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THE PRODUCTION OF BIO-BASED POLYURETHANE FOAMS FROM BIODIESEL RESIDUES

MASTER THESIS

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LIST OF ABBREVIATIONS

CG: Crude Glycerol

CG-10: Polyurethane Foam (containing 10% crude glycerol, 90% polyether polyol)

CG-30: Polyurethane Foam (containing 30% crude glycerol, 70% polyether polyol)

CG-50: Polyurethane Foam (containing 50% crude glycerol, 50% polyether polyol)

CG-80: Polyurethane Foam (containing 80% crude glycerol, 20% polyether polyol)

CHDI: Transcyclohexane Diisocyanate

CPP: Commercial Polyether Polyol

DMCHA: N,N-Dimethylcyclohexylamine

FAME: Fatty Acid Methyl Ester

FTIR: Fourier Transform Infrared Spectroscopy

HBPU: Hyperbranched Polyurethane

HDI: 1,6-Hexane Diisocyanate

HMDI: Dicyclohexane Diisocyanate

IPDI: Isophorone Diisocyanate

KOH: Potassium Hydroxide

MFCG: Methanol-Free Crude Glycerol

MFCG-10: Polyurethane Foam (containing 10% methanol-free crude glycerol, 90% polyether polyol)

MFCG-30: Polyurethane Foam (containing 30% methanol-free crude glycerol, 70% polyether polyol)

MFCG-50: Polyurethane Foam (containing 50% methanol-free crude glycerol, 50% polyether polyol)

MFCG-80: Polyurethane Foam (containing 80% methanol-free crude glycerol, 20% polyether polyol)

MDI: Diphenylmethane Diisocyanate

NaOH: Sodium Hydroxide

NDI: Naphthalene Diisocyanate

PEG: Polyethylene Glycol

PET: Polyethylene Terephthalate

PHD: Polyharnstoff Dispersion

PG: Pure Glycerol

PG-10: Polyurethane Foam (containing 10% pure glycerol, 90% polyether polyol)

PG-30: Polyurethane Foam (containing 30% pure glycerol, 70% polyether polyol)

PG-50: Polyurethane Foam (containing 50% pure glycerol, 50% polyether polyol)

PG-80: Polyurethane Foam (containing 80% pure glycerol, 20% polyether polyol)

PMDETA: Pentamethyldiethylenetriamine

PMDI: Polymeric Diphenylmethane Diisocyanate

PPDI: P-Phenylene Diisocyanate

PTMEG: Polytetramethylene Ether Glycol

PU: Polyurethane

PUD: Polyurea Dispersion

PUF: Polyurethane Foam

SEM: Scanning Electron Microscopy

TDI: Toluene Diisocyanate

TGA: Thermogravimetric Analysis

THF: Tetrahydrofuran

TMXDI: Meta-tetramethylxylene Diisocyanate

TPU: Thermoplastic Polyurethane

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SUMMARY

Polyurethanes are important polymers as their mechanical, thermal, chemical properties can be controlled by the reaction of various polyols and diisocyanates. Polyurethanes have wide application areas, insulation foams, furniture applications, automotive, coatings, and biomedical, many other uses. In this study, commercial and biobased polyurethane foams were produced and required properties were determined. Commercial (polyether), crude glycerol, methanol-free crude glycerol and pure glycerol were used as polyols. All types of polyols were reacted with polymeric diphenyl methane diisocyanates (PMDI) for the production of insulation foams. Crude glycerol is a by-product of the biodiesel production, and it is a kind of biofuel residues, so its purification cost is high for Small and Medium Sized Enterprises. Methanol-free crude glycerol is a kind of crude glycerol whose methanol recovered for reuse the biodiesel production. Thermal properties of polyurethane foams were examined by thermogravimetric analysis (TGA) and thermal conductivity tests. The structures of polyurethane foams were confirmed by Fourier Transformed Infrared (FTIR). Changes in surface structure were investigated by Scanning Electron Microscopy (SEM). Mechanical properties of polyurethane foams were determined by compression tests. This study identifies the critical aspects of polyurethane foam formation by the use of various polyols and furthermore offers new uses of crude glycerol and methanol-free crude glycerol which are waste products from biodiesel industry.

BİYODİZEL ATIKLARINDAN BİYO-KÖKENLİ POLİÜRETAN KÖPÜK ÜRETİMİ

ÖZET

Poliüretan çeşitli polioller ve diizosiyanatların reaksiyonu ile mekanik, termal, kimyasal özellikleri kontrol edilebilen önemli polimerlerdendir. Yalıtım köpükleri, mobilya uygulamaları, otomotiv, kaplama ve biyomedikal gibi geniş uygulama alanına sahiptirler. Bu çalışmada ticari ve biyo-kökenli poliüretan köpükler üretilip özellikleri incelenmiştir. Ticari (polieter) poliol, ham gliserol, metanolü uzaklaştırılmış ham gliserol ve saf gliserol poliol olarak kullanılmıştır. Tüm polioller polimerik difenilmetan diizosiyanat (PMDI) ile reaksiyona sokularak yalıtım köpükleri üretilmiştir. Ham gliserol biyodizel üretiminin yan ürünlerinden biridir ve saflaştırılması Küçük ve Orta Ölçekli İşletmeler için yüksek maliyetlidir. Biyodizel üretiminde metanol tekrar kullanıldığı için ham gliserolden metanol uzaklaştırılarak metanolü uzaklaştırılmış ham gliserol elde edilir. Poliüretan köpüklerin termal özellikleri Termogravimetrik Analiz (TGA) ve ısı iletkenlik testi, yapıları Fourier Dönüşümlü Kızılötesi Spektrum (FTIR), yüzey yapısındaki değişiklikler Taramalı Elektron Mikroskobu (SEM) ile incelenmiştir. Mekanik özellikleri basma testi ile tespit edilmiştir. Bu çalışma, çeşitli poliollerin kullanımı ile poliüretan köpüğü üretiminin kritik yönlerini tanımlamaktadır. Ayrıca ham gliserol ve metanolü uzaklaştırılmış ham gliserol gibi sanayi atık ürünlerine yeni kullanım alanları sunmaktadır.

1. INTRODUCTION

Polymers are large, long-chain molecules that are vital to our life. Proteins and enzymes in our body, cellulose and starch in the plants are some examples of the polymers. However, generally plastics and rubbers are known as polymers in daily life.

Polymers are formed with the covalent bonding of n times small molecules which are called as monomers. They are used in all areas due to some properties, such as easy shaping and low production cost. There are three types of polymers based on the physical properties; thermosets, thermoplastics and elastomers.

Thermoplastic polymers are melting and re-formable polymers when they heated. Once melting, then they reshape with the common techniques which are injection and extrusion molding. Thermoplastic polymers' chains are found in linear and branched structure, not crosslinked. Polyethylene, polypropylene, polystyrene, polyvinylchloride and polycarbonate are some common examples of thermoplastic polymers.

Elastomers, which are crosslinked rubbery polymers, elongate very highly under tensile force. When the force is removed, they return the first length. The most commonly used and known elastomers are polyisoprene (natural rubber), polybutadiene, polyisobuthylene and polyurethane. The differences between thermoplastics and elastomers are mechanical properties. The elastomeric materials have elasticity or bouncing. On the other hand, thermoplastics are elastic to the specific point, and then they deform and break.

