ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

PREPARATION AND CHARACTERIZATION OF MELAMINE FORMALDEHYDE MICROCAPSULES FILLED WITH FLAME RETARDANT MATERIALS

M.Sc. THESIS

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Department of Polymer Science and Technology

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ISTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

ALEV GECİKTİRİCİ MALZEME DOLGULU MELAMİN FORMALDEHİT MİKROKAPSÜLLERİN ÜRETİMİ VE KARAKTERİZASYONU

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FOREWORD

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ABBREVIATIONS

EVA **:** Ethylene-vinyl acetate
FTIR **:** Fourier transform infrared spectroscopy
PE **:** Polyethylene
PP **:** Polypropylene
TCPP **:** Tris (2-chloro-1methylethyl)
PU **:** Polyurethane
PVA **:** Poly (vinyl alcohol)
SDBS **:** Sodium Dodecyl Benzenesulfonate
SEM **:** Scanning Electron Microscopy
ZB **:** Zinc Borate

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PREPARATION AND CHARACTERIZATION OF MELAMINE FORMALDEHYDE MICROCAPSULES FILLD WITH FLAME RETARDANT MATERIALS

SUMMARY

Polymers have been used extensively in our lives especially in recent years. Polymers are preferred for each area because they are much lighter than materials like metal and ceramics. They are light but they have high strength. Easy processability and financial suitability are also reasons why polymers are preferred. At the same time, some physical and chemical improvements can be applied to make the polymers more suitable for the areas to be used. Applications for physical or chemical improvements enhance the functionality of polymers and increase the rate of preference. To increase these properties, appropriate additives and fillers are added to the polymer according to the structure of the polymer, intended use and the areas of usage. These additives can be listed as flame retardants, plasticizers, antioxidants, colorants, UV and heat stabilizers and lubricants.

Since polymers have been used in place of metals, ceramics and glass in recent years, efforts to solve problems caused by plastic materials have increased. Fires that cause loss of life and property can sometimes occur due to polymeric materials, or polymers can cause these fires to progress. Some improvements are applied in polymers, in order to prevent fires or to reduce the loss of life and property fires that may be caused by polymer. For this purpose, polymers with self-flame retardant properties may be used, a flame retarding monomer can be added to the chain during the polymerization or the flame retardant additive may be added directly to the polymer.

The flame retardant additives can be added directly to the polymers or they can be added by coating with another material with the microencapsulation technique. It is possible to improve many properties of flame retardants by microencapsulation process. Reducing the water solubility of flame retardants, increasing the polymers and flame retardant compatibility, changing the appearance and physical properties of flame retardants, increasing the pyrolysis temperature and preventing the release of flame retardant toxic gases are advantages of the flame retardant microcapsulation process.

Microencapsulation is a technique which provides entrapping to various chemicals as a small solid particle or a liquid droplet in a suitable shell stated liquid, gas or solid in micron diameter size. It is possible to apply microencapsulation treatment to medicines, proteins, antimicrobials and flame retardants. The material to be coated by the microencapsulation technique is called the core while the coating material is called the shell.

Zinc borate is a flame retardant that has been widely used in recent years as a boron compound with abundant reserves in our country. Zinc borate, which is compatible with resins, is not toxic. Tris (1-chloro-2-propyl) phosphate (TCPP) is a liquid flame retardant. When the TCPP is added to the polymer in liquid form, it can be separated from the polymeric material over time and migrate to the surface of the material and it may also cause the release of toxic gases into the atmosphere.

In this study, it is aimed to produce flame retardant microcapsules for using in polyurethane (PU), which have a very common usage today. It is aimed that the shell material of the produced microcapsules is melamine formaldehyde resin and the flame retardant additives are used as the core material.

Firstly, microencapsulation process of zinc borate was tried. For this purpose, melamine formaldehyde pre-polymer was synthesized and a zinc borate solution prepared according to the desired core / shell mass ratio was added to the synthesized resin. After that the pH of the medium was acidified to cure the resin.

FTIR analysis was performed on the product obtained and analysis showed peaks of melamine formaldehyde resin was encountered but peaks of zinc borate was not observed. The reason is the absence of zinc borate that the acid used for curing dissolves zinc in the zinc borate in the resulting product. Secondly, in order to prevent the dissolution of zinc borate, the same experiment was repeated with the aim of curing the resin in a basic environment without changing other process conditions. However, at the end of the experiment, it was observed that when the mixing was stopped, the resin did not cure, the pre-polymer and the zinc borate solution remained separately.

In this study, microencapsulation was also tried using TCPP (tris (1-chloro-2-propyl) phosphate) as the core material. Likewise, melamine formaldehyde pre-polymer was synthesized at first. Then TCPP was combined with synthesized pre-polymer by adding poly (vinyl alcohol) (PVA) as an emulsifier and Sodium Dodecyl Benzenesulfonate (SDBS) as a surfactant to the aqueous solution of TCPP. The medium was adjusted acidic to try to cure the resin.

As a result of the FTIR analysis on the obtained product, the appearance of characteristic peaks of both melamine formaldehyde resin and TCPP indicates that the microencapsulation process is successful. At the same time as a result of optical microscope images and SEM analysis of the samples, occurring spherical forms were seen. Experiments were repeated by changing parameters such as mixing speed, core / shell weight ratio, SDBS and PVA ratio used and the effects of these parameters on the microsphere diameter, microsphere diameter range and the product yield were investigated.

As a result of the analyzes, it was seen that the increased mixing speed caused the decrease in the sphere diameter, the increased core / shell ratio increased the yield, reducing the use of SDBS provides homogeneity in sphere diameters, and the increase in the PVA ratio was also effective on the sphere size reduction.

ALEV GECİKTİRİCİ MALZEME DOLGULU MELAMİN FORMALDEHİT MİKROKAPSÜLLERİN ÜRETİMİ VE KARAKTERİZASYONU

ÖZET

Polimerler özellikle son yıllarda hayatımızda çok fazla alanda kullanılmaktadır. Kolay proses edilebilirliği, metal ve seramik gibi malzemelere oranla çok daha hafif olmaları, hafif olmalarına karşın sahip oldukları yüksek mukavemetli oluşları, mali açıdan uygunluğu gibi özellikler polimerlerin her alanda tercih edilebilme sebeplerindendir. Aynı zamanda polimerlere, alanlar için daha elverişli hale getirmek amacıyla bazı fiziksel ve kimyasal bir takım iyileştirmeler uygulanabilmektedir. Fiziksel veya kimyasal iyileştirme amacıyla uygulamalar yapılabilmesi polimerlerin fonksiyonelliğini arttırmakla birlikte tercih edilme oranının da artışına sebep olmaktadır. Bu özellikleri arttırmak amacıyla kullanılacak olan polimere, polimerin yapısı, kullanım amacı ve kullanılacağı alan da göz önünde bulundurularak uygun katkı ve dolgu maddeleri eklenmektedir. Bu katkı maddelerinin başlıcaları alev geciktiriciler, plastikleştiriciler, antioksidanlar, renklendiriciler, UV ve ısı stabilizatörleri ve yağlayıcılar olarak sıralanabilir.

Polimerlerin son yıllarda metal, seramik, cam gibi malzemelerin yerine kullanılabiliyor olması, yaşanabilecek plastik malzeme kaynaklı sorunların giderilmesine yönelik çalışmaları arttırmıştır. Can ve mal kaybına sebep olan yangınlar kimi zaman polimer malzemeler sebebiyle çıkabilir veya polimerler bu yangınların ilerlemesine sebep olabilirler. Polimer kaynaklı yaşanabilecek yangınları önlemek veya oluşabilecek yangınlar sonucunda yaşanabilecek can ve mal kaybını en aza indirebilmek amacıyla polimerlerde bir takım iyileştirmeler yapılmaktadır. Bu amaçla kendiliğinden alev geciktiricilik özelliğine sahip polimerler kullanılabileceği gibi, polimerizasyon sırasında alev geciktirici bir monomerin zincire eklenerek veya bazı katkı maddelerinin ilavesi ile de sağlanabilir.

Alev geciktirici katkı maddeleri polimerlere doğrudan eklenebilecekleri gibi mikroenkapsülasyon tekniği ile başka bir malzemeyle kaplanarak da ilave edilebilirler. Mikrokapsülasyon işlemi ile alev geciktiricilerin birçok özelliğini geliştirmek mümkündür. Alev geciktiricilerin suda çözünürlüğünün azaltılması, polimerler ve alev geciktirici uyumluluğunun arttırılması, alev geciktiricilerin görünüm ve fiziksel halinin değiştirilmesi, piroliz sıcaklığının arttırılması ve alev geciktirici kaynaklı toksik gazların serbest bırakılmasının engellenmesi mikrokapsülasyon işleminin alev geciktiriciye sağladığı avantajlardandır.

Mikroenkapsülasyon fonksiyonel olarak aktif maddelerin uygun ortamlarda kullanılabilmesi için, koruyucu bir polimerik malzeme ile kapsüllenerek içi boş mikro kürelerin içinde saklanması yoludur. İlaçlar, proteinler, antimikrobiyaller ve alev geciktiricilere mikroenkapsülasyon işlemini uygulamak mümkündür.

Mikroenkapsülasyon sonucu elde edilen üründe kaplanacak olan malzeme çekirdek olarak adlandırılırken kaplama malzemesine de kabuk adı verilir.

Ülkemizde de bolca rezervi bulunan borun bileşiği olan çinko borat son yıllarda yaygın olarak kullanılan alev geciktiricilerdendir. Reçinelerle uyumlu olan çinko borat zehirli de değildir. Tris (1-kloro-2-propil) fosfat (TCPP) ise sıvı halde bulunan bir alev geciktiricidir. TCPP'nin polimere sıvı halde eklendiğinde zaman içerisinde polimerik malzemeden ayrılarak malzeme yüzeyine göç edebilmekte ve aynı zamanda atmosfere zehirli gazların salınımına neden olabilmektedir.

Bu çalışmada çinko borat ve TCPP (tris (1-kloro-2-propil) fosfat) alev geciktirici malzemelerinin, kendisi de alev geciktirici özelliğe sahip olan melamin formaldehit reçinesi ile kaplanması hedeflenmiştir.

Bu çalışmada öncelikle çinko boratın mikroenkapsülasyon işlemi denenmiştir. Bu amaçla melamin formaldehit pre-polimeri sentezlenmiş ve sentezlenen reçineye istenilen çekirdek/kabuk kütle oranına göre hazırlanan çinko borat çözeltisi ilave edilmiştir. Daha sonra reçineyi kürleştirmek amacıyla ortamın pH'ı asidik yapılmıştır.

Elde edilen ürüne FTIR (Fourier Transform Infrared Spectroscopy) analizi yapılmış ve analiz sonucunda melamin formaldehit reçinesine ait piklere rastlanmış ancak çinko borata ait pikler görülmemiştir. Elde edilen üründe çinko borata rastlanamamasının sebebi kürleşme için kullanılan asidin çinko boratı çözmesidir. İkinci olarak çinko boratın çözünmesini engellemek amacıyla diğer proses koşulları değiştirilmeden aynı deney reçinenin bazik ortamda kürleştirilmesi hedeflenerek tekrarlanmıştır. Ancak deney sonunda karıştırma durdurulduğunda reçinenin kürleşmediği, çinko borat çözeltisinin pre-polimerin birbirinden ayrıldığı gözlemlenmiştir.

Bu çalışmada aynı zamanda çekirdek materyali olarak TCPP (tris (1-kloro-2-propil) fosfat) kullanılarak mükroenkapsülasyon işlemi denenmiştir. Yine aynı şekilde önce melamin formaldehit pre-polimeri sentezlenmiştir. TCPP (tris (1-kloro-2-propil) fosfat) sulu çözeltisine emülsifiyan olarak poli(vinil alkol) (PVA) ve sürfaktan olarak da Sodium Dodecyl Benzenesulfonate (SDBS) ilave edilerek sentezlenen pre-polimer ile birleştirilmiştir. Deney ortamı asidik olarak ayarlanarak reçinenin kürleşmesi sağlanmaya çalışılmıştır.

Elde edilen ürüne yapılan FTIR (Fourier Transform Infrared Spectroscopy) analizi sonucunda hem melamin formaldehit reçinesine hem de TCPP'ye ait karakteristik piklerin görülmesi mikroenkapsülasyon işleminin başarılı olduğunun düşünülmesine sebep olmuştur. Aynı zamanda numunenin mikroskop görüntüleri ve SEM (Scanning Electron Microscopy) analizleri sonucunda da oluşan küre formları görülmüştür. Karıştırma hızı, çekirdek/kabuk ağırlık oranı, kullanılan SDBS (Sodium Dodecyl Benzenesulfonate) ve PVA (poli (vinil alkol)) oranı gibi parametreler değiştirilerek deneyler tekrarlanmış ve bu parametrelerin mikroküre çapı, mikroküre çap aralığı ve elde edilen ürün verimi üzerine etkileri incelenmiştir.

Yapılan analizler sonucunda artan karıştırma hızının küre çapında azalmaya sebep olduğu, artan çekirdek/kabuk oranının verimi arttırdığı, SDBS (Sodium Dodecyl Benzenesulfonate) kullanımının azaltılmasıyla küre çaplarında homojenliği sağladığı, PVA (poli(vinil alkol)) oranın artmasının da küre çapını küçültme üzerine etkisi olduğu görülmüştür.

1. INTRODUCTION

Reducing the fire caused by plastic materials is a subject that has been investigated especially in recent years. Today, there are many different types of chemical materials with flame retardant properties in the industry. Flame retardancy for plastic materials is one of the important issues investigated both in academic and industrial settings. Nowadays, thermoplastic and thermoset polymers are frequently used. When we look around, it is possible to encounter many polymeric materials from polyurethane (PU) foams, polyethylene (PE) bags, to polypropylene (PP) produced containers. These materials can be very damaging during the fire.

It is possible to prevent this damage by making the polymer material resistant to fire with flame retardancy. Flame retarding can be obtained in general by using self-flame resistant polymeric material, addition of flame retarding monomers to polymer chains during polymerization and adding flame retardant materials and additives. Some polymers have self-flame retardant properties. Poly (vinyl chloride) is an example of this is halogen-containing materials. The most efficient method is to bind flame retardant chemicals to the polymer chains during polymerization. However, this method is not easily applicable to the industry because many plastics producers in the industry directly purchase and process the raw material. In this case the use of additives is more functional. The choice of flame retardant can vary widely depending on the polymer to be added, the process characteristics and requirements, the desired mechanical properties, the product properties (color, shape, etc.), and the thermal properties of the product. For example, the carbon black used for coloring is also a type of flame retardant and also a thermal stabilizer.

At present, studies on the application of flame retardant additives to polymers are continuing. One of these studies is the microencapsulation technique which targets the availability of the flame retardant material and the polymer. By microcapsulation of flame retardant material, reduction of the water solubility of the flame retardants, increase of the compatibility of the flame retardants in the polymers, change of the appearance and physical state of the flame retardants, increase of the pyrolysis temperature of the flame retardants and release of toxic gases can be provide.

2. THEORETICAL PART

2.1 Microencapsulation

Microencapsulation is a technique which provides entrapping to various chemicals as a small solid particle or a liquid droplet; such as drugs, proteins, flame retardants, antimicrobials, dyes or cosmetics in a suitable shell stated liquid, gas or solid in micron diameter size. Core is the encapsulated material and the coating material is called shell or wall material. In Figure 2.1 scheme of microcapsule is shown. Radius of core is symbolized with r_c and radius of microsphere is symbolized with r_m [1]. Protective shell is made by using monomers which forms a polymeric membrane around the core material or it can be formed by the prepared polymer materials [2].

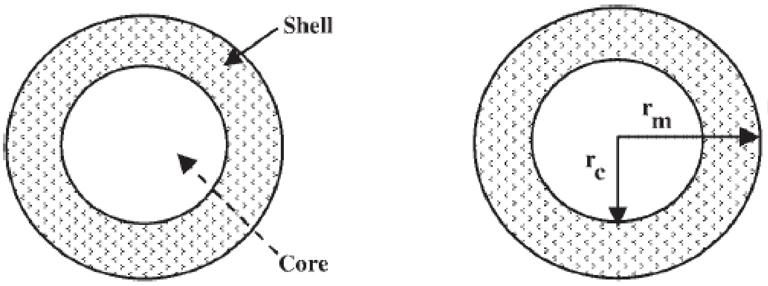


Figure 2.1: Scheme of microcapsule.

Capsules are stated as nanocapsules which is smaller than 1 µm moreover they are identified as macro capsules which is greater than 1000 µm. Usually commercial capsules have between 3 and 800 µm size and 10 to 90% core material [3].

The main purpose of encapsulation a core material into a shell is protection and isolation of the core material from the external influences. When the core material is fluid, encapsulation technique is used for block the core leaving. Otherwise encapsulation can prevent the evaporation of core material in the cases where the core is a volatile material. To preserve the smell of the core material for a long time and to prevent oxidation of the core if it oxidized or degraded in contact with air the microencapsulation is an appropriate method. Moreover, encapsulation is suitable for preventing interference of core to the surrounding structures before the desired time [4].

Shell material vary according to obtain desired effect, process conditions and core material. It can be classified as natural and synthetic. Agar, albumin, alginate, gum arabic, starch, gelatin, cellulose, casein, pectin, chitosan are natural polymers for shell material in addition acrylics, aliphatic polymers, polyethylene glycol, polyamide, polyurethane, polystyrene, silicones, derivatives of cellulose are synthetics [2].

The morphology of microcapsules changes basically according to core material and microcapsulation process. It can form in regular or irregular shapes. Mononuclear, polynuclear and matrix are the types of microcapsules on the basis of their morphology [1]. Figure 2.2. shows that the morphology of microcapsules.

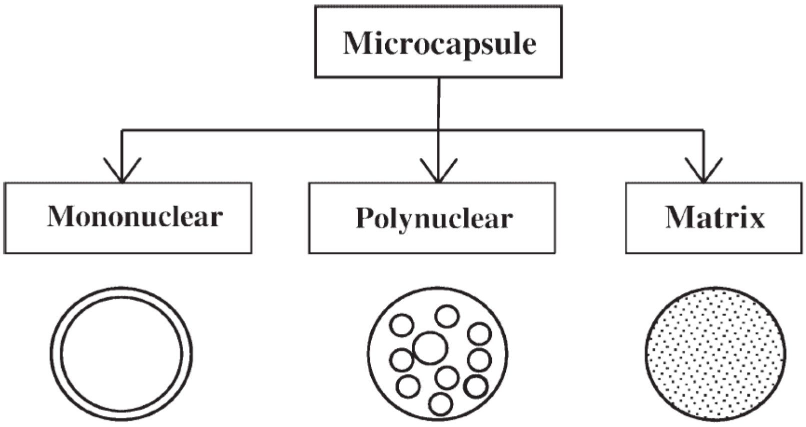


Figure 2.2: Morphology of microcapsules.

