microcapsule Processing and Technology*, Marcel Dekker, Inc., New York, 1979).

Certain techniques and processes contribute to this view of microencapsulation as an art, primarily because of the broad range of scientific and engineering disciplines they encompass, as well as the interconnettivity of these disciplines.

Consider, for example, the process called complex coacervation. Conceived in the 1930's it was the first process used to make microcapsules for carbonless copy paper. In complex coacervation, the substance to be encapsulated is first dispersed as tiny droplets in an aqueous solution of a polymer such as gelatin. For this emulsification process to be successfull, the core material must be immiscible in the aqueous phase. Miscibility is assessed using physical, chemistry and thermodynamics. The emulsification is usually achieved by mechanical agitation, and the size distribution of the droplets is governed by fluid dynamics.

A second water soluble polymer, such as gum arabic, is then added to this emulsion. After mixing, diluite acetic acid is added to adjuste the pH. Though both polimers are soluble in water, addition of the acetic acid results in the spontaneous formation of two incompatible liquid phases. One phase, called the coacervate, has relatively high concentrations of the two polymers; the other phase, called the supernatant, has low polymer concentrations. The concentrations of the polymers in these two phases, and the pH at which phase separation occurs, are governed by specific properties of physical, chemistry, thermodynamics, and polymer chemistry.

If the material are properly chosen, the coacervate preferentially adsorb onto the surface of the dispersed core droplets, forming microcapsules. Again, physical chemistry and thermodynamics dictate whether the coacervate adsorbs onto the core material. The capsule shells are usually hardened first by cooling (heat transfer), and then by chemical reaction through the addition of a cross-linking agent such as formaldheyde (polymer chemistry). The release characteristics of the microcapsules are governed by materials science (mechanical), heat transport (thermal release) and mass diffusion (diffusion through the wall).

Each aspect of this process is highly dependent upon the others. For example, the thermodynamics of the phase separation affects the composition of the shell material, and this affects the ability of the shell to wet the core phase, as well as determining the barrier properties and release characteristics.

Despite extensive research to fully comprehend the coacervation process, it has been almost impossible to study the influence of each of these factors on an individual basis. Furthermore, answers to some questions – how fast should the pH lowered, how can agglomeration and formation of free coacervates be avoided, what are the effects of rapid cooling – remain qualitative.

Considering the difficult questions involved, the interconnettivity of different process element, and the fact that there are hundreds of encapsulation process variations, it is little wonder that microencapsulation is sometimes regarded as an art.

Microencapsulation is a growing field that is finding application in many technological disciplines. A wide range of core materials in addition to those listed above have been encapsulated. These include adhesives, liquid crystals, repairing agents, phase change materials (PCMs), agrochemicals, catalysts, living cells, flavor oils, pharmaceuticals, vitamins, and water. There are many advantages to microencapsulation. Liquids can be handled as solids, odor or taste can be effectively masked in a food product, core substances

can be protected from the deleterious effects of the surrounding environment, toxic materials can be safely handled, and drug delivery can be controlled and targeted.

There are four typical mechanisms by which the core material is released from a microcapsule – mechanical rupture of the wall, melting of the wall, dissolution of the wall and diffusion through the wall. Less common release mechanism include ablation (slow erosion of the shell) and biodegradation.

Two well known applications of microencapsulated products rely on mechnical rupture of the shell to release the core content. Scratch-and-sniff perfume advertisements work because tiny perfume-filled microcapsules are coated onto the magazine page. When scratched, the shell wall ruptures, releasing the perfume. Carbonless copy paper utilizes the same release mechanism. Small capsules, 1-20 microns in diameter, coat the underside of the top sheet of paper. The capsules contain a dye precursor – a clear chemical that by itself will not put a mark on the lower page, but darkens in color when exposed to an acidic component (such as an attapulgite clay or phenolic resin). This acidic component coats the top of the lower sheet. When subjected to the high local pressure beneath a pen point, the capsules break, the two reactants mix, and the copy appears on the lower sheet.

Another area where microencapsulation has been widely applied is in the detergent industry. Some powder detergents contain protein reactive enzymes such as protease, used in removing blood stains. The enzymes are encapsulated in a water- soluble polymer, such as polyethylene glycol, for aestethic reasons and safe handling purposes. Released upon shell dissolution in the washing machine, the enzymes attach the blood protein, thereby helping to remove the blood stain.

Many packaged baking mixes include encapsulated ingredients to delay chemical reactions until proper temperatures are reached. Sodium bicarbonate is a baking ingredient that reacts with food acids to produce leavening agents, which give baked goods their volume and lightness of texture. To delay and control the leavening process, the sodium bicarbonate is encapsulated in a fat, which is solid at room temperature but melts at a temperature of about 125° F. Release of the core material is delayed until the proper temperature is reached.

Microencapsulation products in the pharmaceutical industry are very common, particularly when sustained release of a medication is required. Aspirin provides effective relief for fever, inflammation and arthritis, but direct doses of aspirin can cause peptic ulcers and bleeding. The drugs is therefore sometimes encapulated in ethyl cellulose or hydroxypropyl methylcellulose and starch (aspirin tablets are formed by pressing together

collection of these microcapsules). Rather than being released all at once, the aspirin diffuses through the shell in a slow, sustained dose.

CHAPTER 1

MICROENCAPSULATION & MICROCAPSULES

1.1.Introduction

Microencapsulation is a fascinating process in which tiny droplets or particles are wrapped with a protective coating yielding capsules for countless applications.

In simple terms a capsule is a miniature container (**Figure 1**) that protects its contents from evaporation, oxidation and contamination until its release is triggered.

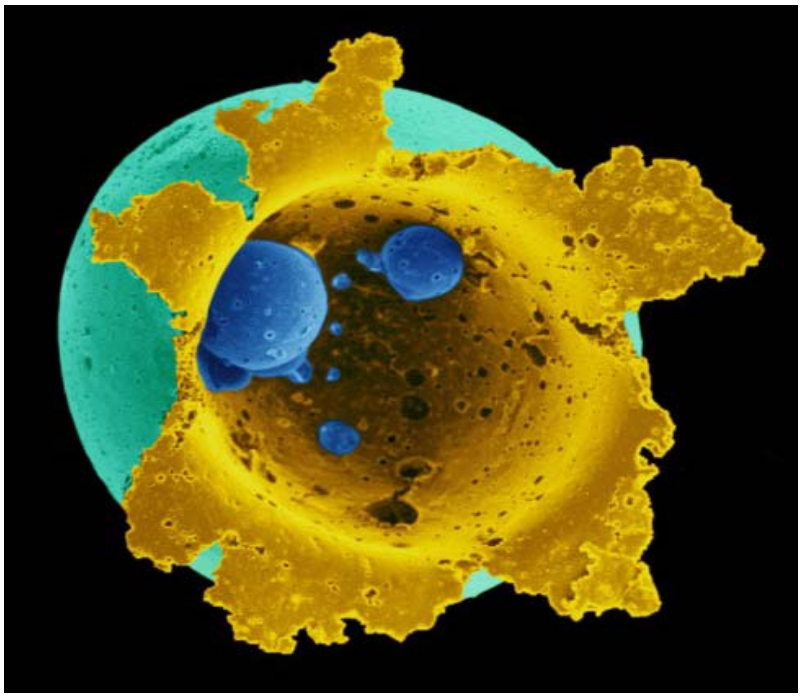


Figure 1. Schematic representation of a microcapsule

The size is always tailored to suit the end product and the relevant processes involved in order assuring survival in sometimes hostile manufacturing conditions. For most applications the particle diameter is only a few microns across. This means that the product remains invisible to the naked eye but high power microscopes open up an exciting insight into this curious dimension.

For example, an area of one square centimetre (cm^2) would contain one million capsules if placed side by side in a standard coated paper application. This allows multiple releases in the same area until finally all capsules are broken.

The most common applications are the coating of paper and board resulting in a wide variety of end products such as disposable handkerchiefs, drawer liners, giftwrap, stationery, greeting cards, advertising, brochures, samplers, books, cartons, labels etc. other substrates such as textiles, certain plastics and even metal surfaces are becoming increasingly popular with encapsulate applied.

There are special applications where the encapsulation is used to keep two or more reactive substances in isolation from each other to provide better shelf life and also new formulation opportunities. The suggestions above are only some of the possible uses.

The development of new methods and the ever-increasing range of new polymeric materials suitable for many different techniques in encapsulation are a constant challenge.

This is resulting in new product opportunities driven by customer demand or sometimes discovered as 'spin off's' resulting from focused research in a multitude of different projects.

One of the great achievements is the variety of different coating processes possible, meaning that in most cases the existing plant can be used without any special know how or modifications.

Long term studies show that coated surfaces can remain intact for decades, the oldest and still working sample was printed in 1958! This enables savings in the packaging costs, since no airtight wrapping is needed.

Microencapsulation is the only cost effective and long lasting method in storing volatile substances over very long periods of time.

In advertising or in launching new products encapsulation becomes a very useful and powerful tool by being invisible and coming to life at the slightest touch.

The rather impressive shelf life performance provides a key benefit organising production of print runs which usually have to be planned some time ahead before the actual article is inserted into a magazine for instance.

Another popular and useful application comprises of a “purchaser testing panel” printed directly onto the product or its packaging (e.g. deodorant, aftershave, room spray, etc.). This would give the potential purchaser a chance to sample the fragrance without the undesired tampering with the actual content (i.e. opening the item, dispensing some of the contents and returning it to the shelf with tampered packaging and reduced fill). A number of major manufacturers use encapsulation to prevent tampering whilst providing sampling at the same time as standard on their products.

1.2. Theoretical background

1.2.1.About microencapsulation

Approximate 40 years ago, encapsulation processes were developed. It involves the coating and entrapment of a pure material or mixture into another material. The coated or entrapped material is usually a liquid but can be a solid or gas. This material is also known as the core material, actives, fill, internal phase or payload.

The coating material can also be called the capsule, wall material, membrane, carrier or shell (**Figure 2).** Natural examples include birds' egg shells, plant seeds, bacterial spores, skin and seashells.

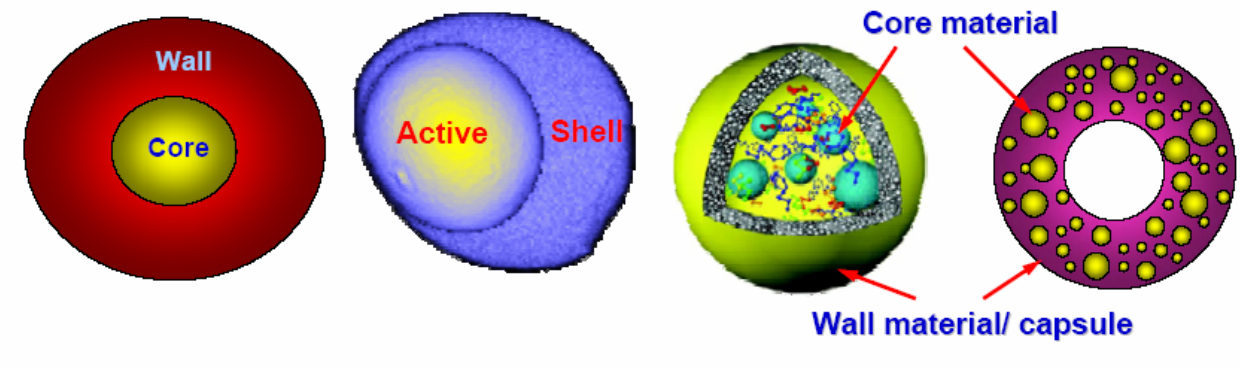


Figure 2. Some examples of microcapsules

Microencapsulation is a technique to prepare tiny packaged materials called microcapsules that have many interesting features[1-3]. This technique has been employed in a diverse range of fields from chemicals [4,5] and pharmaceuticals [6,7] to cosmetics [8,9] and printing [10]. For this reason widespread interest has developed in microencapsulation technology.

The first industrial product employing microencapsulation was carbonless copy paper developed by

Green and Schleicher in the 1950s. The microcapsules used in it were prepared by complex coacervation of gelatin and gum arabic [11]. To this day, carbonless copy paper is one of the most significant products to utilize microencapsulation technology, and is still produced commercially. The technologies developed for carbonless copy paper have led to the development of various microcapsule products in recent years.

Further function integration in microcapsules is essential to make products with excellent properties.

Likewise, strategies should be considered to make smaller microcapsules with thinner membranes. This direction of microencapsulation research is suited to current needs and matches the features of nanotechnology efforts initiated in the United States of America in 2000.

It have been developed, so far, microcapsules with functions for separation and purification [12-17], controlled release of drugs [18-30], and the triboelectric property required by toner microparticles [31, 32]. Hollow microcapsules and microcapsules enclosing microorganisms have also been prepared [33, 34].

1.2.2.Microencapsulation terminology

First, some of the more basic information on the methods of preparing microparticulate formulations must be discussed. The terminology used to describe microparticulate formulations can sometimes be inconsistent and confusing to readers unfamiliar with the field. Essentially, the term "microparticle" refers to a particle with a diameter of 1–1000 μm, irrespective of the precise interior or exterior structure. Within the broad category of microparticles, "microspheres" specifically refers to spherical microparticles and the subcategory of "microcapsules" applies to microparticles which have a core surrounded by a material which is distinctly different from that of the core. The core may be solid, liquid, or even gas. Despite the specific and logical subcategories, many researchers use the terms interchangeably, often to the confusion of the reader. It is usually assumed that a formulation described as a microparticle is comprised of a fairly homogeneous mixture of polymer and active agent, whereas microcapsules have at least one discrete domain of active agent and sometimes more. Some variations on microparticle structures are given in **Figure 3**. As the domains and subdomains of active agent within microcapsules become progressively smaller, the microcapsules become microparticles.

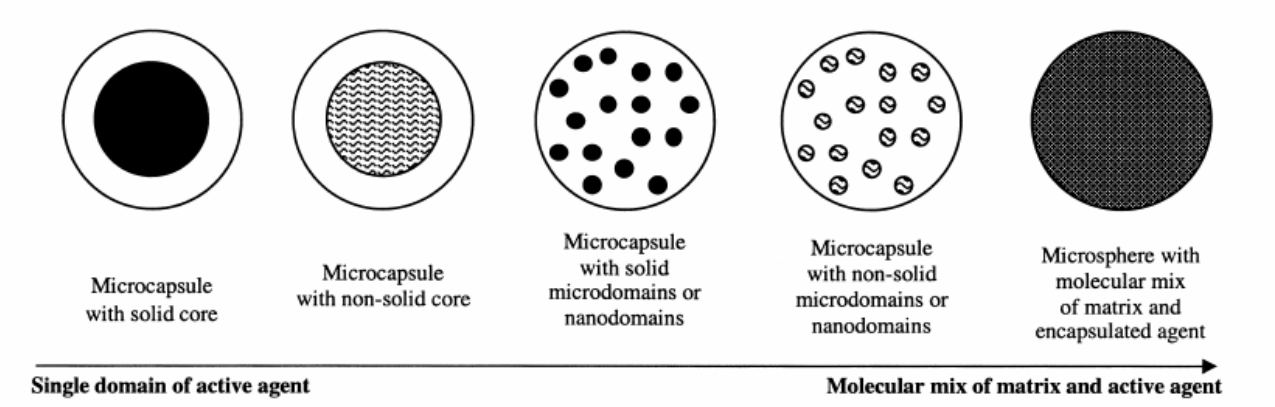


Figure 3. Variations of microparticle formation

1.3.Microencapsulating materials

The core of microcapsules, also called the fill or internal phase, `is the mass to be encapsulated.` Core material may be in any physical state: liquid, solid, gases, dispersions in liquids or complex emulsions. The initial step in encapsulating a active ingredient is the selection of a suitable coating material, referred to as the encapsulation matrix.

Coating substances that are basically film forming materials can be selected from a wide variety of natural or synthetic polymers, depending on the material to be coated and the characteristics desired in the final microcapsules. The coating composition is the main determinant of the functional properties of the microcapsule and of the method to be used to improve the performance of a particular ingredient. An ideal coating material should have the following properties:

1. Good rheological properties at high concentration and ease of manipulation during the process of encapsulation.
2. Ability to disperse or emulsify the active material and stabilize the emulsion produced.
3. Non-reactivity with the material to be encapsulated both during processing and on prolonged storage.
4. Ability to seal and hold the active material within its structure during processing or in storage.
5. Complete release of the solvent or other materials that are used during the process of encapsulation, under drying, or other desolventization conditions.
6. Ability to provide maximum protection to the active material against environmental conditions (e.g., heat, light, humidity).
7. Solubility in solvents acceptable in the food industry, e.g., water, ethanol, etc.
8. Chemical non-reactivity with the active material.

9. Ability to meet specified or desired capsule solubility properties and active material release properties.

Because almost no coating material can meet all the properties listed above, in practice they are used in combination with other coating materials and/or modifiers, such as oxygen scavengers, antioxidants, chelating agents, and surfactants. Generally, water-insoluble polymers are used to microencapsulate the aqueous core while the converse is true for organic core materials [35]. Thickness of coat is manipulated to alter permeability and stability of microcapsules.

1.4.Types of the microencapsulation technology

Microencapsulation is a remarkable technology, which is easy to handle and offers several advantages with respect to protecting the environment. As it comes into increasing use, it can be expected to contribute to the development of new technology and new products.

The microencapsulation technologies most widely used can be roughly categorized in three different types or "formulations," each of which includes a wide variety of methods. They are listed in the table below.

	Formulation	**Overview of formulation**	**Sample wall material**	**Sample Use**
Chemical formulation	Surface polymerization	Polymerizing the core material on a dispersion intermediary surface	Polyurethane, polyamide, and polyurea	Thermal-sensitive papers, pressure-sensitive copying papers, adhesives, and agricultural chemicals
	In Situ polymerization	Supplying monomer from either inside or outside of the core material and polymerizing it on the surface of the core material	Urea, PVA, and melamine	Cosmetics, pressuresensitive copying papers, inks, adhesives, and perfumes
	Submerged curing coating method	Dripping a polymer solution containing the core material from an orifice into a bath of the curing agent	Alginic acid and gelatin	Medications and perfumes
Physical and chemical formulation	Phase separation from a water solution	Separating the phases of a polymer solution containing the core solution by applying an electric charge	Gelatin	Pressure-sensitive copying papers, perfumes, adhesives, medications, and display materials
	Phase separation from organic solvent	Separating the phases of a polymer organic solvent containing the core material by adding nonaqueous solvent	Ethylcellulose	Medications and enzymes

	Submerged drying	Enclosing drops of a water solution containing the core material by a polymer solution, and drying by a method such as heat or decompression	Polystyrene, gelatin, and PVA	Medications
	Dissolution decentration cooling	Coating the core material with a substance that dissolves with heat but solidifies at room temperature	Paraffin and polyethylene	Medications, perfumes, and feed
Mechanical formulation	Spray drying	Dispersing or spraying the core material into a polymer solution and making it into particles, and then drying the solution	Gelatin, starch, PVA, and cellulose	Food, medication, agricultural chemicals, and cosmetics
	Air-suspension coating	Suspending the core material on a fluidized bed and coating it by spraying the material of capsule wall on it	Polymers, alumina, and carbon	Medications and agricultural chemicals
	Dry blending	Physically energizing the particles of core material and raw wall material, and bonding the wall material to the particles of the core material	Nylon and acrylic materials	-

An overwhelming majority of methods used for encapsulating drugs in a submillimeter spherical polymer matrix involve the use of liquid emulsions. A simple definition of an emulsion as applied to liquids is the dispersion and stabilization of one liquid within another to which it is immiscible. The most common emulsion type is oil-in-water (**Figure 4**), however, oil-in-oil and multiple emulsions (water-oil-water, oil-oil-water, solid-oil- water, and so on) are used frequently (36.49).

The main criterion for creating an emulsion is that the dispersed phase (solution containing polymer and drug) must be immiscible (or nearly so) in the continuous phase (external phase containing dissolved surfactant).

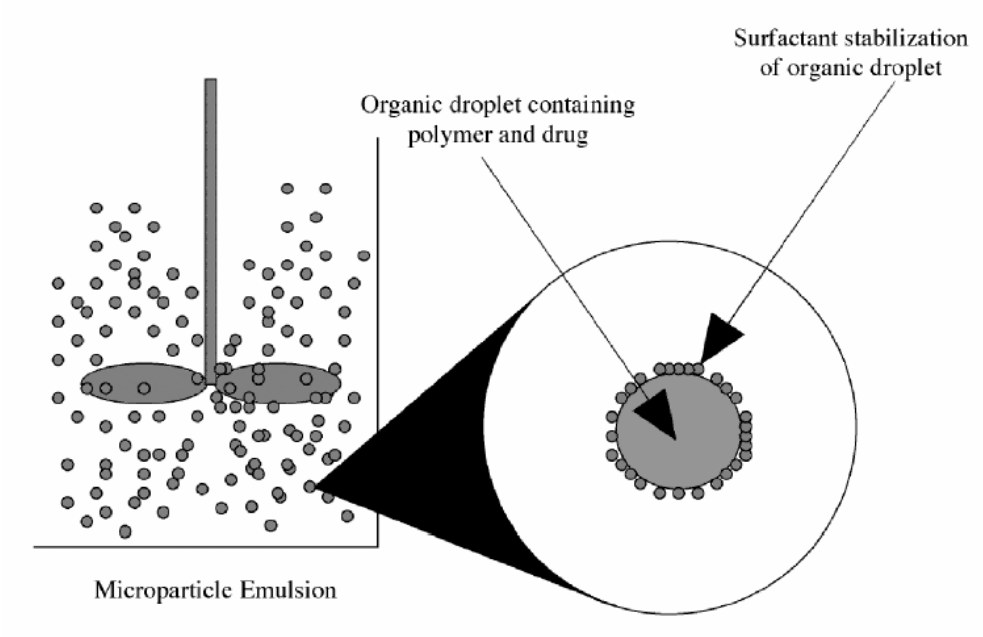


Figure 4. Encapsulation using oil-in-water emulsion technique

A surfactant is also included in the aqueous phase to prevent the organic droplets from coalescing once they are formed. Once the droplets are formed via physical means, the organic solvent leaches out of the droplet into the external aqueous phase before evaporating at the water–air interface. Emulsions are simply created by using a propeller or magnetic bar for mixing the organic and aqueous phases.

1.5. General features of microcapsules

Microcapsules are tiny vessels in which a liquid or solid material called "core material" is encapsulated with a membranous sheath made of, for example, polymer or membranous material. Although their size is not clearly specified, microcapsules ranging from 5 to 300μm are generally used.

The most significant feature of microcapsules is their microscopic size that allows for a huge surface or interface area. Through selection of the composition materials (core material and membrane), it is possible to endow microcapsules with a variety of functions. Generally, membrane materials are chosen in order to pronounce the effects of microencapsulation. Therefore, not only synthetic and natural polymers but also lipids and inorganic materials are used for the preparation of microcapsules.

Microcapsules can be classified into three basic categories according to their morphology as mono-cored, poly-cored, and matrix types, as shown in **Figure 5**. Morphological control is

important and much effort has been given to controlling internal structures, which largely depend on the protocol and the microencapsulation methods employed.

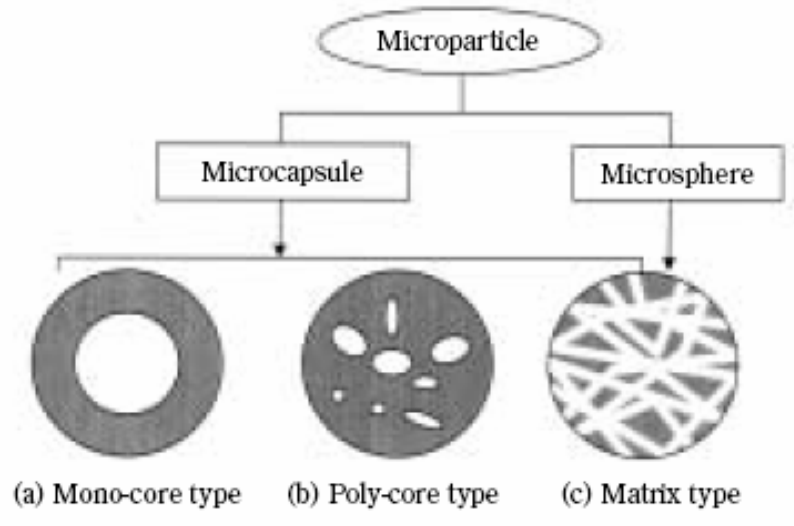


Figure 5. Classification of microparticls from their morphology

Generally speaking, the microcapsule has the ability to modify and improve the apparent shape and properties of a substance. More specifically, the microcapsule has the ability to preserve a substance in the finely divided state and to release it as occasion demands.

Microcapsules are fabricated beforehand so that core material can be extracted by breaking membrane with desired means such as pressure, heat, light, acid, or chemical. In addition, microcapsules can release core material gradually through small holes on the membrane even though the membrane is not broken.