Thermoset polymers are cured at the critical temperature and not softened when they heated again. Thermosets are often rigid materials because cross-links, which are formed with covalent bonds, restrict the movement of polymer chains. The properties of thermosets depend on the degree of cross-linking. The rigidity, high impact resistance, dimensional stability, thermal equilibrium, high temperature resistance, and solvent resistance are increased with the degree of cross-linking. Nowadays, the popular thermoset resins are phenolic resins, urea and melamine based thermosets which are formed with formaldehyde by condensation reaction. Other thermoset resins are epoxies, unsaturated polyesters, urethane foams, surface coatings alkydes.

1.1 Polyurethanes

The debut of Nylon 66, invented by W. Carothers of E.I. DuPont de Nemours & Co. in the mid-1930s, was a big stimulus to chemists for pioneering synthetic polymers. Since then, many exploratory studies in polymer synthesis have been carried out worldwide. Polyurethanes, which are in the family of polymers, were first investigated by Otto Bayer and his collaborators [1].

Polyurethanes, also referred to as urethanes, are characterized by the urethane linkage:

$$\text{-NH-C(=O)-O-}$$

The linkage is formed by the reaction of organic isocyanate groups with hydroxyl groups as shown by the model reaction in Reaction 1, although other groups, such as ether, ester, biuret, allophanate, amide, and others may be present in the polymer molecule [1].

$$\text{R-NCO}+\text{R}^{'}\text{-OH}\rightarrow\text{R-NH-C(=O)-O-R}^{'} \qquad (Rxn\ 1)$$

In this reaction, diisocyanate groups have NCO groups and hydroxyl (OH) groups are called as polyol. These reactants have six kinds of reactions: addition, condensation, dimerization, cyclotrimerization, radical polymerization and thermal dissociation of addition compounds.

Diisocyanates are named according to their NCO content and functionality. They are divided into two; aliphatic and aromatic diisocyanates.

Aliphatic diisocyanates were first synthesized by Wurtz in 1849 [1]. The common types of aliphatic diisocyanates are 1,6-hexane diisocyanate (HDI), isophorone diisocyanate (IPDI), dicyclohexane diisocyanate (HMDI), meta-tetramethylxylene diisocyanate (TMXDI), transcyclohexane diisocyanate (CHDI).

Another type, aromatic diisocyanates were first produced with pyrolysis of symmetric diphenyloxamide in 1950 by Hoffmann. Toluene diisocyanate (TDI); two isomers 2,4 and 2,6, diphenylmethane diisocyanate (MDI); three isomers 4,4', 2,4' and 2,2', P-phenylene diisocyanate (PPDI), naphthalene diisocyanate (NDI) are the common types.

In addition, there are also modified diisocyanates which are prepared by incorporating at least one modifier linkage into monomeric diisocyanates. Such linkages include urethane, carbodiimide, allophanate, biuret, amide, imide, isocyanurate, 2-Oxazolidone. These modifications give some advantages, for example, lower vapor pressure, increased viscosity for stabilized foaming, and controllable reactivity. Some examples of them include isocyanate-terminated quasi-prepolymers (semi-prepolymers), urethane-modified MDI, carbodiimide-modified MDI, isocyanurate-modified TDI, and isocyanurate-modified IPDI [1].

Other reactant is polyol in the polyurethane production. Polyols are liquid oligomers or polymeric compounds with at least two hydroxyl groups [1]. Polyols are divided into two; petrochemical based and biobased polyols. The petrochemical based polyols are polyether and polyester polyols. Biobased polyols are lignin based and hydroxyl-containing vegetable oils, such as castor oil, soybean oil, palm oil, sunflower oil, etc.

In the petrochemical based polyols, the first polyol type is polyether polyol which are classified into four groups: polyoxyalkylene polyols, graft polyols, polyharnstoff dispersion (PHD) polyols, and polytetramethylene ether glycol (PTMEG). These polyol types are explained below:

1. Polyoxyalkylene polyols are prepared by the anionic polymerization of alkylene oxides, such as ethylene or propylene oxides.
2. Graft polyols, which are also called as polymer polyols or copolymer polyols, appeared in the mid-1960s. They include acrylonitrile-grafted as well as acrylonitrile- and styrene-grafted polyether polyols [1]. They have high percent of grafting in the commercial polyols about 30-50%.
3. Polyharnstoff dispersion (PHD) polyols are also known as polyurea dispersion (PUD) polyols. PHD polyols, which were developed by Mobay Corp., are usually produced by reacting TDI with hydrazine-containing polyether polyols under vigorous stirring [1].
4. Polytetramethylene ether glycol (PTMEG) is the last polyol type which is produced with the ring-opening polymerization of cyclic ethers such as tetrahydrofuran (THF). PTMEG is used for producing thermoplastic polyurethanes (TPUs), elastomers, fibers, and films.

Another polyol for the petrochemical based polyols is polyester polyols that have two kinds: aliphatic and aromatic polyols. Aliphatic polyester polyols are formed by the polycondensation reaction of dibasic acids with glycols, for example, ethylene glycol, propylene glycol, diethylene glycol, 1,4 butanediol, and 1,6 hexanediol. In this reaction, dibasic acids can be adipic acid, phthalic acid, and sebacic acid. This type of polyols is also prepared by the ring-opening polymerization of lactones, such as epsilon-caprolactone. Second kind of polyol is aromatic polyester polyols which are produced by the trans-esterification of recycled polyethylene terephthalate (PET).

The biobased polyols are derived from lignin and more kinds of vegetable oils by several different techniques.

Firstly, lignin is the second most abundant biopolymer in the world. The most important aspect of these findings is to find new applications for lignin. Lignin is produced as by-product from pulp- paper and lignocellulosic biofuel industries. It is mostly burned and used as energy source at a low price. The value added uses of lignin is another important area that plant scientists try to discover. Lignin is used for obtaining new types of engineering plastics due to these advantageous properties, like relative numerous reactive functional groups, moderate biodegradability, good adhesive, great variety of modification options, compatibility with various basic chemicals, adsorption and solution properties. On the other hand, its chemical structure and molecular weight depend on the plant species and extraction method, giving difficulties in use. New polymer is synthesized using polyurethane chemistry, with lignin polyols.

In 1996, Tan M. T. T. was used lignin with cardanol, which is a natural alkyl phenol from cashew nut shell liquid, as a polyol and TDI to produce polyurethane films [2]. Evtuguin D.V. *et al.* were used oxygen-organosolv lignin, isolated from spent liquors after delignification of wood in different acidic organic solvent-water media, with oligoethyleneoxide diisocyanate to manufacture crosslinked elastomeric polyurethanes in 1998 [3]. Alcoholysis and kraft lignin-based polycaprolactones (LigPCL) were synthesized by the polymerization of ε-caprolactone which was initiated by the hydroxyl (OH) group in lignin to produce polyurethane sheets with using MDI by Hatakeyama T. et al. in 2002 [4]. Cateto C.A. *et al.* produced the lignin-based polyurethane from polycaprolactonediol, lignin and MDI in 2008 [5]. In the next year, Cateto C.A. *et al.* also converted four types of lignin, Alcell, Indulin

AT, Curan 27-11P, and Sarkanda, into liquid polyols by a chain extension reaction with propylene oxide to manufacture rigid polyurethane foams [6]. In 2011, polyether polyol was synthesized from enzymatic hydrolysis lignin (EHL) by liquefaction with using the mixed solvents, polyethylene glycol (PEG) and glycerol by Jin Y. *et al*. [7].