In mononuclear microcapsules only one continuous shell surrounds the core material however there are many cores enclosed inside the shell in polynuclear microcapules. It is called that matrix encapsulation which have homogeneous core distribution into the shell material [1].

Microcapsules have several release mechanisms such as pressure or shear stress, melting the wall, dissolving the wall, action of solvent, enzyme attack and hydrolysis or slow disintegration [5].

2.2 Microencapsulation Methods

There are various microencapsulation methods in the collected works. Microencapsulation techniques are divided into two groups as chemical and physical. Frequently used chemical and physical microencapsulation methods are given in Table 2.1 [1].

Table 2.1: Frequently used chemical and physical microencapsulation methods.

CHEMICAL METHODS	PHYSICAL METHODS
Interfacial polymerization	Co-extrusion
In-situ polymerization	Spray-drying
Coacervation	Fluidized-bed technology
Rapid expansion of supercritical fluids	Spinning disk

In selecting the microencapsulation method, the type of core material, the permeability of shell material, the desired particle size and required properties of microcapsules are important. Table 2.2 gives the particle sizes that can be obtained according to the microencapsulation methods [1].

Table 2.2: Particle sizes according to microencapsulation methods.

Microencapsulation Method	Particle Size (µm)
Interfacial polymerization	0.5 – 1000
In-situ polymerization	0.5 – 1100
Coacervation	2 – 1200
Co-extrusion	250 – 2500
Spray-drying	5 – 5000
Fluidized-bed technology	20 – 1500
Spinning disk	5 – 1500

2.2.1 Chemical microencapsulation methods

2.2.1.1 Interfacial polymerization

Interfacial polymerization is the formation of a film that the various monomers react with each other at the interface of two liquid phases do not mix which trap the disperse phase. Generally, two reactive monomers are present. One of them is dissolved in aqueous phase containing the solution of core material or dispersion. The another is dissolved in the non-aqueous phase after emulsification. A suitable emulsifier must be added as stabilizer to form emulsion. The monomers are polymerized as a thin coating at the interface. Average polymerization degree depends on reactivity of monomers, concentration of monomers and temperature [6].

Emulsion polymerization

Emulsion polymerization is similar to suspension polymerization, but there are three different points. In the emulsion polymerization the initiator is present in aqueous phase in the beginning. As a result of more intensive stirring, the particle size is usually below 100 µm and also often below 1 µm. The surfactant concentration is much higher and usually above the critical micelle concentration.

High molecular weight polymerization at very high speed and the reduction of the reaction temperature during the reaction are the advantages of emulsion polymerization. Unreacted monomers which present at high concentration is the disadvantage for emulsion polymerization.

The rate of mixing is important parameter to determine the diameters of microcapsules [6,7].

2.2.1.2 In-situ polymerization

In-situ polymerization is quite similar to interfacial polymerization. In the interfacial polymerization, the monomers are present in both phase and the polymerization takes place in the encapsulation reactor. However, in the in-situ polymerization there is no reactive agent in the core material phase. Polymerization occurs only in the continuous phase and continuous part of interface which is formed by disperse core material and continuous phase. Polymerization of the low molecular weight prepolymer increases the size then it precipitates on the disperse core material from the continuous phase, thus microcapsulation takes place.

Urea-formaldehyde, melamine-formaldehyde and urea-melamine formaldehyde are the most widely used monomers in in-situ polymerization. They are used in the microencapsulation of water-insoluble liquid and solid core materials.

An aqueous emulsion of the core material is formed with a suitable mixer and surfactant. After the formation of the emulsion, the pre-polymer is added. The pH and temperature are brought to the appropriate conditions to continue the polymerization [1].

2.2.1.3 Coacervation

Coacervation method is also known as phase separation method. There are two different processes for the coacervation method as simple and complex coacervation. The microcapsule formation for these two processes is basically the same. The feature that distinguishes these two methods is how the phase separation is obtained. In the simple coacervation phase separation requires a desolvation agent, while in the complex coacervation phase separation is achieved by using two oppositely charged polymers [1].

There are three basic steps in the coacervation method: Dispersion or emulsion preparation, core encapsulation and stabilization of the encapsulated particles. Figure 2.3 shown that the formation of microcapsules with coacervation method in schematically. According to scheme, in the first stage core material dispersion in shell polymer solution is appeared. Secondly, shell material precipitates onto the core material. Finally, the stabilization of microcapsules is happened.

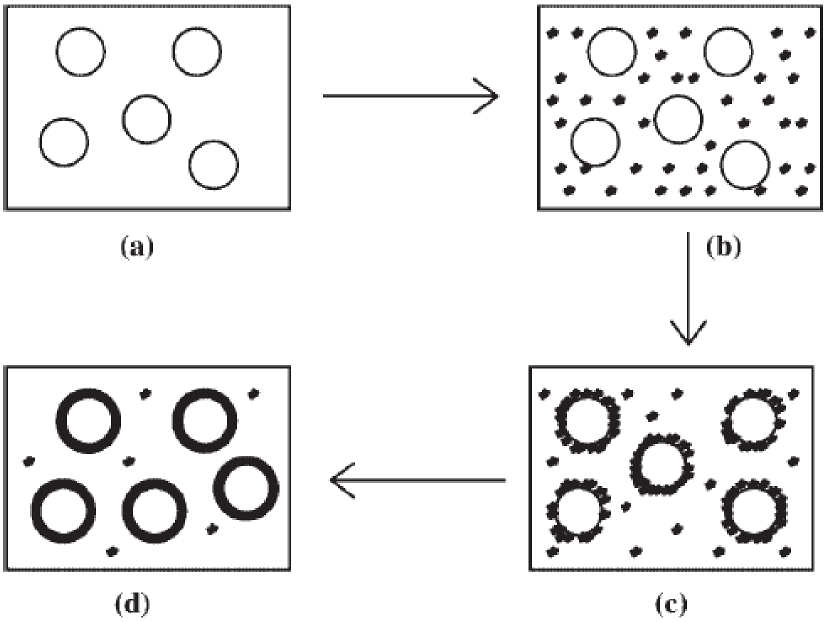


Figure 2.3: Scheme of coacervation process (a) core material dispersion in the shell polymer solution, (b) coacervate separation from the solution, (c) core material coation by coacervate microdrpolets, (d) coalescence of coacervate to form continuous shell around core particles.

Simple coacervation is accomplished by the addition of highly water-soluble substances such as salt or alcohol. If the temperature, pH, solvent, and salt are selected at appropriate rates, any aqueous polymer solution undergoes simple coacervation. The added substances cause the formation of two phases, one of which is dense in terms of colloid droplets and the other of which is diluted. Due to the formation of separate phases, the polymer solidifies around the core material. Depending on the polymer and system, the shell is hardened with additional cross-linkers.

Complex coacervation is performed by using two colloids with different charges. After the preparation of aqueous solution of hydrophilic colloid, the second colloid is added at different charges. The colloids are collected around the core, when the addition of the second colloid. Thus, microcapsulation happens according to complex coacervation [2].

2.2.1.4 Rapid expansion of supercritical fluids

Supercritical fluids are gases that exhibit both fluid and gas properties and are highly compressible. Pesticides, pigments, pharmacological substances, vitamins, odor and flavor compounds and dyes can be encapsulated by this method. Many shell materials are used that are soluble or insoluble.

In this method, the supercritical fluid containing the core and shell materials is exposed to the pressure. The mixture which is under the pressure is sent to an atmospheric pressure medium with a nozzle. The decrease in pressure reduces the solubility of the shell material in the fluid then provides converging of the core material. Microcapsulation with rapid expansion of supercritical fluids is shown in Figure 2.4 [1].

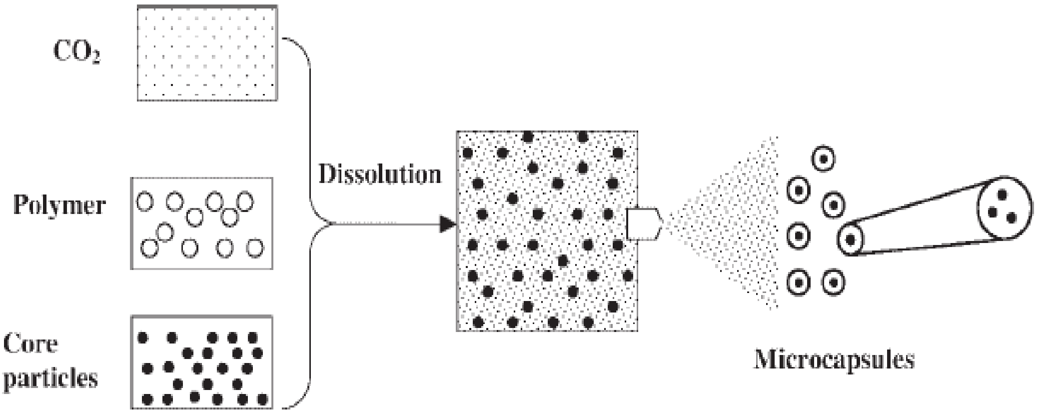


Figure 2.4: Microcapsulation with rapid expansion of supercritical fluids.

2.2.2 Physical microencapsulation methods

2.2.2.1 Co-extrusion

In the co-extrusion method, the core material mixed with melted polymer. As shown in Figure 2.5 liquid core and shell materials pumped through tubes and forms droplets by the applied vibration. The molten polymer starts to cool below the glass temperature to form the shell material. The shell material can be extruded with the desired viscosity by dissolving it in a suitable solvent. In this case, the solvent is removed by hot air at the outlet of the extruder and solidified or transferred to the coagulation bath to provide gelation [1,3].

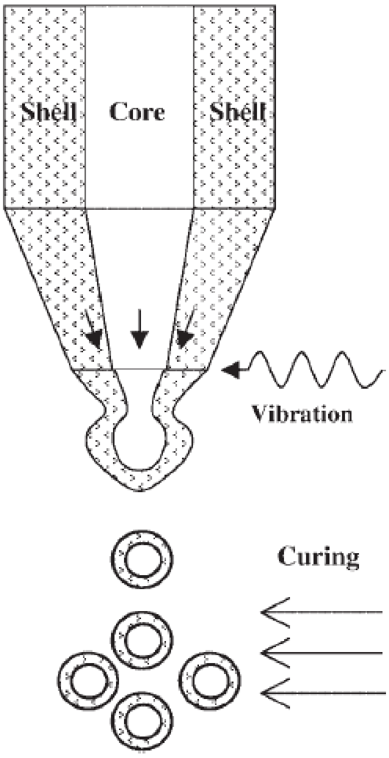


Figure 2.5: Microencapsulation by co-extrusion method

2.2.2.2. Spray-drying

In the spray drying, the shell material is dissolved in a polymer solution. The solution is pumped through the nozzle and sprayed into a cabinet containing hot air as an aerosol. Due to the hot air in the cabinet, the solvent is removed and a microcapsule is formed. The ratio of core-shell material, viscosity, concentration and temperature of initial solution affect the properties of microcapsules [8]. Spray-drying method is illustrated in Figure 2.6 [1].

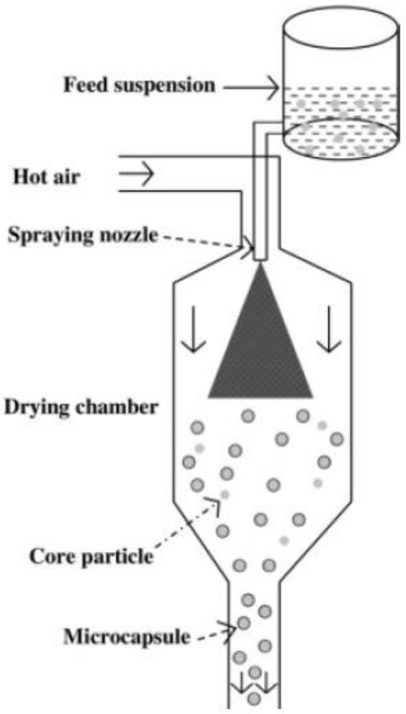


Figure 2.6: Spray-drying method.

2.2.2.3 Fluidized-bed technology

This method is also known as Wurster method. The powdered core material is suspended in air using a fluidized bed then the solution that will form the capsule wall is sprayed in the form of suspension or emulsion. With solvent removal it is provided that the shell material covers the core material. High production capacity, to be suitable for encapsulation of every particle and suitable drying conditions are the advantages of this process. However, dispersion is difficult when the particles are smaller than 75 μm which are coated [9].

Three different fluidized-bed coaters are used as top spray, bottom spray and tangential spray shown in Figure 2.7 [1].

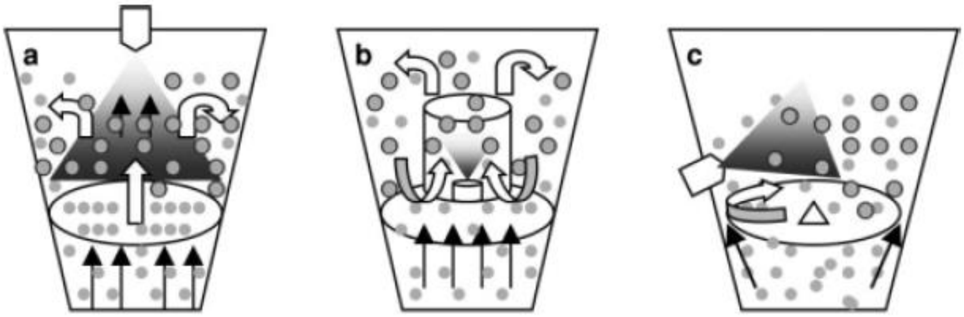


Figure 2.7: Types of a fluid-bed coater. (a) Top spray, (b) bottom spray, (c) tangential spray.

2.2.2.4 Spinning disk

The core material is fed onto the rotating disk together with the dispersed form of the shell formulation. The core material, which rises with the shell material at the edge of the disk, is trapped in the capsule by cooling and solidifying of shell material. Flat, conical or bowl shaped disks can be used. This method is low cost and fast. The obtained microcapsules have sizes below 15 µm. In order to obtain good results in this method, the core material must be supplied in the sphere form. The viscosity of the shell material is important. Though it can be worked with many shell materials as hot melt, the viscosity should be lower than 5000 cP. Figure 2.8 shows scheme of spinning disk method [1,3].

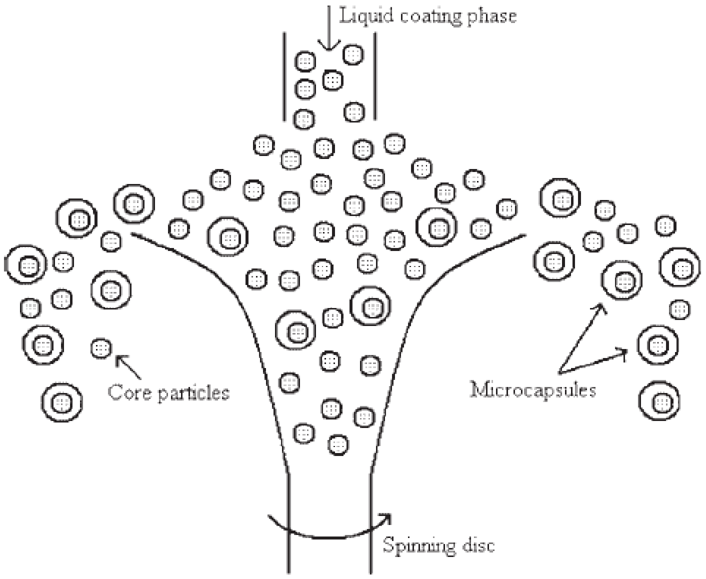


Figure 2.8: Scheme of spinning disk method.

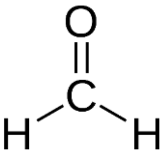
2.3 Melamine Formaldehyde Microcapsules

Resins are generally referred to as low molecular mass or oligomeric compounds. They are generally using as raw materials, for binders, curable molding compositions adhesives and coatings. They behave brittle in solid states. They are classified as natural and synthetic. Phenol-formaldehyde resins, urea-formaldehyde, melamine-formaldehyde resins, polyesters resins, silicone resins, ketone-aldehyde resins, epoxy resins, acrylic resins and alkyd resins are the most significant synthetic resins [10].

In terms of processing and implementation melamine-formaldehyde resin is similar to urea-formaldehyde resin. But melamine-formaldehyde resins are more moister resistant, harder and stronger.

Melamine-formaldehyde resin is a synthetic resin which is formed by polycondansation of melamine and formaldehyde. Melamine is a crystalline solid obtained from the derivation of urea and methane is used for procurement of formaldehyde. Some properties of monomers melamine and formaldehyde is given in Table 2.3 [11].

Table 2. 3: Properties of melamine and formaldehyde

	Melamine	Formaldehyde
Chemical Formula	$C_3H_6N_6$  	CH_2O 
Molar Mass	126,12 g/mol	30,026 g/mol
Color	White solid	Colorless
Melting point	345°C	-15 °C
Solubility in water	3240 mg/l	High

In the reaction between formaldehyde and melamine, formaldehyde is added to the amine groups (2,4,6-triazine-1,2,3,4-triazine) in the melamine to give derivatives containing different numbers of methylol groups. The water-soluble methylol is converted to melamine-formaldehyde resin at high temperatures by cross-linking over methylene or ether bridges [12].

With the disperse polycondansation technique, monodisperse melamine formaldehyde microcapsules are formed. The nucleation and progress of the polymerization are accomplished in short times. Even in the media which contains surfactants, a continuous coagulation happens [13]. Melamine and formaldehyde are polymerized around the core material in appropriate conditions with the in-situ polymerization as shown in Figure 2.9 [14].