Contents of microcapsules are released by a variety of mechanisms [35, 50, 51]. The coating may be mechanically ruptured, for example, by the act of chewing (physical release) [52]. Coatings may melt when exposed to heat (thermal release) [52] or dissolve when placed in solvents. Changes in pH may alter the permeability of polymer coatings and thereby control leaching. Water soluble core materials diffuse into aqueous media. Protein or lipid coatings may degrade by the action of proteases and lipases respectively. Several fundamental equations governing controlled release of active substances were described [53-57].

General purposes for microencapsulation are to make liquids behave like solids; separate reactive materials; reduce material toxicity; provide environmental protection to compounds; alter surface properties of the materials; control release of materials; reduce volatility or flammability of liquids; and mask the taste of bitter compounds [35,52, 58-60].

Consequently, microencapsulation can be employed to enhance, time or tune the effect of functional ingredients and additives such as processing aids (leavening agents and enzymes); preservatives (acids and salts); fortifiers (vitamins and minerals); flavors (natural and synthetic), and spices [61].

Major benefits brought about by microencapsulation of active ingredients and additives are summerized in a number of reasons :

1) To reduce the reactivity of the core in relation to the outside environment (e.g., light, oxygen, and water);
2) To decrease the evaporation or transfer rate of the core material to the outside environment;
3) To promote easier handling of the core material;
4) To control the release of the core material in order to achieve the proper delay until the right stimulus;
5) To mask the core taste; and to dilute the core material when it is used in only very small amounts, but achieve uniform dispersion in the host material [58,62].

More detailed features of microcapsules are summarized in books by Gutcho [63] and Arshady [64], and in review papers by Makino [65], Arshady [66], Kondo [67], Hatate, et al. [68], and Yoshizawa [69-71].

1.6. Microcapsule Design

The architecture of microcapsules is generally divided into several arbitrary and overlapping classifications. One such design is known as matrix encapsulation. In this design the matrix particle resembles that of a peanut cluster. The core material is buried to varying depths inside of the wall material. The most common or well known type of microcapsule is that of a spherical or reservoir design. It is this design that most approaches a hen's egg. It is also possible to design other microcapsules that have multiple cores where the multiple cores may actually be an agglomerate of several different types of microcapsules. (**Figure 6**)

If the core material is an irregular material, such as occurs with a ground particle, then the wall will somewhat follow the contour of the irregular particle and one achieves an irregular microcapsule. The last well known design for a microcapsule is that of a multiple wall. In this case the multiple walls are placed around a core to achieve multiple purposes related to the manufacture of the capsules, their subsequent storage and controlled release.

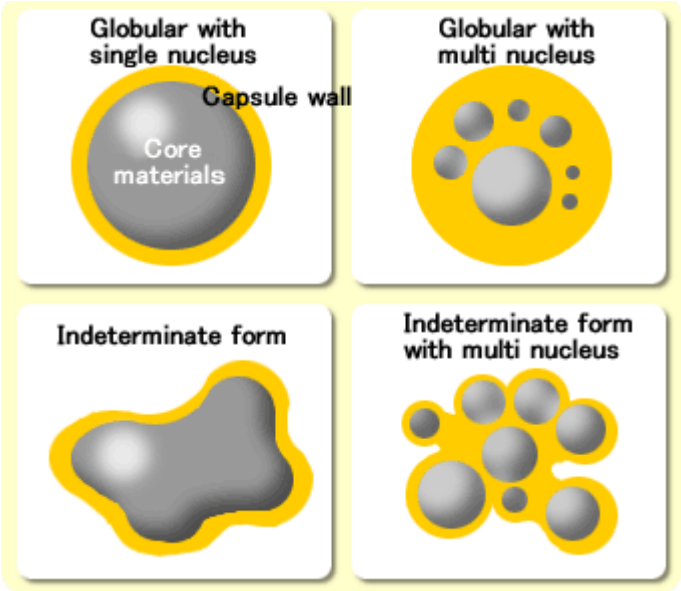


Figure 6. Structure of microcapsules

The total process of microencapsulation actually covers three separate processes on a time scale. The first process consists of forming a wall around the core material. The second process involves keeping the core inside the wall material so that it does not release. Also, the wall material must prevent the entrance of undesirable materials that may harm the core. And finally, it is necessary to get the core material out beginning at the right time and at the right rateMicrocapsule Uses

1.7.Functions of Microcapsules

Microcapsules offer superior functions compared to non-capsulation applications: their uses since the initial coacervation work in the 1940's are many and varied. The uses of microcapsules that are of interest here include the following:

1) Reduce the reactivity of the core with regard to the outside environment, preventing the active ingredient from deterioration

The membrane of the capsule protects the active ingredient it contains-the core material-against degradation, by insulating it from external moisture, light, and oxygen.

2) Decrease the evaporation or transfer rate of the core material to the outside environment

Typical usages of this function are microencapsulated aroma and organic solvent. These are advertisement leaflets and tissue papers that produce aroma of lemon and/or apple when scratched their part of pictures by nail, and cigarettes that are processed with encapsulated menthol.

3) Improve the workability

a. Prevent lumping;

b. Promote the easy mixing of the core material.

c. Position the core material more uniformity through a mix by giving it a size and outside surface like the remainder of the materials in the mix

d. Convert a liquid to a solid form

Because the membrane segregates its contents, capsules can contain and mix different, mutually reactive ingredients, and preserve them for a long time. Even liquids can be prepared in what appears to be a powder or particles. This makes a material easily workable.

3) Promote the safety of handling of the core material

Once toxic materials such as insecticides, weed killers, and disinfectants that are used in the agricultural field, are microencapsulated, they can be handled safely. In addition, when curing agents for epoxy resins are microencapsulated, the materials can be handled with no risk of rash.

4) Taste and odor mask the core

When a medicine that has a disagreeable taste or smell is encapsulated, it can be taken easily.

5) Dilute the core material when it is only used in very small amounts; but, achieve uniform dispersion in the host material.

6) Control of the release of the core material so as to achieve the proper delay until the right stimulus

a. Release the core material when needed

One method of releasing the core material is to break the membrane by applying pressure or heat, so that the core material is released all at once. This method is appropriate for pressure-sensitive copying paper, adhesives, and aroma impregnated printing.

b. Gradual release of the core material

Another method is to have the core material penetrate the membrane so that it is released moderately and gradually, at a speed that can be controlled. This method is useful for medicines, aromatic substances, and agricultural chemicals such as fertilizers. For the last of these, microencapsulation makes it possible to use less of the core material, and disperse it more infrequently, thus saving resources.

1.8.Release Mechanisms

A variety of release mechanisms have been proposed for microcapsules; but in fact, the number that have actually been achieved and are of interest here are rather limited. These are as follows:

1. A compressive force breaks open the capsule by mechanical means; (**Figure 7**)

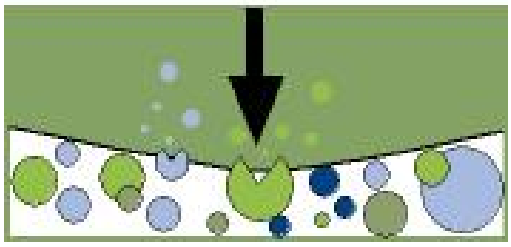


Figure 7. Activation of microcapsules under pressure

2. The capsule is broken open in a shear mode ;

3 . The wall is dissolved away from around the core such as when a liquid flavoring oil is used in a dry powdered beverage mix;

4. The wall melts away from the core releasing the core in an environment such as that occurring during baking; and,

5. The core diffuses through the wall at a slow rate due to the influence of an exterior fluid such as water or by an elevated temperature. (**Figure 8**)

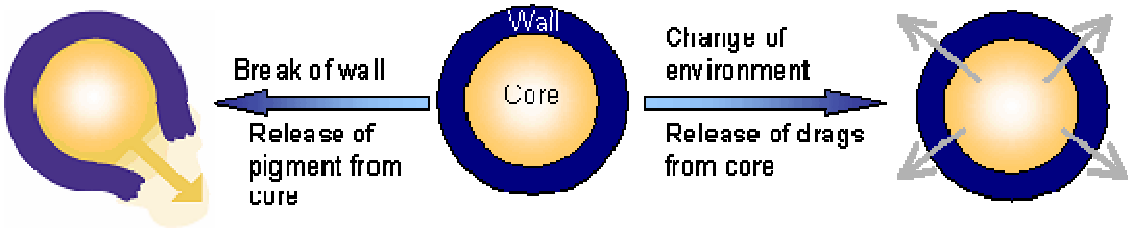


Figure 8. Release mechanisms

1.9. Application Examples of Microcapsules

Although the applications of microcapsules are limited, as previously discussed, they are used in fields that absolutely require microcapsules (**Figure 9**). Discussed below are some application examples.

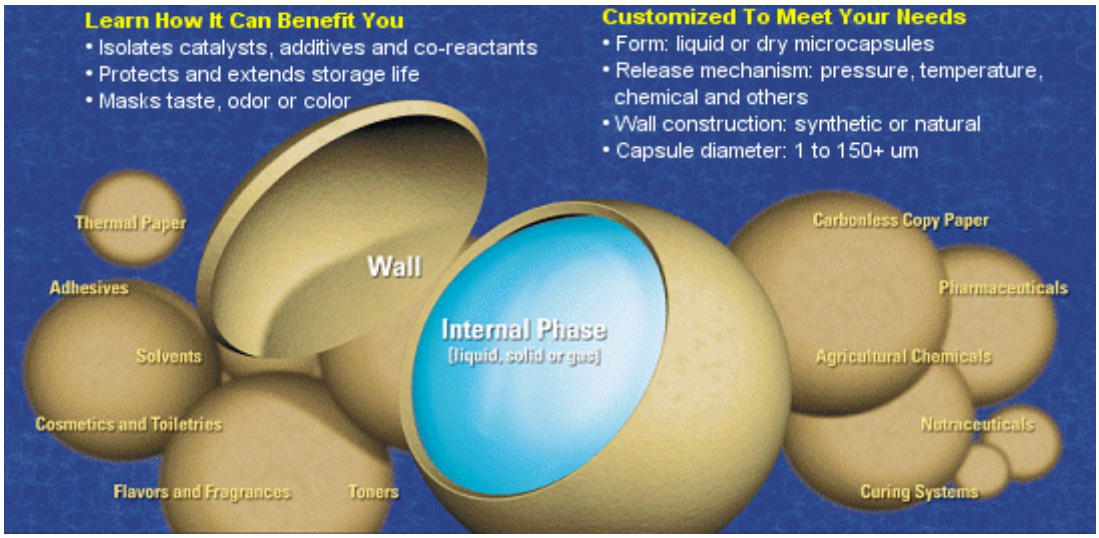


Figure 9. Some application examples of microcapsule applications

1.9.1. "Smart" Paper or carbonless copy paper

Many people know that pressure-sensitive copying paper is a typical application example of microcapsules, but few are aware of the mechanism involved. Most people believe that ink is microencapsulated, and the microcapsules are then broken when characters are written by a ballpoint pen, releasing the ink to generate color. This is not an accurate description of the actual mechanism.

Pressure-sensitive copying paper consists of two or three different types of sheets. In two-sheet copying paper, a top sheet whose back surface is coated with microcapsules (coated back CB) is combined with a bottom sheet whose front surface is coated with developer (coated front CF). In three-sheet copying paper, a middle sheet whose front surface is coated with developer and back surface is coated with microcapsules (coated front nd back CFB)is sandwiched by top and bottom sheets (**Figure 10**)

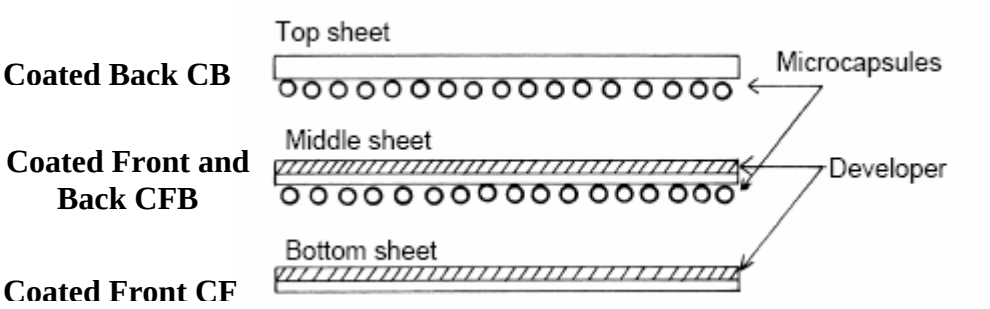


Figure 10. Schematization of a three-sheet copying paper

CB sheets have a layer of microcapsules, microscopic capsules, that contain an invisible ink. The CF sheet has a coating of a coreactant, which when exposed to the colorless inks in the microcapsules reacts with them to produce color (**Figure 11**)

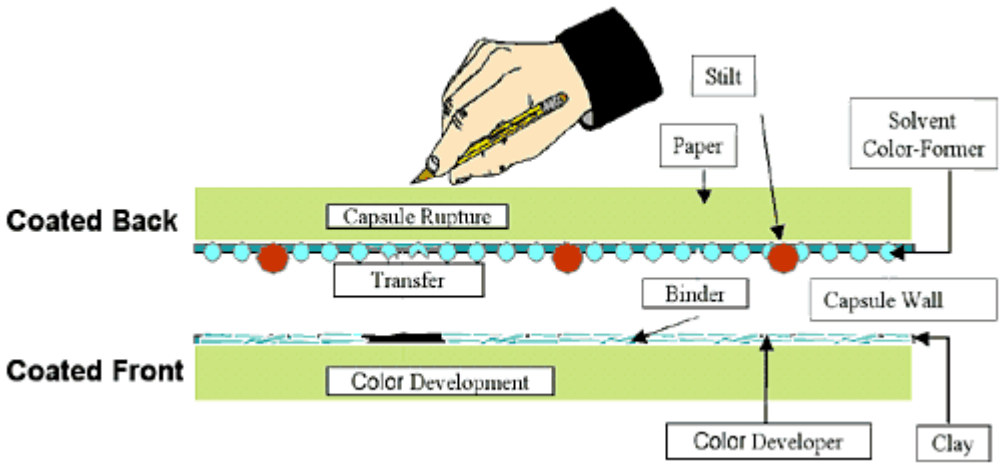


Figure 11. Schematization of a two-sheet copying paper

The benefit of the microcapsules is that they keep the reactants away from each other until you want color to develop, which is when you write on the top sheet of paper. Writing on the top sheet produces mechanical pressure that bursts the microcapsules, allowing them to release their colorless ink leading to development of color on the facing sheet of paper.

Thermal paper was developed in the late 1950s as a response to NASA's need for a printer the size of a cigar box. When it was first developed, thermal paper had a negative reputation for its fragility. Now thermal paper has been developed for a much broader range of applications and can be specifically designed to withstand harsh environments. Technically,

thermal paper is a heat sensitive medium through with images or designs are produced by the application of heat energy. (**Figure 12**)

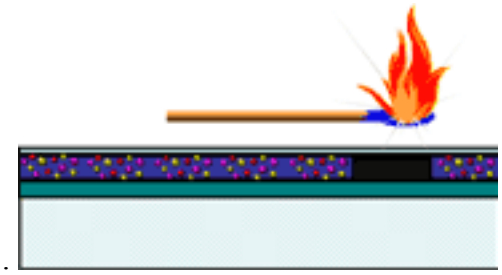


Figure 12. Schematic representation of thermal paper

Thermal paper is comprised of three layers: a base sheet, a base coating, and a thermosensitive coating. The thermosensitive coating contains a colorless dye (the color former), a bisphenol or acidic material (the color developer), and a sensitizer. Dyes are typically basic substances which become colored when oxidized by acidic compounds or bisphenol compounds. In these dye-developer systems, sensitizers are typically mixed with the dyes to form a blend with a reduced melting point. This reduces the amount of heat necessary to melt the dye and obtain reaction with the color developer. The components of the thermosensitive coating are often determined by the operating requirements. These components are sensitive to the environment (heat, humidity and pressure) and many materials (organic solvents, cleaners, petroleum solvents, ammonia, some oils, plasticizers). The main type of thermal printing is known as Direct Thermal printing, where heat is generated in the printhead which activates the ink in the paper to develop color.

1.9.2. Pharmaceuticals

To deliver health-giving substances it is important that they reach the right part of the body. One way of doing this is through microencapsulation - the packaging of small particles of solid, liquid or gas within a secondary material and delivering them in small particles.

The three major reasons that microencapsulate medicines are as follow:

1) To eliminate disagreeable taste or odor when a medicine is taken

2) To prolong the effect of a medicine (The capsule is not broken immediately, so the content will leach out little by little.)

3) To protect medicine from degradation by the surrounding environment.

Consumers may choose to eat food products containing microencapsulated ingredients, which once ingested, move through the body until they reach a targeted area of the gut. At this point the capsules release their contents of healthy ingredients, providing specific health benefits to the target area.

Microencapsulation is now used by formulation scientists to protect sensitive or unpalatable bioactives from harsh external environments. Forms of encapsulation can vary from simple membrane coatings to multiwalled structures or numerous cores within a single walled structure.

The encapsulated bioactive can be released by external triggers such as pH, temperature, pressure, solvent-activation or by degradation by bacteria in the human gastrointestinal tract. The encapsulant materials that are being used for food applications are limited to natural sources derived from lipids, proteins and carbohydrates. Controlled release of the encapsulated bioactive can be achieved by designing tailor-made materials that can deliver the encapsulated bioactive at a specific site in the gastrointestinal tract.

Recently, research into encapsulation has been examining the potential of controlled release of bioactives which could be used to mitigate the onset of diseases. The successful incorporation of these targeted bioactives will potentially lead to the future development of novel functional foods

1.9.3. Flavors and flagrances

Food ingredients have been microencapsulated since the 1930's when flavours were spray dried using acacia gum as the coating material. Nowadays food ingredients are encapsulated to make their handling easier and to improve their stability to food processing conditions, including controlling or sustaining their release when food is processed or eaten. The variety of encapsulated ingredients now includes acids, bases, artificial sweeteners, colourants, preservatives, leavening agents, antioxidants and agents with undesirable odours and tastes. Encapsulated ingredients have been incorporated into cheese processing, spreads, breads, fruit juices, energy bars, baby foods and yoghurt.

The use of microcapsules in food is generally that of an additive. By regulatory definition, a food additive is any substance which becomes added to food either intentionally or unintentionally other than food itself This includes both compounds added directly and those that are added indirectly such as migrating from packaging materials. We will limit our discussion here to direct, intentional additives. This means, for example, that the Vitamin C in orange juice is not an additive but the Vitamin C added to orange juice is. There are several

hundred types of microcapsules being used as a food additive in the U.S. today. Most of these are used in the development and production of artificial flavors or natural flavors and spices. Microcapsules as food additives may be added to enhance or alter appearance. Food is not only consumed for its calories or nutrients. It is also part of our cultural experience and it must be appealing in all of its aspects. It is not just a biological necessity, its consumption is a social activity, an aesthetic experience and an expression of cultural and personal experiences. This means that food must not only taste good but it also must have the right color, texture and aroma.

The use of microcapsules can improve or enhance nutrition. The processing required to produce many of the food products used today and the long shelf life needed to provide a variety of foods available far from the place where they were grown often results in the loss of nutritional value. The products are often restored to their natural nutritional values through the addition of vitamins, minerals and in some cases, proteins.

Microcapsules can be used as preservatives. Most food preservation originally was accomplished by curing, smoking or pickling which were primarily effective in changing the moisture content or water activity in foods. Then came canning, pasteurization, freezing and chemical preservatives. Microcapsules can also enhance the convenience of food products. Changing lifestyles and the limited time available for food preparation require an increasing variety of high quality, nutritious and convenient food products today.

1.9.4. Healing agents

The design and development of self-healing polymer composites (**Figure 14)** is aimed towards making new materials that are capable of assessing their internal damage and performing self-repair leading to extended service life with good mechanical properties. To repair a damaged polymer composite and improve its strength the geometrical stress concentrations initiated by the crack must be relieved. This can be achieved by 1) crack-closure or 2) crack-filling processes. The crack closing process may be achieved by the use of shape memory alloys or shape memory polymer. Use of these approaches can provide for mechanical bonding. On the other hand the process of repair using crack-filling can be potentially achieved by rebonding using crosslinkable polymers or by dissolution of the polymer in a good solvent and provide subsequent opportunity for chain entanglement at the crack interface. The process of crack-filling involves three important features, 1) a method for the storage of a healing agent, 2) a process for the transport of the healing agent and 3) a suitable method for initiation of repair. The storage of the healing agent may be accomplished

by use of spherical microencapsulated particles. The transport is envisioned to occur by local stresses, which would initiate the rupture and release of the healing agent and flow owing to capillary action. The repair would occur by the polymerization of the healing agent utilizing an embedded catalyst in the matrix.

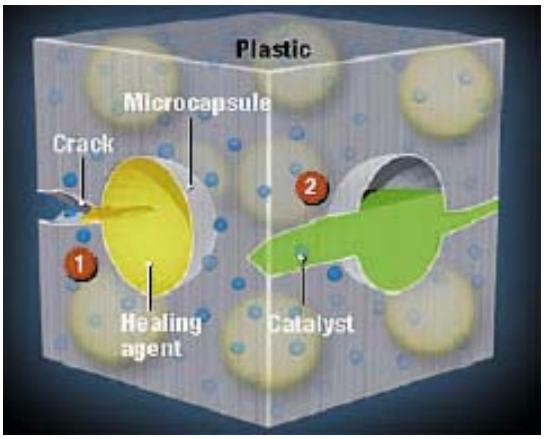


Figure 13. Schematic representation of a self-healing composite

The concept of self-healing is illustrated in **Figure 14**. White and coworkers [72] have developed an approach to perform the crack-filling process. The healing agent (reactive monomer) is stored in micron-sized microcapsules embedded in the matrix material. When a crack develops, it approaches the microcapsule, ruptures it, and releases the microencapsulated healing agent into the crack by capillary action. Rapid polymerization of the healing agent in the crack reduces the crack tip stress concentration, bonding the interfaces together and improving the mechanical strength.

Figure 14. The self-healing concept: i) crack is drawn to the microcapsules, ii) crack is filled with the healing agent, reducing crack tip stresses, iii) healing agent undergoes polymerization bonding the crack planes together.

Capsule wall thickness, toughness and relative stiffness of the microcapsules, and the strength of the interface between the microcapsule and the matrix appeared to be relevant parameters.

It was found that the microcapsule stiffness should be less than the matrix stiffness in order to attract the crack toward the microcapsule.

A similar healing concept uses hollow fibres instead of microcapsules. Hollow fibres based on glass fibre are filled with either resin or hardener, which are released into the damaged area when the fibres are fractured. Both a resin and a hardener fibre have to break for healing to occur. When the resin and the hardener contact in the crack plane, the resin hardens, thus repairs the crack. Sufficient volume of resin and hardener for repair can be released from the tube by means of heating.

When comparing the fibres to the microcapsules, we find first note that fibres used should be small, because otherwise multiple healing events will not be favoured. No catalyst is needed, because of the use of a two-component hardener resin system. It is hard to use a two-component system with microcapsules, because the distribution of the microcapsules in the matrix can hardly be controlled. On the other hand, using the fibre concept, two fibres of different type have to break for healing to occur. Comparing the results of both studies is hard, because the authors make use of different tests, using other parameters and measuring other variables. One conclusion can be drawn: The research in the microcapsule field is much more ahead. Parameters have already been explored in this field, while the research on fibres was concerned with the making of the material. The microcapsule concept is much closer to really proving its use. Same tests have to be done on microcapsules and fibres to be able to compare.

1.9.5. Phase Change Materials (PCMs)

A Phase Change Material (PCM) is a substance with a high heat of fusion which, melting and solidifying at certain temperatures, is capable of storing or releasing large amounts of energy. The only phase change used for PCMs is the solid-liquid change. Liquid-gas PCMs are not yet practical for use as thermal storage. Although they have a high heat of transformation, the increase in volume during the phase change from liquid to gas makes their use impractical. Initially, the solid-liquid PCMs perform like conventional storage materials; their temperature rises as they absorb solar heat (**Figure 14**). Unlike conventional storage materials, however, when PCMs reach the temperature at which they change phase (their melting point) they absorb large amounts of heat without getting hotter. When the ambient temperature in the space around the PCM material drops, the PCM solidifies, releasing its stored latent heat. PCMs therefore absorb and emit heat while maintaining a nearly constant temperature. Within the human comfort range of 20° to 30°C, latent thermal storage materials are very effective.

They store 5 to 14 times more heat per unit volume than conventional storage materials such as water, masonry, or rock. Microencapsulated phase change materials (MicroPCMs) provide a portable heat storage system. For this reason they have attracted more and more attention since the 1990s. Microcapsules contain in their core a storage medium of waxes. On heating and cooling, the wax in the reservoir capsules melts and solidifies, respectively.