The technology for polyurethanes enables to manufacture polyurethanes from bio-based system. Currently, there are numerous manufacturers of polyols from vegetable oils that have been commercialized and available at the large scale. In 2008, Tanaka R. et al. worked on palm oil-based polyol (PO-p) to prepare the polyurethane foams. They converted palm oil to monoglycerides as a new type of polyol by glycerolysis with using alkali catalyst and a solvent [8]. The soy-based polyols were produced by ring opening the epoxy groups in epoxidized soybean oil with various alcohol and a catalyst by Dai H. *et al*. in 2009 [9]. Deka H. *et al*. prepared *Mesua ferrea L.* seed oil-based hyperbranched polyurethane (HBPU) in 2010. *Mesua ferrea L.*, which is called as Ceylon ironwood, Indian rose chestnut, or Cobra’s saffron, is a species in the family Calophyllaceae. The oil was isolated by the solvent-soaking method and purified by the alkali-refining technique. Monoglyceride of the oil was prepared by the standard glycerolysis procedure [10]. In 2013, Das B. *et al*. manufactured sunflower (*Helianthus annuus L.*) oil-based polyols for hyperbranched polyurethane (HBPU) and linear polyurethane (LPU) as a film form by using TDI [11].

Nowadays, researchers are focused on plant based polyols for renewable resources. The oils are extracted from various plants and converted to polyols with certain reactions. In 2005, Araújo R.C.S. *et al*. used the *Eucalyptus* biopitch as a polyol which was obtained from wood tar distillation to produce flexible polyurethane foams with using MDI [12]. The wheat straw was liquefied in the mild condition with solvent mixture of ethylene glycol and glycerol by Wang H. *et al*. to prepare biodegradable polyurethane foams in 2007 [13]. The molasses and glycerol, which was by-product of biodiesel from palm oil, based polyols were synthesized with polyethylene glycol by Tay G.S. *et al*. in 2011, and they used also palm empty fruit bunches into the polyurethane [14]. In 2012, Hu S. *et al*. were produced biopolyols with the liquefaction of soybean straw into the crude glycerol, which was unrefined, to produce polyurethane foams [15].

Types of Polyurethanes

Polyurethanes are classified into five groups according to their application areas; CASE, synthetic leathers, biomedical, thermoplastic polyurethanes (TPU), and foams.

CASE is abbreviation of the Coatings, Adhesives, Sealants and Elastomers. Typical uses for this group include leather coatings, fabric coatings and adhesives, industrial maintenance and corrosion-resistant finishes, floor varnishes, seamless flooring, marine finishes, magnet wire coating, and concrete sealing [16].

Polyurethane coatings opened the door for automotive applications with the development of low-cost polyether polyols. Also, formulations and processing techniques continuously developed. Today, polyurethane coatings can be found on many different materials, such as in construction; building floors, steel trusses and concrete supports, to improve their appearance and lifespan [17-19]. There are three important components in the production of polyurethane coatings; di- or polyol, di- or polyisocyanate and chain extender. Polyurethane coatings are classified as belonging to one of five ASTM classifications, which are chiefly related to the curing mechanism: oil modified, moisture cure, blocked, prepolymer plus catalyst, and two components [16, 20].

In addition, polyurethane is often used as an adhesive, as well as a coating. Polyurethane adhesives adhere well to many substrates. The adhesion can be reinforced by hydrogen bridge bonds, which the polymerizing polyurethane can develop to many substrates. Moreover, free isocyanate groups present in the adhesive film can react with slight traces of moisture in or on the substrate surface. Every adhesive must be capable of flow for a certain time, so that it can be applied to the parts to be joined. It wets the substrate surfaces and yields initial adhesion that is not yet a load-bearing bond between the two parts. The adhesive joint attains the necessary cohesion by subsequent hardening [21]. Polyurethane adhesives are divided into four groups; polyurethane reactive adhesives, solventborne polyurethane adhesives based on hydroxyl polyurethane, polyurethane dispersion adhesives, polyurethane hot-melt adhesives.

Polyurethane sealants are useful for both industrial and commercial applications. A quality sealant will adhere to masonry, wood, concrete, steel, aluminum, and most plastics. The typical polyurethane sealant is hydrocarbon-based.

With the advances in water-based polyurethane technology, effective water-based or latex, sealants are now available. Polyurethane sealants may be pressed, layered, sprayed, or brushed onto joints, but the most common method of application is with a caulk gun. Most sealants are sold in tubes that fit the caulking gun.

Elastomers are used for the definition of flexible materials. Polyurethane elastomers are used in daily life and plastic, steel industry. Most importantly, they are alternative polymeric structures economically for rubber. Polyurethane elastomers have extremely flexible range of applications from little gasket to big griddle or cyclone so they have lower production costs than the other elastomers. Compared to other elastomers, polyurethane elastomers have excellent wear resistance, tear and tensile strength, high elongation and modulus values. In addition, their structures are non-deformable under load and permanent deformation values are excellent.

Natural leathers are used for some properties, such as beautiful appearance, softness and porous structure. These properties give them high water absorption and vapor permeability. On the other hand, they are less in the market due to their price and awareness of protecting animals. Synthetic leathers are alternative based on nonwoven support material coated with polyurethanes. Advantages of the synthetic leather are soft handle, crease resistance, strength and elongation at break, hygroscopic ability, ventilation, easy-care, easy volume-producing [22].

Polymer science and technology have developed in parallel with modern medicine. Polyurethanes are also developed in biomedical science. New families of polyurethanes have been designed and improved for the certain applications by a few small commercial firms. The first biomedical application of polyurethane is that polyester-urethane foam was used in breast implant in 1958 by Pangman. 1,4 butanediol, 1,6 hexanediol and ethylene glycol are generally used as chain extender in the biomedical applications. The sterilization process is an essential requirement for all medical polymers and defined as elimination of microbial life. There are three main sterilization methods; heat (dry heat and steam heat), gas (ethylene oxide) and radiation (gamma radiation and electron beam sterilization).

Polymers are usually mixed with some additives to produce suitable products for the end-use applications. For the biomedical polyurethanes, additives are divided into four groups; antioxidants, lubricants, plasticizers and additive functional groups. Biomedical polyurethanes are used in cardiovascular, ortho-rhino-laryngology, dentistry, regulation, esthetics, tissue reconstruction, contraception, reproductive systems, general surgical applications, orthopedics and biomechanics [23-37].

Thermoplastic polyurethane (TPU) is a kind of polymer with different characteristics that can be processed as it is soft when heated and the group without losing the structural integrity of the processing of multiple times, is capable of being cooled. TPUs are block polymer which are produced with three basic raw materials (polyol or long chain diol, chain extender, or short chain diol and diisocyanate) in specific way. Thermoplastic polyurethanes consist of two blocks, soft and hard. Soft block is polyol part, gives the flexibility and elastomeric characteristics. Hard block is composed of between diisocyanate with a chain extender, returns the physical toughness and performance characteristics in TPU. There are two types of TPU production; batch and continuous process. The main sectors are used as follows; shoe soles, automotive: interior, exterior, bonnet and six, engineering: hydraulic and pneumatic, medical: serum bag, wound dressing, surgical drapes, pipe, hose and tubing, wire and cable, film and sheet [38].