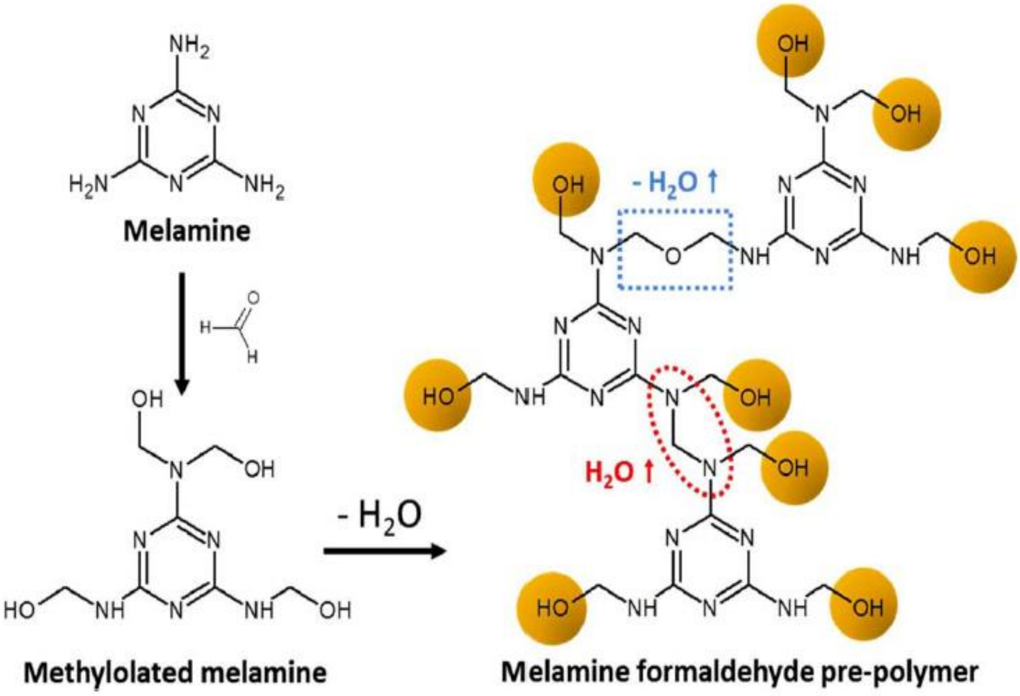


Figure 2.9: Reaction mechanism of melamine-formaldehyde resin

2.4 The Advantage of Microencapsulation of Flame Retardants

The microencapsulation process can be used to improve many of the properties of flame retardants. Decreasing the water solubility of flame retardants, increasing the compatibility of flame retardants in polymers, changing the appearance and physical state of flame retardants, increasing the pyrolysis temperature of flame retardants and preventing the release of toxic gases are the primarily advantages of microcapsulation of flame retardants [15].

When the polymer composites have been in high moisture environments for a long time, flame retardant can dissolve because of its poor water resistance and migrate to the surface of composite material. Consequently, mechanical properties of composite are decreased. So, flame retardants can be capsulated due to reduce the water solubility [16].

Because of the different polarity between the flame retardant and the polymer, the compatibility of the two material is weak. Thus, the dispersion of the flame retardant in the polymer matrix gets difficult and it causes weakening the mechanical properties of the composite material. Flame retardant is coated with a suitable shell material which is suitable for polarity of polymer to prevent the mechanical properties from weakening [15].

A liquid flame retardant may be microencapsulated into a solid shell to stop migration and evaporation of the flame retardant during or after the microcapsulation process. So that blending of the flame retardant with the polymer is also facilitated [17].

To increase the use temperature of flame retarder having a low pyrolysis temperature, it can be coated with a shell material having a better thermal stability.

Flame retardants having irritating odor and toxic gases will be covered with the microencapsulation process moreover will not be spread around [15].

2.5 Combustion and Flame Mechanism

Combustion process is defined that a reaction of a substances which is ready to ignite and oxygen when in contact with a flame sources. If the flammable material is heated up to the ignition temperature which is a characteristic temperature value for itself, it will start to burning by flaming in the oxygen atmosphere. The high heat generated during combustion ensure the combustion of combustible gas and solid waste produced by the burning material and combustion continue until there is no flammable material or oxygen in the environment [18].

Ignition source, fuel and oxygen are the three important elements required for the proceeding the combustion process. The combustion progression can be stopped by blocking one of these three components [19].

Burning causes the production of many free radicals. The free radicals produced provide the continuity of the combustion reaction and two radicals generated in the chain branching reaction accelerate the combustion. Combustion reaction ends due to the reduction or termination of free radicals in the environment. $H\cdot$, $OH\cdot$ and $O\cdot$ are the radicals that carry the flame in the combustion process and ensure the continuity of the burn [20]. Equation 2.1, 2.2 and 2.3 show combustion reactions for polymers [19].

$$RH \rightarrow R\cdot + H\cdot \ \text{(Start)} \tag{2.1}$$

$$H\cdot + O_2 \rightarrow HO\cdot + O\cdot \ \text{(Branching)} \tag{2.2}$$

$$HO\cdot + CO \rightarrow CO_2 + H\cdot \ \text{(Propagation)} \tag{2.3}$$

If the polymer material is exposed to heat for enough time, the macromolecule begins to thermally decompose, which is called pyrolysis. In any flame application, a small amount of oxygen reaches the polymer surface and combustible gases are produced under the control of the pyrolysis phenomenon. The mixture of flammable gas which is produced causes the polymer material to ignite and not start to burn. The fillers, pigments, stabilizers and flame retardant materials on it affect the burning behavior. Other atoms such as nitrogen, chlorine, fluorine, sulfur and phosphate in the structure of the material reduce the flammability [21].

2.6 General Flame Retardant Mechanism

A flame retardancy, a process that stops or suppresses combustion. Flame retardants act chemically and/or physically as solid, liquid and gas.

There are numerous physical effects of flame retardants in combustion process: by cooling, by performing protective layer, by dilution.

a) By cooling: It occurs when the additive material lowers the temperature of the substrate below the temperature required for the flaming process, in the endothermic process. Aluminum Hydroxide (Trihydrate) is a good example for cooling.

b) By formation of protective layer formation of protective layer: A protective layer known as physical barrier is formed from flame retardant material. In this approach known as intumescence phenomenon, the additive material acts for decreasing heat transfer from the heat source. A protective vitreous barrier can generate from phosphorus containing additives due to their pyrolysis. Also, boric acid based additives, inorganic borates, or low melting glasses affects similarly.

c) By dilution: Inert substances and additives are based on the principle of avoiding escalation of the ignition mixture level as a result of dilution of the solid or gas-phase fuel because of releasing the inert gases. Aluminum Hydroxide is also used for this purpose [22].

Flame retardant additives prevent the combustion process as chemically in the solid and gaseous phases. In gas phase inhibition the flame retardant prevents the mechanism of combustion process in the gas phase. The exothermic process stopped in this way, the system begins to cool and with the reducing flammable gases in the environment extinction takes place. On the other hand, partially burned products which have high toxicity produced by flame reactions and these products are generally cause increasing the toxicity of fire gases and reducing the development of fire [23].

In the solid phase, there are two kinds of reactions. In the first of these reactions, the decomposition of the polymer is accelerated by the flame retardant and the separated parts are carried by flow to another part of the polymer so that the combustion cut off. The peroxide group of the expanding polystyrene is an example of this mechanism. In the second type of reaction, the flame retardant causes carbonization of the carbon on the polymer surface. As a result of dehydration double bonds are formed in the flame retardant polymer. Consequently, a cyclic structure and cross-linking occur. Phosphorus compounds are examples of this group [24].

2.7 Basic Types of Flame Retardants

2.7.1 Halogen flame retardants

The activity of halogen-containing flame retardants increase with the sorting of F < Cl < Br < I. Fluoride and iodine based flame retardants are not used in practice. Since fluorine bonds strongly with carbon, it is not effective in gas phase radical capture. On the contrary, Iodine makes a weak bond with carbon. So even a very low energy it released; polymer properties like light stability are affected and flame retarding properties are lost even at the pyrolysis temperature. Brominated and chlorinated compounds have good thermal stability and they are effective as fire retardant, but they can cause corrosion in plastics processing marinas. However, some of the brominated compounds, which are more expensive than the chlorinated ones, also protect the plastic material against UV rays and increase the thermal stability of the material. Although halogen-containing flame retardant additives are still in widespread use, studies are carried out for halogen-free species.

Halogen-containing flame retardants prevent the progress of the radical chain mechanism in the gas phase. The high-energy HO· and O· radicals formed by chain branching are removed from the medium by halogen-containing flame retardants. At first flame retardant ionizes. In the reactions shown below, X represents Cl or Br. Equation 2.4, 2.5, 2.6 and 2.7 show halogen flame retardant for polymers.

$$RX \rightarrow R\cdot + X\cdot \tag{2.4}$$

$$X\cdot + RH \rightarrow R\cdot + HX \tag{2.5}$$

$$HX + H\cdot \rightarrow H_2 + X\cdot \tag{2.6}$$

$$HX + OH\cdot \rightarrow H_2O + X\cdot \tag{2.7}$$

2.7.2 Inorganic flame retardants

In contrast to organic compounds, inorganic flame retardants do not evaporate under the influence of heat. Moreover, they decompose and act as a shield against oxygen attack and thermal recycling at the polymer surface by removing non-flammable gases such as carbon dioxide or water. Recently, Aluminum Hydroxide $Al(OH)_3$ and Magnesium Hydroxide $Mg(OH)_2$ are the most commonly used flame retardants in inorganic flame retardants. Because they are cheap and they are easy to join the plastics.

2.7.2.1. Zinc borate

Zinc borate is a chemical substance contains boron in its structure that has been used increasingly in recent years as a flame retardant. The most commonly used zinc borate is $2ZnO \cdot 3B_2O_3 \cdot 3,5H_2O$.

Zinc Borate is used as fire resistant, a smoke suppressant, an anti-corrosion additive material, and a friction modifier additive in oils.

Due to its high dehydration temperature (290 – 300 °C) it is widely used in the manufacture of high temperature resistant plastic materials. Zinc borates are used in automotive / aircraft interior parts, textile and paper industries, in cables, in fire-resistant paints, in fabrics, in electrical / electronic parts, in flameproof covering carpets. It is used instead of the other flame retardants because they are a much more effective smoke suppressant compared to other flame retardants and are cheaper than other flame retardants. In recent years, the combined use of zinc borate in different applications with other flame retardants has been increasing. For example, zinc borate has the ability to be used with $Al(OH)_3$ and $Mg(OH)_2$ in systems with and without halogen.

Zinc borate with the molecular formula $2ZnO \cdot 3B_2O_3 \cdot 3,5H_2O$ or $4ZnO \cdot 6B_2O_3 \cdot 7H_2O$ is a white, non-desiccant, viscous, powdered product. Zinc borate permits high temperature polymer processes by maintaining the hydration water up to 290 – 300 °C. Some of the physical properties of Zinc Borate are given in Table 2.4. and Figure 2.10. shows the main molecular structure of Zinc Borate [25,26].

Table 2.4: Physical properties of zinc borate.

Refractive Index	1,58
Average Particle Size	7-12 µm
Solubility (25 °C)	< % 0,28 g/ml water
Specific Weight	2,77 g/ml

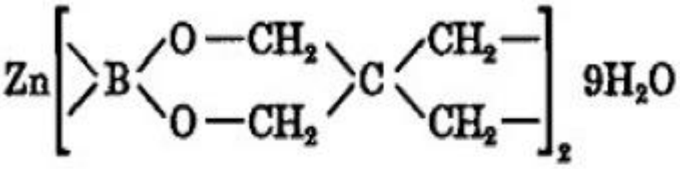


Figure 2.10: Molecular structure of zinc borate.

2.7.3 Phosphorus-containing flame retardants

Phosphorus-containing flame retardants act in the condensed phase, especially in oxygen-containing plastics. Phosphorus containing flame retardants are very diverse, as opposed to those containing halogen. In this group, phosphinites, phosphite oxides, phosphonium compounds, phosphonates, natural red phosphorus, phosphites and phosphates are used as flame retardants. In addition, if the phosphorus compounds contain halogen, especially if they contain bromine, the flame retarding property of the compound increases positively. Most phosphorus compounds are liquid and plasticizer. Commercially available phosphoric acid esters, such as aryl phosphates and alkyl substrate derivatives, are used as additives in PVC, polyamide, polyphenylene ether applications [24,27].

2.7.3.1 Tris (1-chloro-2-propyl) phosphate (TCPP)

Tris (1-chloro-2-propyl) phosphate (TCPP) is chlorine-phosphorous based flame retardant. It is insoluble in water; Soluble in most organic solvents and compatible with resins. It is used as flame retardant in the production of acetate, ethylene-vinyl acetate (EVA), PVC, polyurethane foams, and phenolic materials. At the same time, it is resistant to low temperatures and moisture and it has antistatic property enhancing effect. It is resistant to low temperatures and moisture and it has antistatic property enhancing effect. Physical and chemical properties of TCPP are shown in Table 2.5. and Figure 2.11 illustrates the main molecular structure of TCPP [28].

Table 2.5: Physical and chemical properties of TCPP.

Empirical Formula	$C_9H_{18}Cl_3O_4P$
Molecular Weight	327,56
Melting Point	-42 °C
Flashing Point	218 °C
Relative Density	1,28-1,29 g/cm^3 (25 °C)
Solubility	1,6 g/l in water
Refractive Index	1,4630-1,4645
Appearance	Colorless or light-yellow transparent liquid

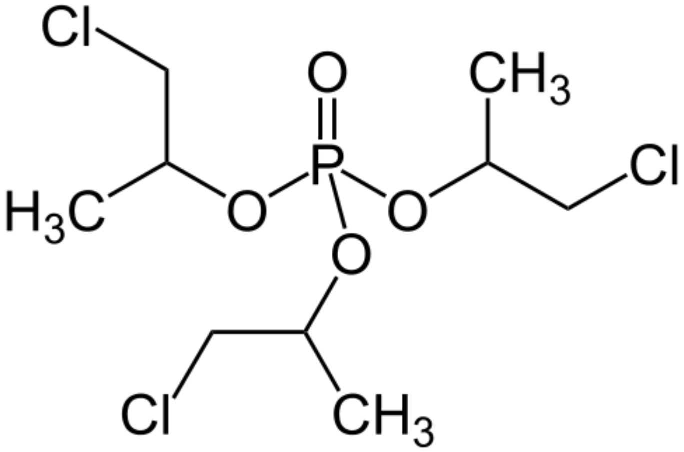


Figure 2.11: Molecular structure of TCPP

3. EXPERIMENTAL PART

Information about used materials in the experiments is given in this part. Applied procedure of microcapsule preparation is explained methodically. It is also indicated that characterization methods applied for microcapsules.

3.1 Materials

Used chemicals and used equipment are given in Table 3.1 and Table 3.2.

Table 3.1: Used chemicals.

Chemicals	**Supplier**
Melamine	Merck
Formaldehyde	Merck
Sodium Dodecyl Benzenesulfonate	Sigma Aldrich
Poly (vinyl alcohol)	Sigma Aldrich
Zinc borate	Merck
Tris (2-chloro-1methylethyl)	Flokser Group
Acetic acid	Sigma Aldrich
Sodium hydroxide	Sigma Aldrich
Acetone	Sigma Aldrich

Table 3.2: Used equipment.

Equipment	**Supplier**
Mechanical stirrer	Heidolph, RZR 2020
Heater	Heidolph, MR 3001 K
Optical Microscope	Hund WETZLAR, V300
FTIR	Bruker, ALPHA
SEM	Philips, XL30 ESEM-FEG

3.2 Preparation methods of microcapsules

In this study, in-situ polymerization is used in preparation of microcapsules, adapted by Meng et al [29]. Microcapsules were produced in three-neck round-bottom flask under mechanical stirrer.

3.2.1 Preparation of melamine-formaldehyde prepolymer

Formaldehyde solution; ACS reagent, 37 wt. % in H_2O, contains 10-15% Methanol as stabilizer (to prevent polymerization) and melamine 99%; 2,4,6-Triamino-1,3,5-triazine, sym-Triaminotriazine were used for synthesis of melamine-formaldehyde pre-polymer. Desired molar ratio of melamine/formaldehyde is 0,2. According to molar ratio of melamine and formaldehyde, required mass of chemicals were calculated. Desired melamine and formaldehyde were mixed with 50 ml deionized water and added to a three-neck round-bottom flask. By addition of 2 wt % NaOH solution under mechanical stirring, pH of mixture was kept at the range of 8,5 - 9. The heat of system was regulated to (65 – 70) °C. Prepolymer of melamine and formaldehyde were obtained after 30 min, by indication of colorless mixture.

3.2.2 Preparation of zinc borate filled microcapsules

Required amount of Zinc Borate which was calculated according to desired core/shell weight ratio were added to distilled water. After aqueous Zinc Borate solution was stirred 30 minutes, it was added to the prepolymer solution. To obtain a stable emulsifiable solution, the mixture stirred about 30 minutes. After the pH of mixture was regulated to desired value by 5 wt. % acetic acid or NaOH solution, the temperature was stabilized to 65°C, reaction was continued during 6 hours under high mechanical stirring. At the end of the reaction the resulting mixture was cleaned with water in order to get rid of the unreacted materials. Tale 3.2. shows the experimental sets preparation of Zinc Borate filled microcapsules.

Table 3.1: Experimental sets preparation of zinc borate filled microcapsules.

Sample ID	Dispersion Rate (rpm)	Feeding weight ratio of core/shell	pH	Reaction T (°C)	Time (h)
ZB-1	800	2	4	65	6
ZB-2	800	2	8.5	65	6
ZB-3	1000	2	4	65	6

3.2.3 Preparation of tris (2-chloro-1methylethyl) filled microcapsules

Sodium Dodecyl Benzenesulfonate (SDBS) technical grade Dodecyl benzene sulfonic acid sodium salt and poly (vinyl alcohol) (PVA) Mw 85,000-124,000, 99+% hydrolyzed were used as an emulsifier and for protecting colloids. TCPP with a density of 1290 kg/m^3 was used as core material. 100 ml aqueous solution of Sodium Dodecyl Benzenesulfonate (SDBS) and Poly (vinyl alcohol) (PVA) was prepared. Required amount of Tris(2-chloro-1methylethyl) (TCPP) which was calculated according to desired core/shell weight ratio and the aqueous SDBS, PVA solution were added to the prepolymer solution. To obtain a stable emulsifiable solution, the mixture stirred about 30 minutes. After the pH of mixture was reduced to 3,8 – 4,1 by 5 wt. % acetic acid solution and the temperature was stabilized to 65°C, reaction was continued during 6 hours under high mechanical stirring. At the end of the reaction the resulting mixture was cleaned with water in order to get rid of the unreacted materials including TCPP then microspheres were dried at room temperature. Table 3.2. shows the experimental sets preparation of TCPP filled microcapsules.

Table 3.2: Experimental TCPP filled microcapsules.

Sample ID	Dispersion Rate (rpm)	Feeding weight ratio of core/shell	Emulsifier content (%w)		Washing Material
			SDBS	PVA	
TCPP-1	400	2	1	0.3	Acetone
TCPP-2	1000	2	1	0.3	Water
TCPP-3	1000	0.5	1	0.3	Water
TCPP-4	1000	1	0	0.45	Water
TCPP-5	1000	0.5	0	0.45	Water
TCPP-6	1000	2	0	0.6	Water

3.3 Characterization Methods of Microcapsules

3.3.1 FTIR (Fourier Transform Infrared Spectroscopy)

Determination of the presence of the core and shell materials in the samples Fourier transform infrared spectroscopy analyzes were carried out. ALPHA FTIR Spectrometer from Bruker was used for recording infrared spectra. The data obtained directly from the sample. Firstly, FTIR spectra of melamine-formaldehyde resin, Zinc Borate and TCPP were analyzed. Then, they were compared with the samples.