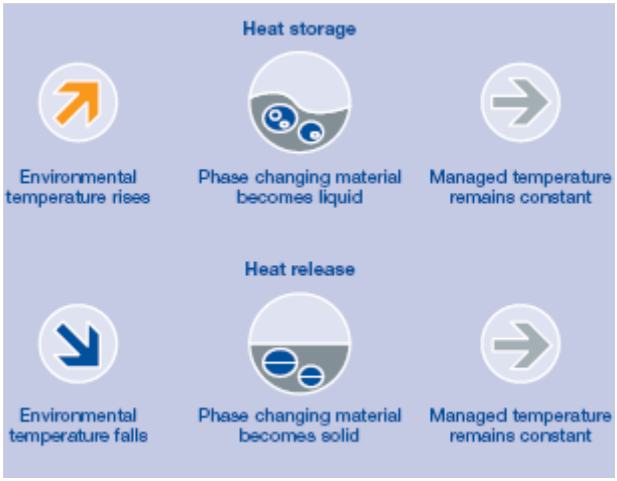


Figure 14. Room temperature response function of PCM

When the temperature rises, the phase changing materials absorb heat. When the temperature falls, they emit heat. During the phase change, the temperature remains constant. This stored heat which is 'concealed' in the phase change is known as latent heat. It is a reversible process which occurs within the melting range of the wax. Once the room temperature rises to above melting temperature the microcapsules begin their 'work'. Surplus heat is dissipated into the wall to be stored there. As a consequence, temperature peaks are cut off, thus ensuring a more uniform room temperature. So, there is an incredibly broad range of potential applications, specifically for thermal insulation during the summer season.

MicroPCMs have been widely studied as an active or pumped coolants [73-76], solar and nuclear heat storage systems [77] and in a packed bed as a heat exchanger [78]. MicroPCMs have also been used in the manufacture of thermo-regulated fibers (**Figure 15-16**), fabrics, and foams [79]. MicroPCMs have been synthesized with urea-formaldehyde [73, 74], cross-linked nylon [74], melamine-formaldehyde [76], gelatin-formaldehyde [78], and polyurethane [80] as shell materials and were usually used at a temperature lower than 150 °C. Calcium

silicate [81] and aromatic polyamide were used as shell materials to fabricate stable microcapsules [82].

Figure 15. Heat exchange through fibers containing encapsulated PCM.
(a) cooling effect; (b) warming effect

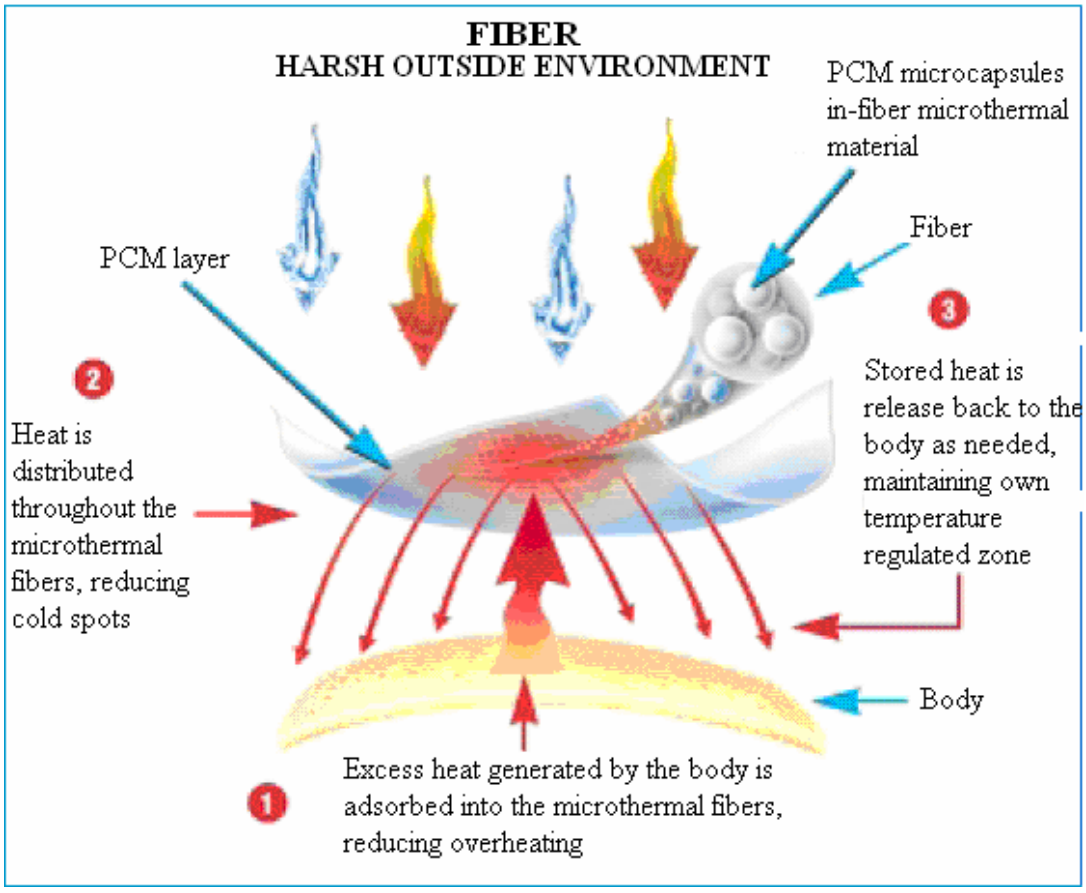


Figure 16. Thermo-regulated fiber assembling

1.9.6. Adhesives

Microcapsule-type adhesives make ordinal two-part adhesives to one-part adhesives by encapsulating either one of two-part adhesive agents. However, from the viewpoint of practical use, there are some problems. Specifically, it is uncertain whether microcapsules are completely broken, and also whether the broken content can be sufficiently mixed with another agent.

In addition, there are risks of problems that microcapsules may be broken by the shutter mechanism in the automatic adhesive coating system, and also that the agent may leach from capsules through the membranous sheath to gel in the bottle.

Screw-locking agent is an optimal application of microcapsules as adhesives usage, since the microcapsules are completely broken by the resistance generated when screws are tightened, and agents are automatically mixed by the screwing effect.

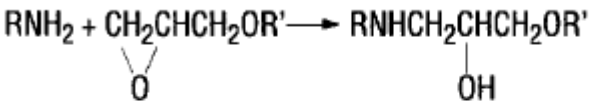
CHAPTER 2

EXPERIMENTAL

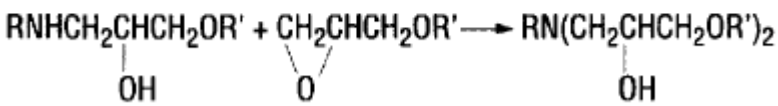
2.1. Materials

2.1.1. Epoxy resin

Epoxy resins are polymer-forming systems containing two principal components that interact to produce highly cross-linked products with exceptional toughness, adhesion, and chemical resistance. The key player in the polymerization is epoxy functionality—a strained, three membered ring consisting of one oxygen and two carbon atoms. This is also known as an oxirane group. This structure reacts with active hydrogen compounds that add to the ring to open it and yield a secondary hydroxyl compound. When the active hydrogen compound is a primary amine, the product contains both a secondary hydroxyl group and a secondary amine **(Equation 1**). The hydroxyl group is not sufficiently reactive to engage the epoxy group, but the secondary amine is only moderately less active than the primary amine. It can react with an oxirane group to provide polymer formation with polyfunctional epoxy monomers (**Equation 2**).



(1)



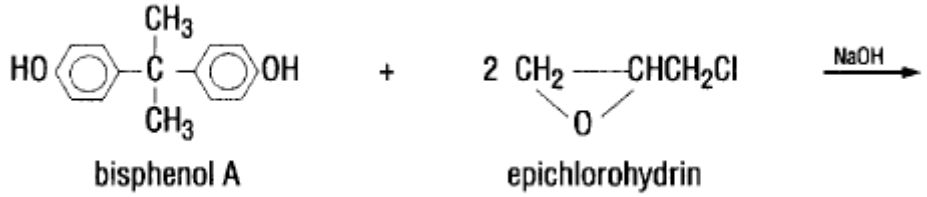
(2)

Polymerization occurs without the formation of condensation by-products or off gases and generally with less than 5% bulk shrinkage. Preferably the active hydrogen compound should contain several primary and secondary amines. The high reactivity of appropriate amines enables the resin to cure at relatively low temperatures, i.e., at or near ambient. The product will have a large proportion of nitrogen and oxygen heterofunctionality. Many strong adhesives derive their desirable bonding properties from the intramolecular presence of both oxygen and nitrogen. Mechanical hooking and covalent bonding each play a role in epoxy polymers that function as adhesives, but the major mechanism for adhesion is the sharing of

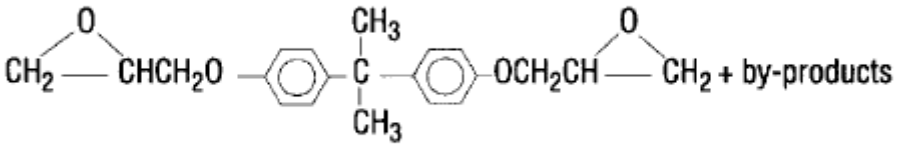
electrons between the polymer and the substrate, i.e., coordinate bonding. The availability of both nitrogen and oxygen atoms provides the variety of spatial and electronic configurations needed to match more of the diverse receptor configurations of the substrate.

2.1.1.1. The Epoxy Component

Cured resins with widely differing properties can be obtained by changing the structure of the epoxy compound. Industrial chemists have succeeded in synthesizing and making commercially available a broad variety of these monomers. However, almost all of the various products sed have been based on bisphenol A diglycidyl ether, **Equation 3**. This material is produced from common petrochemical building blocks—propane and benzene—through a series of well-established manufacturing steps that culminate in the base-catalyzed condensation between epichlorohydrin and bisphenol A.



bisphenol A epichlorohydrin **(3)**



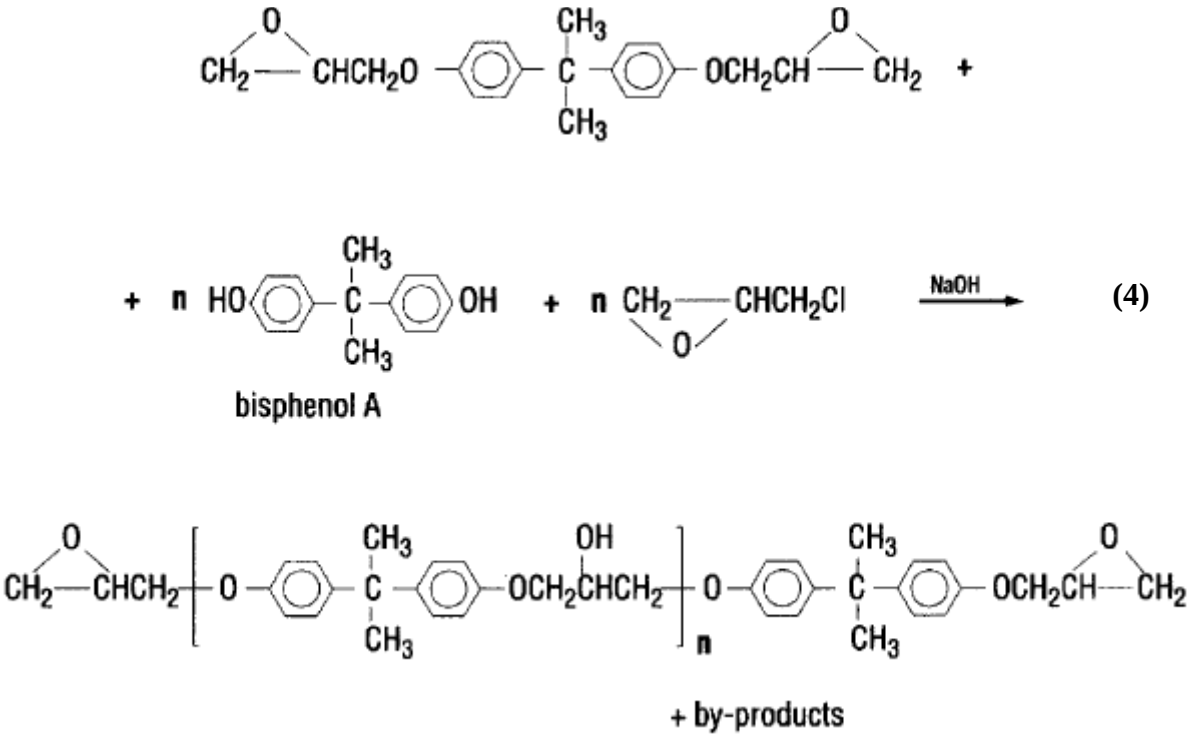
diglycidyl ether of bisphenol A

Two types of side reactions can occur in this step to make the composition of the condensation product somewhat more complicated than the diglycidyl of bisphenol A. The active hydrogen on another bisphenol A molecule can add to the oxirane ring (**Equation 4**). As a result, commercial resins are mixtures in which n varies from zero to approximately 20. In addition, other components and impurities react with some of the oxirane rings to leave a product averaging 1.9 or fewer epoxy rings per molecule.

As **n** increases, the resin becomes more viscous, and when **n** is 2 or more the product is solid. The largest volume and most important product commercially is a mixture made up primarily of pure bisphenol A diglycidyl ether and much smaller amounts of oligomers.

The composition consists of 87-88% diglycidyl ether with **n** = 0, 11% with **n** = 1, and 1-2% with **n** = 2. This provides a resin with an average molecular weight of about 370, which is prepared by using a very high ratio of epichlorohydrin to bisphenol A to minimize **Equation 4**.

Products obtained in this manner have epoxy equivalent weights of 180-200 and viscosities at 25 °C of 10,000-18,000 cP. Typical example of this material is Epon 828 (Shell). Resins such as Epon 825, which are essentially free of oligomers, have much lower viscosities, 4000-5500 cP at 25 °C



(4)

2.1.2. Urea-Formaldehyde resin

Urea-formaldehyde (UF) resins are the most important type of the so-called aminoplastic resins. They are based on the manifold reaction of two monomers, urea and formaldehyde. By using different conditions of reaction and preparation a more or less innumerable variety of condensed structures is possible. UF resins are thermosetting duromers and consist of linear or branched oligomeric and polymeri molecules, which also always contain some amount of monomer. Non-reacted urea is often beneficial to achieve special effects, e.g. better stability

during storage. However, the presence of free formaldehyde is ambivalent. On the one hand, it is necessary to induce the hardening reaction. On the other, it causes displeasing formaldehyde emission during the processing .

After hardening UF resins form an insoluble, three-dimensional network and cannot be melted or thermoformed again. In their stage of aapplication UF resins are still soluble or dispersed in water or in the form of spray dried- powders, which, in most case however, are redissolved in water for application.

There are several papers and monographs concerning UF resins in the literature [83-90], which contain considerable additional information.

2.1.2.1.Chemistry of urea- formaldehyde resins

Despite the fact that UF resins consist of only two main components, namely urea and formaldehyde, they present a broad variety of possible reactions and structures. The basic characteristics of UF resins can be explained at the molecular level by:

- their high reactivity;
- their water solubility; and
- the reversibility of the aminomethylene link, which also explains the low resistance of UF resins against the influence of water and moisture, aspecially at higher temperatures

The reaction of urea and formaldehyde is basically a two-step process: usually an alkaline methylolation followed by an acid condensation.

2.1.2.1.1.Methylolation and condensation reaction

Methylolation refers to the addition of up to three (four in theory)molecules of the bifunctional formaldehyde to one molecule of urea to give the so-called methylolureas. The formation of tetramethylolurea is disregarded because the literature has found only negligible amounts of this copmpound

Main reactions

Methylolation (addition) reactions

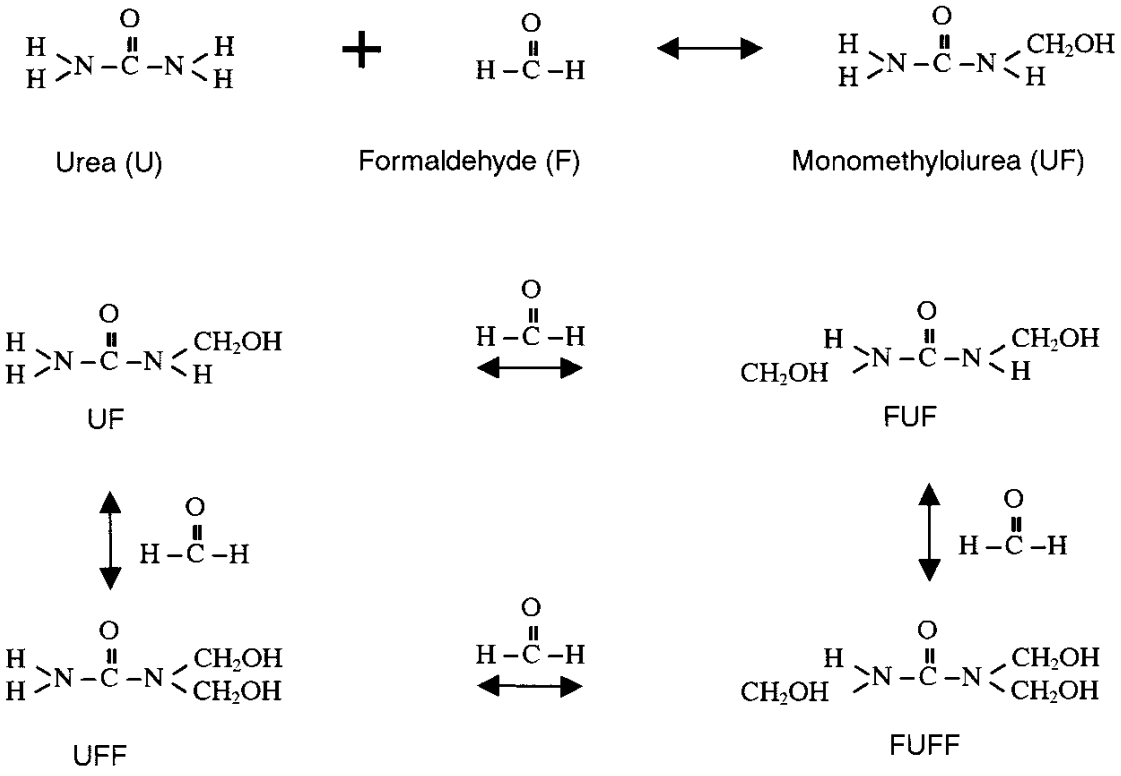


Figure 1. Methylolation reaction network. (UFF and FUF are NN and NN' dimethylolureas)

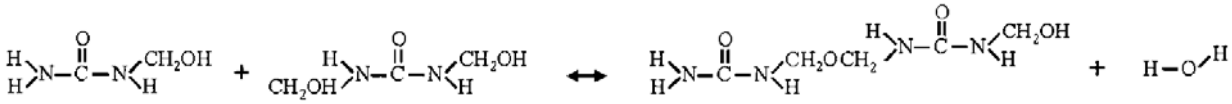
The reversibility of this reaction is one of the most important features of UF resins, and is responsible for both the low resistance against hydrolysis caused by the attack of moisture or water and the subsequent frormaldehyde emission. This is so because emittable formaldehyde results from the slight hydrolysis of weakly bonded formaldehyde. The formation of methylol groups mostly depends on the F/U molar ratio, with higher molar ratios increasing the tendency to form highly methylolated species [91,92]. Products of side reactions are acetals, hemiacetals and etherified products, with residual methanol always present in small amounts from the production of formaldehyde. The methylol groups are more or less stable in slightly alkaline conditions[93], but this is of no industrial importance. Starting the reaction of urea and formaldehyde in the usual molar ratio but under acidic conditions gives methylene-linkrd ureas which tend to be insoluble in water with ca. five or six urea units [94-97].

2.1.2.1.2.Condensation reaction

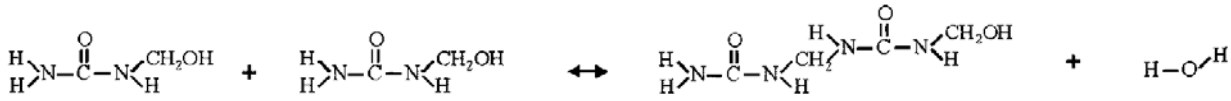
The UF polymer builds up in the acid condensation step: the methylols, urea and free formaldehyde still present in the system react to give linear and partly branched molecules with medium and even higher molar masses. The type of bond between the urea molecules

depends on the conditions used: low temperatures and only slightly acidic pH favour the formation of methylene ether bridges
(-CH_2-O-CH_2-), while higher temperatures and lower pHs lead to the more stable methylene (-CH_2-) bridges. Ether bridges can rearrange to methylene bridges by splitting off formaldehyde. One ether bridge meeds two formaldehyde molecules and it is not as stable as a methylene bridge. Hence it is recommended to avoid such ether group in UF resins under today's common conditions of low formaldehyde content by virtue of low molar ratio of the resins.
Summarizing there are two different types of condensation reactions thet form larger UF molecules:

1) Dimethylene ether linkages (-N-CH_2-O-CH_2-N-). These are reaction between two methylol groups, e.g. between monomethylolurea and dimethylolurea.



2)Methylene linkages (-N-CH_2-N-). These are reaction between a methylol group and an amino hydrogen, e.g. between two monomethylolurea molecules



In **figure 2** an illustration of amacromolecule is shown.

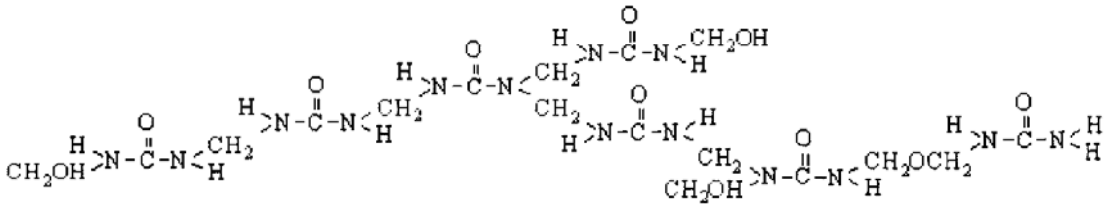
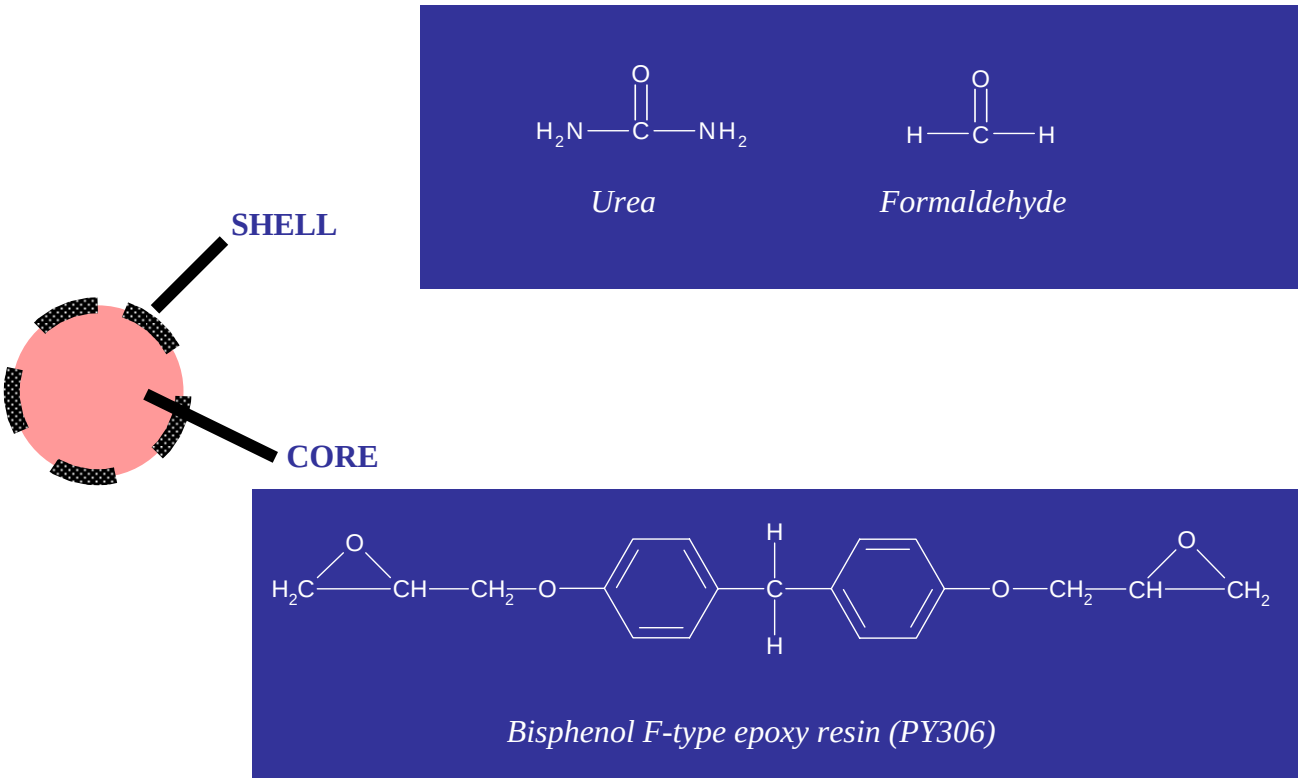


Figure 2. Illustration of poly(urea-formaldehyde) macromolecule

2.2. Synthesis

2.2.1. Urea-formaldehyde microcapsules



Formation of urea-formaldehyde microcapsules was achieved by *in situ* polymerization in an oil-in-water emulsion.