Polyurethane Foams

Polyurethane foams debuted over 70 years ago. At the present time these types of foams are the largest segment in the foam industry. Polyurethane foams are block polymers that prepared by the reaction of polyols with diisocyanates in the presence of catalysts, surfactants and blowing agents. The characteristics of polyurethane foams are changed with the properties of reactants, such as, molecular weight and functionality of polyols. Diisocyanates act as the jointing agent of polyols [1].

Blowing agents are the key materials for foams. Gas generation is an essential part of foam formation. There are two kinds of gas generation in the foam preparation, chemical and physical. In chemical gas generation, chemical compounds react with the isocyanate groups and generate carbon dioxide gas. Water, boric acid and enolizable organic compounds are some blowing agents which are used for chemical gas generation.

Physical blowing agents are liquids that have low boiling points and non-reactivity to isocyanate groups; they vaporize by the exotherm of foaming reaction. Some examples are fluorine containing compounds, such as C5-hydrocarbons, azeotropes with or without halogen, and liquefied carbon dioxide.

Catalysts for the preparation of polymeric foams are classified five types, such as gelling, blowing, cyclotrimerization, oxazolidone and carbodiimide catalysts. For the polyurethane foams, there are two kinds of reactions due to this reason two types of catalysts are necessary, tin catalysts “gelation catalysts” for the reaction between isocyanate and hydroxyl groups, tertiary amine catalysts “blowing catalysts” for the isocyanate and water reaction.

Silicone surfactants appeared as commercial products in about 1958 [1]. They are used with the catalysts (DABCO, tertiary amine, tin). The major factors of silicone surfactants are structural parameters of them, such as the ratios of ethylene oxide (EO)/(EO+PO), and (EO+PO)/Si.

Polyurethane foams are produced by mixing polyol, catalysts, surfactant, blowing agent and diisocyanate at the room temperature. In the two component system, there are three types of foaming methods; the one-step, the quasi-prepolymer, and the full-prepolymer (**Figure 1.1**). The one-step and quasi-prepolymer methods are generally used for the production of flexible and rigid foams. However, the full-prepolymer method was used only in early years of polyurethane foam industry [1].

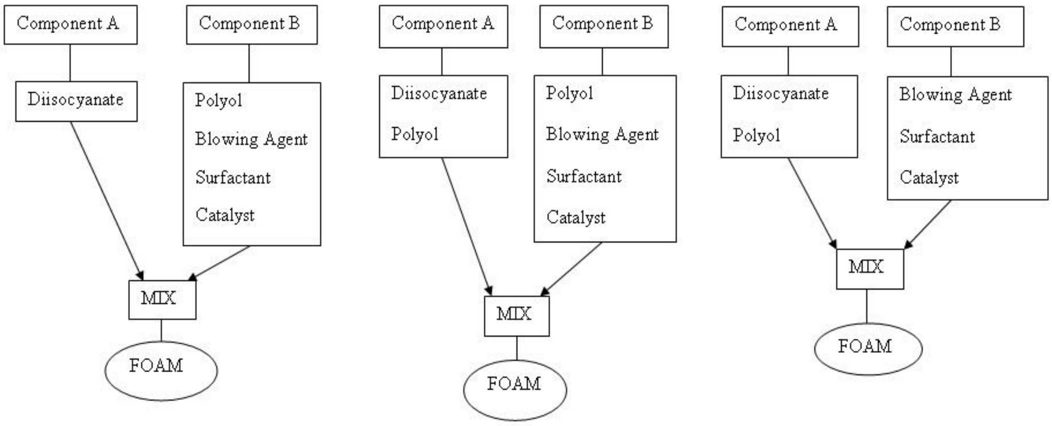


Figure 1.1 Polyurethane Foam Production Methods

There are three steps for the foaming processes; cup foaming, box foaming, and machine foaming. Cup foaming is also called as hand mixing. It is a simple method of evaluating foaming systems for comparison of raw materials and resulting foam properties. After optimum formulation obtained by cup foaming, box foaming and then machine foaming are employed. In the box foaming, the sizes of the box range from 15x15x15 cm to 30x30x30 cm. the necessary amount of raw materials is calculated depending upon the foam density expected. Last foaming step is machine foaming which has several types, such as large-box foaming, slabstock foaming, pour-in-place foaming, sandwich foaming, molding, spraying, and frothing process [39, 40].

Polyurethane foams are classified into two categories: flexible and rigid foams. In some cases semirigid foams and semiflexible foams are distinguished by the compression recovery phenomena [1]. Semirigid foams have high stiffness, low resiliency, and complete recovery after deep compression as flexible foams. On the other hand, they have incomplete recovery as rigid foams. Some important values of polyurethane foams are given in **Table 1.1**.

Table 1.1 Classification of polyurethane foams

Polyol	Rigid Foam	Semirigid Foam	Flexible Foam
OH number	350-560	100-200	5.6-70
OH equivalent no.	160-100	560-280	10,000-800
Functionality	3.0-8.0	3.0-3.5	2.0-3.1

Firstly, flexible polyurethane foams can be classified based on process into slabstock and molded foams. Slabstock foam is the continuous loaf of foam made by the continuous pouring of liquid foaming mixture on a moving conveyor. They include conventional polyether foam, high-resilience foam, viscoelastic foam, super-soft foam, energy-absorbing foam, semiflexible foam, and flexible polyester foam. Molded foams have been used for producing intricately shaped products, such as automotive seats, child seats, head restraints, vibration damping, arm rests, furniture cushions, and mattresses by the hot or cold molding processes.

Another type of polyurethane foams is rigid foams that consist of high percent of closed cells and have the following unique characteristics. Foams are prepared at ambient temperature without heating. They adhere to many kinds of materials, like steel, wood, thermosetting resins, foams, and fibers. Their densities are in a wide range from 20 to 3000 kg/m^3. They are resistant to petroleum, oils, and other non-polar solvents. Low-density foams have high thermal insulation properties. Due to this reason, rigid polyurethane foams are used as thermal insulation products to energy savings on the earth, such as refrigerators, freezers, refrigerated trucks, refrigerated containers, refrigerated warehouses, building and construction, chemical and petrochemical plants, water heaters, portable ice boxes, and thermos bottles.

1.2 Biobased Polyurethanes

In recent years, the use of biobased polyol has boomed in polyurethane industry and many commercial applications are arising. The isocyanate and the polyols obtained from biological resources are reacted to form biobased polyurethane. Many different forms of these two reactants are used to create different of products and applications with different strength and elongation values.

Nowadays, researchers are focused on plant based polyols for renewable resources. The oils are extracted from various plants and converted to polyols with certain reactions [2-7, 9]. Two types of polyols, castor oil and soy polyol are commonly used [41]. Initially, the castor oil was used owing to its high hydroxyl numbers that reacts with isocyanate groups. Simultaneously, another polyol is obtained from soybean which is one of the available vegetable oil. Despite of this reason, soy polyol based polyurethanes is limited since they have lower mechanical properties, odor arising during processing.

There are some studies to reinforce biobased polyurethanes to overcome the low mechanical properties with glass fiber and natural fibers like lignin. There have been some studies to synthesize polyurethanes from lignin to utilize lignin and to make green materials [42].