3.3.2 Optical Microscopy

Optical microscope images of microcapsules were viewed with a brand of hund WETZLER, V300 optical microscope and recorded. Images were recorded with the zoom 4 times and 10 times.

3.3.3 SEM (Scanning Electron Microscopy)

Morphological properties of microcapsules were determined with scanning electron microscopy. Studies were performed by Philips, XL30 ESEM-FEG SEM. The samples were coated with platinum (Pt) for SEM. SEM was also used for the determination of average diameters of microcapsules.

3.3.4 Core Content Determination

For determination of core content extraction method was applied. At first, microcapsules were crushed in a mortar. Then the weight of the crushed microspheres is measured and put in a bag made of filter paper. Extraction procedure were applied to remove the core material from the sample bag by using acetone as a solvent. After extraction, the sample bag is dried at 70 °C and weighed again. The percentage of the core content in the synthesized microcapsules is calculated by the equation 3.1. W_0 is the weight of the sample bag before extraction and W_1 is the weight of the dried sample bag after extraction.

$$\frac{W_0 - W_1}{W_0} \; x \; 100 \tag{3.1}$$

4. RESULTS AND DISCUSSION

4.1 FTIR Analysis

FTIR result of melamine formaldehyde resin is shown in Figure 4.1. It is indicated in the spectrum of MF Resin stretching vibration peaks of N-H and –OH at 3321,59 cm^{-1}, stretching vibration of C-N in the triazine ring at 1509,14 cm^{-1}, the vibration peak of –C-O-C- at 1170,43 cm^{-1} and the characteristic peak of triazine ring at 804,17 cm^{-1} [30,31].

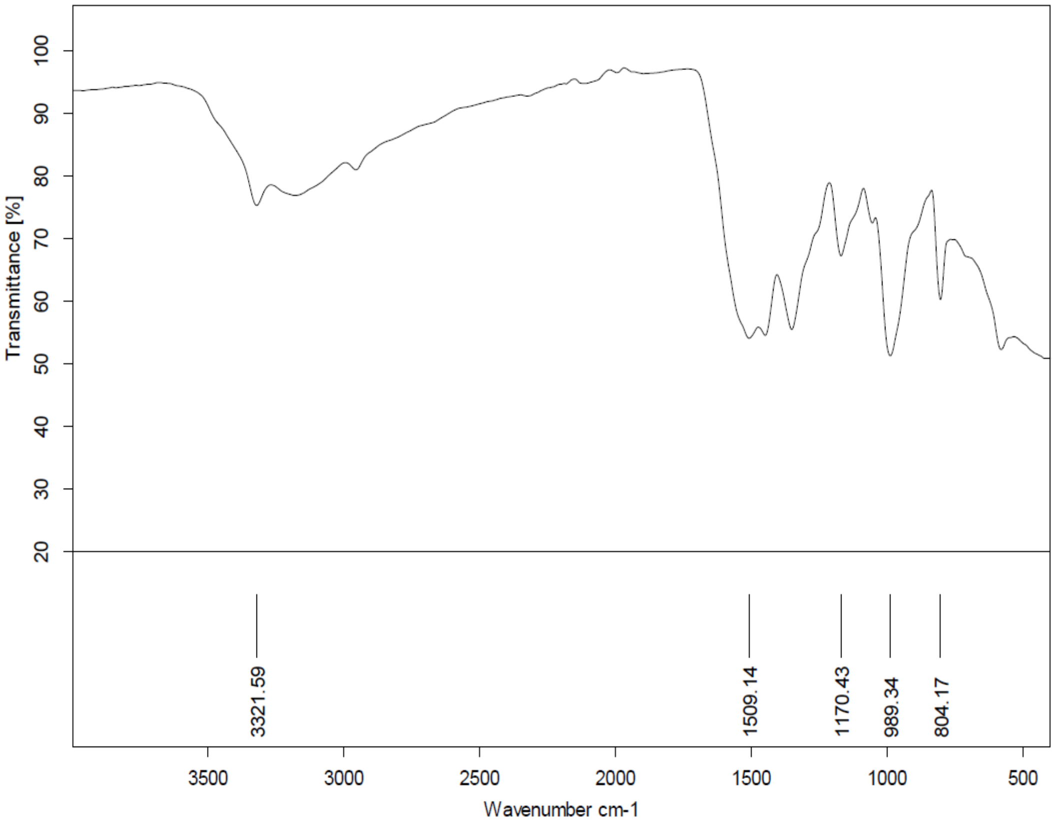


Figure 4.1: FTIR spectrum of melamine-formaldehyde resin.

In Figure 4.2. FTIR result of Zinc Borate is represented. Stretching vibrations of –OH is indicated the band of 3210 cm^{-1}. Because of crystal water containing in Zinc Borate bending vibration peak of H-O-H is observed at 1338 cm^{-1}. Asymmetric stretching vibrations of trihedral (BO_3) groups, asymmetric and symmetric stretching vibrations of tetrahedral (BO_4) borate groups and bending vibrations of trihedral (BO_3) groups cause the peak observation at the band of 1252 cm^{-1}, 1191,78-1061,55 cm^{-1} and 751,7 cm^{-1} respectively [32].

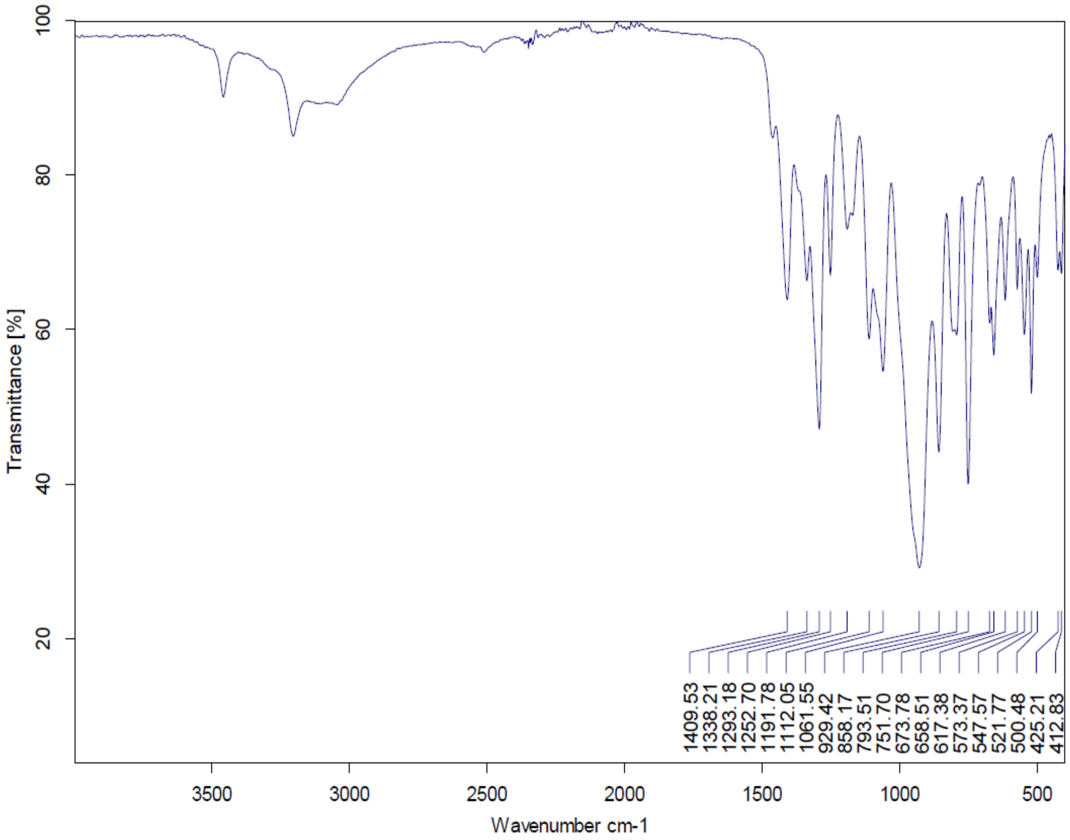


Figure 4.2: FTIR spectrum of zinc borate.

The spectra of ZB-1, ZB and MF resin are shown in the same graph in Figure 4.3. ZB represented by pink curve and MF represented by green curve. As seen in the spectrum of the Sample ZB-1, while the peaks belonging to the MF resin are seen, there are no distinctive peak from zinc borate. It means that there is no zinc borate in the spheres that are supposed to be formed. The zinc borate was dissolved by the acid used for pH adjustment, before coating by MF during the experiments. Therefore, in order to prevent the dissolution of zinc borate, experiment ZB-2 was tried with the aim of curing the melamine formaldehyde in basic medium. However, curing was not achieved at the end of the experiment, and the pre-polymer and zinc borate solution remained in two separate phases.

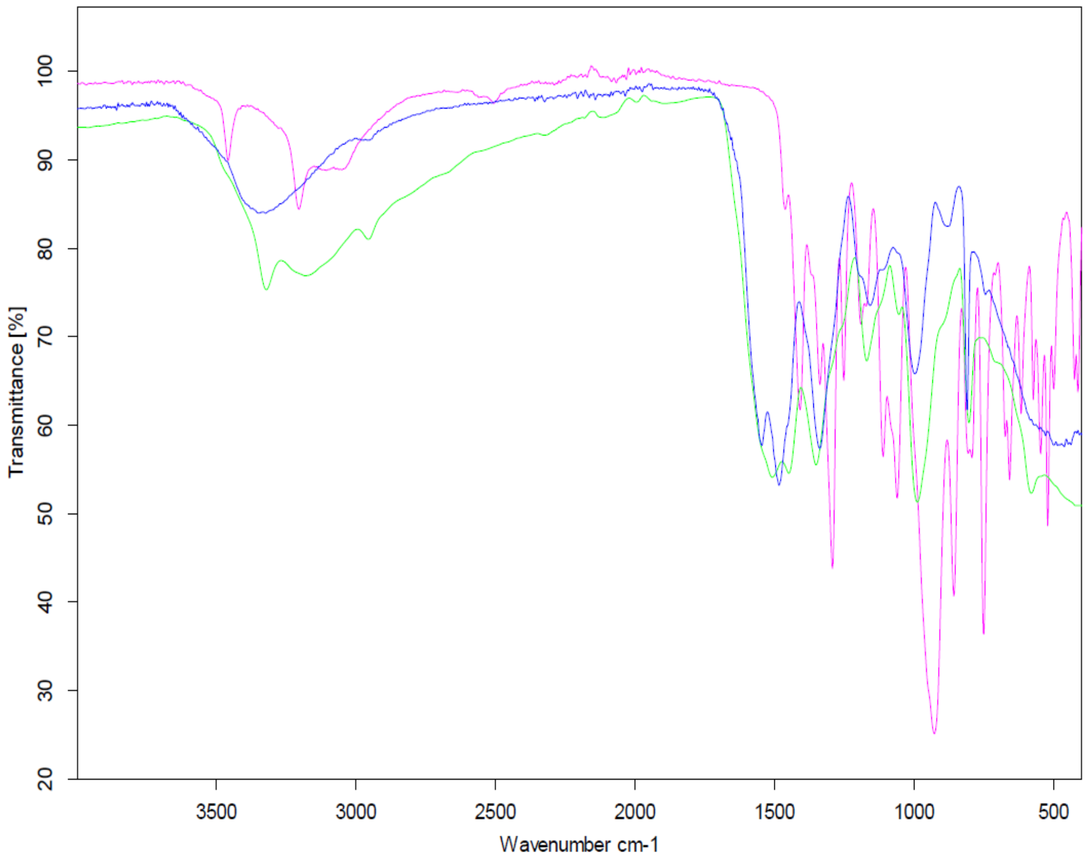


Figure 4.3: FTIR spectra of sample ZB-1, ZB and MF resin.

FTIR result of TCPP is shown in Figure 4.4. In 500 cm^{-1} and 1500 cm^{-1} region there are specific peaks belonging TCPP. The spectra of TCPP, MF resin and the samples from TCPP-1 to TCPP-6 are shown in the same graph in figures from Figure 4.5. to Figure 4.10. respectively. As seen in the spectrum of the samples of TCPP, the peaks belonging to the MF resin are seen and represented with green line and the TCPP peaks are signified with pink line. The third peaks on the graphics are belong the samples of TCPP. The characteristic peaks of both MF resin and TCPP are seen in the sample curves. It means that microencapsulation of TCPP with MF resin was achieved.

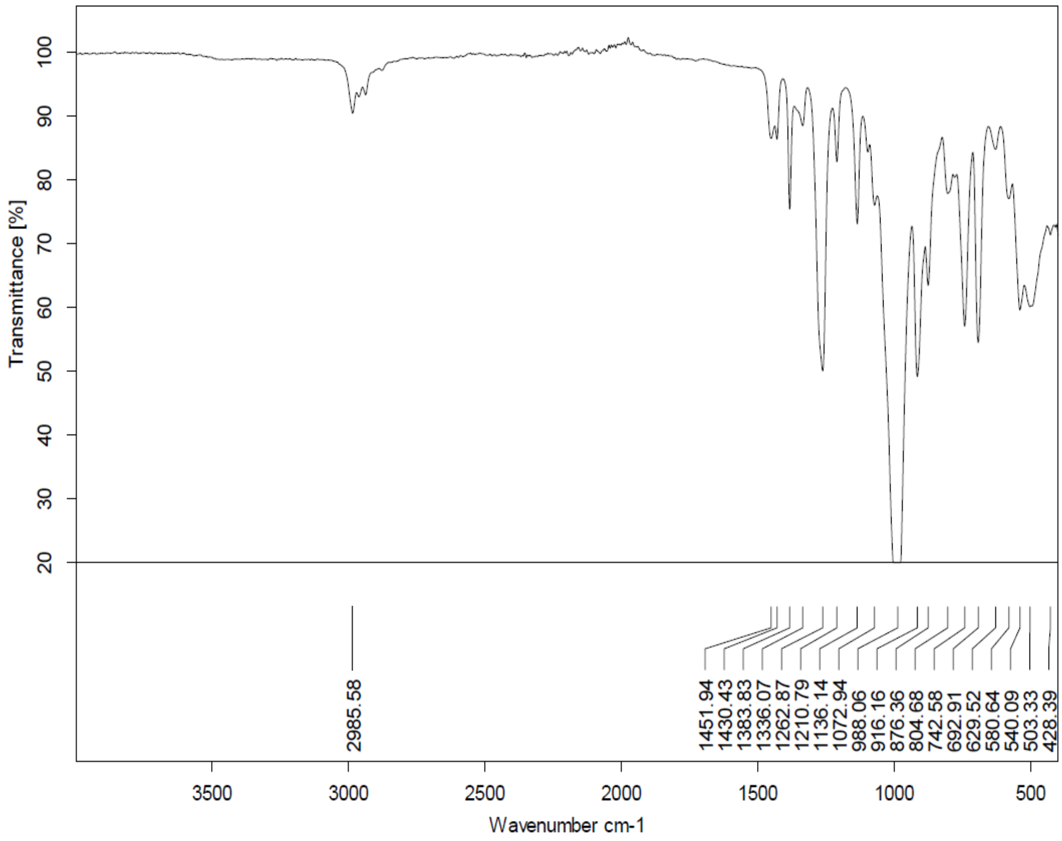


Figure 4.4: FTIR spectrum of TCPP.

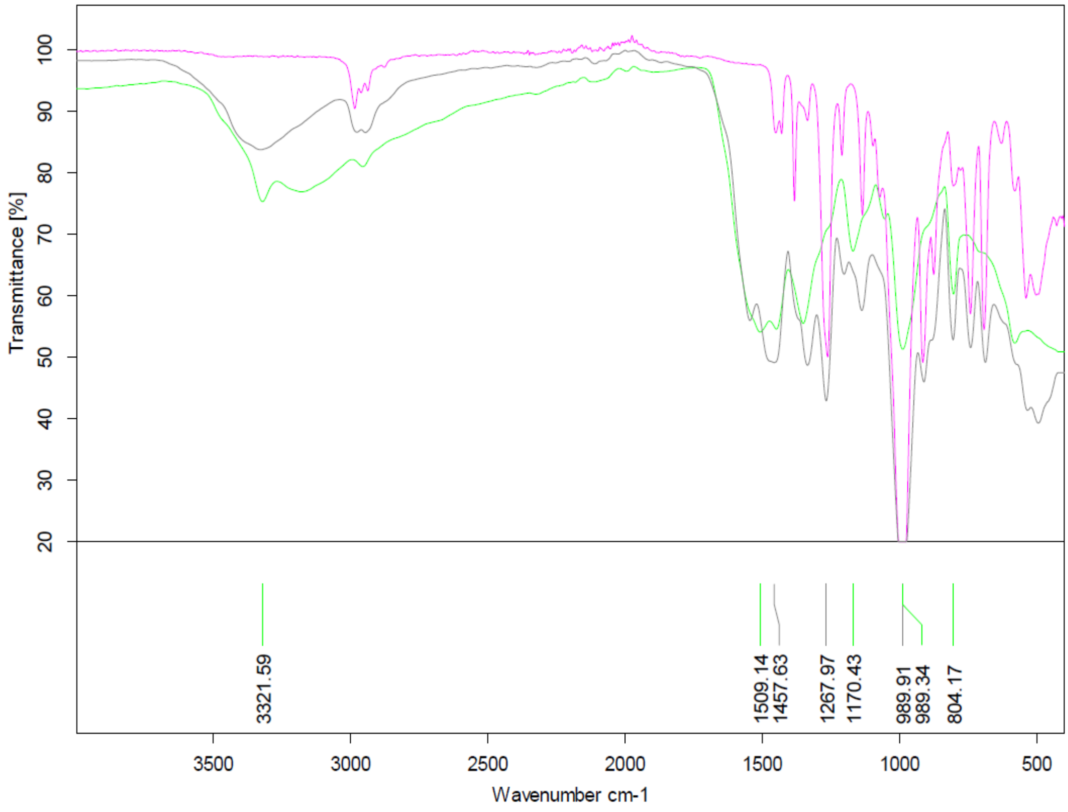


Figure 4.5: FTIR spectra of sample TCPP-1, TCPP and MF resin.