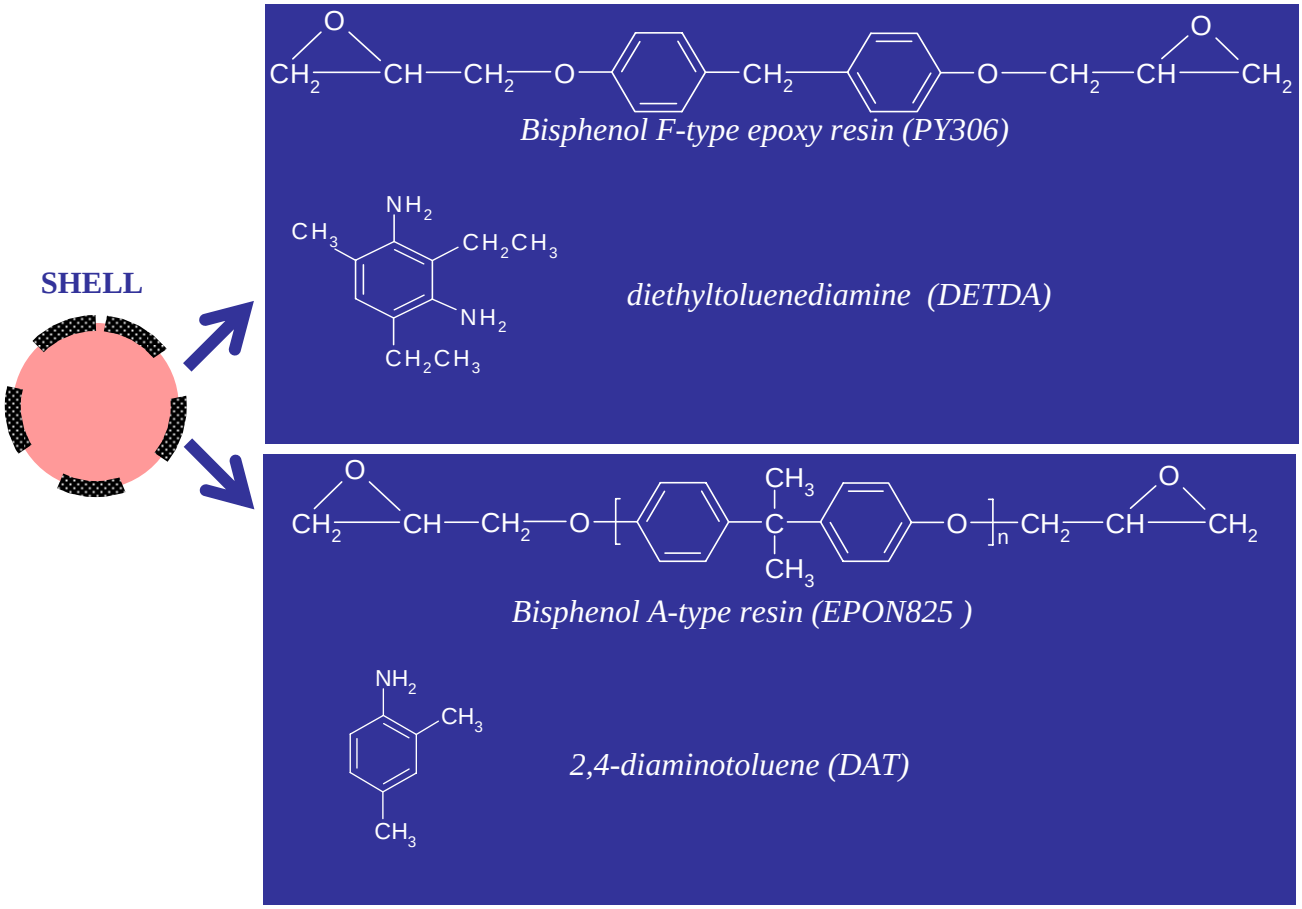
In a typical procedure 2.5 g urea, 0.25 g ammonium chloride and 0.25 g resorcinol were dissolved in water (150 ml), under magnetic stirring and at room temperature.

Since in some cases it may be desirable to use an emulsion stabilizer, a 2.5 wt% aqueous solution of EMA copolymer (50 ml) was added to the reaction mixture. The emulsion stabilizers has the function to form thin layer around the capsule core entities and thereby to stabilize the emulsion. The pH was adjusted to 3.5 using sodium hydroxide (NaOH) and hydrochloric acid (HCl). 30 ml of PY306 were added to the solution to form an emulsion and allowed to stabilize for 10 min. 6.3 g of 37 wt.% aqueous solution of formaldehyde were added to the emulsion to obtain a 1:1.9 molar ratio of formaldehyde to urea. The temperature was raised to the selected value.

After a fixed time of reaction under continuous stirring, the mixer and hot plate were switched off. Once cooled to room temperature, the suspension of microcapsules was

separated under vacuum filtration and then washed with chloroform to eliminate the residual (non encapsulated) epoxy resin. The microcapsules were isolated by filtration and vacuum dried at 40 °C for 24 hours.

2.2.2. Epoxy-based microspheres



The synthesis of epoxy-based microspheres was described in details in a previous work [9]. Briefly, the microspheres were obtained by dispersion polymerization. According to this procedure, the epoxy monomer and the curing agent, taken in a fixed molar ratio, were mixed in polypropyleneglycol, used as solvent, and let react at a selected temperature without stirring, for 15 hours, until the resin particle formation occurred. The solid product was washed with hot methanol and chloroform, filtered and dried under vacuum.

In particular, two types of microspheres were prepared:

- Mic1, obtained from EPON825 + DAT (solute) dissolved in PPG1000 (solvent).
  $T_{reaction}$ = 130°C $t_{reaction}$ = 15 h; solute/solvent = 50 wt.%
- Mic2, obtained from PY306 + DETDA (solute) dissolved in PPG1000 (solvent).

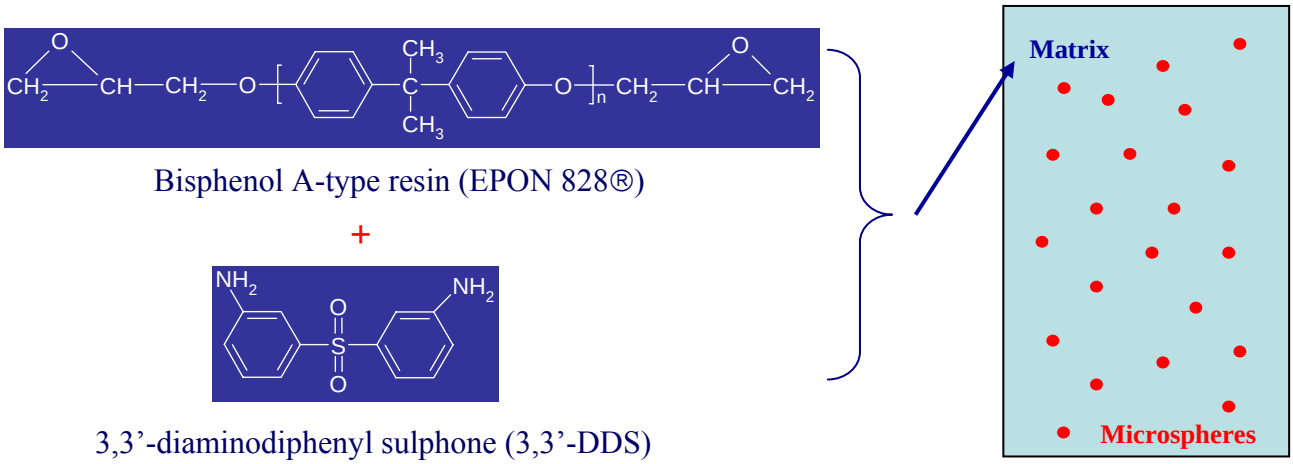
$T_{reaction}$ = 130°C $t_{reaction}$ = 15 h; solute/solvent = 50 wt.%

In both cases a 35 % molar excess of the curing agent was used to be sure that all the epoxy monomer introduced was reacted and to guarantee an excess of curing agent on the surface of the microspheres.

2.2.3. Materials used for rheological analysis

Rheological analyses have been carried out on blends of EPON828 and 3,3'DDS containing two different weight percents of epoxy microspheres, 10 and 20wt. %. In particular, both Mic1 and Mic2 microspheres were used for these studies. The comparison of the four modified systems was made with the EPON828-3,3'DDS neat resin.

In all the cases, the epoxy monomer, the curing agent and the microspheres (when present) were mixed at the temperature of 110°C without solvent.



Later on, we will refer to the five systems as 0%Mic for the neat resin, as 10%Mic1 and 20%Mic1 for the systems containing the 10 and the 20wt.% of Mic1 microspheres, respectively, and as 10%Mic2 and 20%Mic2 for the systems containing the Mic2 microspheres.

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2.2.4.Materials used for Dynamical Mechanical Thermal Analysis (DMTA)

Cured samples were prepared by mixing the microspheres with the EPON828 and stirring the resulting mixture for 30 minutes at T = 120°C. Then the curing agent was added and the mixture was stirred for 1h at T = 80°C. This blended resin was poured in a preheated steel mould and degassed for 30 min at 145°C. Successively, the temperature was increased at

2°C/min up to 180°C and hold at this value for three hours. At the end of the curing cycle the panels were left to cool down slowly at room temperature.

2.3.Instrumental

2.3.1. Properties of urea-formaldehyde microcapsules

Morphological analysis of prepared sample was carried out by means scanning electronic microscopy (SEM) using a Leica Cambridge Stereoscan microscope model 440. Prior to being observed, samples were metallized with a gold layer.

To confirm the microencapsulation process as well as to get a semi-quantitative evaluation of amount of microencapsulated epoxy resin DSC analysis was carried out.

A TA Instruments model 2920 calorimeter was used to detect on thermal behavior of microcapsules core and shell. For each sample, a single scan from 0 °C to 300 °C at a heating rate of 10°C/min, under nitrogen atmosphere, was carried out.

The thermal stability of the microcapsules was investigates by using a thermogravimetric analyzer (Dupont model 951). For each sample a simple scan was performed at a heating rate of 10°C/min from room temperature up to 600°C under N_2 flow

FT-IR spectra of microsphere samples were obtained in transmission mode using a System 2000 spectrometer from Perkin-Elmer (Norwalk, CT). This instrument employs a germanium/KBr beam splitter and a deuterated tryglycine sulfate (DTGS) detector. The instrumental parameters adopted for the spectral collection were as follows: resolution 4 cm^{-1}, optical path difference (OPD) velocity = 0.20 cm s^{-1}, and spectral range 4000-400 cm^{-1} resulting in 3551 collected data points.

To exactly evaluate the amount of epoxy resin encapsulated Raman spectroscopy was used. Raman spectra were collected on a Nicolet Nexus NIR FT-Raman spectrometer from Thermo Nicolet (Madison, WI, USA), equipped with a diode pumped Nd-YAG laser (λ = 1064 nm) as an excitation source operating at 0.85–1.05 W of power, and a room temperature InGaAs photoelectric detector. The backscattered radiation was collected at 180° to the laser beam direction. Typical spectra were recorded in the range 3800 – 200 cm^{-1}, at a resolution of 4 cm^{-1}, co-adding 500 scans to improve the signal-to-noise ratio. The specimens, in the form of finely ground powders were sampled in glass vials. Raman spectroscopy was used for the quantitative evaluation of the encapsulated epoxy resin.

To separate the individual peaks in the case of unresolved, multicomponent bands, a curve resolving algorithm was employed, based on the Levenberg-Marquardt method[31]. In

order to reduce the number of adjustable parameters and to insure the uniqueness of the result, the band shape and the number of components were fixed. The number of components and their initial positions were estimated by looking at the negative peaks of the second-derivative spectra. To account for the fluorescence effect the baseline was simulated by a third-order polynomial function. The program was allowed to calculate, by a non-linear curve fitting of the data, the height, the full width at half height (FWHH) and the position of the individual components. The peak function used throughout was a mixed Gauss-Lorentz line shape[32].

2.3.2. Properties and perfomance of epoxy-based microspheres

Differential Scanning Calorimetry (DSC) (TA Instrument mod.2920) was used to evaluate the glass transition temperatures (T_gs) of microspheres and to follow the curing reaction of bulk systems. For each sample a double heating scan from room temperature to 280 °C at a rate of 10°C/min, under nitrogen atmosphere, was carried out. T_gs of microspheres were obtained from the second heating scans in the DSC analysis.

Scanning Electronic Microscopy (SEM) was carried out in order to study the morphology of particles and to evaluate their sizes, as well as to investigate on the characteristics of fracture surfaces of composites. An Hitachi microscope mod. S-2300 was employed. Prior to being observed, samples were metallized with a gold layer. The particle diameter distribution, their average values and standard deviations were determined using an image analysis software, ImageJ 1.34s Wayne Rasband, National Institute of Health, U.S.A. The statistical histograms were fitted with a Lorentzian function.

Rheological properties of the systems were determined on an Ares Rheometer by Rheometric Scientific. Complex-viscosity η^*, elastic modulus G' ad loss modulus G'' were obtained by oscillatory shear measurements as a function of temperature and by a series of isothermal experiments employing parallel plates (40 mm diameter) separated by a 1,2 mm gap. Isothermal tests were performed by preheating the sample chamber to the fixed temperature, then the sample was quickly inserted and the analysis started. The analysis was done with optimised instrumental parameters of 35% strain and angular frequency of 30 rad/s.

DMTA tests were carried out for cured samples with an Ares Rheometer by Rheometric Scientific at a fixed frequency of 10 rad/sec and 0,1 strain with a 2°C/min heating rate using samples of sizes 12x40x3 mm. Storage modulus and tanδ were obtained by a torsion mode.

PART I

PROPERTIES OF POLY(UREA-FORMALDHEYDE) MICROCAPSULES CONTAINING AN EPOXY RESIN

CHAPTER 3

3.1. Introduction

The effect of polyoxymethylene urea (PMU) microspheres on general purpose epoxy resin were studied. The investigation was motivated by the potential application of microspheres in a crack filling, self-repair composite systems. These composites autonomically heal cracks as they develop in a structure. When a crack forms it ruptures embedded microcapsules that release a healing agent. The agent flows into the crack through capillary action and is polymerized by a catalyst in the matrix of the composite.

Self-repairing materials are inspired by living systems, in which minor damage (e.g., a bump or bruise) triggers an autonomic healing response. A similar system is desirable for composite materials in which crack or delamination damage can be repaired without manual intevention. A composite material with this healing capability would have an increased service life and would have a great advantage in structural applications.

There are several reapair concepts for composite materials that have been developed (**Figure 1**).

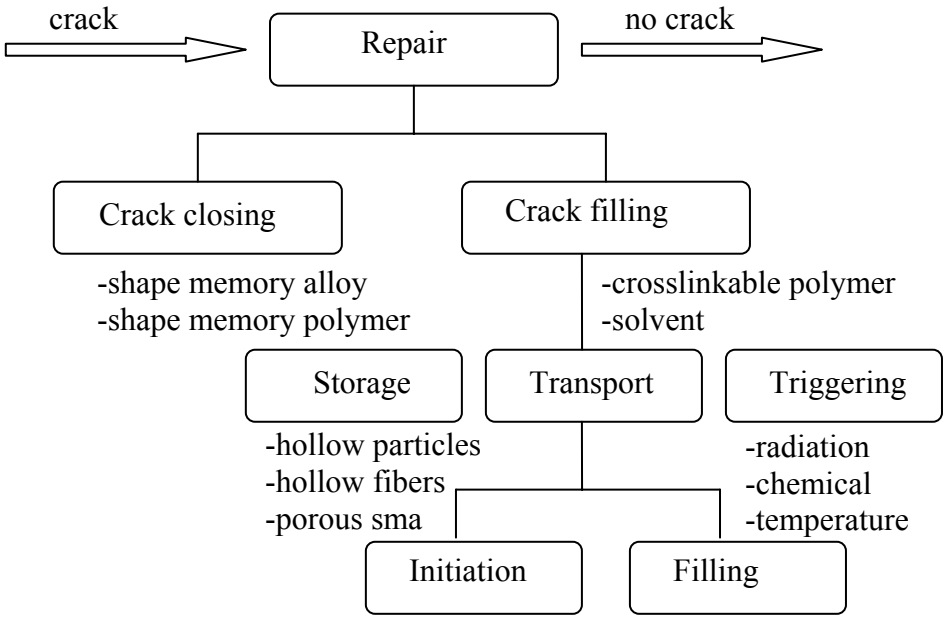


Figure 1. Flowchart of repair schemes and involved issues

The first repair scheme is crack closing, and the second is crack filling. In crack closing, the two crack faces are brought together, thus eliminating the stress concentration at the crack tip. Without this stress concentration, the crack will no longer propagate, and the material has in essence been healed.

In the second repair scheme, the crack is filled with a repair agent to heal the crack.the repair agent could be some type of cross-linking polymer that would form a bond between the two crack faces. Two-part epoxy adhesives have been explored for polymer matrix composites[98,99], and three-part methylmethacrylate adhesive has been applied to concrete [100]. Low viscosity epoxy resins have also been used to repair delaminations in graphite/epoxy aircrafts panel components [101,102]

With a crack filling repair scheme, there are three issues that must be considered. These issues are the storage of the repair agent, the transport of the repair agent to the damage site, and the triggering of the healing action (**Figure 1**). In the manual repair of delaminations and impact damage, the repair agent (e.g., an epoxy resin) is typically delivered under pressure to the damaged area. The repair agent is stored external to the structure. Mixing the resin and the curing agent starts the cross-linking reaction that will eventually bond the two crack faces (i.e., trigger the healing reaction).

To obtain a self-repairing composite the polymeric matrix has to contain a self-repair system that does not affect the material's overall properties or performance. It must also be able to sense damage, and then be able to react to that damage and initiate healing. Finally, it must restore the material's original properties (strength and stiffness, for example).

The present work focuses on the preparation and characterization of microcapsules to store the epoxy resin to be used as a repair agent for a crack filling repair scheme.

The wall material has to avoid leakage and diffusion of the encapsulated agent for considerable time. Moreover, when used as fillers for composites, a high bond strength to the host polymer combined with a moderate strength microcapsule shell are required to remain intact during processing of the polymeric matrix. For this purpose a urea-formaldheyde based material was selected. UF resins are the most important type of the so-called aminoplastic resins that consist of linear or branched oligomeric and polymeric molecules, which also always contain some amount of monomer [103]. After hardening UF resins form an insoluble, three-dimensional network and cannot be melted or thermoformed again.

Epoxy resin was chosen as the encapsulated agent of interest thanks to its extreme versatility, as it has found use in many advanced fields, ranging from electrical/electronic to aircraft/aerospace and automotive industries [104].

Factors determining the microencapsulability of the core material were described. In particular, our interest was devoted to a better understanding of the influence of the reaction parameters on the microcapsule properties.

In order to evaluate the relation between the experimental conditions and the encapsulability

a set of urea-formaldehyde microcapsules containing an epoxy resin was prepared by *in situ* polymerization in an oil-in-water emulsion, in which reaction time and temperature and stirring speed were modulated.

Scanning electronic microscopy (SEM) was performed to investigate on microcapsule size and surface morphology. TGA, DSC, Raman and FT-IR analyses were carried out with the aim of evaluate the thermal stability of the microcapsules, the extent of microencapsulation and the shell features.

Infrared and Raman spectroscopy are complementary tools for obtaining vibrational spectra. Depending on the nature of the vibration, which is determined by the symmetry of the molecule, vibrations may be active or forbidden in the infrared or Raman spectrum. Infrared active are all vibrations which modulate the molecular dipole moment. Raman active are vibrations which modulate the molecular polarizability. Based on the different selection rules of these two spectroscopic techniques, polar bonds tend to yield strong IR and weak Raman bands, whereas non-polar groups give rise to strong Raman and weak IR bands [105]. Further advantages of Raman compared to mid infrared are the lack of interferences from water vapour and glass, which is very convenient because glass sample containers can be used during experiments.

3.2 Results and discussion

Urea-formaldehyde microcapsules were synthesized as described in the *Experimental part*. In particular, five different samples were prepared varying the experimental conditions, such as reaction time and temperature and stirring rate, as summarized in **Table 1**.

Neat urea-formaldehyde was also prepared in the same condition of sample A.

Table 1: Reaction parameters (temperature, time and stirring rate) selected for the preparation of urea-formaldheyde microcapsules

Sample	***Reaction temperature (°C)***	***Reaction time (hour)***	***Stirring rate (rpm)***
Neat UF	60	4	2000

A	60	4	2000
B	60	6	2000
C	40	4	2000
D			1600
E			1200

3.2.1. Chemical reaction in urea-formaldehyde resins

The synthesis of UF resins from urea and formaldehyde is basically a two step process [86-108]: the first is the so-called methylolation reaction, which is catalysed by both acids and bases and leads to the formation of hydroxymethyl compounds (monomethylol, dimethylol and trimethylolurea). Methylolation refers to the addition of up to three molecules of the bifunctional formaldehyde to one molecule of urea. It is known that tetramethylolurea has never been isolated [88]. The formation of methylol groups mostly depends on the F/U molar ratio, with higher molar ratio increasing the tendency to form highly methylolated species [90,91]. Molar ratio lower than ca. 1.8 lead to some precipitation during the following acid condensation step, causing inhomogenities in the solution.

In a second step, the condensation reaction between the various methylol species and urea takes place. This reaction is mainly acid catalysed and leads to a complex mixture of low molecular weight UF oligomers. The condensing moieties link together by methylene (N-CH_2-N) or by dimethylene ether (-N-CH_2-O-CH_2-N-) groups. At low pH, the as produced UF resins cure irreversibly to form a cross-linked network. This reaction can be induced by addition of catalyst or hardeners (ammonium chloride and ammonium sulphate) and/or of further branchers, such as resorcinol, involved in the co-condensation reaction with urea and formaldehyde [109,110]. The incorporation or resorcinol improves the low resistance of UF bonds to the influence of water. Moreover, it proceeds quickly upon heating resulting in the formation of tridimensional networks and ultimately a thermosetting resin that is no longer thermoformable.

3.2.2. Microcapsule morphology

In order to examinate the morphological features of synthesized microcapsules SEM analysis was carried out, as reported in the micrographs of **Figures 2-7.** As reference SEM image of sample composed by pure UF has been reported (**Figures 2**).