1.3 Waste Management

Waste is a kind of hazardous substance given to the receiving environment as a result of the production and use, to damage the human health and the environment directly or indirectly. Waste management includes reducing waste at source, separation on the specification, collection, temporary storage, recycling, transportation, disposal and control after disposal. A sub-focus in recent decades has been to reduce waste materials' effect on the natural world and the environment and to recover resources from them.

Waste management can involve solid, liquid or gaseous substances with different methods and fields of expertise for each. Waste management practices differ for developed and developing nations, for urban and rural areas, and for residential, industrial, and commercial producers. Waste management for non-hazardous residential and institutional waste in metropolitan areas is usually the responsibility of local government authorities, while management for non-hazardous commercial and industrial waste is usually the responsibility of the generator.

1.4 Biodiesel and Biodiesel Residues

Biodiesel has a better property as a solvent than standard diesel, since it cleans the engine. It is important due to increasing energy needs all over the world; fossil fuels have limited resource, alternative sources are needed, in the growing countries need more and more energy.

Biodiesel is an alternative and renewable fuel for diesel engines and it is also non-toxic and biodegradable. It is also used directly in most diesel engines without requiring extensive engine modifications [43]. Biodiesel is produced by transesterification reaction with fat or oil and alcohol; ethanol or methanol, in the presence of a catalyst; such as potassium hydroxide (KOH) or sodium hydroxide (NaOH) (**Figure 1.2**).

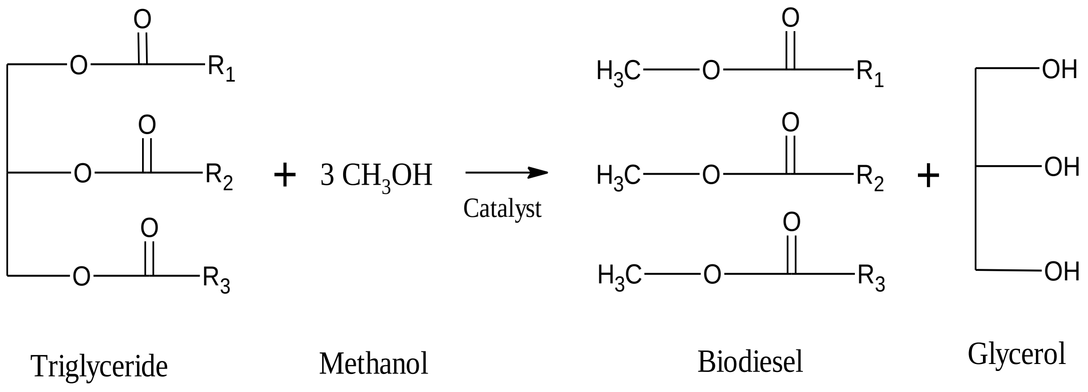


Figure 1.2 Transesterification Reaction

Biodiesel can be manufactured from animal fats, vegetable oils, used cooking oils, and new generation material; algae. Soybean, corn, canola, palm, sunflower, beef tallow, pork land are common used fats or oils as raw materials of biodiesel production. The product of the reaction is fatty acid methyl esters, FAME, which are known as biodiesel, and glycerol which is co-product [43, 44].

In the biodiesel process, there are four production steps; oil purification if the waste oil used, oil neutralization, transesterification in the reactor, settling and separation. In the purification step, oil is filtered to remove dirt, charred food, and other non-oil material. In addition, water is removed since it hydrolyses fats to form free fatty acids, which then form soap (**Figure 1.3**).

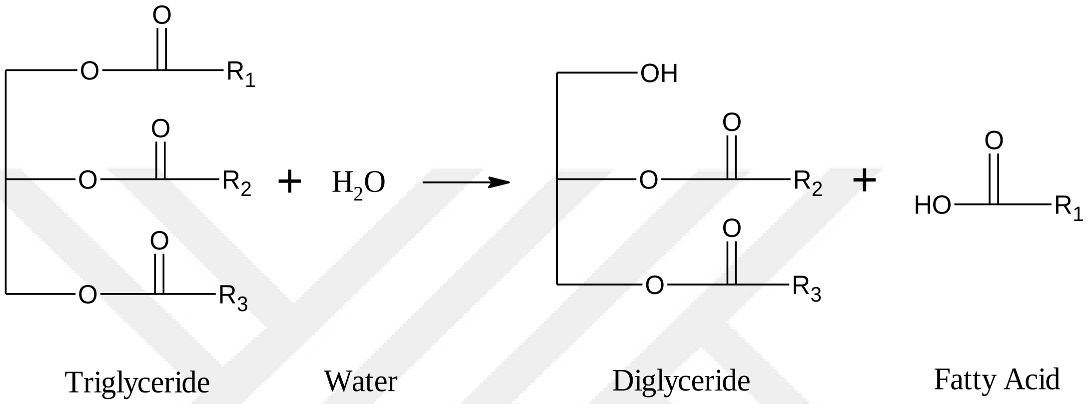


Figure 1.3 Fatty Acid Formation

Another step is neutralization for free fatty acids, oil is titrated in order to determine their concentration in the oil sample, and then the quantity of base required to neutralize.

After oil purification and neutralization steps, oil is reacted with excess amount of methanol in the presence of catalyst about 1-2 hours at 60°C. In the outlet stream of the reactor, there are the products of transesterification reaction; biodiesel and glycerol, also in different amount of catalyst, methanol, and soap.

Biodiesel and glycerol are separated in the settling; upper part is biodiesel, methanol and catalyst, crude glycerol is in the bottom. After catalyst, soap and methanol removal, biodiesel is obtained. With every 3 gallons of biodiesel, 1 kg of crude glycerol is produced and it shows very low value because of its impurity.

Crude glycerol is a kind of solution which includes glycerol (50-60% purity), methanol, catalyst, soap, salt and water. Firstly, methanol is removed from the crude glycerol to reuse in the production. From methanol-free crude glycerol (80-90% purity), other components are separated with some purification techniques, and then pure glycerol is attained [45-47] (**Figure 1.4**).