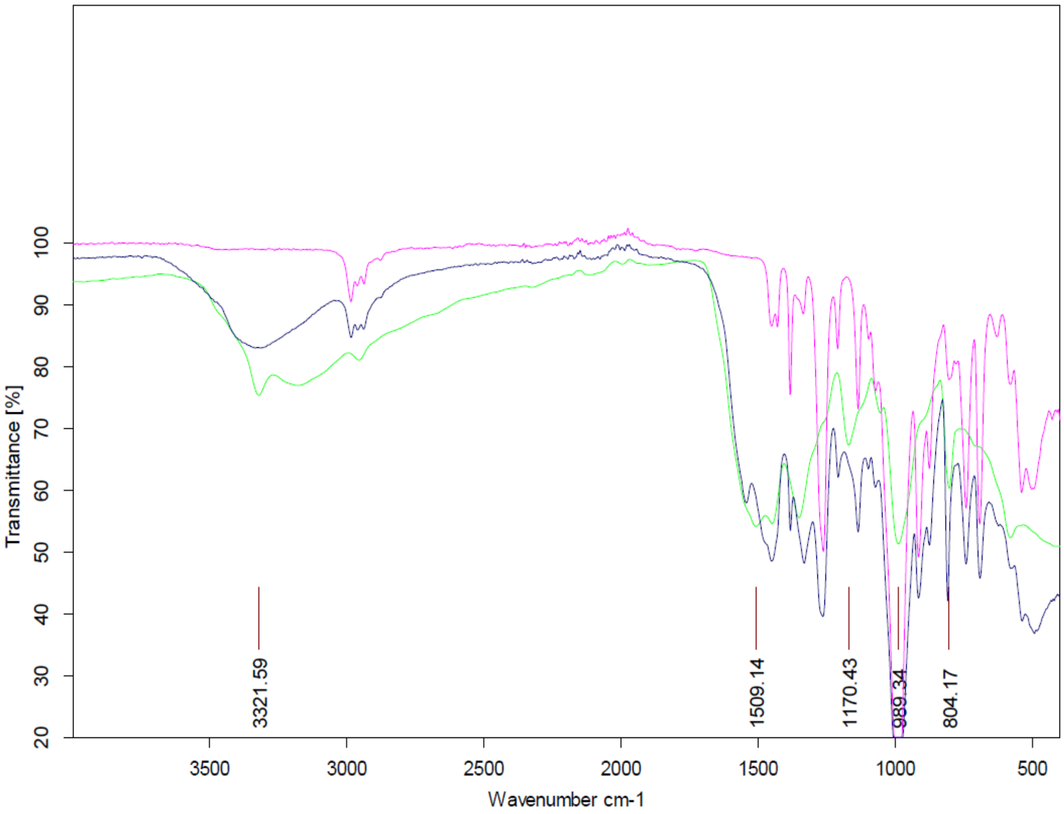


Figure 4.6: FTIR spectra of sample TCPP-2, TCPP and MF resin.

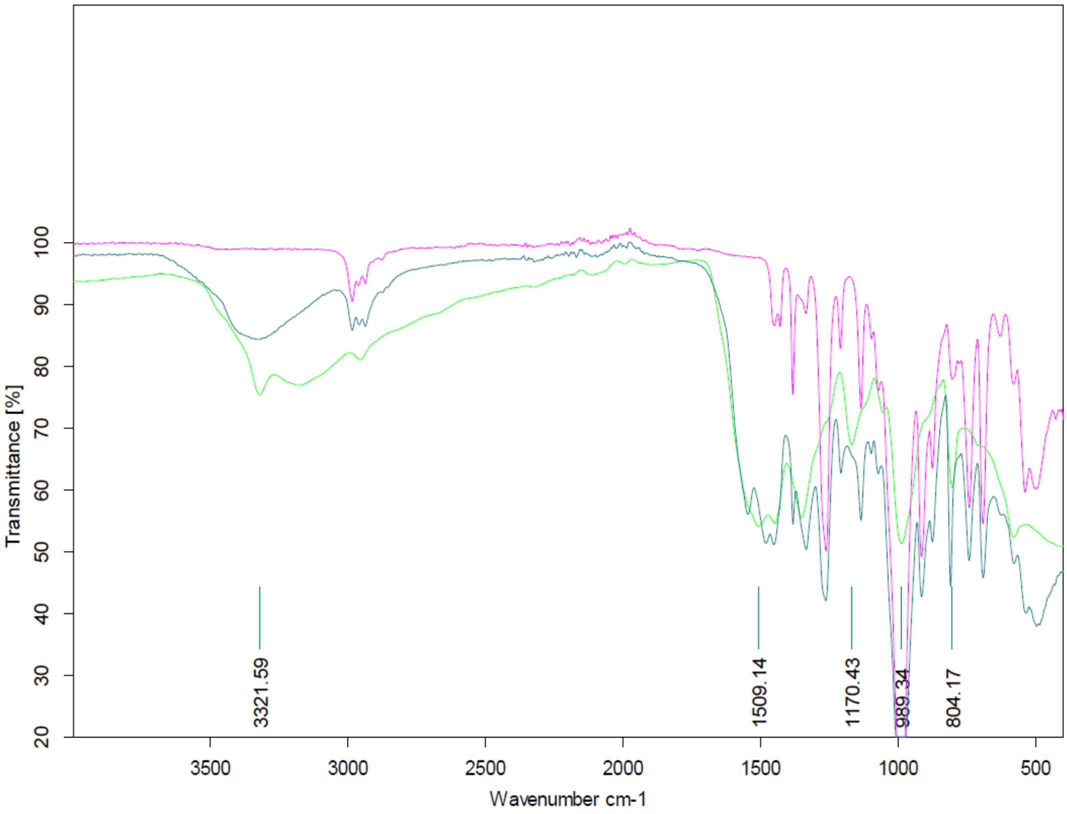


Figure 4.7: FTIR spectra of sample TCPP-3, TCPP and MF resin.

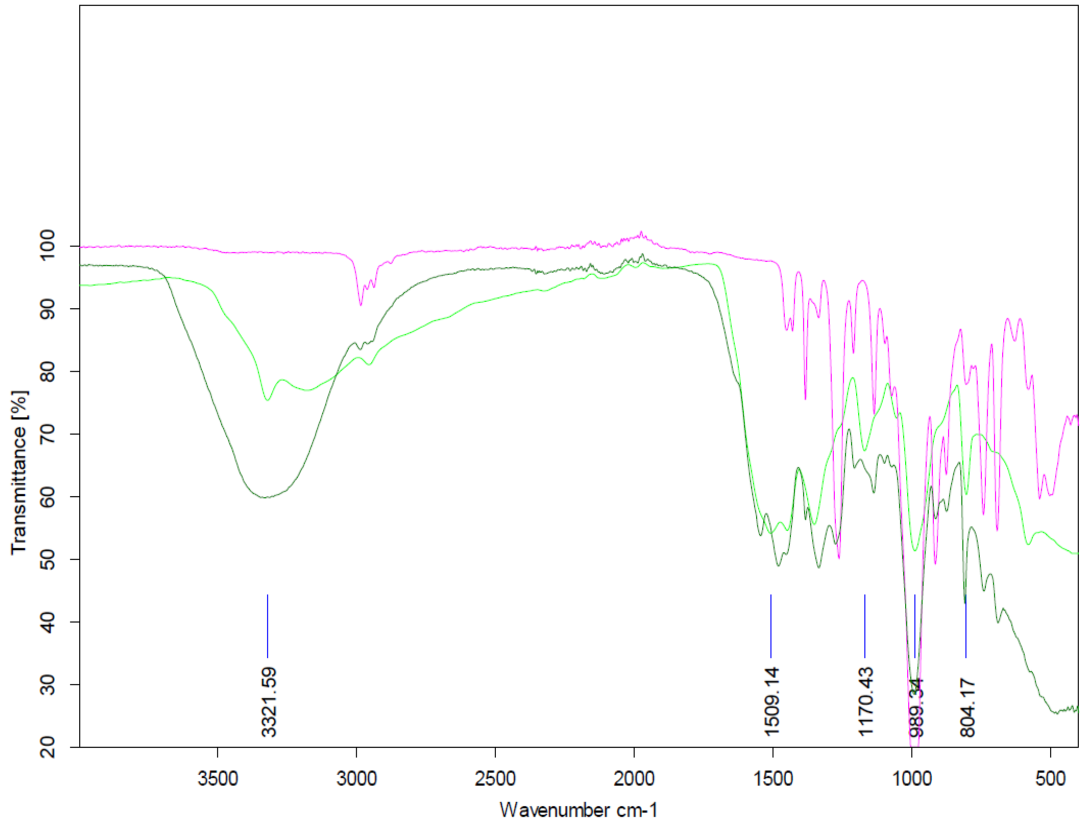


Figure 4.8: FTIR spectra of sample TCPP-4, TCPP and MF resin.

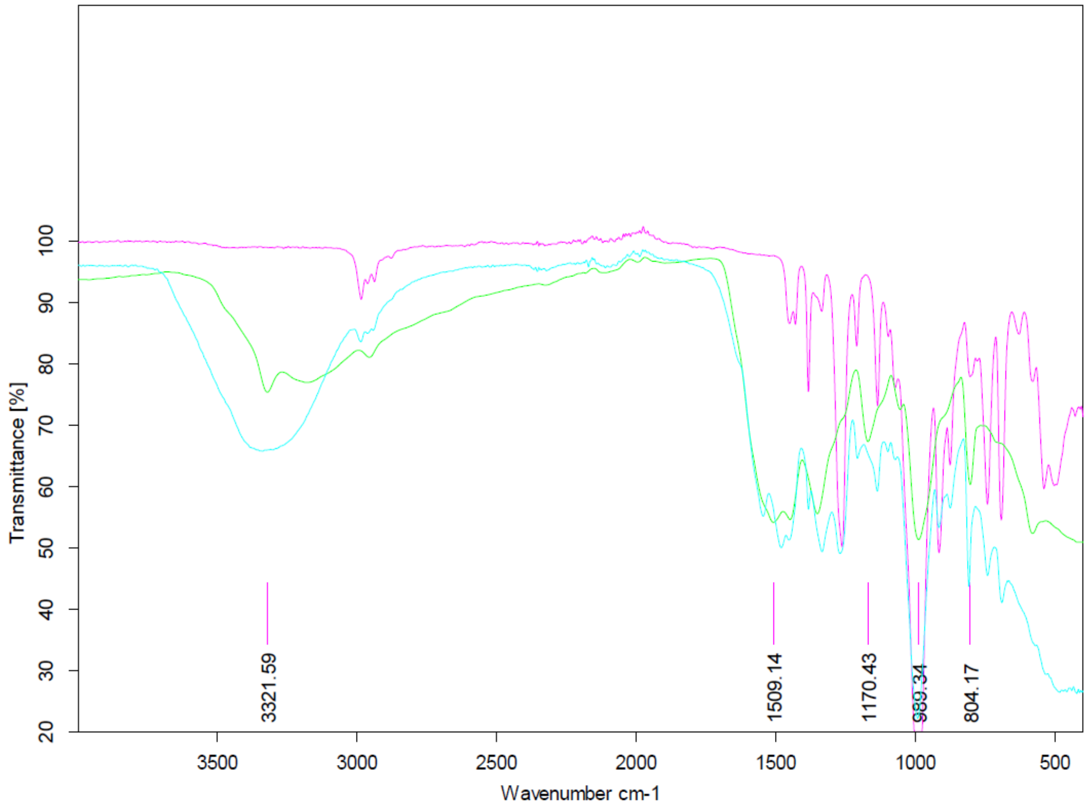


Figure 4.9: FTIR spectra of sample TCPP-5, TCPP and MF resin.

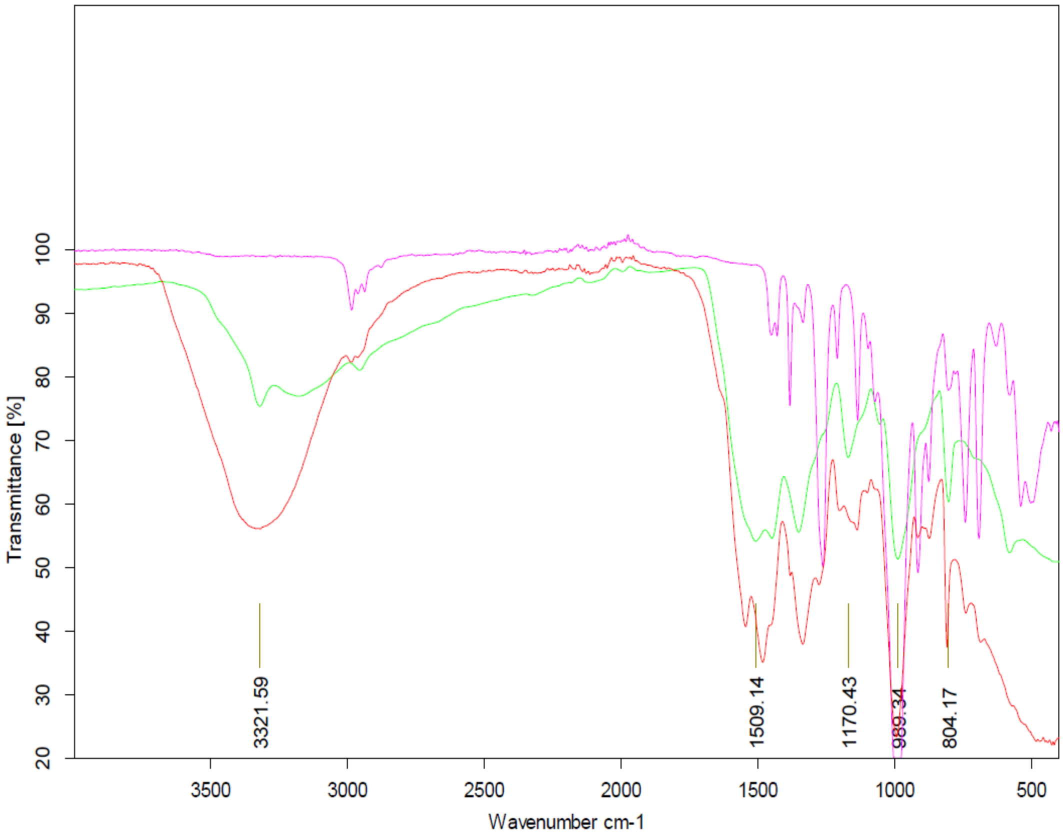


Figure 4.10: FTIR spectra of sample TCPP-6, TCPP and MF resin.

4.2 Visual Analysis of MF Microcapsules filled with TCPP

The structure of microcapsules was examined with optical microscope and SEM. In Figure 4.11. the structure of TCPP-1 is presented with optical microscopy images and Figure 4.12., Figure 4.13. and Figure 4.14. show the SEM images of TCPP-1. They have spherical structure. After the synthesis of TCPP-1, acetone was used in washing process. Therefore, the shell of these microspheres was damaged as shown in the figures.

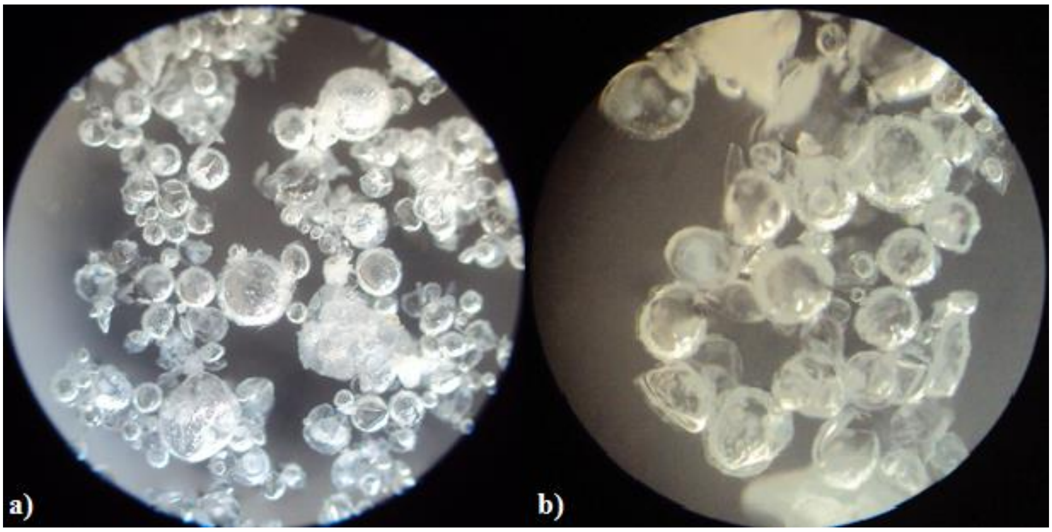


Figure 4.11: Optical microscope images of TCPP-1 a) x4 magnification, b) x10 magnification.

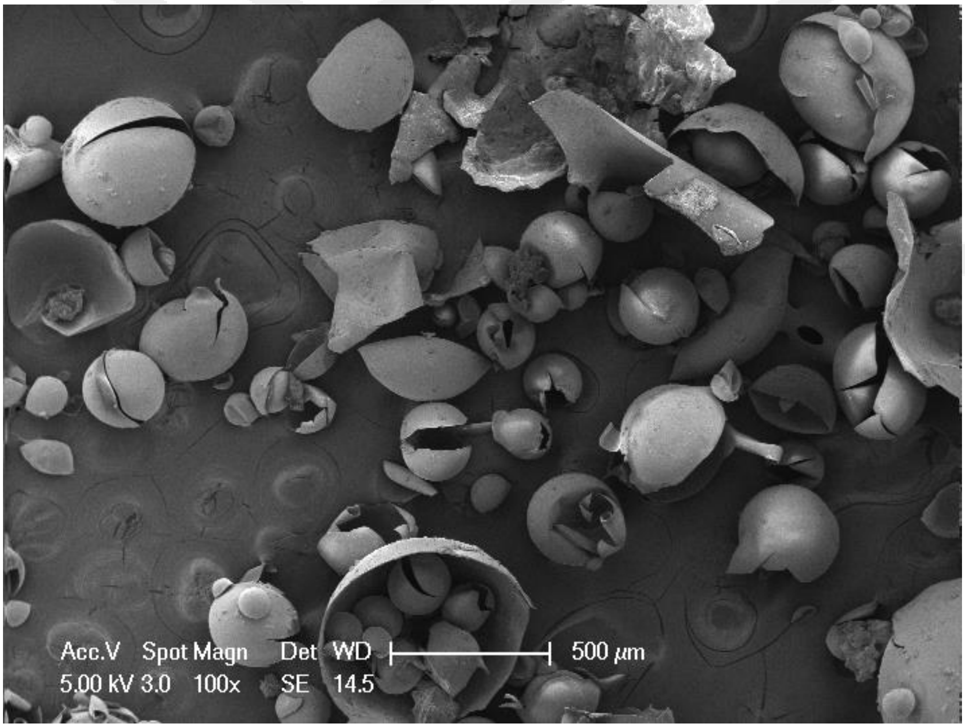


Figure 4.12: SEM image of TCPP-1 with x100 magnification.