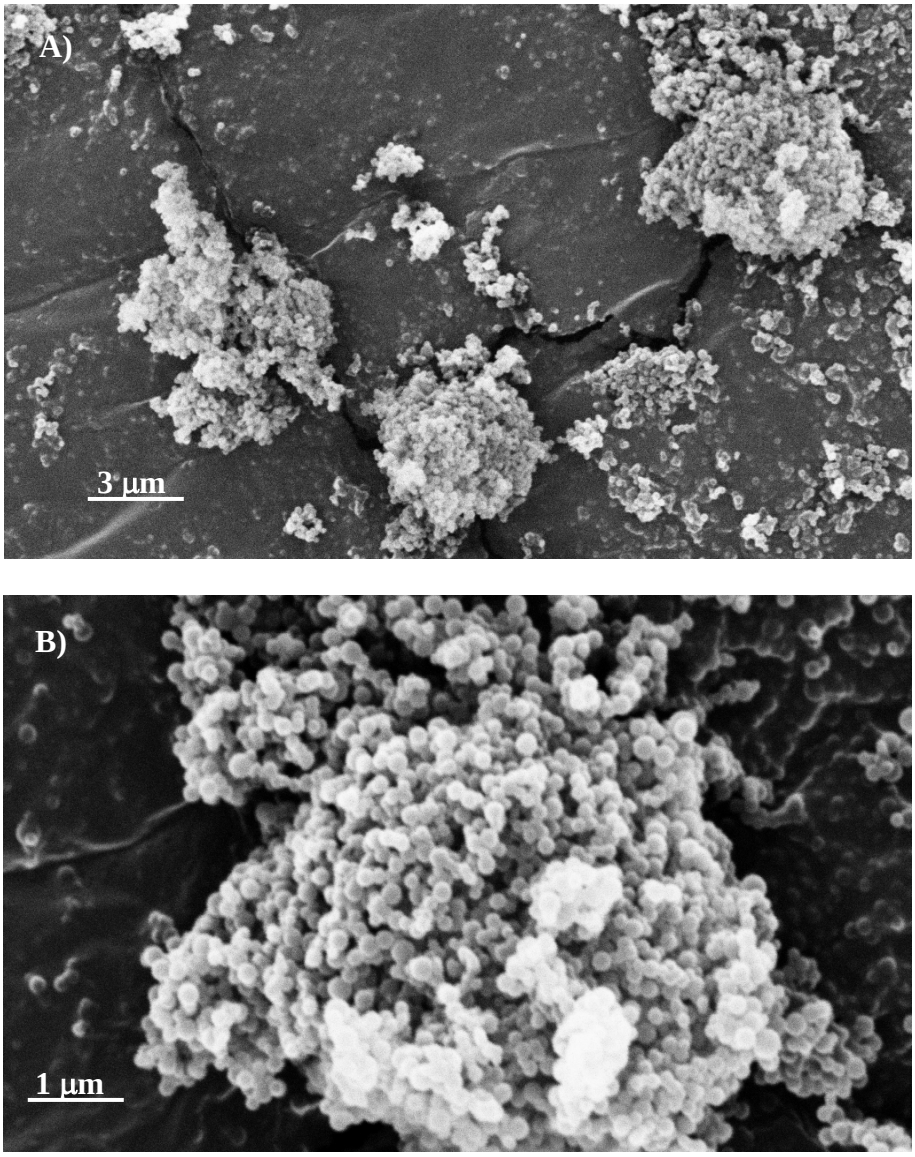


Figure 2 : SEM micrographs of pure urea-formaldheyde at **A)** 10KX and **B)** 30KX magnification

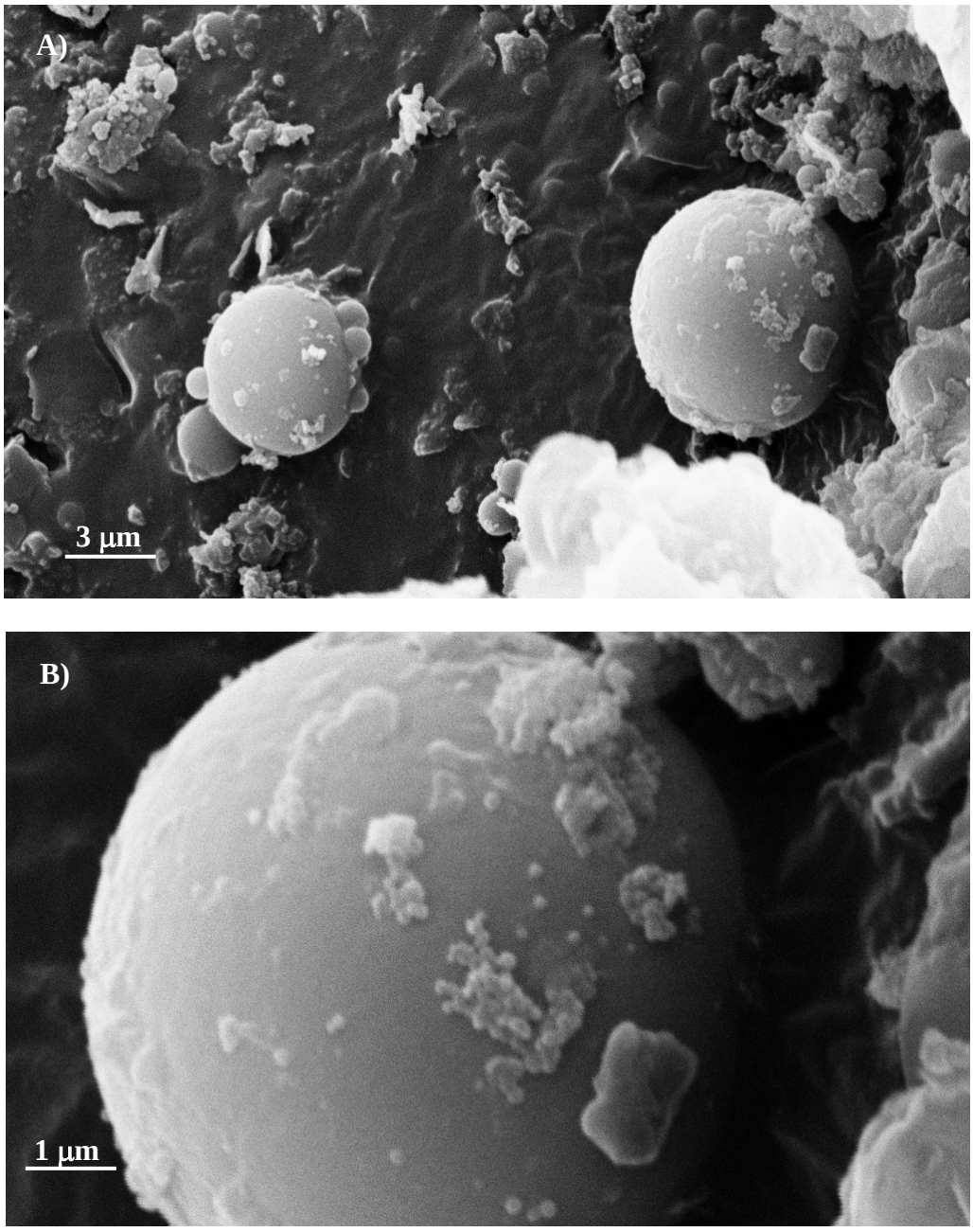


Figure 3: SEM micrographs of sample A at **A)** 10KX and **B)** 30KX magnification

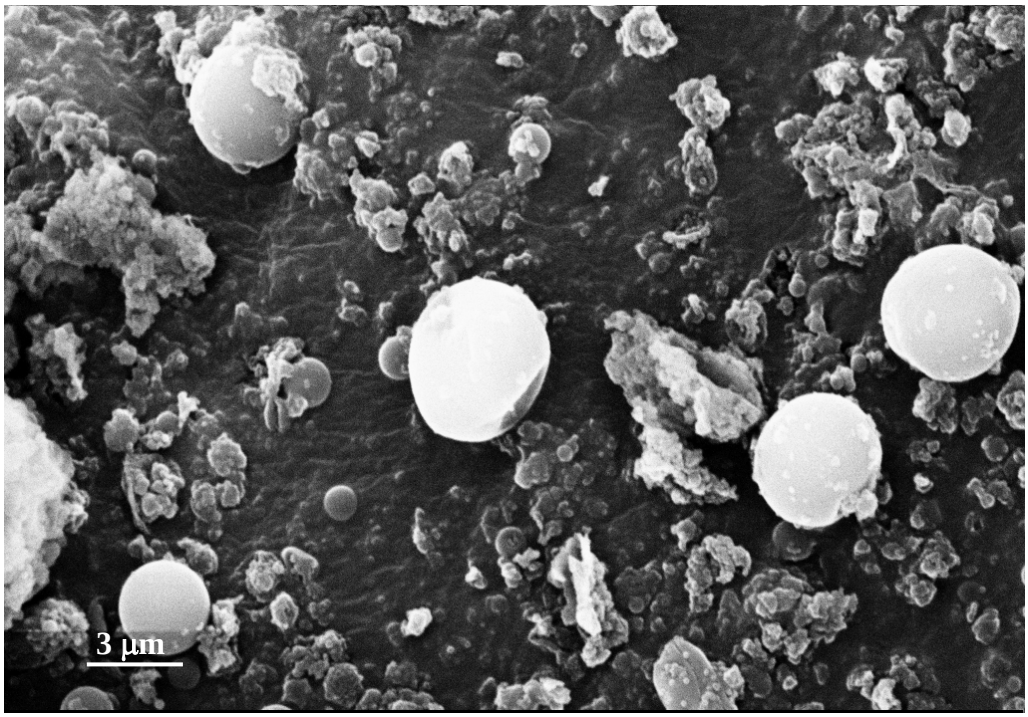


Figure 4: SEM micrographs of sample B at 30KX magnification

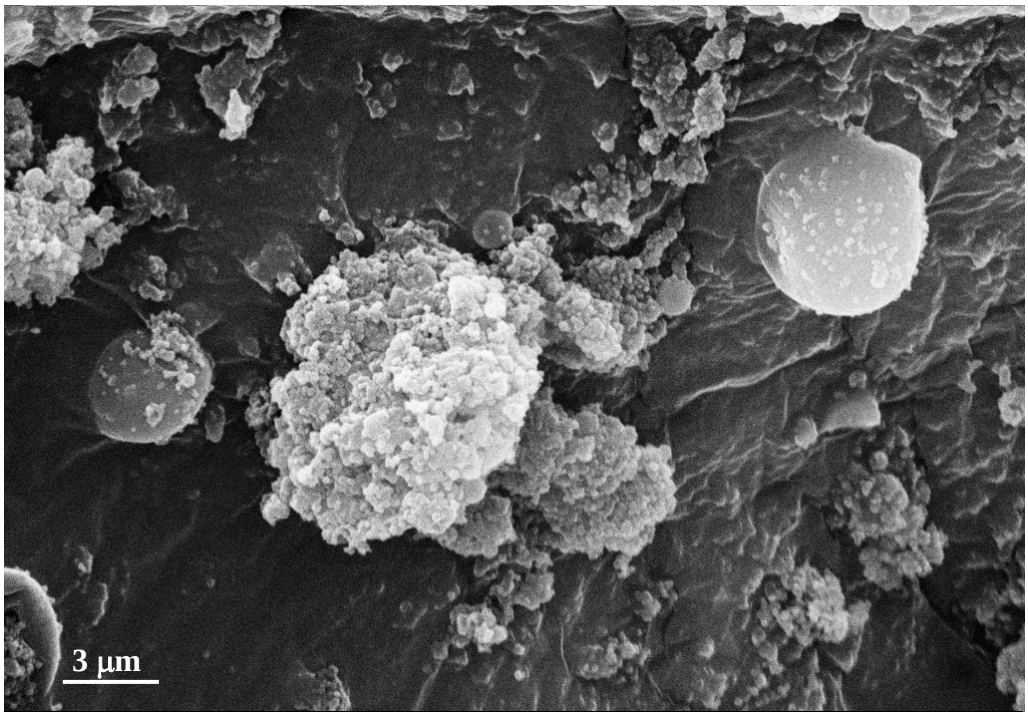


Figure 5: SEM micrographs of sample C at 30KX magnification

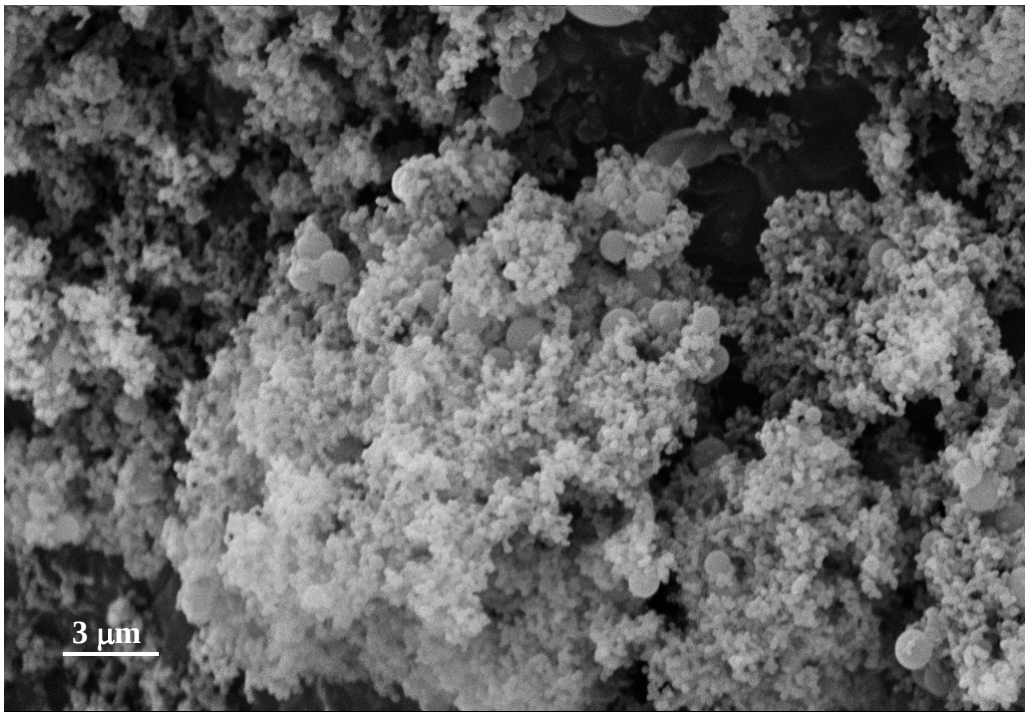


Figure 6: SEM micrographs of sample D at 30KX magnification

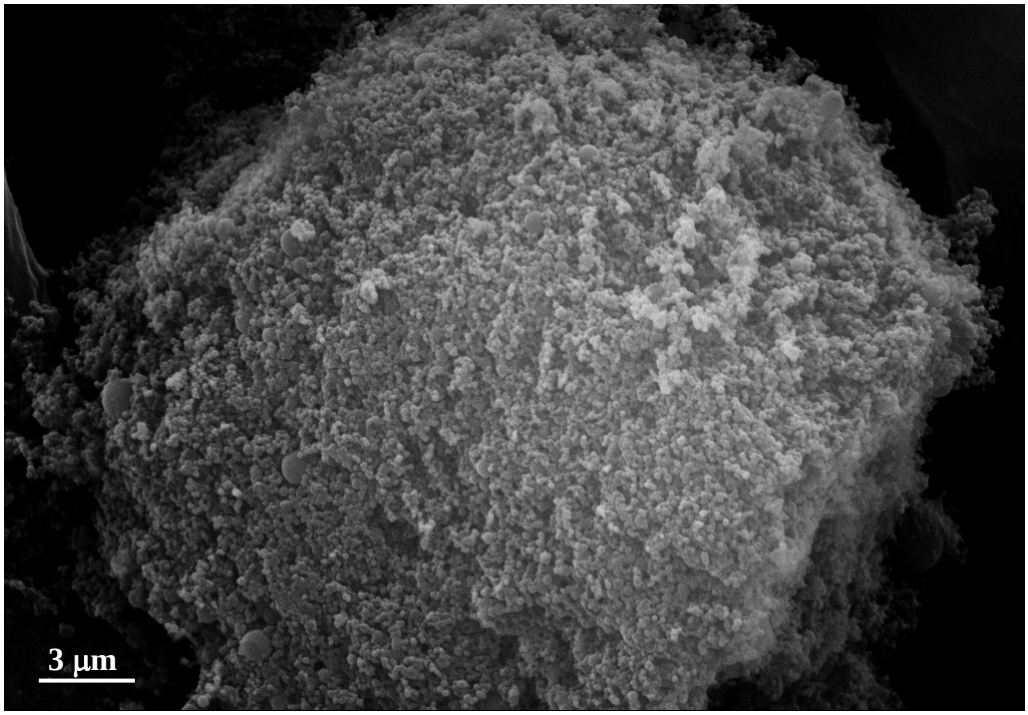


Figure 7: SEM micrographs of sample E at 30KX magnification

All the samples exhibit a complex morphology, characterized by micro-sized beads with a partially rough outer surface (single oil droplets), and/or clusters of nanocapsules. Irregularly shaped capsules (termed as *aggregates*) were also observed, in which the core material was subdivided into a number of parts embedded in a continuum of wall material.

Encapsulation proceeds via liquid-liquid phase separation. Polymerization between urea and formaldehyde is initiated in the water phase where a low molecular weight pre-polymer forms. As the molecular size increases, the polymer deposits at the organic-aqueous interface, in which the organic phase is constituted by the epoxy monomer [111]. The polymerization continues to give a highly cross-linked urea-formaldehyde capsule wall in the presence of resorcinol and ammonium chloride. The formation of urea-formaldehyde nanoparticles is attributed to precipitation of higher molecular weight pre-polymer in the aqueous solution and their agglomeration and deposition on the capsule surface.

The sample morphology is further complicated by the development of a wide variety of structures in the UF pre-polymers which are undoubtedly present after the cure, as reported above.

According to the mechanism proposed above for the case of a sample composed by pure UF (**Figure 2**) clusters of nanocapsules formed by precipitation of the cured, high-molecular weight portions was found. No evidence of micro-sized particles was detected. In this case, the reaction between urea and formaldehyde occurred exclusively in the aqueous phase, since the epoxy-based droplets, acting as a substrate for the interfacial polymerization, were absent.

As far as the microcapsules containing the epoxy resin concerns, a different and more complex morphology is evident in SEM micrographs. **Figure 3** shows the SEM images of sample A which is very similar to that observed for the samples B and C, differing on the reaction time and temperature used for their preparation respectively (see **Table 1**). The microcapsule diameters are in the range between 5 and 15 microns in both cases. The morphology of sample A, as well as of samples B and C (**Figures 4-5**), is characterized by the presence of microcapsules, *aggregates* and agglomerates of nanoparticles.

Samples D and E were obtained using a reaction temperature T = 40 °C and two different stirring rates (**Table 1**). Their morphology was very similar to that observed for the sample composed by pure UF and it was characterized by a widespread amount of agglomerated nanosized particles (**Figures 6-7**) and). Most probably, in both cases, due to the lower reaction temperature and stirring rate the organic phase was not well dispersed in the aqueous medium and the urea-formaldehyde system reacted predominantly in the water phase.

3.2.3. Thermal analysis

In order to investigate on the presence of the epoxy resin into the capsules, a thermal analysis by DSC was carried out. The collected data provided also information about the extent of polymerization of the UF walls. The results are summarized in **Table 2**.

Table 2: ΔH and temperature values associated to the epoxy resin homopolymerization in the microcapsules

Sample	$T_{rection}$ *(°C)*	$t_{reaction}$ *(h)*	***stirring rate*** ***(rpm)***	$\Delta H_{homopol}$ *(J/g)*	$T_{homopol}$ *(°C)*
Neat UF	60	4	2000	-	-
A	60	4	2000	390	223
B	60	6	2000	391	228
C	40	4	2000	330	229
D	40	4	1600	101	200
E	40	4	1200	13	212

The DSC curves of the samples A and B are reported in **Figure 8** in comparison with the thermogram of hollow UF capsules with the aim to evaluate the effect of the reaction temperature on the encapsulating capability.

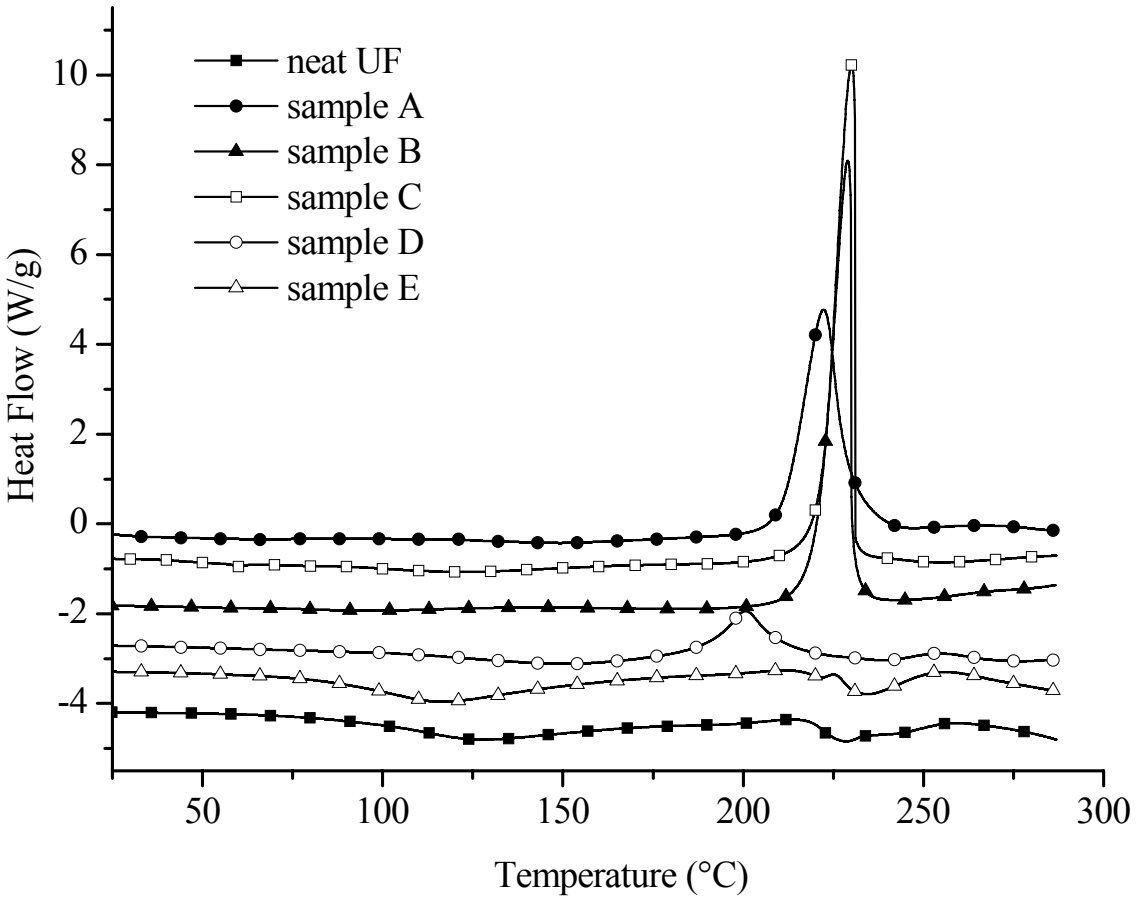


Figure 8: DSC thermograms of prepared microcapsules

For this purpose, the peak centred at T = 225 °C was taken into account, since it was not possible to refer to the melting point of the epoxy resin as a diagnostic peak indicating the achievement of the encapsulation. In fact, once the epoxy resin was melted to be added to the reaction solution, it was not able to recrystallize, retaining its viscous state for a long time.

The peak at T = 225 °C is likely to be attributed to the homopolymerization of the epoxy monomer. It is known that epoxies are reactive towards self-polymerization to polyethers at high temperatures (T ≈ 200 °C) and in the presence of impurities, such acidic and basic compounds [112, 113]. These species most probably were captured into the capsules during the wall formation.

Since the ΔH associated to the homopolymerization reaction is unchanged for sample A and B, that differ to each other only on the reaction time used for their preparation (see Table 1), it can be asserted that the reaction time does not affect the epoxy resin encapsulability.

On the other hand, the ΔH associated to the homopolymerization reaction is higher for sample A (ΔH = 390 J/g) with respect to the sample C (ΔH = 330 J/g), indicating a superior amount of encapsulated resin in the first case. This can be explained in terms of a more efficient dispersion of the core agent with increasing the temperature in the case of sample A. In fact, at T = 60 °C the epoxy resin is above its melting point and its reduced viscosity favours the homogeneous emulsification throughout the aqueous phase. Moreover, at this temperature the urea-formaldehyde system is more reactive, leading to a complete polymerization within the fixed reaction time (t = 4 h). This was also confirmed by the absence of the two broad endothermic peaks centred at T = 127 °C and T = 228 °C respectively, associated to the unreacted formaldehyde, urea, and UF oligomers.

The same peaks are easily detectable in the case of neat UF and in the samples D and E.

As far as the neat UF concerns, although the reaction temperature was set at T = 60 °C it seems that the polymerization did not reach the completion. This could be ascribed to the absence of the epoxy resin droplets, which somehow act as seeding sites for the UF polymerization.

Finally, the peak diagnostic for the epoxy resin appears weak in the curve of sample D, while it is not detectable in the thermogram in the case of sample E, analogously to hollow UF particles. Most probably, due to the lower stirring rate, the epoxy resin/water interfacial surface was reduced and the UF polymerization occurred predominantly in the water phase.

From these results it can assumed that both the temperature and the stirring rate affect the extent of polymerization of the UF wall. Low reaction temperature and stirring rate force the monomer to react in the aqueous rather than at the epoxy/water interface, leading not only to different chemical urea-formaldehyde derivatives but also to a decreased encapsulation capability.