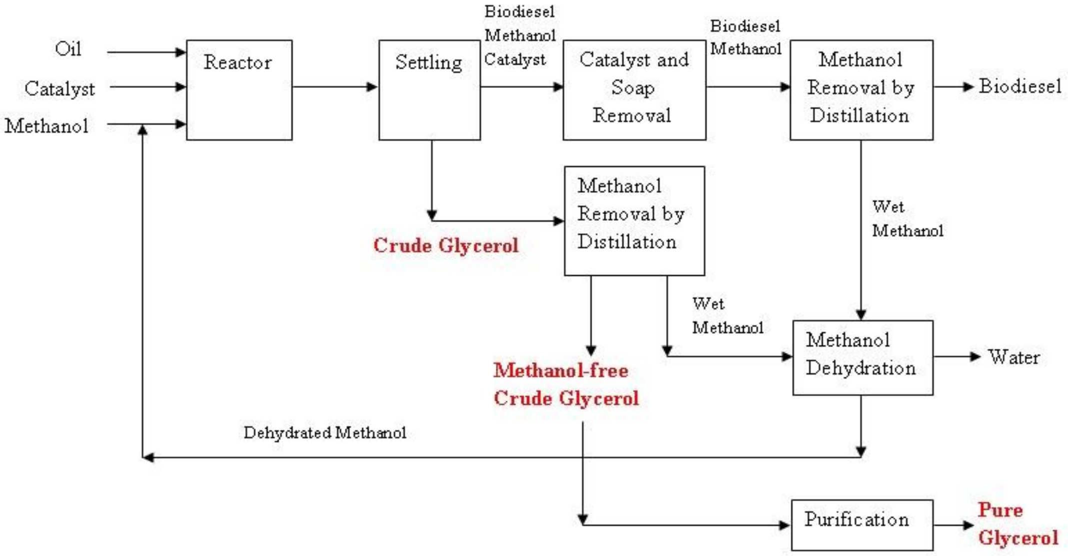


Figure 1.4 Biodiesel Process

As the global biodiesel production increases exponentially, the resulting crude glycerol is extensively high and become issues due to their disposal of effective utilization. On the other hand, pure glycerol is used in animal feeds, hand creams, toothpaste, soaps, and lubricants. In order to upgrade the crude glycerol to those high end applications, it should undergo various purification stages such as bleaching, deodoring, and ion exchange. Normally, this is not affordable or economically feasible for most of the small and medium ranges industries. Hence, it is necessary to investigate the value-added uses of crude glycerol in various biomaterial applications such as chemicals/monomers, plasticizer, hydrogen generation, carbon source for bacterial growth, and polyesters production [48].

In this study, the effect of the polyol-glycerol composition on the properties and structure was investigated by FTIR, TGA, SEM, mechanical and thermal tests.

2. EXPERIMENTAL

This study has two main parts; polyurethane foam preparation and their characterization.

2.1 Materials

In this research, four different types of polyurethane foams were prepared with one-step foaming method by cup foaming. Polyether polyol, crude glycerol, methanol-free crude glycerol, pure glycerol and PMDI are the raw materials. Other additives for the PUF preparation are two types of catalysts, surfactant and pure water as a blowing agent.

Polyether polyol (CPP) was provided from Oltchim S.A. (Valcea, Romania) with the hydroxyl number is 400 mg KOH/g and functionality value is 4.5. It has a commercial name of Petol PS 400-4G.

Crude glycerol (CG) and methanol-free crude glycerol (MFCG) were obtained from DB Agricultural Energy Co. (Izmir, Turkey) with the hydroxyl numbers were calculated (ASTM D 4274-05, Test Method B) as 1850 mg KOH/g and 1770 mg KOH/g, respectively. Crude glycerol contains approximately 50.0% glycerol, 25.0% water, 16.5% methanol, 5.0% soap, 3.0% sodium hydroxide, and 0.5% salt. Methanol-free crude glycerol includes 84.8% glycerol, 7.7% water, 4.5% soap, 2.3% sodium hydroxide, 0.5% salt and 0.2% methanol. These contents were measured by using Headspace Gas Chromatography Mass Spectroscopy (HS-GCMS), Agilent Technologies 7697A Headspace 7890A GC System, in Suleyman Demirel University.

Pure glycerol was provided from Akdeniz Kimya A.S. (İzmir, Turkey) with the hydroxyl number was calculated (ASTM D 4274-05, Test Method B) as 1865 mg KOH/g. Some values of raw materials are given in the **Table 2.1**.

Table 2.1 Some important values of raw materials

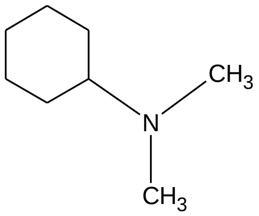
	Characteristics	**Values**
Polyether Polyol	**Hydroxyl Number**	400 mg KOH/g
	Viscosity	3000-5000 cP
	Functionality	4.5
Crude Glycerol	**Hydroxyl Number**	1850 mg KOH/g
Methanol-free Crude Glycerol	**Hydroxyl Number**	1770 mg KOH/g
Pure Glycerol	**Hydroxyl Number**	1865 mg KOH/g

Polymeric MDI (PMDI) was obtained from Bayer MaterialScience AG (Leverkusen, Germany) with 31.5% NCO content. The commercial name of PMDI is Desmodur 44V20L.

Two types of tertiary amine catalysts were used in this research; pentamethyldiethylenetriamine and N,N-dimethylcyclohexylamine are taken from Evonik Industries AG (Essen, Germany). Their commercial names are Tegoamin PMDETA and Tegoamin DMCHA, respectively. Silicon surfactant was obtained from Air Products Chemicals (Hamburg, Germany) and it has a commercial name of Dabco DC193. Chemical formulas of catalysts are given below:

Pentamethyldiethylenetriamine: $[(CH_3)_2NCH_2CH_2]_2NCH_3$

N,N-dimethylcyclohexylamine:



2.2 Preparation of Polyurethane Foams

Polyurethane foam with CPP was prepared by mixing approximately 100% polyether polyol, 1% surfactant, 0.4% catalyst, 0.4% co-catalyst and 2.5% water at the beginning forming the pre-mixture. Then PMDI was added about 102% at room temperature with mixing for the reaction occurs. Molecular ratio of isocyanate to hydroxyl groups (NCO/OH ratio) was kept at 1.18 for all samples.

Another type of polyurethane foams, with CG, were prepared by mixing polyether polyol and crude glycerol at different amounts, 90%-10%, 70%-30%, 50%-50%, and 20%-80%. Then 2% surfactant, 0.4% catalyst, 0.4% co-catalyst and 2.5% water were added into the polyol mixture. After forming the pre-mixture, PMDI was added at the same NCO/OH ratio.

Third type of polyurethane foams, with MFCG, were prepared by mixing polyether polyol and methanol-free glycerol at different amounts, 90%-10%, 70%-30%, 50%-50%, and 20%-80%. Then 1.5% surfactant, 0.4% catalyst, 0.4% co-catalyst and 2.5% water were added into the polyol mixture. After forming the pre-mixture, PMDI was added at the same NCO/OH ratio.

The last type of polyurethane foams, with PG, were prepared by mixing polyether polyol and pure glycerol at different amounts, 90%-10%, 70%-30%, 50%-50%, and 20%-80%. Then 1% surfactant, 0.4% catalyst, 0.4% co-catalyst and 2.5% water were added into the polyol mixture. After forming the pre-mixture, PMDI was added at the same NCO/OH ratio.

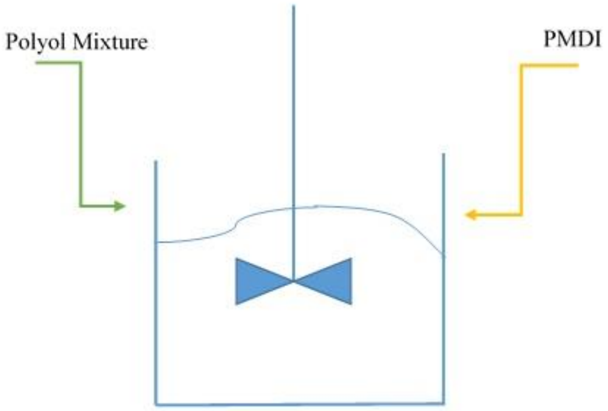


Figure 2.1 Mechanical Mixing

All samples were mixed with the mechanical mixer (Velp Scientifica, Overhead Stirrer, 0-2000 rpm) at 1500 rpm about 12 seconds, with crude glycerol mixing speed is 1000 rpm due to rapid foaming as a consequence of methanol presence (**Figure 2.1**) (**Table 2.2**).