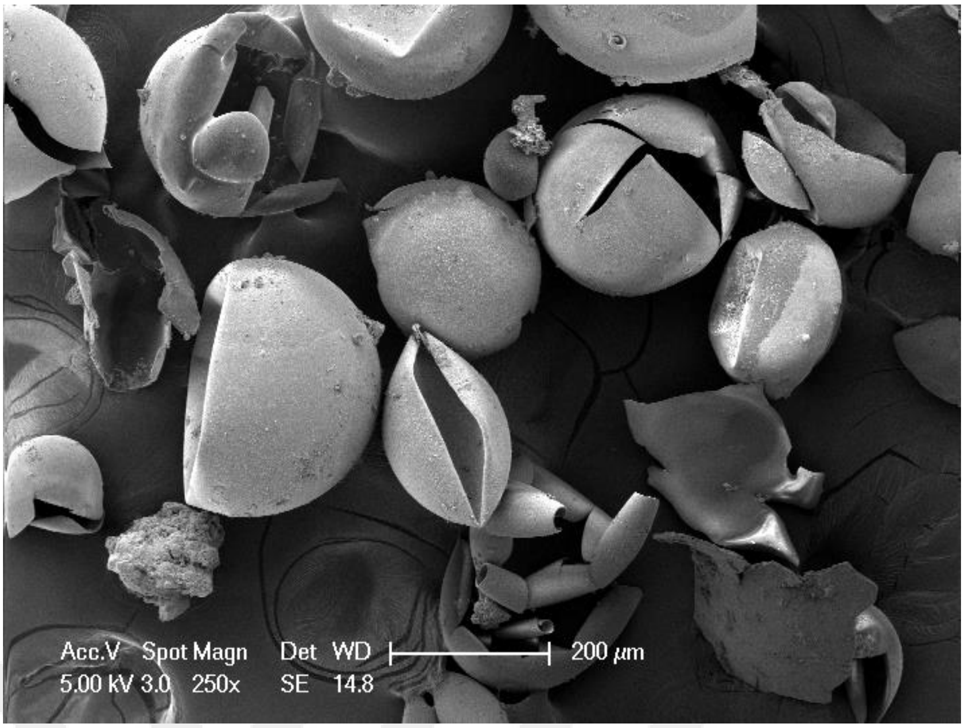


Figure 4.13: SEM image of TCPP-1 with x250 magnification.

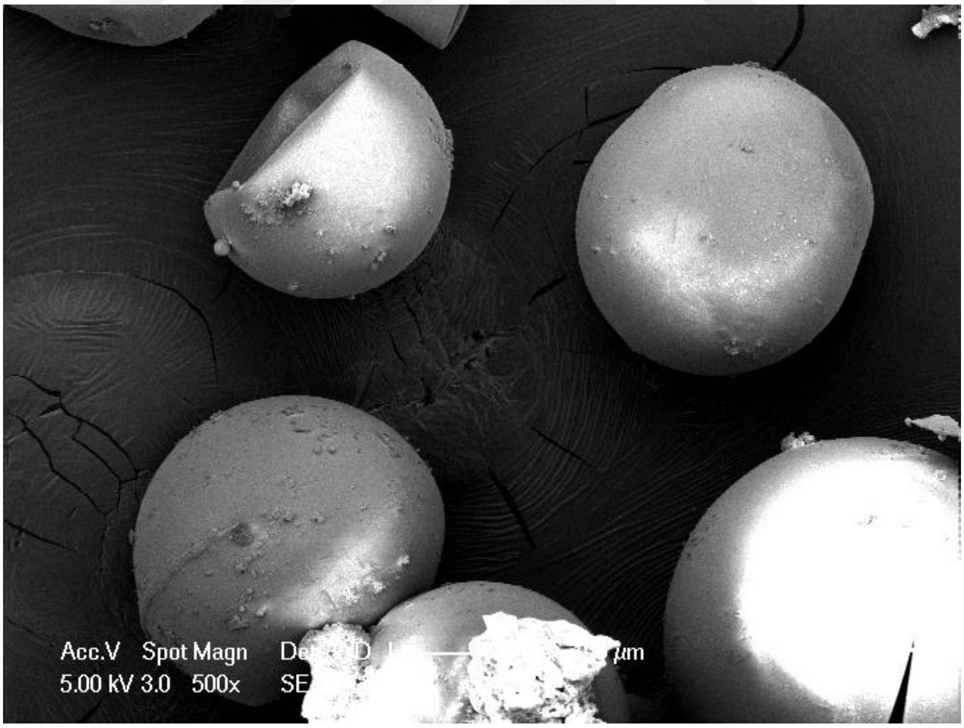


Figure 4.14: SEM image of TCPP-1 with x500 magnification.

Figure 4.15. illustrates the images of sample TCPP-2 obtained from optical microscopy and Figure 4.16., 4.17. and 4.18. are the SEM images. When the results of sample TCPP-1 and TCPP-2 are compared, in sample TCPP-2 the diameters of

microspheres are smaller than the sample TCPP-2. Differences between the dispersion rate in the experiments was caused decreasing of the diameters. After the synthesis of TCPP-2, water was used in washing process. In consequence, a smaller amount of damages was observed in TCPP-2, when it is compared with TCPP-2.

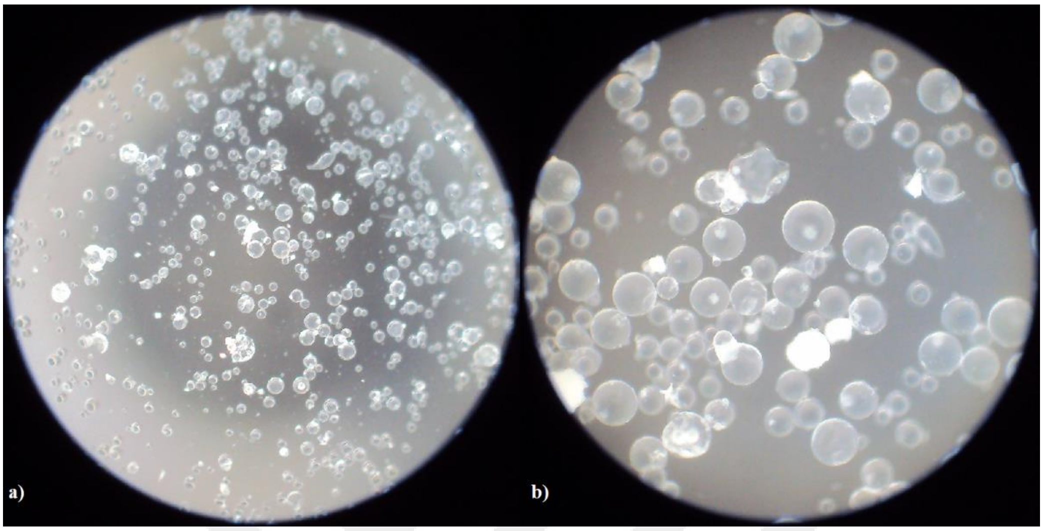


Figure 4.15: Optical microscope images of TCPP-2 a) x4 magnification, b) x10 magnification.

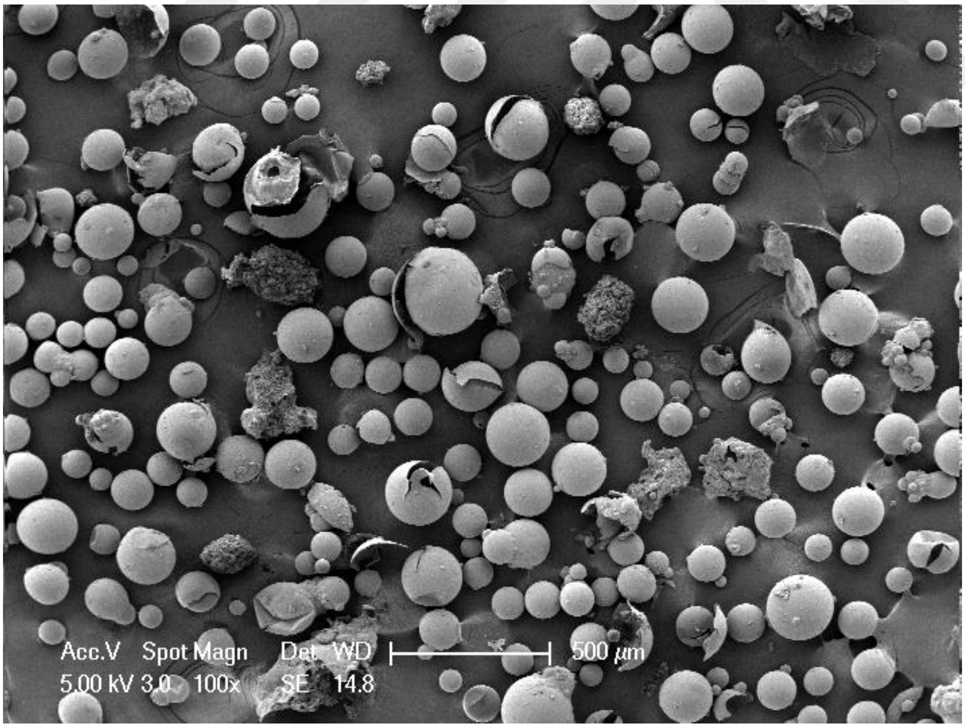


Figure 4.16: SEM image of TCPP-2 with x100 magnification.

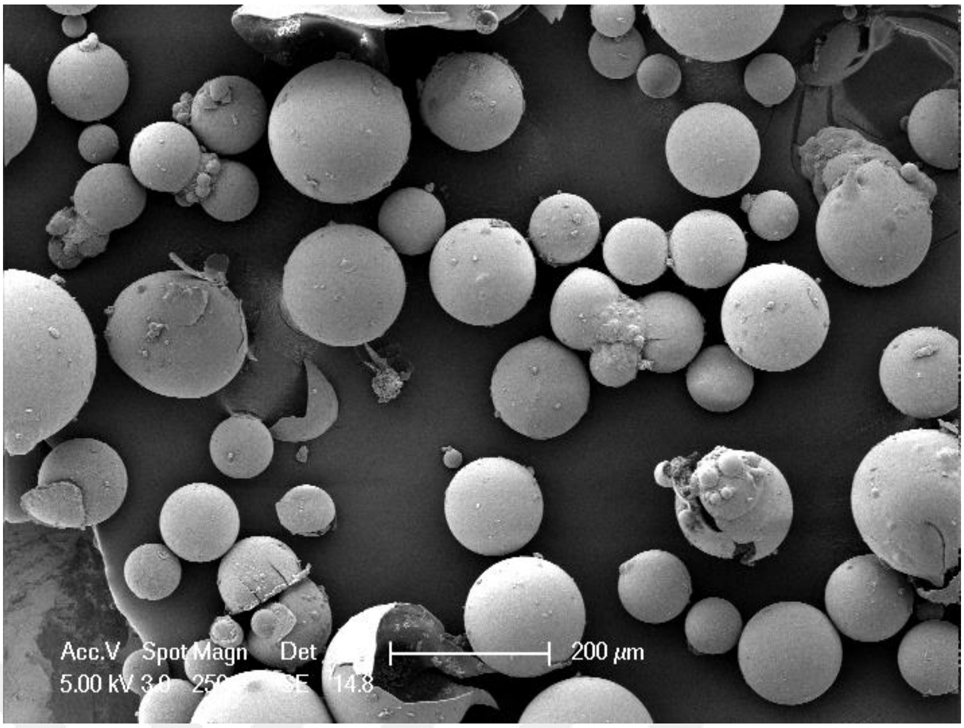


Figure 4.17: SEM image of TCPP-2 with x250 magnification.

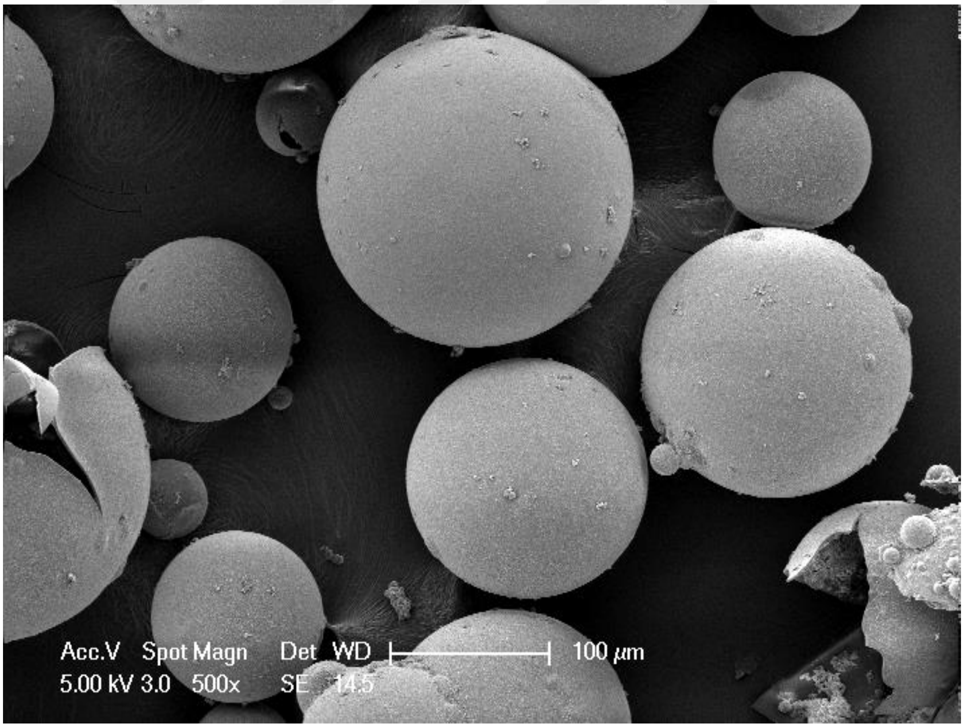


Figure 4.18: SEM image of TCPP-2 with x500 magnification.

In Figure 4.19. the structure of TCPP-3 is presented with optical microscopy images and Figure 4.20., Figure 4.21. and Figure 4.22. show the SEM images of TCPP-3. Smaller spherical diameters were obtained in TCPP-3 than the samples of TCPP-1 and

TCPP-2 because of decreasing in feeding weight ratio of core/shell. However, too much foaming was observed during the experiment, leading to a decrease in yield.

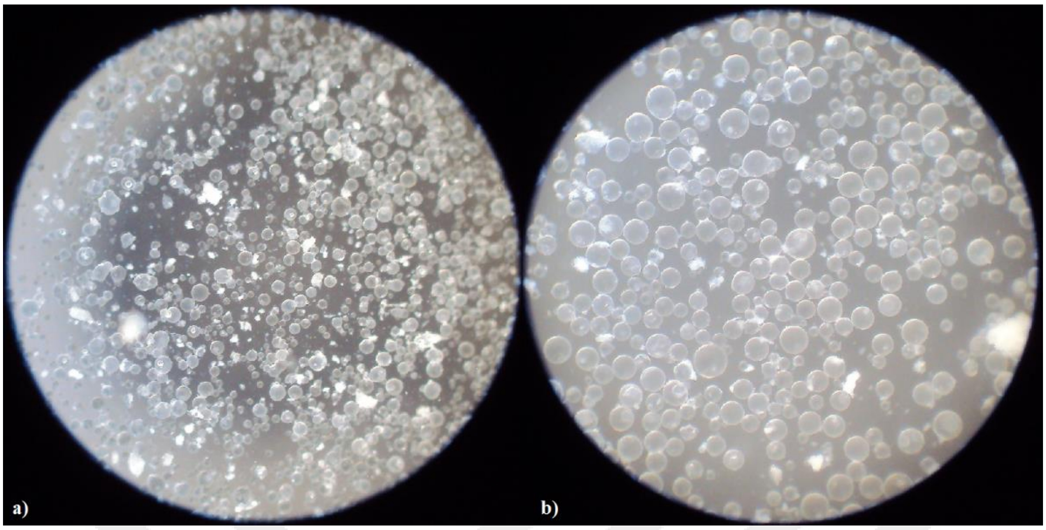


Figure 4.19: Optical microscope images of TCPP-3 a) x4 magnification, b) x10 magnification.

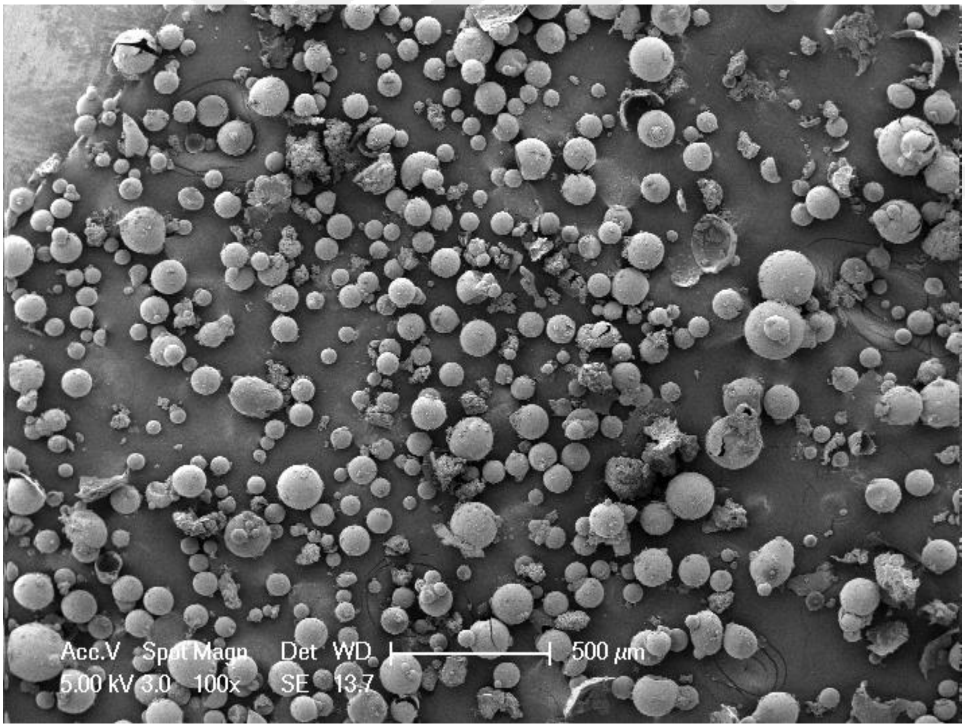


Figure 4.20: SEM image of TCPP-3 with x100 magnification.