3.2.4. Vibrational analysis (FTIR and Raman spectroscopies)

The FTIR spectrum of the pure urea-formaldehyde resin in the 4000 – 400 cm^{-1} range is reported in **Figure 9.**

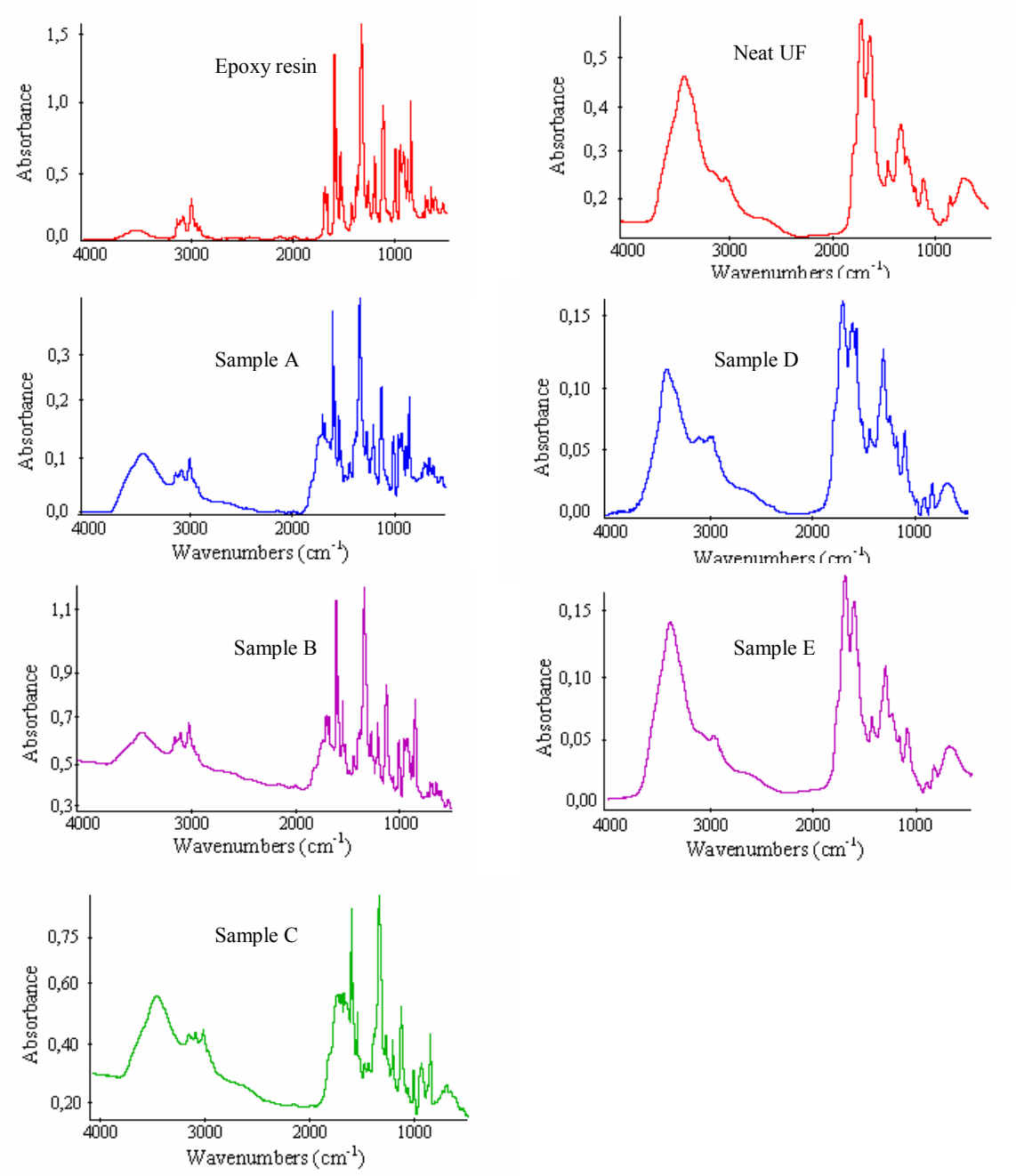


Figure 9 : FT-IR spectra of prepared microcapsules

A broad absorption centered at around 3379 cm^{-1} is likely related to a considerable amount of absorbed water, with possible contributions from the stretching vibrations of residual amine groups. Prominent spectral features are observed at 1630 – 1559 cm^{-1}, corresponding, respectively, to the amide I mode (mostly C=O stretching) and the amide II mode (prevailingly N-CO stretching). A well defined shoulder is detected at higher wavenumbers (1710 cm^{-1}). The complex profile observed in the carbonyl region reflects the multiplicity of molecular structures formed upon curing.

The FTIR spectrum of the neat epoxy resin **(Figure 9)** is richer and considerably more resolved. Residual hydroxyl groups, formed during the synthesis, together with absorbed H_2O, produce the broad band centered at 3512 cm^{-1}; the CH_2/CH stretching modes give rise to the complex multiplet in the 3100 – 2800 cm^{-1} region. The p-substituted aromatic rings produce intense absorptions at 1610, 1585, 1509, 1178, 840 and 756 cm^{-1}; the highly coupled C-O-C stretching modes absorb at 1298 and 1242 cm^{-1}. The epoxy ring gives rise to a well resolved peak at 916 cm^{-1} (ring deformation) and to a second peak at around 860 cm^{-1}, partly superimposed onto an aromatic absorption band. The spectra of the investigated microcapsules, in the form of powders dispersed in KBr, are reported in **Figure 9.** Spectra of samples A and B are dominated by the contribution of the epoxy resin, although the UF skin is readily detectable both in the ν_{OH} and in the carbonyl region. Spectrum of sample C is intermediate; spectra of samples D and E closely resemble the spectrum of the neat UF resin, but some of the more intense peaks of the epoxy component (i.e. at 1509 and 1452 cm^{-1}) are still readily detectable.

From the powder spectra of **Figure 9** it is possible to isolate the epoxy resin spectrum by subtracting out the contribution of the UF resin. The results of such an analysis, relative to sample B, is displayed in **Figure 10**.

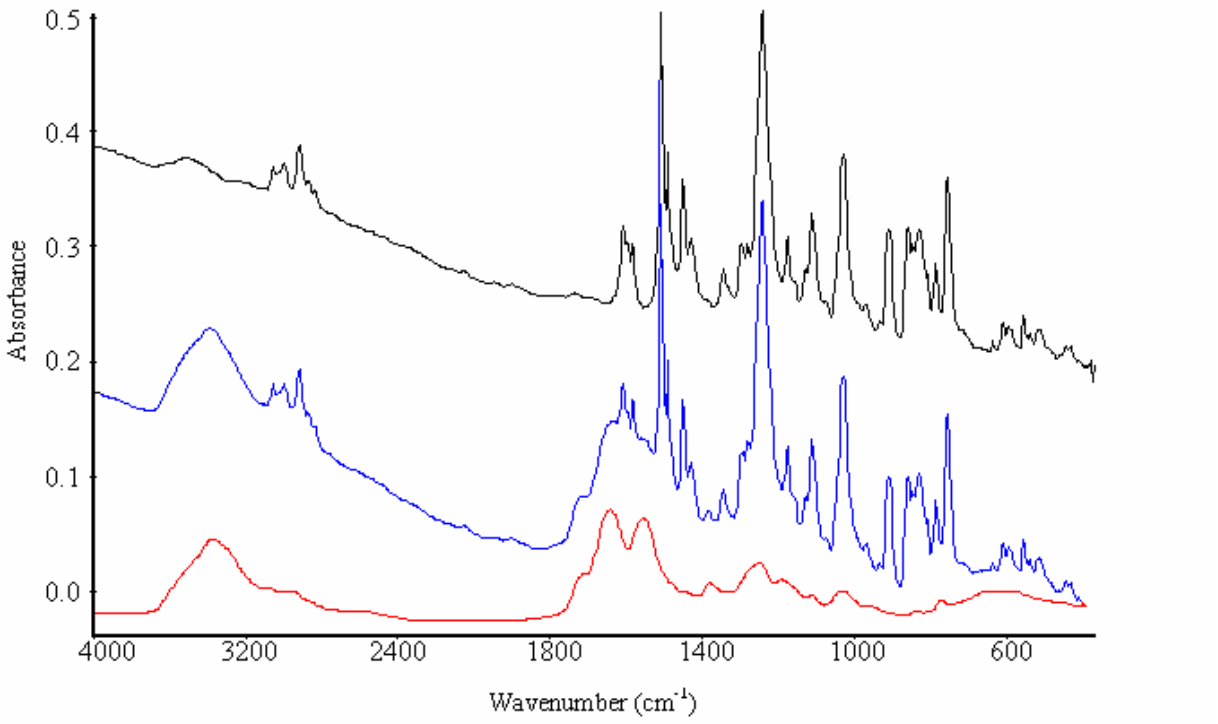


Figure 10 : FT-IR spectra of **A)** urea-formaldheyde resin, **B)** sample B and **C)** difference spectrum between sample B and urea-formaldheyde resin

The difference spectrum obtained in this way is essentially coincident with that of the neat epoxy resin (compare **Figure 9** and **Figure 10**), apart from the sloping base-line from 4000 to 1800 cm^{-1} in spectrum of sample C, due to the scattering of solid microcapsules having the same size of the incident IR radiation (2.5 – 5.5 μm). This effect is not observed in the spectrum of the neat epoxy resin, which is liquid at room temperature. The ratio between the absorbance of a peak characteristic of the epoxy ring, i.e. at 916 cm^{-1}, (A_{916}) over that of a peak expected to be invariant under the condition used to prepare the samples (typically a well resolved aromatic absorption like the one at 756 cm^{-1}, A_{756}) is proportional to the concentration of epoxy groups. This ratio is equal to 0.63 ± 0.025 for samples A and C, 0.64 ± 0.025 for sample B and 0.63 ± 0.025 for the pure epoxy resin. Samples D and E, gave unreliable difference spectra due to the very low amount of epoxy resin incorporated in the microcapsules. The analysis demonstrates that no side reactions leading to the consumption of epoxy groups take place in the conditions used to prepare the microcapsules. In terms of the relative ratio of the two components in the microcapsules, the FTIR data qualitatively indicate that encapsulation has been successfully achieved for samples A and B, for which the amount of epoxy resin considerably exceeds that of the surrounding UF skin. Sample C displays a roughly one-to-one ratio between the two components, while for sample D and even more so for sample E, the encapsulation procedure is to be considered inefficient. However, difficulties related to the estimation of the total sample content and to the achievement of a perfectly homogeneous dispersion, limit the usefulness of KBr powder spectra in providing reliable quantitative data (uncertainities ≥ 10%). For a more precise analysis of the samples composition we turned our attention to Raman spectroscopy.

The Raman spectra of the microcapsules prepared in the present study are reported in **Figure 11** along with the spectra of the pure components for comparison.

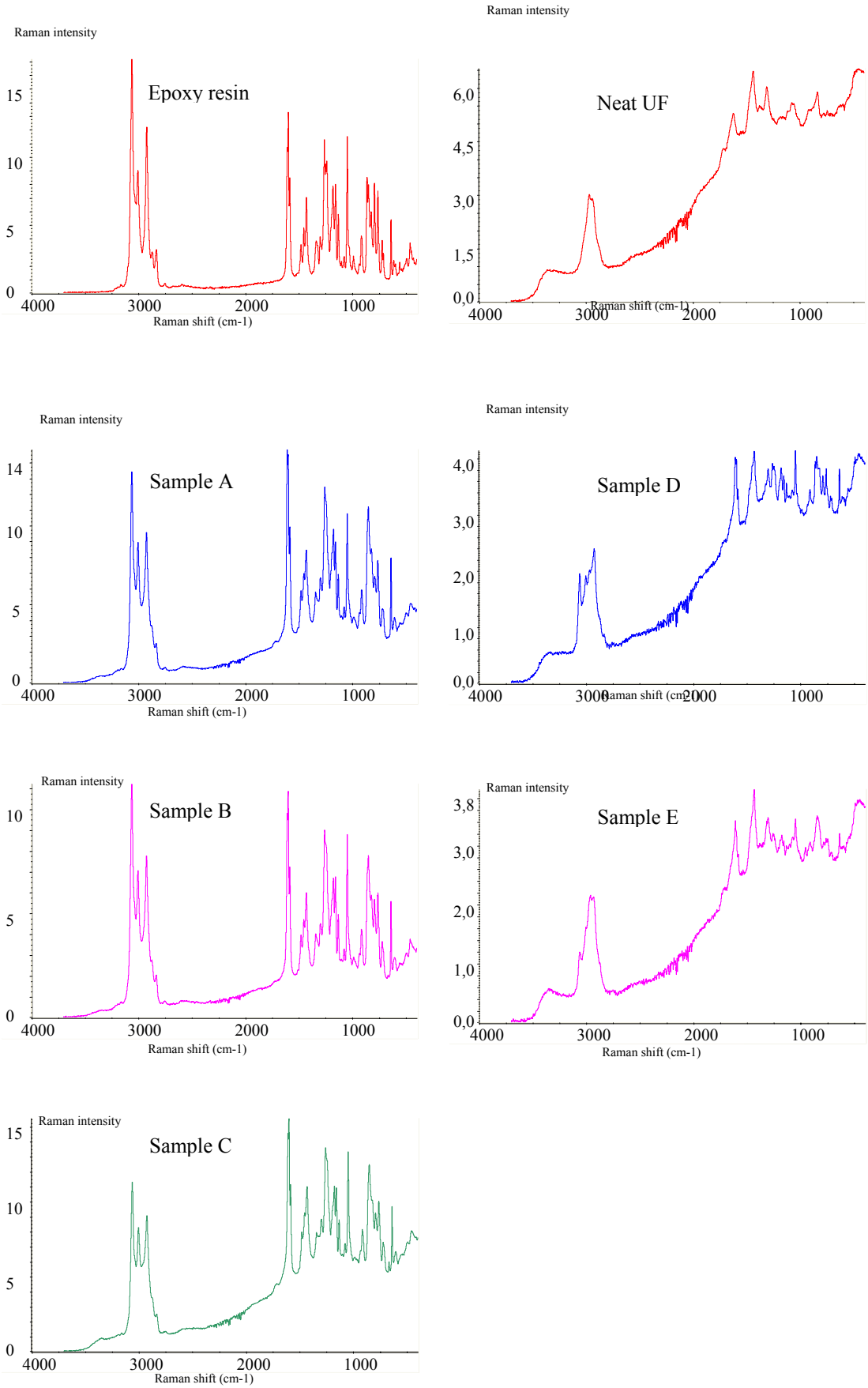


Figure 11: Raman spectra of prepared microcapsules

The epoxy resin gives rise to an intense Raman scattering, in the 4000 – 400 cm^{-1} range, thus producing an essentially noise-free spectrum. As generally found, the Raman peaks are considerably sharper than their infrared counterparts, thus providing a more resolved spectrum. The ν_{CH} region displays fully resolved components at 3063 cm^{-1} (ν Ar-H), 3008 cm^{-1} (ν CH epoxy), 2925 (ν_{asym} CH_2 ether) 2873 (ν_{sym} Ar–CH_2–Ar) and 2836 cm^{-1} (ν_{sym} CH_2 ether). Of particular relevance for the present investigation is a well resolved triplet with maxima at 1609, 1600 and 1587 cm^{-1}, assigned to ring stretching modes of the disubstituted aromatics. The epoxy group gives rise to several characteristic peaks at 1263, 1132, 917 and 864 cm^{-1}. The UF resin produces a much lower amount of Raman scattering with respect to the epoxy, and a correspondingly worse spectrum, characterized by intense fluorescence, as indicated by the steep slope of the baseline. In spite of the low intensity and the poor signal-to-noise ratio, several peaks can be identified and assigned. A broad band in the region 3050 – 2800 cm^{-1} originates from the methylene groups, while the amide carbonyls produce an unresolved multiplet with maxima at 1716 and 1623 cm^{-1}. Again, the multicomponent profile in the carbonyl stretching region is a consequence of the complexity of the resin structure. [113, 114].

Two bands at 1470 (shoulder) and 1438 cm^{-1} are assigned, respectively, to the bending mode of methylene units in the N-CH_2-N and in the CH_2-OH structures [113,115].

The spectra of samples A, B and C are very similar to the spectrum of the epoxy resin. However, the fluorescence increases in going from sample A to sample C, which reflects the growing contribution of the UF phase to the overall scattering process. Spectra of samples D and E closely resemble the spectrum of the UF resin, thus indicating that in these two cases the UF component is largely predominant. As for the FTIR spectra, however, also in these cases the more intense peaks of the epoxy resin, notably those in the 1660 – 1560 cm^{-1} range, remain clearly detectable.

Raman spectroscopy is well established as a quantitative analytical technique. In fact, by assuming a direct proportionality between the normalized intensity of a characteristic Raman peak and the concentration of the scattering species, we may write:

$$\frac{I_{UF}}{I_{EPO}} = \frac{I_{1722}}{I_{1585}} = k\frac{C_{UF}}{C_{EPO}} \qquad \textbf{(1)}$$

from which

$$\left(\frac{C_{EPO}}{C_{UF}}\right)_S = \left(\frac{I_{1722}}{I_{1585}}\right)_{STD} \cdot \left(\frac{I_{1585}}{I_{1722}}\right)_S \cdot \left(\frac{C_{EPO}}{C_{UF}}\right)_{STD} \qquad \textbf{(2)}$$

where I_{1722} and I_{1585} are the intensities of two peaks characteristic, respectively, of the UF and the epoxy resins and C_{EPO} and C_{UF} refer to their concentration, expressed in weight %. The subscripts *S* and *STD* indicate, respectively, the sample being analysed and a standard mixture of known composition prepared by mechanical mixing of the two resins.

Because of severe peak overlapping in the region of interest, a curve fitting analysis was performed to evaluate I_{1722} and I_{1585}. The results are displayed in **Figure 12** for the UF resin, for the epoxy resin and for a representative microcapsule sample (sample C).

In all cases the correspondence between the simulated and the experimental profiles is excellent and the peak parameters, i.e. the full width at half height (FWHH), the position and the band-shape, as evaluated from the spectra of the pure resins closely correspond to those obtained for the composite spectra. This confirms the reliability of the method. The percentage of epoxy resin over the total sample weight, as evaluated from Eq. 2 for all the investigated specimens is reported in **Table 3**.

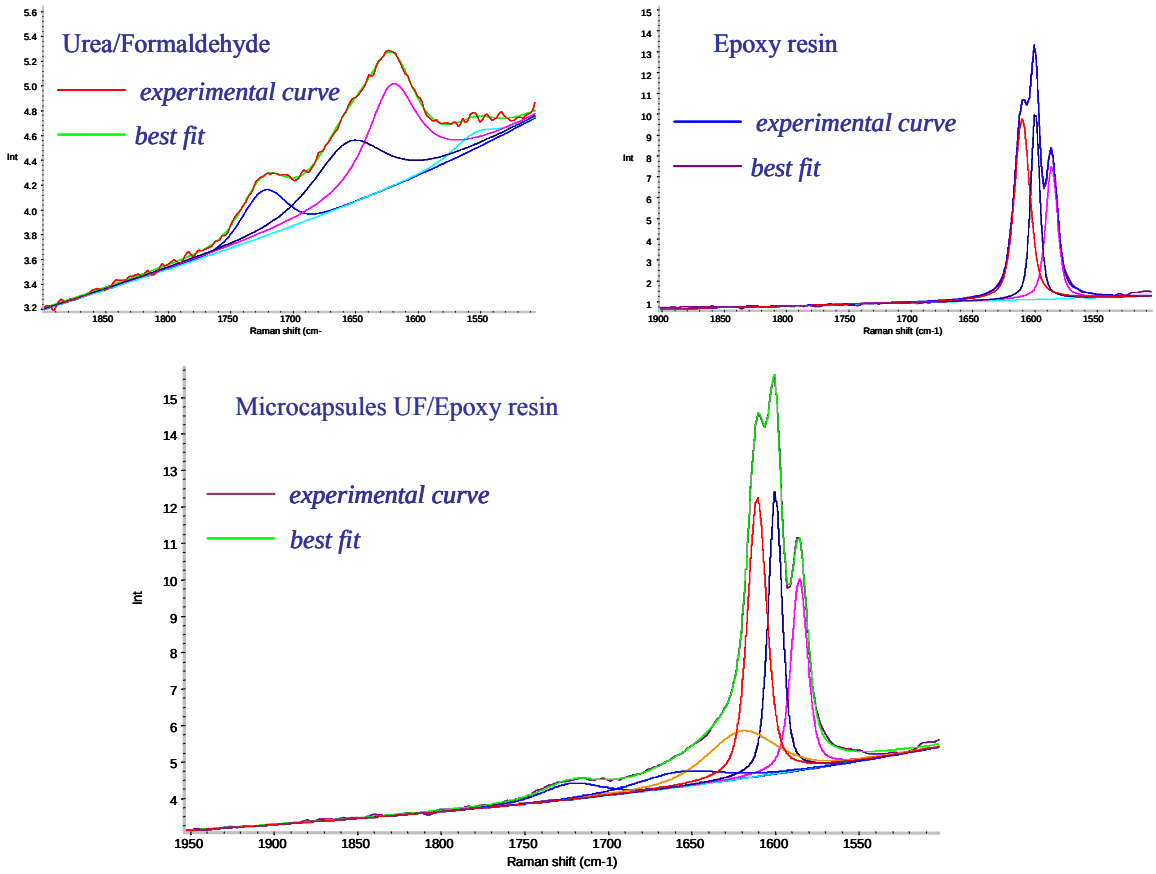


Figure 12: Fittings curves of Raman spectra of **A)** urea-formaldheyde resin, **B)** epoxy resin and **C)** sample C

Table 3: Summary of quantitative analysis by Raman spectroscopy

Sample	***I(1722)(A.U.)***	***I(1585)(A.U.)***	***I(1722)/I(1585)***	W_{epo}/w_{UF}	***%epoxy resin***
Epoxy resin	-	93.5	-	-	100
Neat UF	21.34	-	-	-	0
A	15.22	96.09	0.16	2.72	73.1
B	13.5	72.6	0.19	2.32	70
C	23.95	80.21	0.3	1.43	59
D	8.65	6.94	1.25	0.34	25.6
E	11.84	3.68	3.22	0.13	11.8

3.2.5. TGA analysis

Figure 13 shows the weight loss percentage for a representative set of microcapsules (samples A, C and E) with respect to that of neat UF and of epoxy resin, as a function of temperature. The collected data are summarized in **Table 4**.

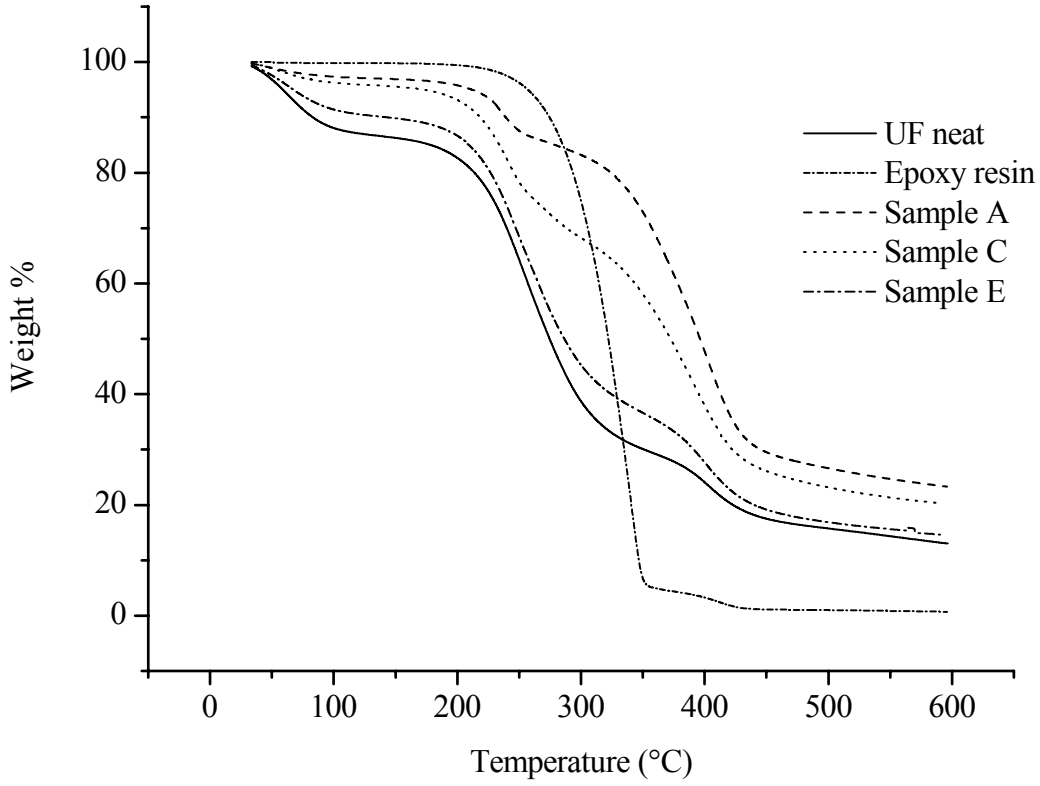


Figure13 : Thermogravimetric curves of analyzed samples

Table 4: Thermal properties of epoxy resin, neat UF and microencapsulated epoxy resin

	I degradation step		**II degradation step**	
Sample	***T_d^1 (°C)***	***weight loss (%)***	***T_d^1 (°C)***	***weight loss (%)***
Epoxy resin			321	95.1
Neat UF	256	62	390	11
A	244	15	382	60
C	241	28	386	47.6
E	258	54	402	20

[1]The temperature when the weight loss percentage of the sample was 50 wt%

The thermograms of the samples A, C and E exhibit two weight loss steps. In order to analyse each degradation step the curves of neat UF and epoxy resin were taken into account.

The most significant weight loss (62 wt%) of neat UF occurs in a range between 150°C and 300°C, while the epoxy resin thermal decomposition starts at T ≈ 225 °C, to reach the 50 wt% loss at T_d = 322 °C.

If we analyse the curve of sample A, in the temperature range between 150 °C and 300°C, a 15 wt% loss occurs, associated to the decomposition of the UF shell. Moreover, a second marked degradation step involving the core material (60 wt%) is evident at higher temperatures. It is worth noting that the weight loss temperature of microencapsulated epoxy resin is higher than that of the bulk. This is due to the presence of homopolymerized species which formed during the heating process, as evidenced from DSC analysis (**Figure 8**) and to the shielding effect of UF shell on the encapsulated, unreacted epoxy resin.

In the case of the samples C and E, that differ from the sample A on the reaction temperature and stirring rate used for their preparation (see **Table 1**) the same steps are detectable. However, the weight loss associated to the decomposition of epoxy resin portion are significantly reduced with respect to that observed in the case of sample A, while in the temperature range associated to the decomposition of the UF shell, a 28 wt% (sample C) and 54 wt% (sample E) loss occurs.

The small step observed at lower temperatures in the thermograms of samples C and E as well as in the case of neat UF could be ascribed to the decomposition of the UF oligomers.

These results are in agreement with the DSC data demonstrating that low reaction temperature and stirring rate lead not only to different low molecular weight UF species but also to a decreased encapsulation capability.