Table 2.2 Mixing Values of Samples

		CPP	**CG**	**MFCG**	**PG**
Polyol Mixture	**Polyether Polyol**	100%	90%, 70%, 50%, 20%	90%, 70%, 50%, 20%	90%, 70%, 50%, 20%
	Glycerol	-	10%, 30%, 50%, 80%	10%, 30%, 50%, 80%	10%, 30%, 50%, 80%
	Surfactant	1%	2%	1,5%	1%
	Catalyst	0,4%	0,4%	0,4%	0,4%
	Co-catalyst	0,4%	0,4%	0,4%	0,4%
	Water	2,5%	2,5%	2,5%	2,5%
Diisocyanate	**PMDI**	102%	102%	102%	102%
Mixing speed	**(rpm)**	1500	1000	1500	1500
Mixing time	**(s)**	12	8	12	15

2.3 Characterization

2.3.1 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

FTIR analysis was conducted with Thermo Scientific, Nicolet iS5 FT-IR Spectrometer (ATR Mode) with 4000 and 400 cm^{-1} scan range to investigate the polyurethane structure and to determine if there is any free NCO in the polyurethane foams.

2.3.2 Mechanical Properties, Compression Testing

Compressive strength of PU foams were measured in accordance with BS EN ISO 844:2009. The dimensions of the samples were right prism with 50 x 50 x 50 mm. The maximum strength of the samples was measured with Shimadzu AGS-X 5 kN testing machine (**Figure 2.2**).

Figure 2.2 Compression Test Device

2.3.3 Thermal Conductivity

Thermal conductivity of the samples was measured with C-Therm TCi Thermal Conductivity Analyzer (**Figure 2.3**). Each sample was measured five times to find the optimum value.

Figure 2.3 Thermal Conductivity Device

2.3.4 Thermogravimetric Analysis (TGA)

Perkin Elmer Diamond TG/DTA was used for TGA analysis. The measurements were done from 30 °C to 630 °C with a heating rate of 10 °C/min under nitrogen atmosphere at atmospheric pressure. The analysis was used to determine the solid content left when the polymer was heated up to 630 °C.

2.3.5 Scanning Electron Microscopy (SEM)

Scanning electron microscopy, Quanta 400F Field Emission SEM was used at 20 kV. The samples were coated with gold in order to have conductive samples to measure and avoid charging.

3. RESULTS AND DISCUSSION

3.1 Visual Examination

A visual examination of the samples may reveal useful information. For example, the color can be used for identification of the PUF samples. When PMDI content increases, due to the hydroxyl number of polyol mixture, the color turns into yellow from 10% to 80%, respectively (**Figure 3.1**, **Figure 3.2**, **Figure 3.3**).

The shape of foams are disordered while glycerol contents increase. The volume of samples are also different one by one because of the mechanical mixing. Only 10% blends of glycerol types PUF have smooth surfaces, like the commercial one. In addition, while the purity of glycerol increases, the height of foam samples are raise up so the gas formation decreases.

Figure 3.1 PUF from Crude Glycerol

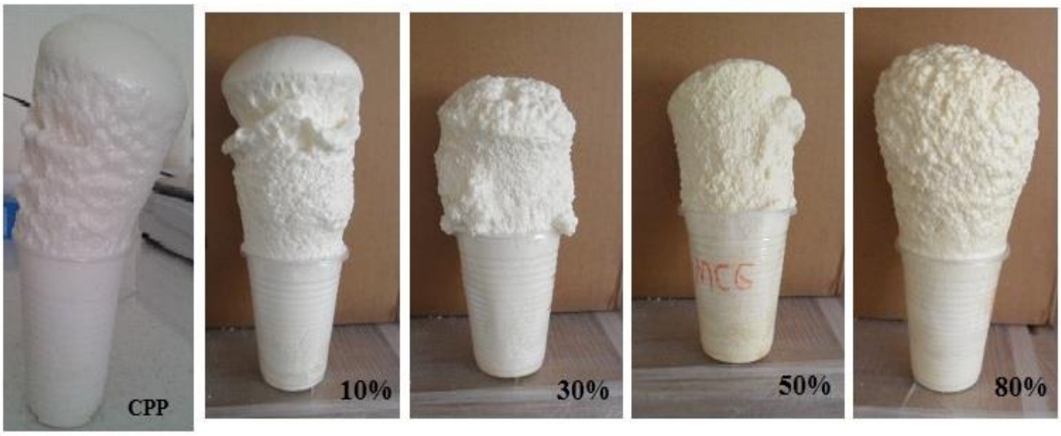


Figure 3.2 PUF from Methanol-Free Crude Glycerol

Figure 3.3 PUF from Pure Glycerol

3.2 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR was used to investigate changes of polyurethane polymerization with different glycerol types and different amounts. The isocyanate absorption band (-NCO vibration) is assigned at 2270 cm^{-1}. This absorbance can be used to monitor the isocyanate group conversion during the polymerization. The hydrogen bonded -NH stretching vibration associated to the urethane group is dominated between 3380 and 3360 cm^{-1}. Other important vibration is urethane (-C=O) vibration assigned at 1720 cm^{-1} (carbonyl region).

Figure 3.4 shows that the –NCO vibration peaks are neglected at 2270 cm^{-1} because of that the peak of CPP is higher than the samples of CG. This means there is no excess isocyanate in the polymerization. And then, for the urethane vibration

CG-10 has the maximum value which is 7,87 x 10^{-2} than the other foams. This type of PUF has also the maximum values for the –NH stretching vibration at approximately 3400 – 3300 cm^{-1}. CG-30 has the similar values of CG-10, 1,59 x 10^{-2} and 1,58 x 10^{-2}.

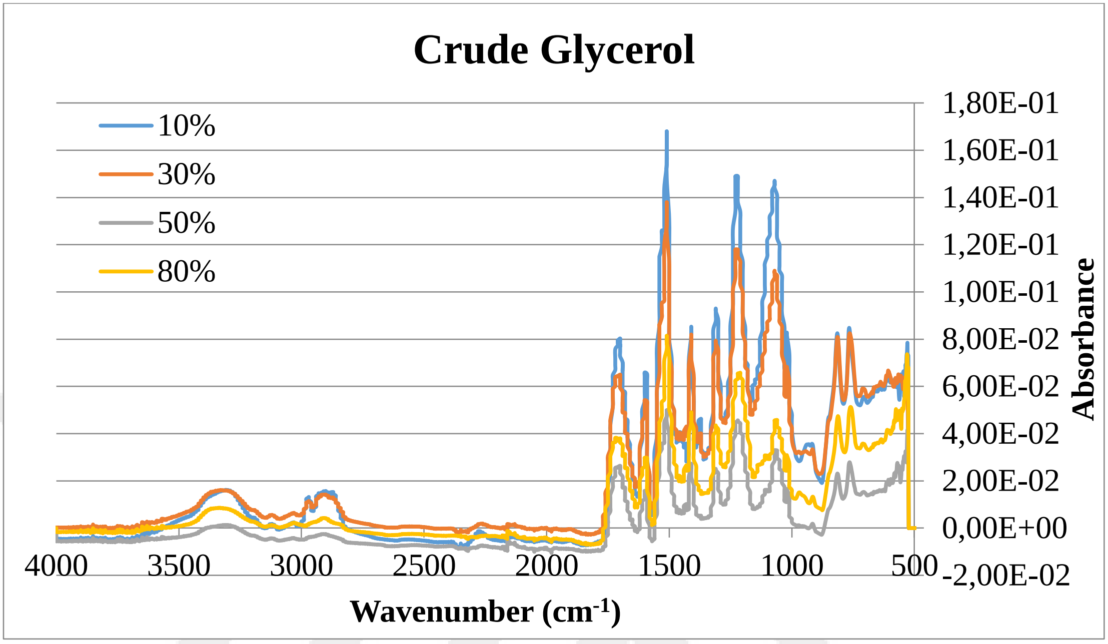


Figure 3.4 FTIR results of PUF with Crude Glycerol

The –NCO vibration peaks are similar for the all samples which are included methanol-free crude glycerol and they are lower than the commercial one, CPP. This means there is small amount of excess isocyanate in the polymerization. For the urethane vibration MFCG-30 and MFCG-80 have the maximum values than the other foams, respectively 9,21 x 10^{-2} and 5,45 x 10^{-2}. On the other hand, for the –NH stretching MFCG-80, 5,91 x 10^{-2}, has higher value than MFCG-30, 2,59 x 10^{-2} (**Figure 3.5**).