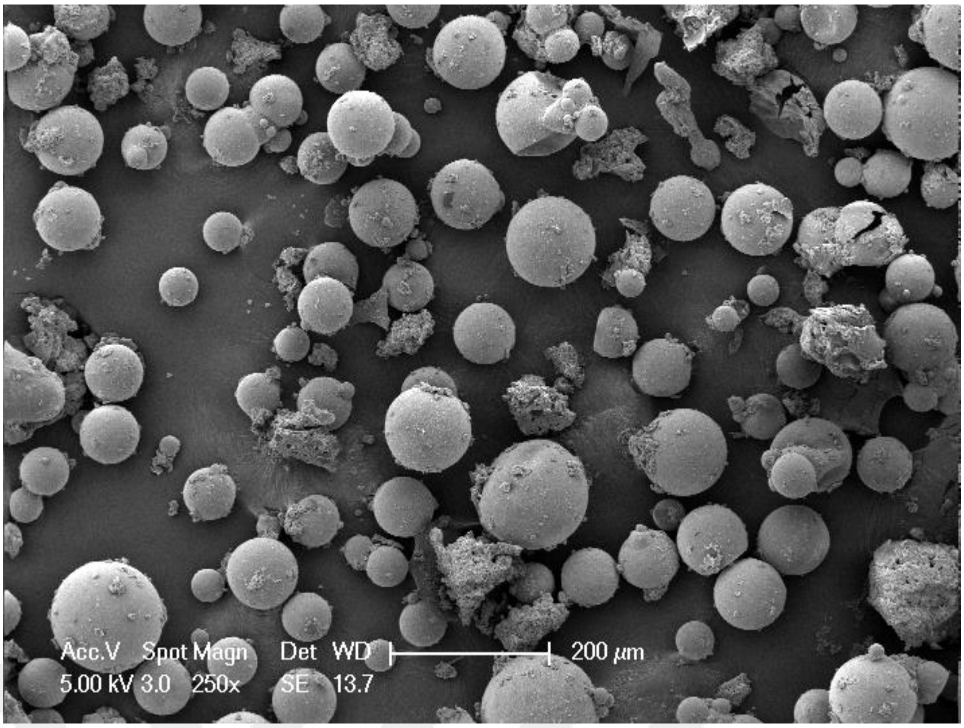


Figure 4.21: SEM image of TCPP-3 with x250 magnification.

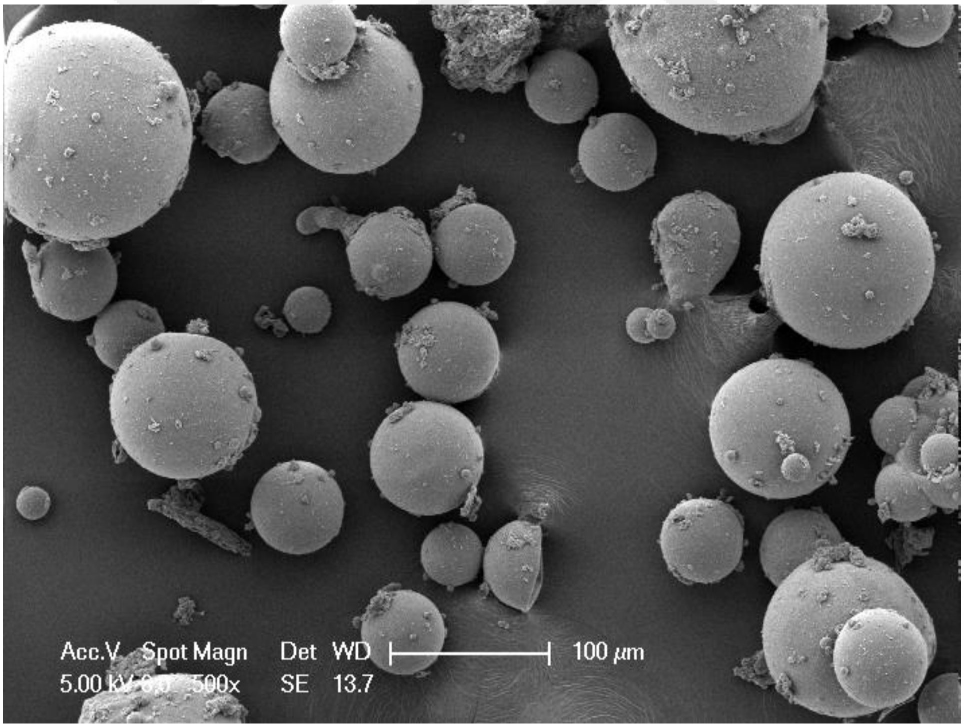


Figure 4.22: SEM image of TCPP-3 with x500 magnification.

SDBS was not used to remove foam formation in the production of TCPP-4. At the same time PVA ratio has been increased. As a result, there was no bubble observation, sphere diameters was reduced and spheres with diameters closer to each other are obtained. In Figure 4.23. the images of sample TCPP-4 obtained from optical microscopy is illustrated and Figure 4.24., 4.25. and 4.26. are the SEM images.

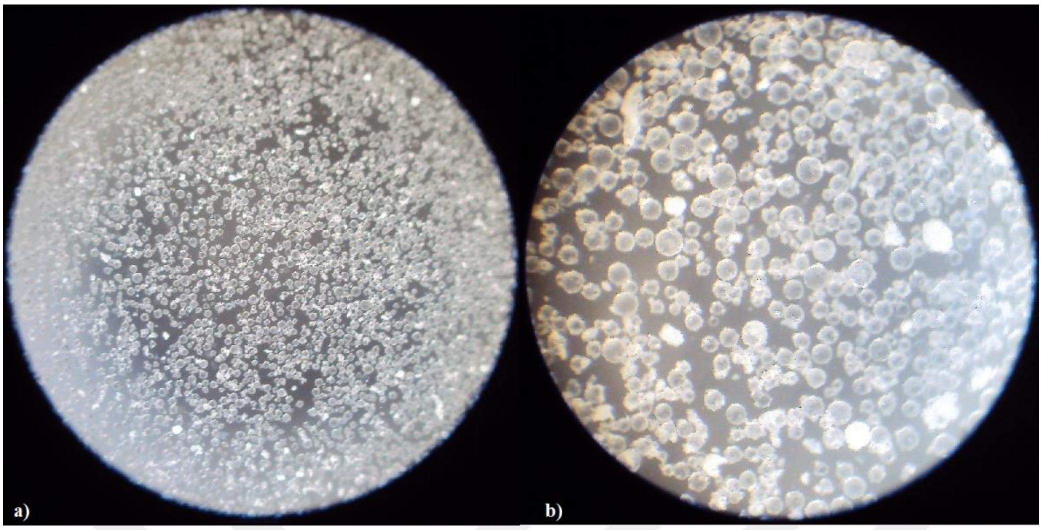


Figure 4.23: Optical microscope images of TCPP-4 a) x4 magnification, b) x10 magnification.

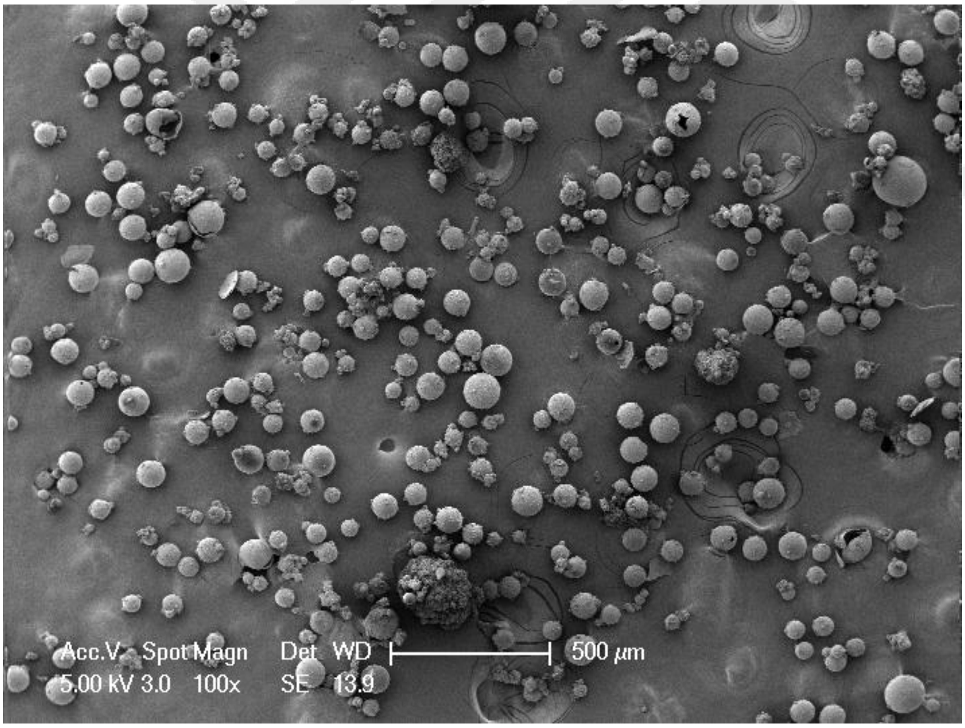


Figure 4.24: SEM image of TCPP-4 with x100 magnification.

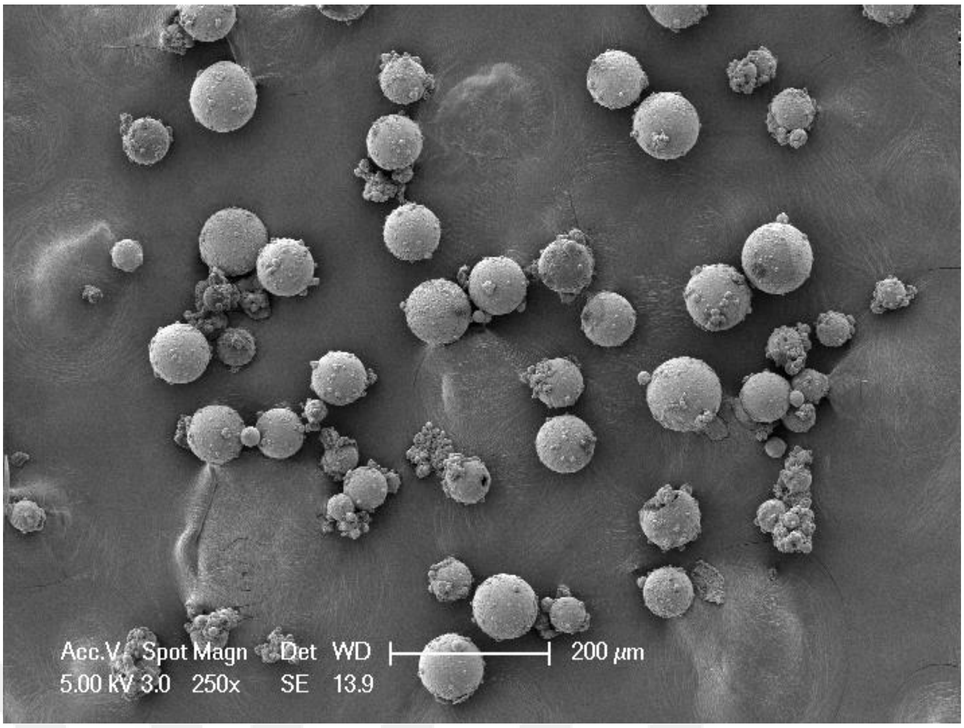


Figure 4.25: SEM image of TCPP-4 with x250 magnification.

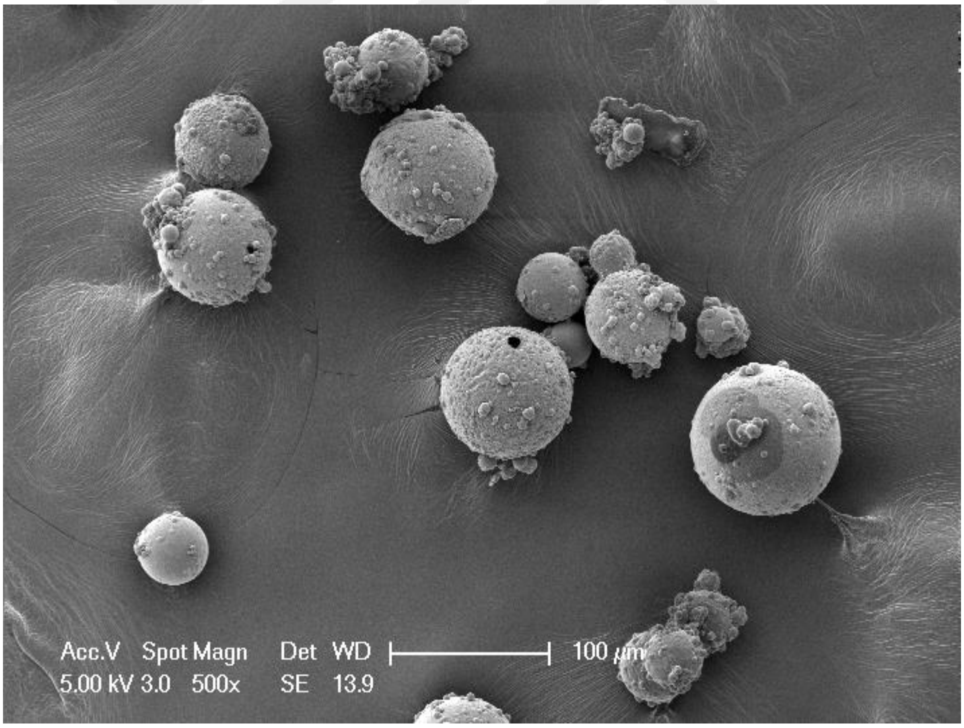


Figure 4.26: SEM image of TCPP-4 with x500 magnification.

After obtaining the desired results in sample TCPP-4, it was aimed to increase the shell thickness by reducing the feeding weight ratio of core/shell in TCPP-5. In Figure 4.27. the structure of TCPP-5 is presented with optical microscopy images and Figure 4.28., Figure 4.29. and Figure 4.30. show the SEM images of TCPP-5. It is realized that with this changing, the diameters. Also, both transparent and more opaque and large spheres which are shown in Figure.4.31. Opaque spheres are thought to be spheres with thicker shell thickness.

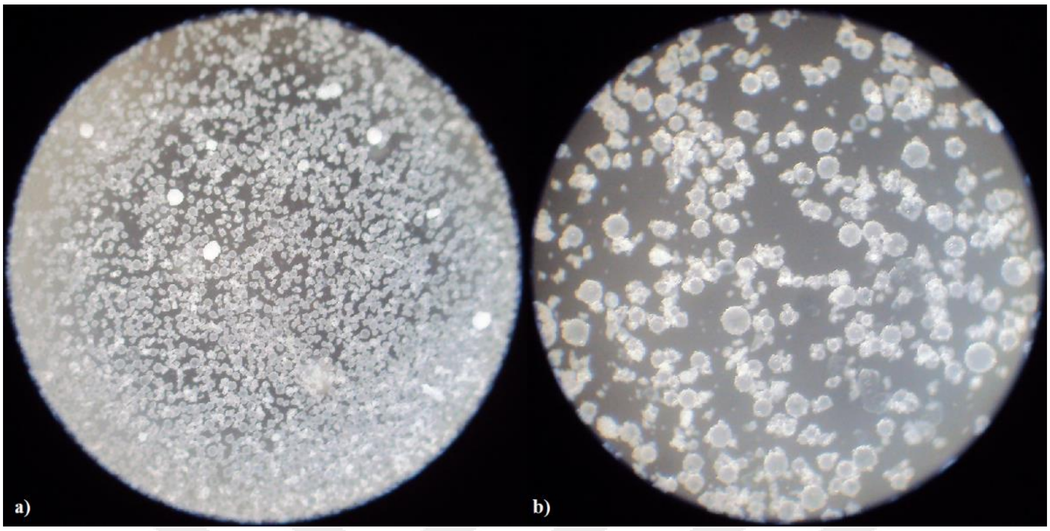


Figure 4.27: Optical microscope images of TCPP-5 a) x4 magnification, b) x10 magnification.

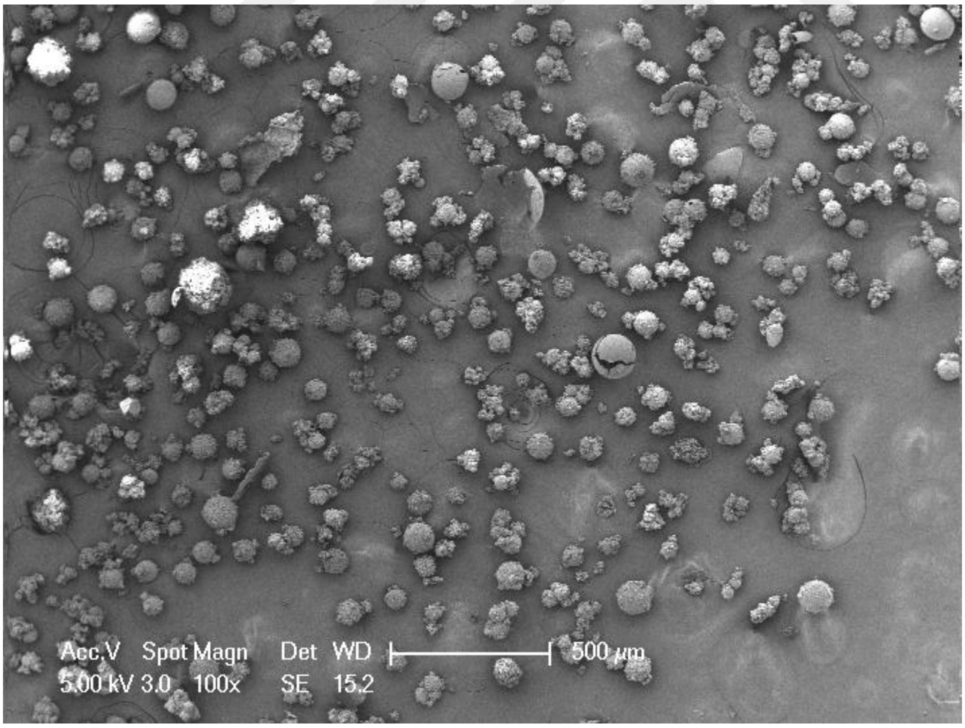


Figure 4.28: SEM image of TCPP-5 with x100 magnification.