Moreover, TGA analysis has been used to asses the reliability of Raman spectroscopy as a quantitative analytical technique.

For this purpose, the weight loss associated to the degradation of UF shell has been taken into account to be used in the following equation:

$$\left(\frac{wt\%loss_{UF}}{C_{UF}}\right)_{neat} = \left(\frac{wt\%loss_{UF}}{C_{UF}}\right) \qquad \textbf{(3)}$$

where C_{UF} and $wt\%loss_{UF}$ refer, respectively, to UF concentration, expressed in weight %, and to the weight loss associated to the decomposition of UF shell. The subscripts *neat* refers to the sample composed by pure urea-formaldheyde, which has been used as reference.

By assuming a UF concentration equal to 100% in the neat UF, it was possible to determine the UF concentration within each microcapsule sample. In particular, if we consider the case of sample A the percentage of UF, as evaluated from Eq. (**3)**, is 24 wt%. The amount of encapsulated epoxy resin, calculated as the complementary value to 100%, is 76wt%.

The TGA results are in agreement with the Raman data confirming the reliability of this spectroscopic analysis as a quantitative analytical technique.

3.3. Conclusions

A series of UF/PY306 epoxy resin microcapsules has been prepared by *in situ* polymerization in an oil-in-water emulsion and the influence of reaction parameters on the microcapsule properties was described.

Morphological analysis showed for the samples A, B and C a complex morphology, characterized by the presence of micro-sized beads with a partially rough outer surface (single oil droplets), and/or clusters of nanocapsules. Irregularly shaped capsules (termed as *aggregates*) were also observed. In the case of samples D and E, obtained at lower reaction temperature and stirring rate, the morphology was different and characterized by a widespread amount of agglomerated nanosized particles.

DSC and TGA results indicated that a decrease of the reaction temperature, as well as of the stirring rate, has a great influence on the microcapsule properties. Low reaction temperature and stirring rate force the monomer to react in the aqueous rather than at the epoxy/water interface, leading not only to different chemical urea-formaldehyde derivatives but also to a decreased encapsulation capability.

FT-IR analysis demonstrated that no side reactions leading to the consumption of epoxy groups take place in the conditions used to prepare the microcapsules. In terms of the relative ratio of the two components in the microcapsules, the FTIR data qualitatively indicate that encapsulation has been successfully achieved for samples A and B. Sample C displays a roughly one-to-one ratio between the two components, while for sample D and even more so for sample E, the encapsulation procedure is to be considered inefficient.

A more precise analysis of the samples composition has been carried out by means Raman spectroscopy. In particular, spectroscopic results confirmed that a decrease of the reaction temperature, as well as of the stirring rate, reduce the microencapsulability of the core material.

The main factor responsible for the epoxy resin microencapsulability seems to be related to the stirring rate. Most probably, the dispersion of the organic phase in the water, which is made progressively adverse by decreasing the reaction temperature, i.e. by passing from sample A to sample C, is further reduced by lowering the stirring rate, i.e. by passing from sample C to samples D and E. As a consequence of the low epoxy/water interfacial surface, the reaction between urea and formaldehyde occurs predominantly in the aqueous phase, according to the same mechanism proposed for the UF sample.

PART II

PROPERTIES AND PERFOMANCE OF EMBEDDED EPOXY-BASED MICROSPHERES

CHAPTER 4

4.1. Introduction

The aim of the present work is to determine the influence of epoxy-based microspheres on the composite material properties. The embedded microspheres are a secondary, dispersive phase in the matrix. As a type of particulate filler, the microspheres could gratly affect the mechanical properties of the matrix.

Modification of epoxy-based materials by the inclusion of additives is a well-known method for improving their physical properties [116-119]. Usually, low modulus thermoplastic or elastomeric particles are used to increase ductility and impact resistance, as they are able to reduce the internal stress of incorporating epoxy resins. Since the extent of local deformation of materials under stress in the crack tip is strongly dependant on the local texture of the epoxy resins, the characteristics of dispersed particles, such as size, interfacial bonding to the epoxy matrix and their content, are the key factors to regulate the toughening performance [117,119].

Over the last years, a growing number of applications have required the use of polymeric microspheres bearing reactive functional groups on their surfaces in order to improve the properties of reinforced materials. For this reason, numerous methods have been developed for the synthesis of functionalized microspheres [120-122] and many studies on the influence of these particles on the mechanical and rheological properties of the composite systems have been carried out [116,117,119,123-125].

Among them emulsion and seeded emulsion polymerization, suspension polymerization and dispersion polymerization in aqueous and non-aqueous media have been traditionally used for the polymerization of vinyl monomers, such as vinyl acetate, acrylate, vinyl chloride, styrene and epoxy resins [117,126-130].

In their work, Falk and Crivello [131] synthesized epoxy functional microspheres through cationic suspension polymerization in both aqueous and non-aqueous media, using onium salt photoinitiators. In the same period, Bécu-Longuet and K.F. Lin and their co-operators [124,118] prepared functionalized core-shell particles and studied the influence of size and surface functionalities on the physical properties of epoxy resins. Numerous other scientific groups have shown interest in this field [116, 125,132].

Some authors [133,134] proposed an alternative method, based on the sol-gel technique, for the in situ generation of silica particles within a thermoset network using tetraethoxysilane (TEOS) as precursor of the inorganic phase. The in-situ built-in inorganic

phase reinforced the rubbery network. Moreover, during polymerization grafting between the epoxide network and silica–siloxane structures occured by condensation of silanol groups with the C–OH group formed at the epoxide–amine reaction [135]. This strategy is advantageous compared to the use of pre-formed particles because it is a one step procedure. However, the shape and dimensions of the silica phase depends on the cure cycle, the catalyst and the resin type. This can be a problem in the industrial practice because it restricts the choice on the processing and formulations parameters.

In this work, we show the influence of epoxy resin microspheres functionalized with amino groups on the rheological and thermo-mechanical properties of a Bisphenol A-based epoxy resin (EPON828) cured with 3,3'-diaminodiphenylsulphone (3,3'DDS). First, the microspheres were synthesized through dispersion polymerization. In particular, two different systems were prepared: a Bisphenol A-type resin (EPON825) cured with 2,4-diaminotoluene (DAT), and a Bisphenol F-based epoxy resin (PY306) crosslinked with diethyltoluenediamine (DETDA). In both cases, the epoxy monomer and the curing agent were dissolved in an organic polyether-based solvent, and let react at high temperature without stirring. An excess of curing agent was used, so that cured microspheres with a surface rich of amino groups were obtained. During the curing reaction, as the molecular weight of the reacting system increased, phase separation occurred. As soon as the reaction reached the completion, the crosslinked material deposited as an insoluble powder, consisting in micro-sized spherical particles. Details about the mechanism responsible for the formation of epoxy microspheres were given elsewhere [123]. The characteristics of final particles, such as size, morphology and functionality were shown to be significantly controlled by the experimental conditions adopted during the synthesis. That is, the reaction temperature, the nature of the medium and the monomers, the affinity between the monomers and the solvent, as well as the solute-to-solvent ratio were found to be the key factors in determining the features of the microparticles.

In a second step, after dispersion of the microparticles into the EPON828-3,3'DDS resin, the rheological and thermo-mechanical behaviour of the blends was investigated. With the aim of determining the influence of both typology and amount of microspheres on the matrix reactivity in the prepared blends rheological test were performed. This particular experimental technique may be considered an efficient method, since it is able to correlate the reactivity of an epoxy system with the measured gel time (t_{gel}). Glass transition temperatures and storage moduli of cured composites in comparison with un-modified resin were evaluated through dynamical mechanical thermal analysis.

Morphological study on the prepared systems was also carried out with the aim of investigating both on the dispersion homogeneity and the extent of adhesion of microspheres in the matrix.

4.2. Results and discussion

4.2.1. Microspheres synthesis and characterization

In this work, two starting epoxy monomers (EPON825 and PY306) were cured with two amino-based curing agents (DAT and DETDA, respectively) with a view to synthesizing two types of thermosetting microspheres. In particular, Mic1 and Mic2 were obtained, as described in the *Experimental* section. The glass transition temperature (T_g) values and the size of microspheres are reported in **Table 1**.

Table 1: Properties of prepared microspheres

Sample	*T_g in-bulk system [°C]*[a]*	*T_g microspheres [°C][a]*	*Microsphere size [m]*
EPON825-DAT	150	143	1.2 – 4.1
PY306-DETDA	132	130	6.70- 10.1

* *T_g in-bulk system* refers to the glass transition temperature of EPON825-DAT and PY306-DETDA systems synthesized in bulk (without solvent) and used as reference
[a] Glass transition temperatures (T_gs) were obtained by DSC measurements

As it can be seen in **Table 1** the two samples exhibited a distinctly single T_g, indicating that the microspheres were likely to be formed by a homogeneous structure. Furthermore, the values of the T_gs were only lightly lower than those of the *in-bulk* cured epoxies, suggesting that the molar excess of curing agent used for the synthesis of microspheres could be responsible for the plasticization of the inner part of the microparticles.

In addition, the microspheres were insoluble in all the common organic solvents, confirming the crosslinked nature of the materials.

Figures 1 and 2 show the SEM micrographs of Mic1 and Mic2, respectively.

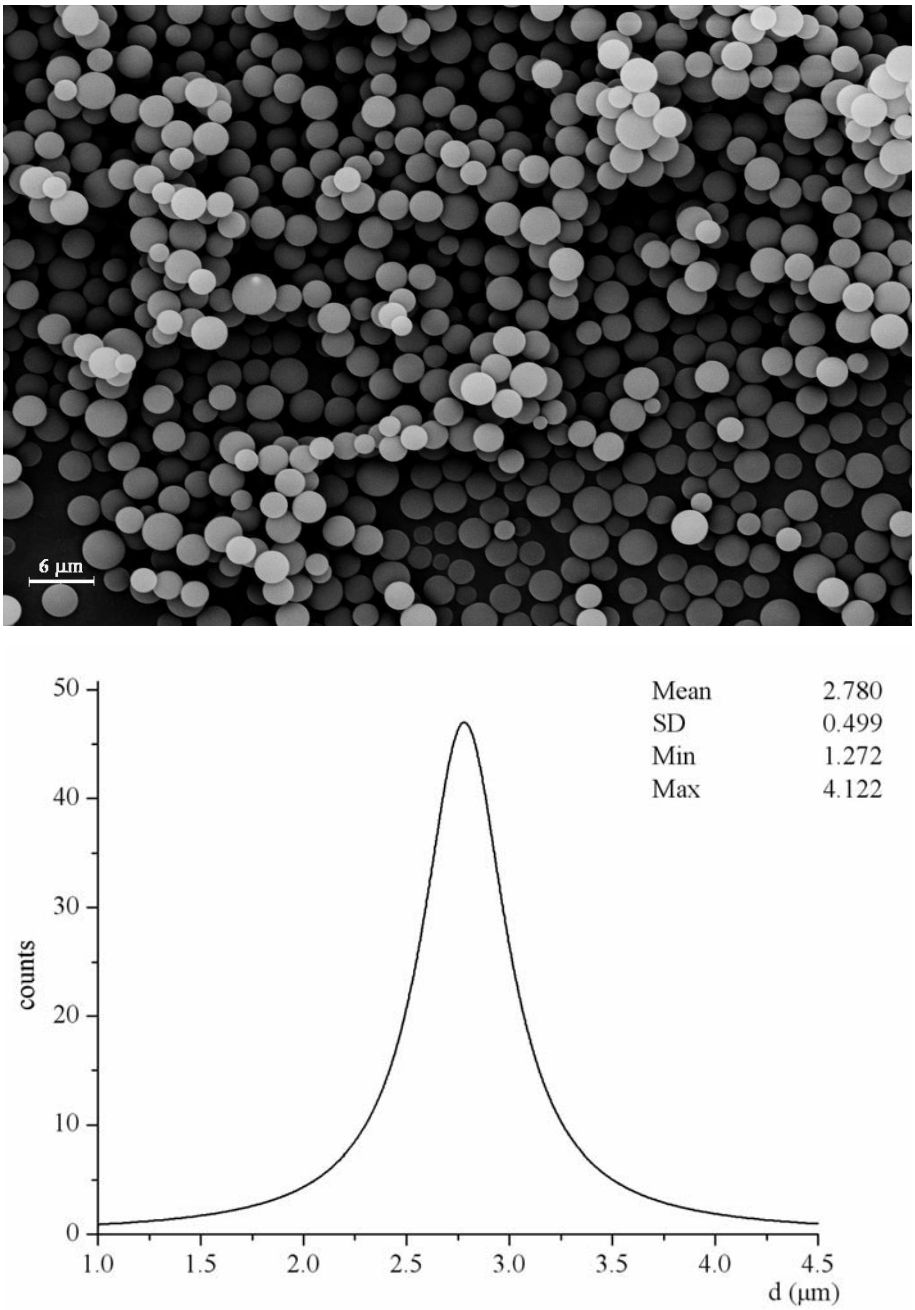
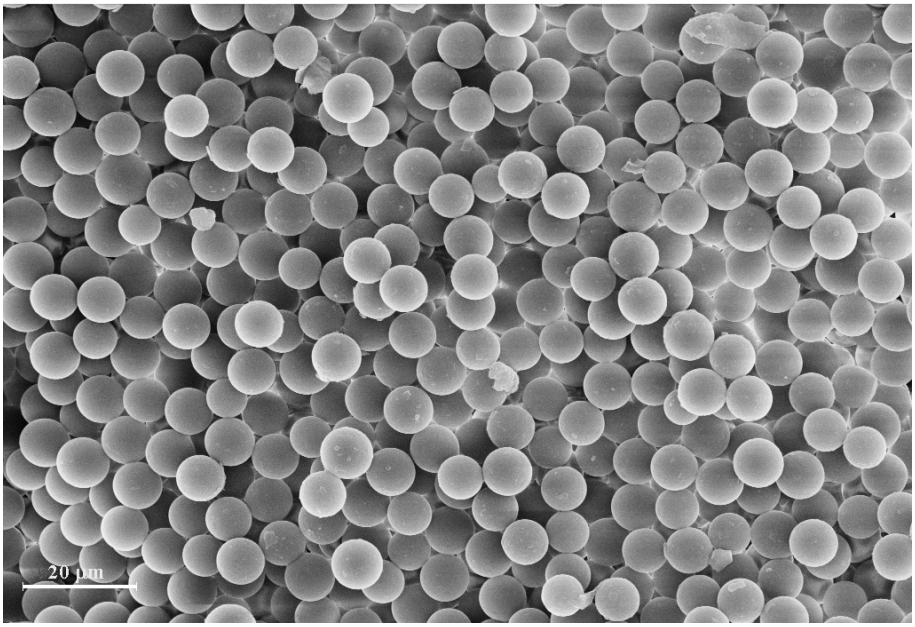


Figure 1. **A)** SEM image of Mic1 microspheres and **B)** their size distribution curve



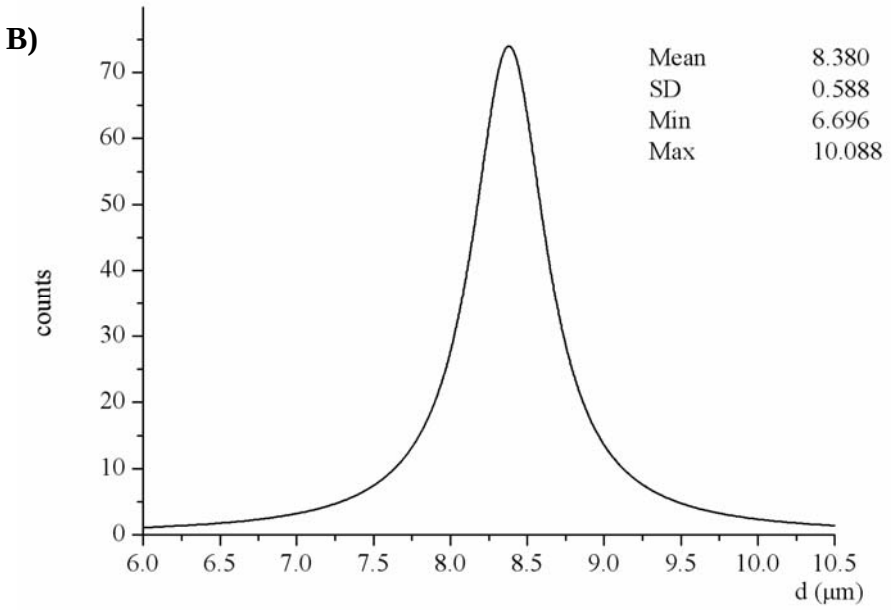


Figure 2. **A)** SEM image of Mic2 microspheres and **B)** their size distribution curve

In both cases the particles appeared very regular in shape. As far as their size concerns, the particle diameter distribution curves indicated that, in the case of Mic1 (**figure 1B**) diameter dimensions ranged between 1.3 and 4.1 μm, whereas in the case of Mic2 (**figure 2B**), between 6.7 and 10.1 μm.

This striking difference could be ascribed to the complex mechanism of particle formation, which includes the curing reaction between the epoxy monomer and the aromatic amine, leading to the crosslinked resin, and the phase separation process. This latter is related to the miscibility of the epoxy-amine reacting system in the solvent. The synergy between

these two processes is responsible for the final properties of the crosslinked microparticles. That is, when the curing kinetic is fast, the induced phase separation occurs in a short time leading to the formation of microspheres characterized by a reduced size.

The optical micrographs in **Figure 3** show the influence of the reacting temperatures on the formation of microparticles based on EPON825-DAT in PPG1000.

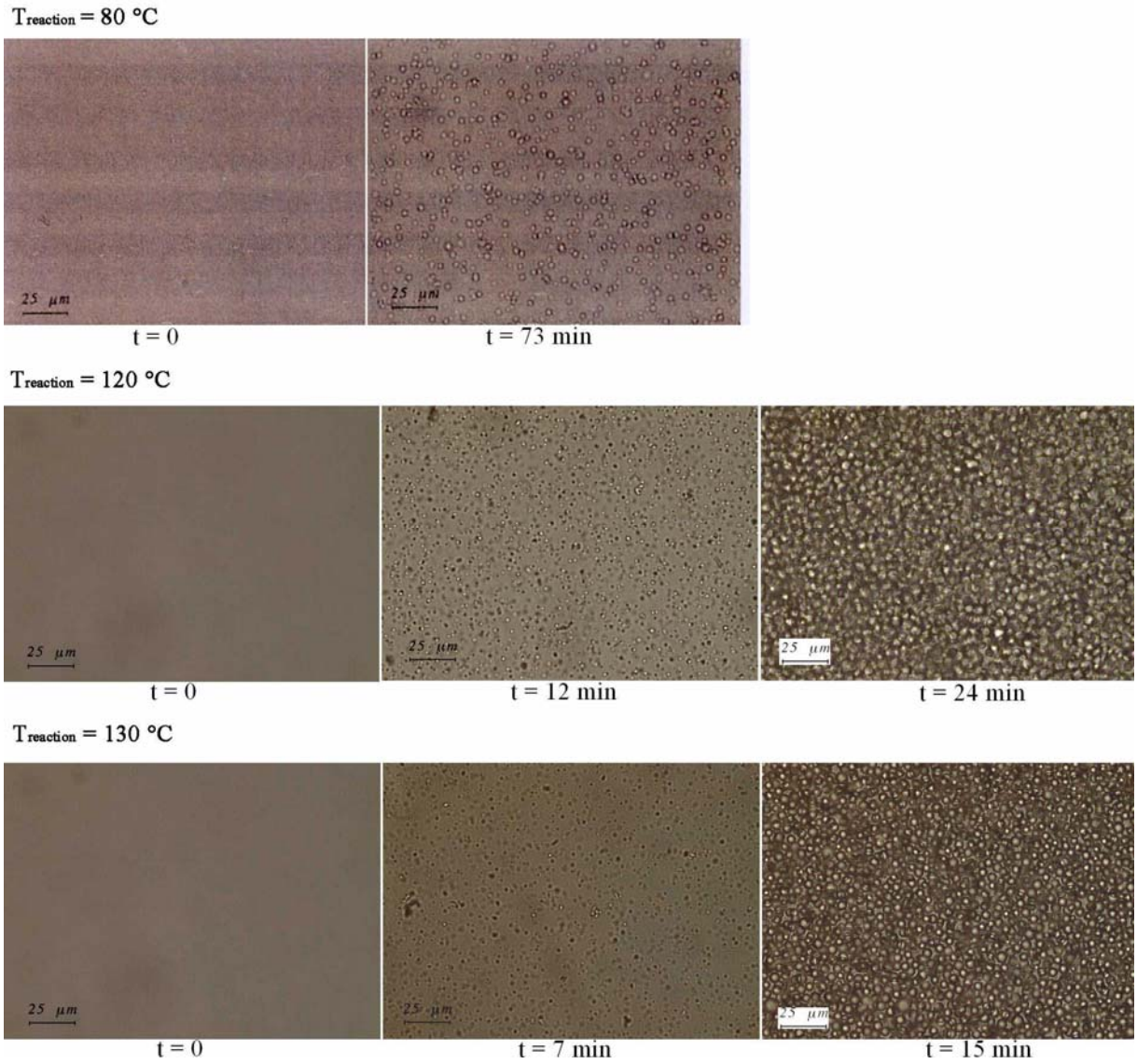


Figure 3. Optical micrographs showing the influence of the reacting temperatures on the formation of EPON-DAT-based microspheres

At high temperatures, the rate of microsphere formation is high and the appearance of the first particles is evident at t = 7 min at $T_{reaction}$ = 130°C ($T_{reaction}$ is the temperature selected for the microsphere synthesis), and at t = 12 min when $T_{reaction}$ = 120°C. As soon as the

temperature is lowered still further ($T_{reaction}$ = 80°C) the particle formation rate decreases. Only after 73 min the first particles are observable, which also exhibit bigger size.

In this study, the reaction temperature was kept constant ($T_{reaction}$ = 130°C); however, the nature of starting monomers and hence their different reactivity towards polymerization affected the curing kinetic and, consequently, the microparticle sizes.

Figure 4 shows the DSC thermograms of EPON825-DAT and PY306-DETDA *in-bulk* systems during the curing reaction.

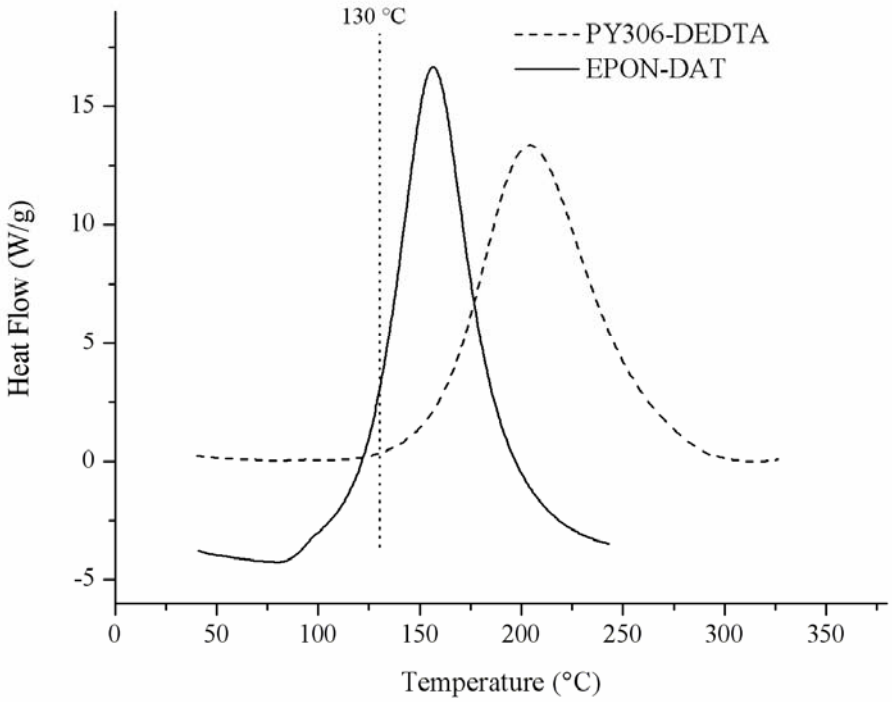


Figure 4.DSC thermograms of *in-bulk* PY306-DETDA and EPON-DAT systems

As it can be observed, the temperature (T_{peak}) corresponding to the exothermic peak associated to the cure of PY306-DETDA is 204°C (T_{onset} = 123°C), whereas, in the case of EPON825-DAT system, a much lower temperature is required to get the polymerization reaction started (T_{onset} = 85°C; T_{peak} = 156°C). In particular, at T = 130°C EPON825-DAT system is more reactive than PY306-DETDA, meaning that the polymerization of PY306-DETDA is activated at much higher temperatures with respect to EPON825-DAT system.

This implies that in the dispersion polymerization process, at the set reaction temperature T = 130°C, EPON825 and DAT reach a high molecular weight soon, giving rise to small particles that separate from the solvent. On the contrary, the reduced reactivity

between PY306 and DETDA delays the demixing and favours the growth of the microspheres before their precipitation. This may explain the difference in Mic1 and Mic2 size.