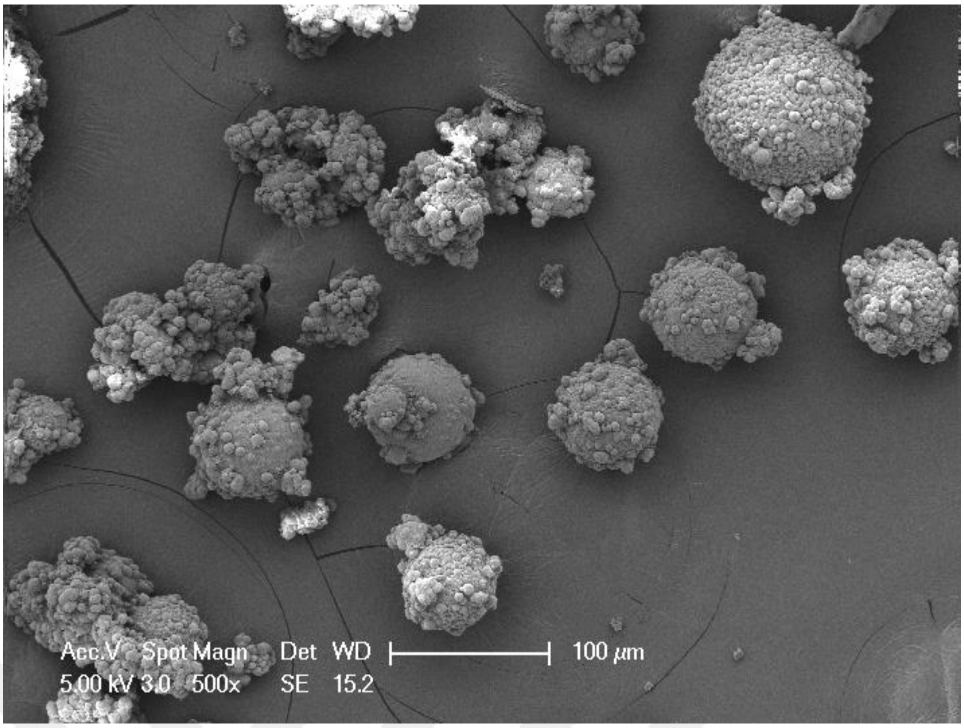


Figure 4.29: SEM image of TCPP-5 with x500 magnification.

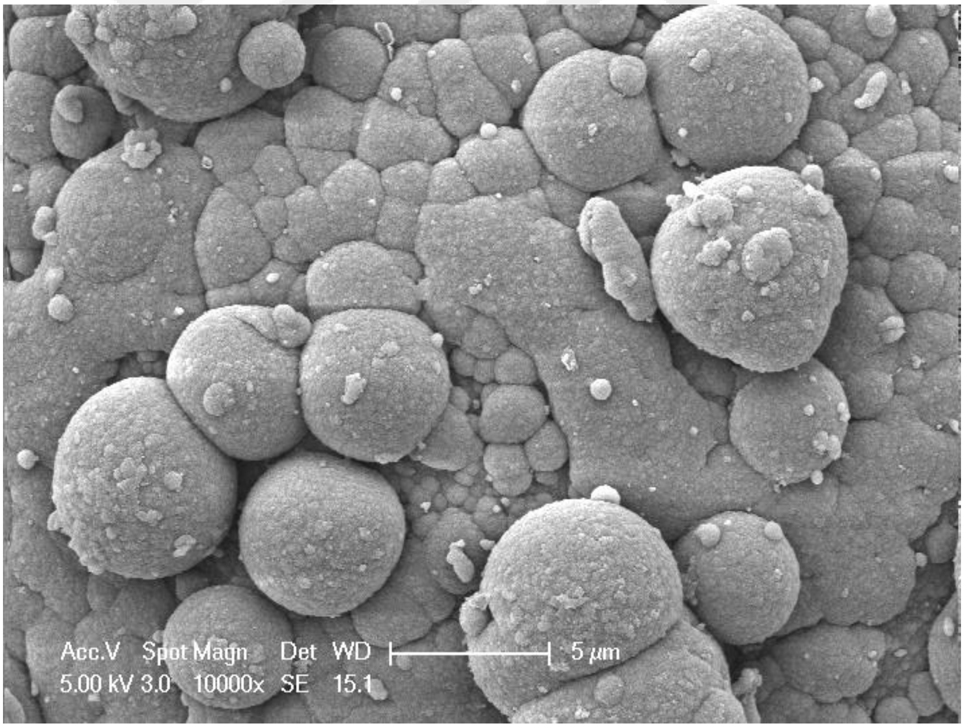


Figure 4.30: SEM image of TCPP-5 with x1000 magnification.

Figure 4.31: Opaque spheres in TCPP-5.

The amount of PVA in the sample TCPP-6 is further increased and consequently it was observed that even small spheres formation. Because the spheres are too small, they stick together. At the same time, small size of the spheres caused difficulty of collapse to the bottom during the washing process. Small spheres were decanted with water which leads to a decrease in the yield. Figure 4.32. illustrates the images of sample TCPP-2 obtained from optical microscopy and Figure 4.33., 4.34. and 4.35. are the SEM images.

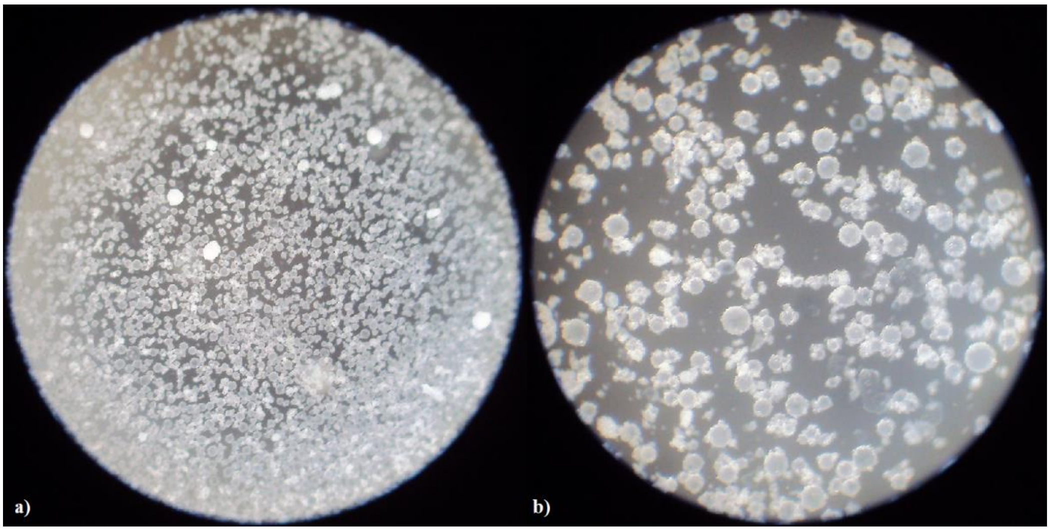


Figure 4.32: Optical microscope images of TCPP-6 a) x4 magnification, b) x10 magnification.

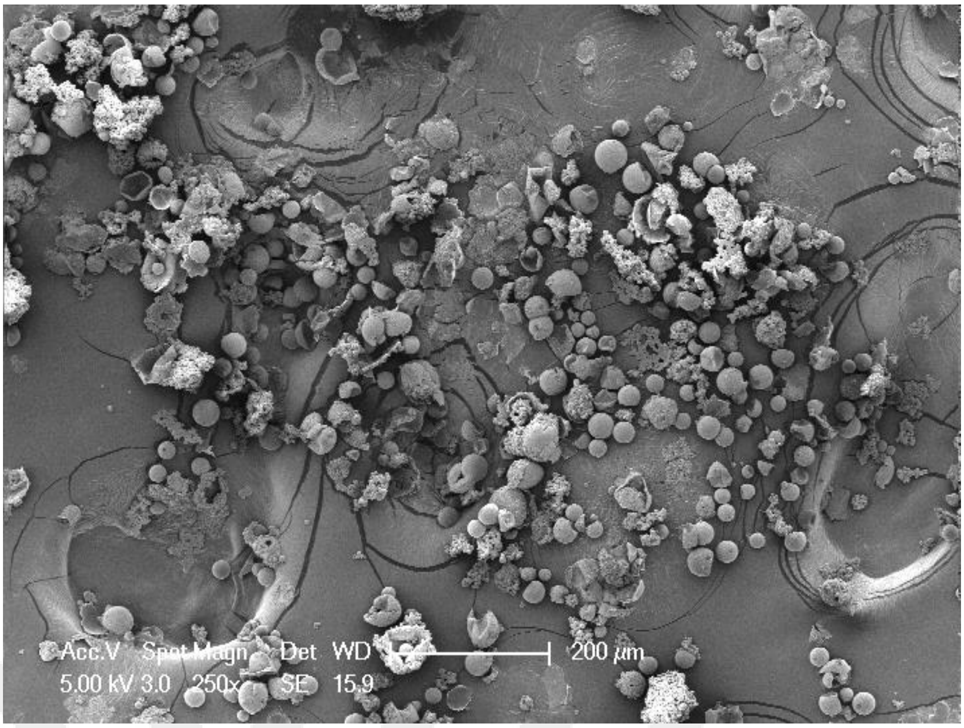


Figure 4.33: SEM image of TCPP-6 with x250 magnification.

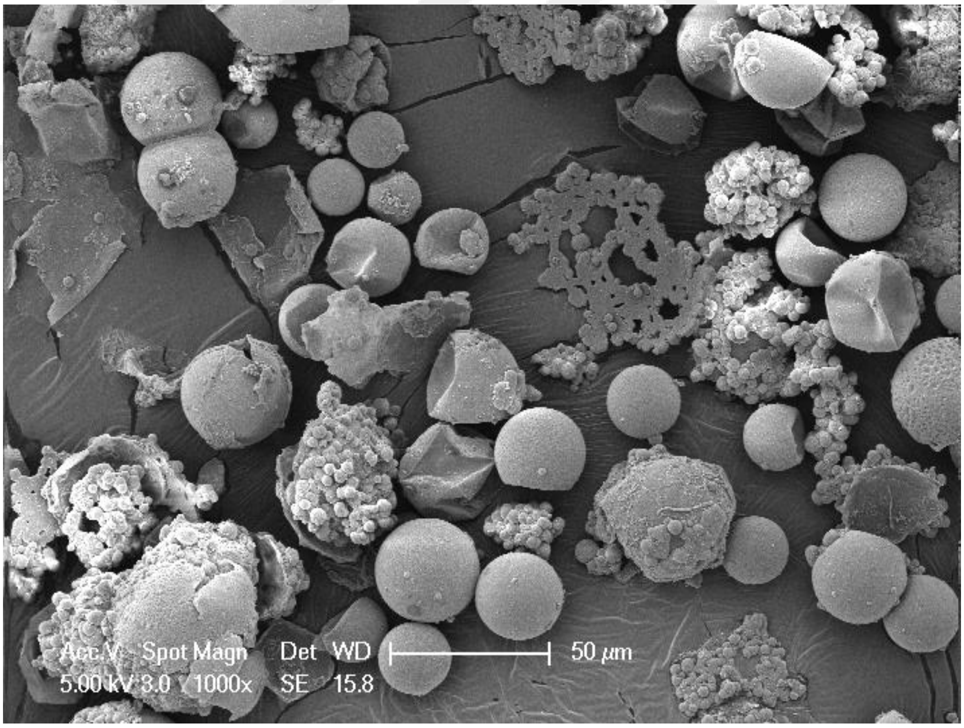


Figure 4.34: SEM image of TCPP-6 with x1000 magnification.

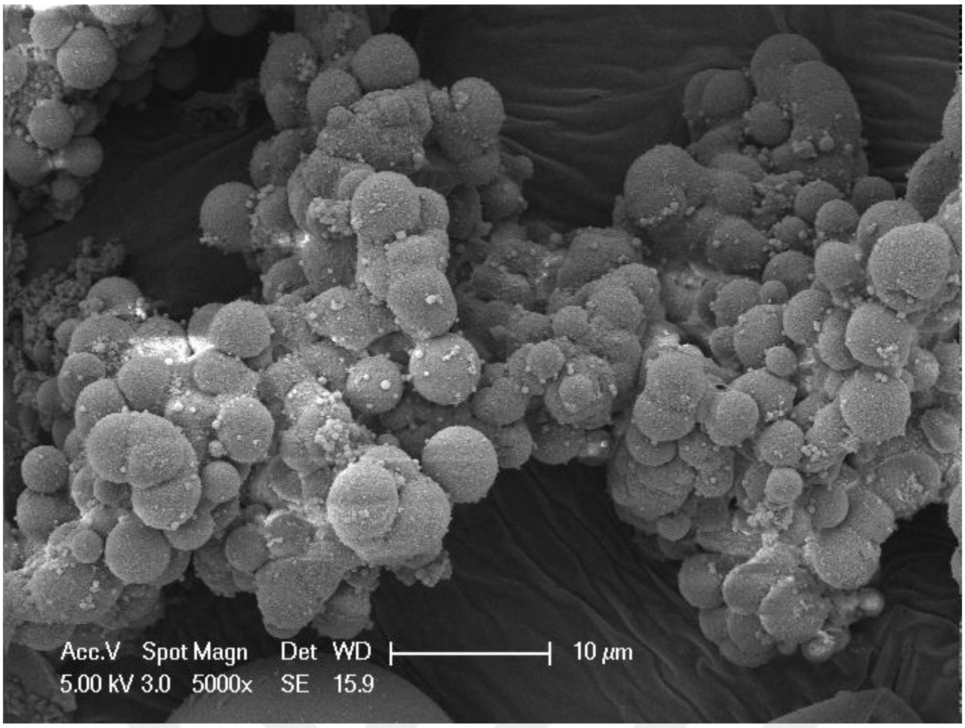


Figure 4.35: SEM image of TCPP-6 with x5000 magnification.

4.3 Determination of Average Diameter of MF Microcapsules filled with TCPP

The average diameters of microcapsules are determined by the help of the images obtained from SEM. Diameters of the selected spheres are marked and measured on images that have been magnified 100 times. average diameter values are given in Table 4.1.

Table 4.1: Average diameters of microspheres.

Sample ID	Dispersion Rate (rpm)	Feeding weight ratio of core/shell	Emulsifier content (%w)		**Diameter Range (µm)**	**Average Diameter (µm)**
			SDBS	PVA		
TCPP-1	400	2	1	0.3	**582 - 67**	**239**
TCPP-2	1000	2	1	0.3	**192 – 37**	**119**
TCPP-3	1000	0.5	1	0.3	**178 – 47**	**99**
TCPP-4	1000	1	0	0.45	**169 – 28**	**69**
TCPP-5	1000	0.5	0	0.45	**81 – 0.5**	**13**
TCPP-6	1000	2	0	0.6	**29 – 0.4**	**10**

According to results in Table 4.1 average diameters of microspheres decrease with reducing dispersion rate and increasing PVA content. Usage of SDBS is effecting on the diameter range of microspheres. When marked diameters are examined in the figures, it is observed that the presence of SDBS causes variations in sphere diameters. Samples TCPP-4, TCPP-5 and TCPP-6 are examples with closer spherical diameter, when compared with samples TCPP-1, TCPP-2 and TCPP-3.

4.4 Determination of Encapsulation Yield

In Table 4.2. the product amounts and yields obtained from the end of the encapsulation process are given.

Table 4.2: Yields of microspheres.

Sample ID	Dispersion Rate (rpm)	Feeding weight ratio of core/shell	Emulsifier content (%w)		**Amount (g)**	**Yield (%)**
			SDBS	PVA		
TCPP-1	400	2	1	0.3	**4.5**	**11.25**
TCPP-2	1000	2	1	0.3	**5.8**	**14.5**
TCPP-3	1000	0.5	1	0.3	**1**	**5**
TCPP-4	1000	1	0	0.45	**5.8**	**22.3**
TCPP-5	1000	0.5	0	0.45	**2.6**	**13.3**
TCPP-6	1000	2	0	0.6	**0.9**	**2.3**

It can be seen that reducing in feeding weight ratio of core/shell decreases the yield, when TCPP-1 and TCPP-2 are compared with TCPP-3. Differently, although TCPP-3 and TCPP-5 have same core/shell ratio, TCPP-5 have higher yield than TCPP-3 because of excess PVA amount. When TCPP-1 and TCPP-2 were examined, it was observed that the stirring rate was not too much of an effect on yield. Despite of high core/shell ratio, TCPP-6 has the lowest yield, because small spheres formed due to high PVA content were decanted with water which leads to a decrease in the yield. The most appropriate feeding weight ratio of core/shell in term of yield is 1 which belong to TCPP-5 with an average PVA amount compared to the others.

4.5 Core Content Determination

In Table 4.3 the percentage of the core content in the synthesized microcapsules are given. According to Table 4.3 decreasing diameter of the spheres reduces the core content because smaller spheres contain less core material.

Table 4.3: Core content of microspheres

Sample ID	Dispersion Rate (rpm)	Feeding weight ratio of core/shell	Emulsifier content (%w)		**Core Content (%)**
			SDBS	PVA	
TCPP-1	400	2	1	0.3	**71**
TCPP-2	1000	2	1	0.3	**65**
TCPP-3	1000	0.5	1	0.3	**71**
TCPP-4	1000	1	0	0.45	**74**
TCPP-5	1000	0.5	0	0.45	**48**
TCPP-6	1000	2	0	0.6	**52**

5. CONCLUSION

Polymers that have many uses in our lives need some mechanical or chemical improvements in order to get better results during their use. Additives like flame retardants, heat and UV stabilizers, colorants, antioxidants, colorants and fillers are added to the polymers in a proper amount, with the aim of providing the desired properties. By the help of using flame retardants in polymers it is aimed that to prevent polymer-based fires or to reduce the damage caused by these fires. To develop the flame resistance of polymers, flame retardant additives have an important role.

Flame retardants have different application varieties on polymers. The microencapsulation technique is one of these applications aimed to reduce the water solubility of the flame retardants, increase the compatibility of the flame retardants in the polymers, change the appearance and physical state of the flame retardants, increase the pyrolysis temperature of the flame retardants and release of toxic gases.

In this study, it was aimed to produce microspheres which contains flame retardant as core material and poly (material melamine-formaldehyde) resin as shell material by in situ polymerization which is one of the microencapsulation techniques. It was tried that to produce microspheres using Zinc Borate and TCPP as flame retardant in the experiments.

Firstly, poly (melamine-formaldehyde) resin was tried to cure in the acidic media in order to encapsulate Zinc Borate. When the products obtained after the experiment were examined by FTIR, poly (melamine-formaldehyde) resin was found in the product, but it was observed that there was no Zinc Borate, because Zinc Borate was dissolved by the used acid. Secondly, in order to prevent the dissolution of zinc borate during the experiment, curing was attempted to be carried out in a basic environment, but the uncured resin and zinc borate remained in separate phases at the end of the experiment.

TCPP was used as flame retardant in the continuation of the study and microencapsulation was tried. Six experimental sets were tested and the success of microcapsulation in each case was demonstrated by FTIR analysis at first and then by optical microscope and SEM images. During the experiment the temperature and time are kept constant in each of the experiments. By changing the parameters like dispersion rate, emulsifier content and feeding weight ratio of core/shell, it is examined that their effects on morphology of microsphere structure, average diameter of microspheres, the range of diameters and the yield of experiments. The results show that the increasing feeding weight ratio of core/shell reduces the microsphere size. The smaller diameter and narrower diameter range is obtained in the experiments where SDBS is not used. Increase of the PVA amount decrease the diameter of the spheres. But due to the loss during the decantation when the very small sphere is obtained, the decrease of the yield is obtained.

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