The dependence of microsphere dimension on the curing kinetics reminds the isothermal crystallization mechanism of crystallisable polymers, in which the rate of crystallization increases as the temperature decreases. In fact, low crystallization temperatures (high $\Delta T = T_{melting} - T_{crystallization}$) lead to faster nucleation and growth of spherulites and, consequently, to small and numerous spherulites with respect to that observed at high crystallization temperatures [24].

In the case of the thermosetting-based microspheres, it can be said that low $\Delta T = T_{peak} - T_{reaction}$ leads to high reactivity and thus to smaller cured particles.

4.2.2. Rheological properties

Figure 5 shows the complex viscosity (η*) for a ramp test carried out at 2°C/min on the uncured blends modified with different amounts of microparticles.

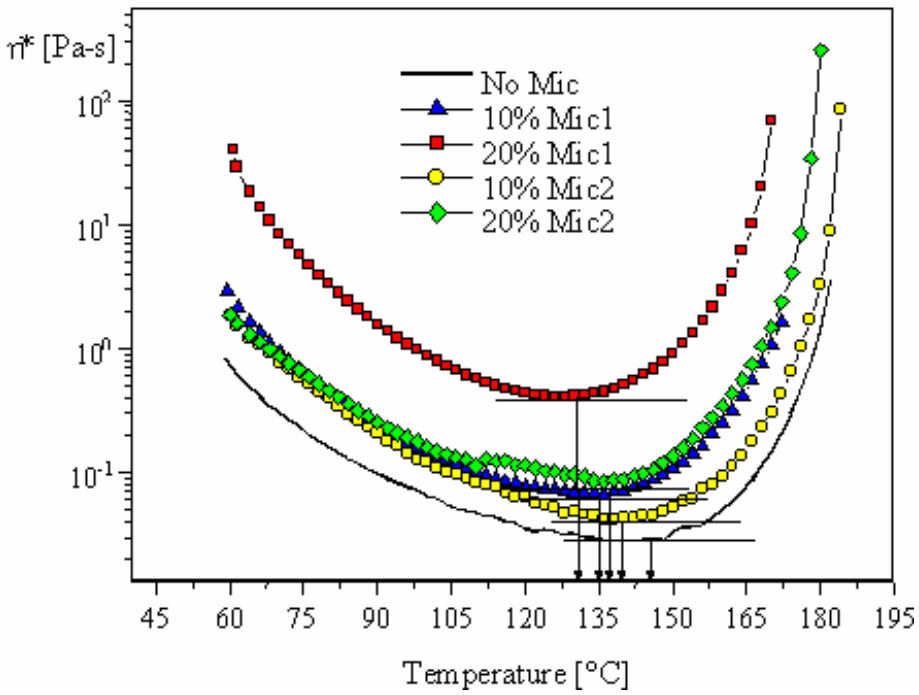


Figure 5. Complex viscosity (η*) traces for uncured blends with different amounts of microparticles

The addition of the microspheres increases the viscosity and the rise is higher when the microspheres percentage is higher. The smaller particles Mic1 raise more the viscosity then the Mic2 because they have higher volume fraction and higher surface area. Bécu-

Longuet et al. [124] found analogous results for epoxy resins modified with core-shell particles of different dimensions. The viscosity increases upon addition of filler is usual also with other filler [138]. However, the microsphere affected also the temperature values at the minimum viscosity that decreases with increasing the percentage of the microspheres in the resin. This result indicates that an increase of the microspheres amount is responsible for the higher reactivity of the system. This effect may be related to the presence of the amino groups on the shell of the microparticles that can react with the epoxy ring in addition to those of the curing agent. The temperature values at the minimum viscosity is also affected by the particle dimensions because the Mic1, which have higher surface area, have reasonably more amino groups on the shell and thus are more reactive. Such effect is unusual for filled systems modified with unreactive particles, which instead usually tend to extend the pot life of the systems because of the delay in the cure reaction [138-140]

The uncured blends have been tested in the rheometer with isothermal test to determine the gel point at various temperatures. The results (**Table 2**) confirmed that the addition of the microparticles reduces the gel times of the epoxy resins. In particular, the blends with Mic1 show higher reduction in accordance with the observation on its reactivity drawn from the ramp test.

Table 2: Gel point times (t_{gel}) at various temperatures (T)

T [°C]	***t_{gel} [min]***				
	0%Mic	*10%Mic1*	*20%Mic1*	*10%Mic2*	*20%Mic2*
120	153.00	130.15	110.52	143.80	135.26
130	97.96	80.78	69.13	89.86	80.02
140	55.58	53.14	45.03	54.85	47.00
150	38.60	34.10	28.17	34.06	27.96

The gel point data can be used to build up a model, which is useful to predict the gel time at temperatures different from those of the test. In fact, an overall activation energy for polymerisation can be obtained from gelation times, assuming that cure reactions may be described by an equation containing one apparent activation energy [141,142] as follows :

$$\frac{dx}{dt} = A\exp\left(\frac{-E_a}{RT}\right) f(x) \qquad \textbf{(1)}$$

where A is a constant, E_a is the apparent activation energy for the overall reaction, R is the gas constant, T is the absolute isothermal cure temperature and f(x) is a function of the reaction mechanism and the extent of reaction x. Integration of this equation from x = 0 to x = x_{gel}, by taking natural logarithms, leads to:

$$\ln \int_0^{x_{gel}} \frac{dx}{f(x)} = \ln A + \ln(t_{gel}) - \left(\frac{E_a}{RT}\right) \qquad \textbf{(2)}$$

Based on the Flory theory [143] the extent of reaction at gelation is constant, so the above equation can be expressed as:

$$\ln(t_{gel}) = C + \frac{E_a}{RT} \qquad \textbf{(3)}$$

Where C is a constant. The model adopted to predict gel times at temperatures different from those used in the experiments is based on a linear interpolation of equation **(3). Figure 6** shows the interpolations obtained for blends modified with the microspheres and the apparent activation energy for each system.

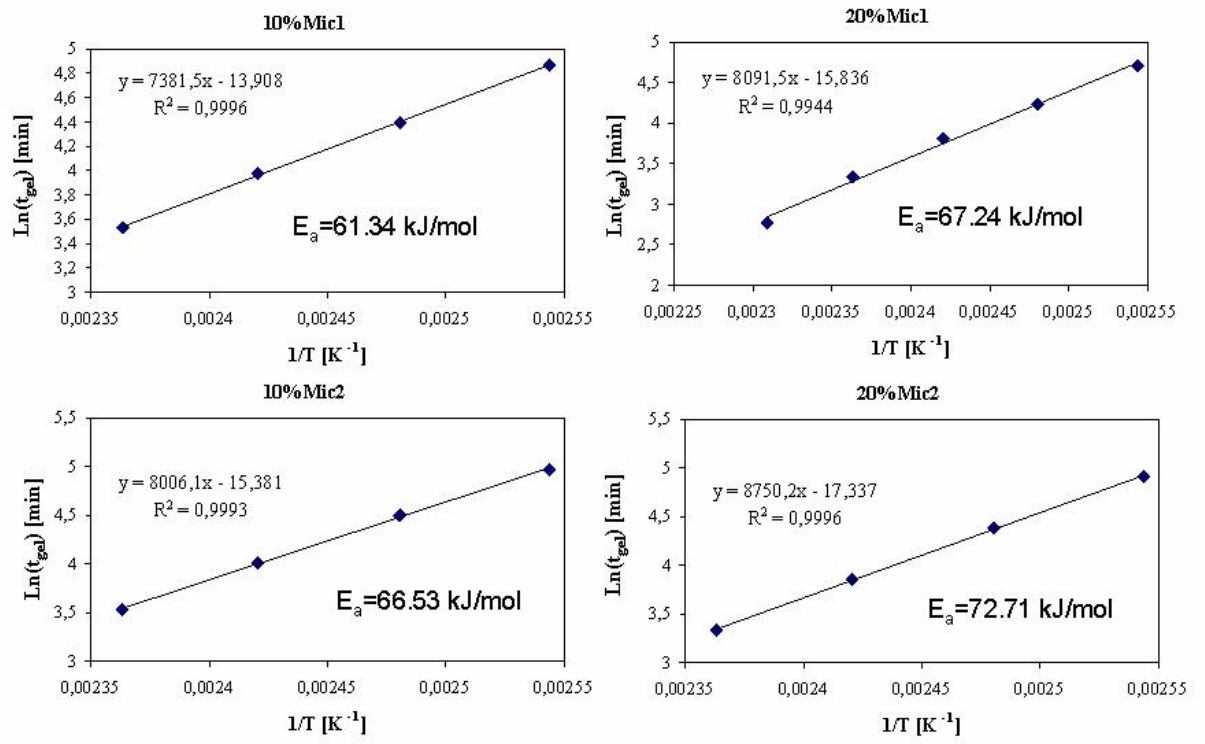


Figure 6. Linear interpolation graphs of the gel point data for the blends modified with the microparticles

Figure 7 reports the comparison of the model curves.

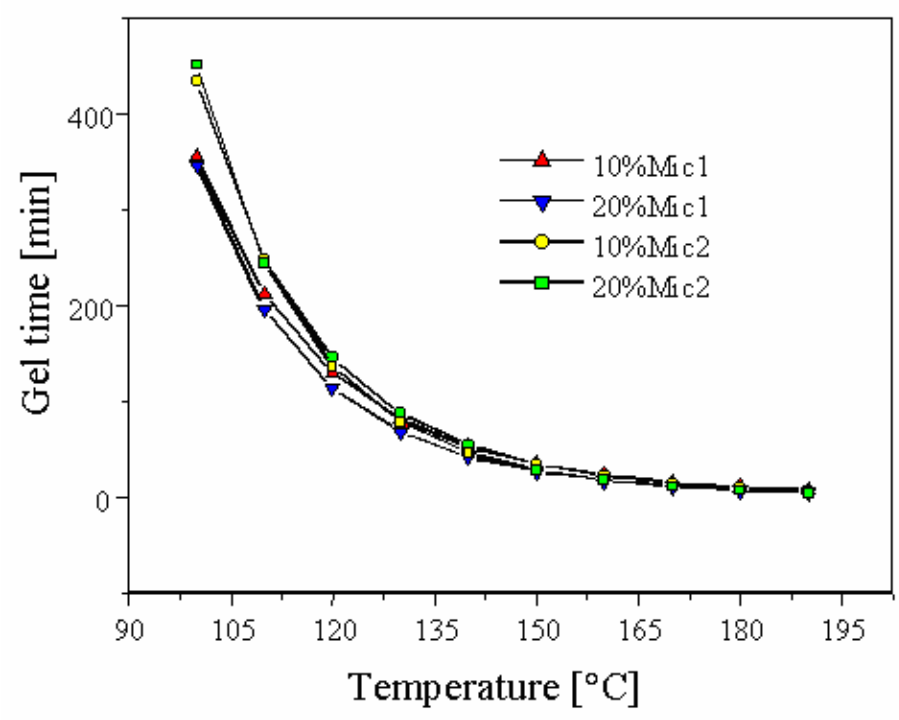


Figure 7. Comparison of model curves to predict the gel point for the modified with the microparticles

The unmodified system presented an activation energy (~64.98 kJ/mol) slightly lower to those found for higher loadings of the microspheres. This results is similar to what reported in literature [144] for epoxy/amine system when the percentage of ammine is increased. This result further supports the previous conclusion on the reactivity of amino groups present on the microsphere surface.

4.2.3. Dynamical mechanical thermal analysis (DMTA)

DMTA analysis on cured samples showed (**Figure 8**) a clear single peak in the tanδ trace for all the blends in correspondence of the glass transition temperatures.

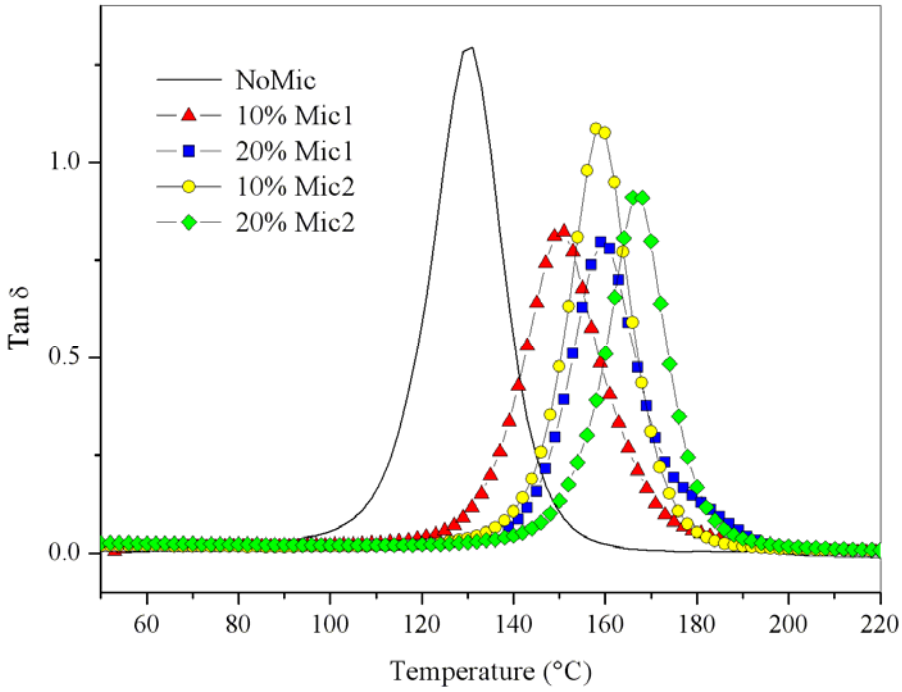


Figure 8. Tanδ traces of the cured blends with different amounts of microparticles

Table 3 summarizes the T_g data obtained from **Figure 8**.

Table 3: Glass transition temperatures T_gs of neat EPON828-3,3'DDS and its composites with Mic1 and Mic2. Data were obtained from DMTA analysis.

Sample	***T_g [°C]***[a]
	131
10%Mic1	150
20%Mic1	158
10%Mic2	157
20%Mic2	166

[a] Values of T_gs correspond to tanδ peaks

The un-modified resin exhibits a T_g of 131°C, while the blends with 20wt. % of Mic1 and Mic2 have correspondingly T_gs of 158°C and 166°C. The increase of the glass transition temperature can be explained as the result of two causes:

- the presence of reactive amino groups on the shell, which leads the microparticles to behave as multifunctional crosslink sites, thus increasing the crosslink densities. Similar results were found for functionalized nanosilica particles by Kim et al. [116] that proved the

efficiency of amine functionalization over other unreactive surface groups. However, the reported T_g increases were considerably lower than those showed here;

- the reduction of the free volume of the epoxy network, caused by the expansion of the microparticles upon heating. This latter factor has been reported by Lin and Shieh [118] to explain the increase of T_g in their systems modified with crosslinked core-shell particles.

The storage modulus G' (**Figure 9**) in the rubbery region is increased by the addition of the microspheres.

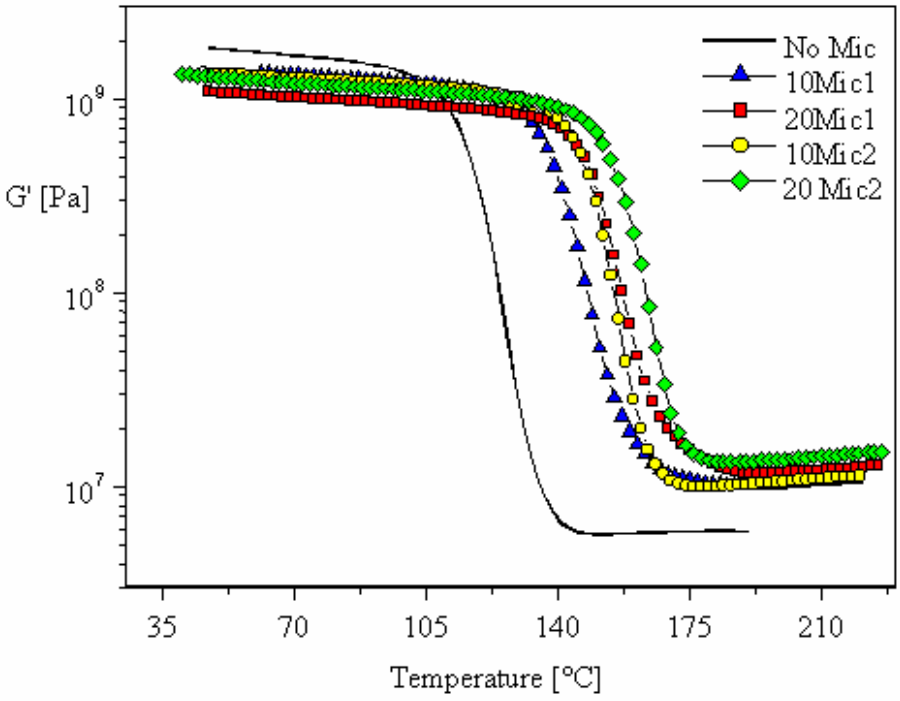


Figure 9. Storage modulus (G') curves for the cured blends with different amounts of microparticles

Therefore, if we consider the relationship **(4)** drawn from the theory of the rubber elasticity [137], that links the molecular weight between the crosslink points (M_c) to the storage modulus G', we can conclude that the network formed by the addition of the microspheres results in higher crosslink densities.

$$M_c = \frac{3\rho RT}{G'} \qquad \textbf{(4)}$$

Where ρ is the density of the resin, R is the universal constant, T is the temperature and G' is the storage modulus in the rubbery region.

In the glassy region, the storage modulus (G') for the modified samples is lower than for the unmodified resin. Bécu-Longuet et al [124] found similar results for the elastic

modulus of their systems, and they attributed the reduction of stiffness to the addition of a low modulus component (the core-shell particles) to the glassy network even though no dissolution of the core-shell particles in the resin occured. The microparticles used in the present study are cured thermoset materials; however, their synthesis is carried out with a molar excess of curing agent (35%) which could then be responsible for the plasticization of the inner part of the microparticles and thus, of the reduction of elastic modulus within the particles. The quantification of the inner modulus can be possible only with local nanoidentation techniques, which are far beyond the scope of this paper. In fact, as reported in the literature [138], an increase in the amine concentration over the stoichiometric ratio has a plastificant effect, which is responsible for a decrease of the bulk elastic properties. The microparticles can thus alter the elastic behaviour in the glassy region of the modified system.

4.2.4. SEM analysis of composite materials

In order to investigate on microsphere segregation, degree of adhesion with the matrix and fracture behaviour, the composite samples were cryogenically fractured and analysed by means of SEM. By a careful observation of the fractured surface of the 10%Mic1 sample (**Figure 10**) two different morphological regions could be detected: in the first (**region I**), the epoxy microspheres appeared to be partially covered by the resin, indicating that the degree of adhesion between matrix and fillers was high. In the other region (**region II**), spherical voids were well detectable, indicating that the fracture carried out in liquid nitrogen proceeded also via interfacial debonding. In any case, the microspheres repeatedly deflected the crack.

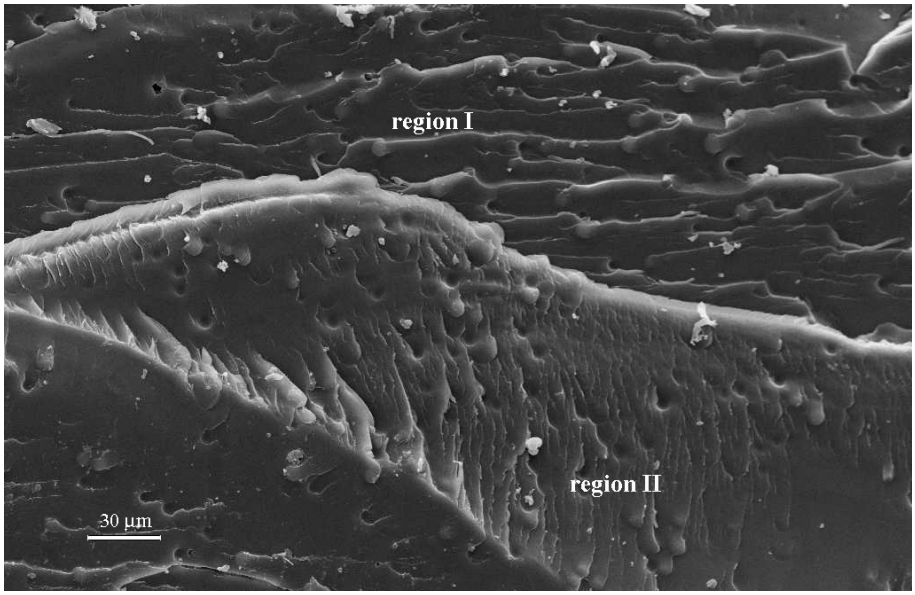


Figure 10. SEM micrograph of cured blends filled with 10%wt of Mic1

Micrographs taken from the fracture surface of the sample modified with 10%wt of Mic2 (**Figure 11**) gave a completely different picture.

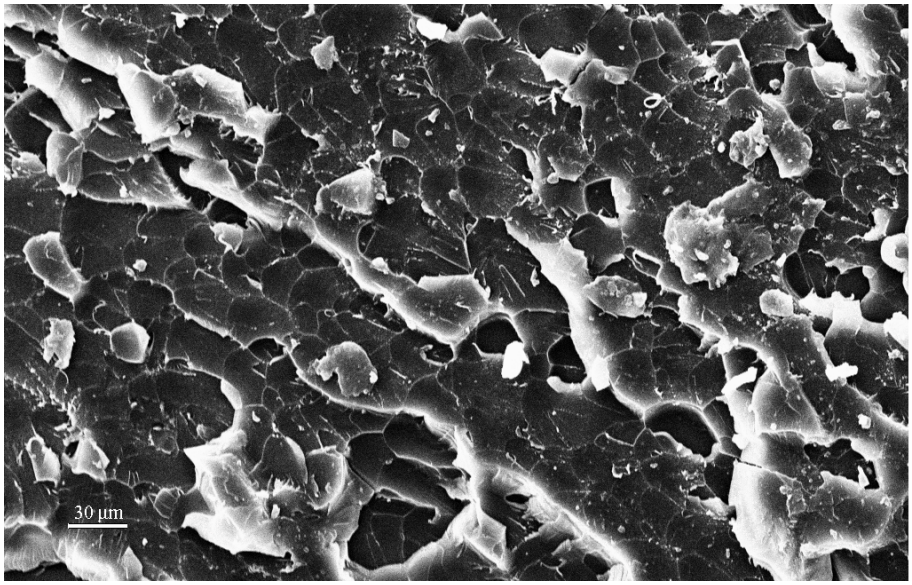


Figure 11.SEM micrograph of cured blends filled with 10%wt of Mic2

The microparticles were not visible because of complete coverage with the matrix and the fracture surface appears more complex with respect to the 10%Mic1 sample. This is likely to be related to the lower crosslinking density responsible for the brittle crack propagation [145]. In fact, as discussed above, the Mic2 microspheres are characterized by bigger size and hence by a reduced surface area. This means that the amino groups on the shell are in lower amount leading and thus lead to a reduced crosslink density.

4.3. Conclusions

In this work, the influence of thermosetting microspheres on the properties of an epoxy resin was investigated. For this purpose, the preparation and the morphological characterization of two types of epoxy-based microparticles was carried out. The microspheres were then added to an EPON828-3,3'DDS matrix to study their influence on the rheological and thermo-mechanical behaviour.

With the aim of synthesizing two types of thermosetting microspheres, two starting epoxy monomers (EPON825 and PY306) were cured with two amino-based curing agents (DAT and DETDA, respectively).

The microspheres obtained were characterized by different dimensions distribution, ranging between 1.3 and 4.1 μm in the case of Mic1 and between 6.7 and 10.1 μm in the case of Mic2. This was related to the different reactivity of the two starting monomers and, hence, to the different curing kinetics of particle formation. DSC measurements indicated that the two particle samples are characterized by a distinct T_g, indicating that the microspheres were likely to be formed by a homogeneous structure. Furthermore, the values of the T_gs were only lightly lower than those of the *in-bulk* cured epoxies, suggesting that the molar excess of curing agent used for the synthesis of microspheres could be responsible for the plasticization of the inner part of the microparticles.

Rheological experiments performed on EPON828-3,3'DDS resin charged with 10% and 20% wt. microspheres leaded to the conclusion that the presence of amino groups on the microsphere surfaces was responsible for a higher reactivity of the system. Moreover, the temperature value for the minimum viscosity decreased as the percentage of microspheres in the sample increased.

The modified blends showed higher values of glass transition temperatures compared to the un-modified resin. These increases were explained as a consequence of the presence of amino groups on the shell of the microparticles, which enhance the crosslink density of the network, as well as of the hindering effect on the free volume growth of the epoxy network. The analysis of the storage modulus in the rubbery region confirmed such increase in the crosslink density.

Furthermore, the control of the dimensions of the microspheres allowed tailoring the reactivity and the viscosity features. In particular, the bigger particles gave the lower increase of blends viscosity. The latter could be considered advantageous in controlling the flow properties of the blends and for diminishing bleeding effects without reducing the processability of the systems.

The micrographs showed that due to the presence of the Mic2-type microparticles the matrix deformed plastically. This could be ascribed to the lower crosslinking density, which in turn is responsible for the brittle crack propagation.

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