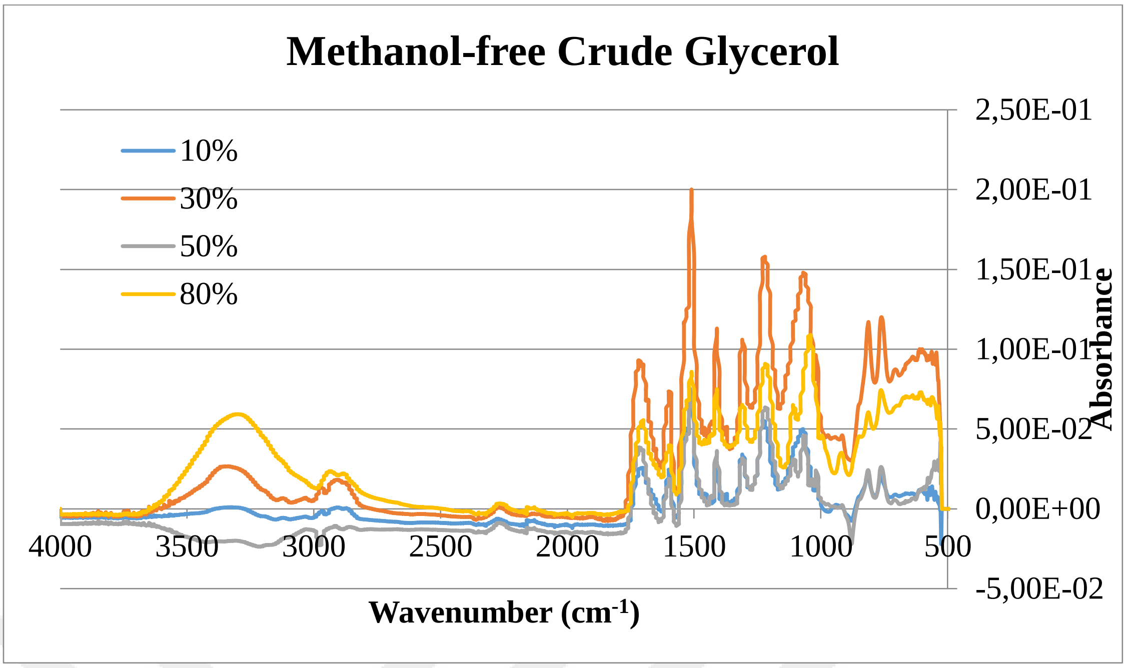


Figure 3.5 FTIR results of PUF with Methanol-Free Crude Glycerol

In the **Figure 3.6**, the –NCO vibration peaks are shown at 2270 cm^{-1} and PG-30 (2,71 x 10^{-2}) has the maximum values. During the polymerization, there is excess isocyanate. In addition, for the urethane vibration PG-80 has the maximum values, 12,9 x 10^{-2}, than the other foams. PG-10 (9,32 x 10^{-2}) has also similar values with PG-80. These amounts of PUF have also the maximum values for the –NH stretching vibration, PG-80 and PG-10, 4,12 x 10^{-2} and 1,82 x 10^{-2} respectively.

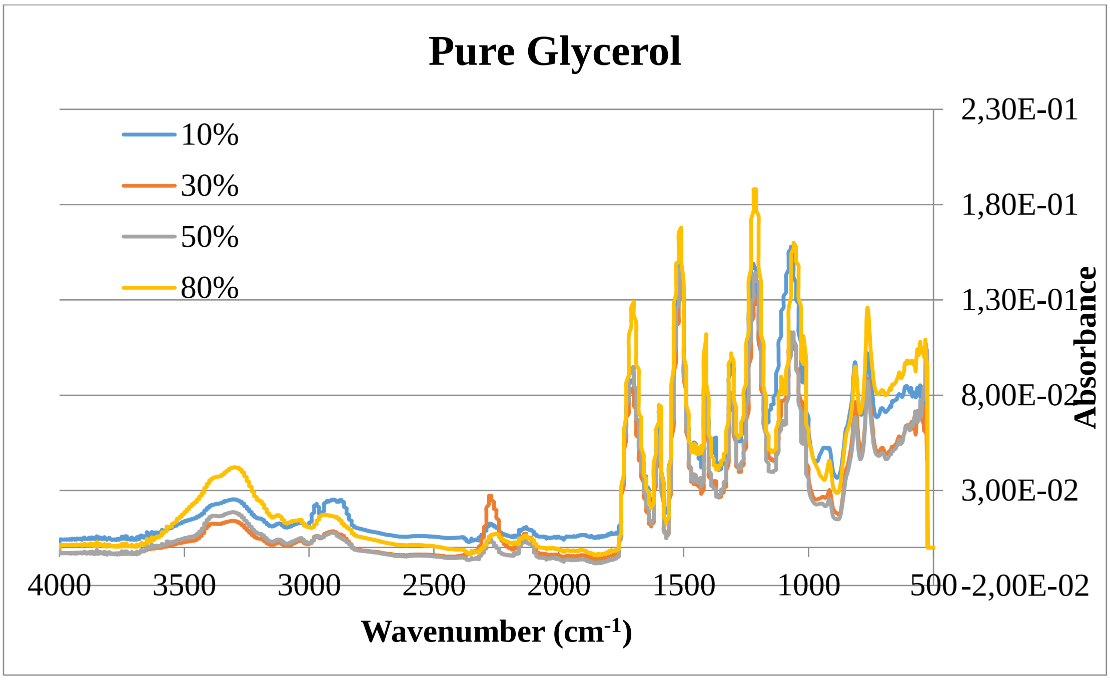


Figure 3.6 FTIR results of PUF with Pure Glycerol

FTIR results were given general information about chemical bonding of foams. If it is not ATR mode and cup foaming method, the results will be more detailed. FTIR results of samples are given in the Appendix Part with their details, sample by sample. All peaks, -NCO, urethane and –NH vibrations are also shown in the spectrums. According to the results, CG-10, CG-30, MFCG-80, MFCG-30, PG-80 and PG-10 are the similar with CPP.

3.3 Mechanical Properties, Compression Testing

A compression test determines behavior of materials under crushing loads. The specimen is compressed and deformation at various loads is recorded. Compressive stress and strain are plotted as a stress and strain diagram.

The results of the compression test are given in **Figure 3.7**.

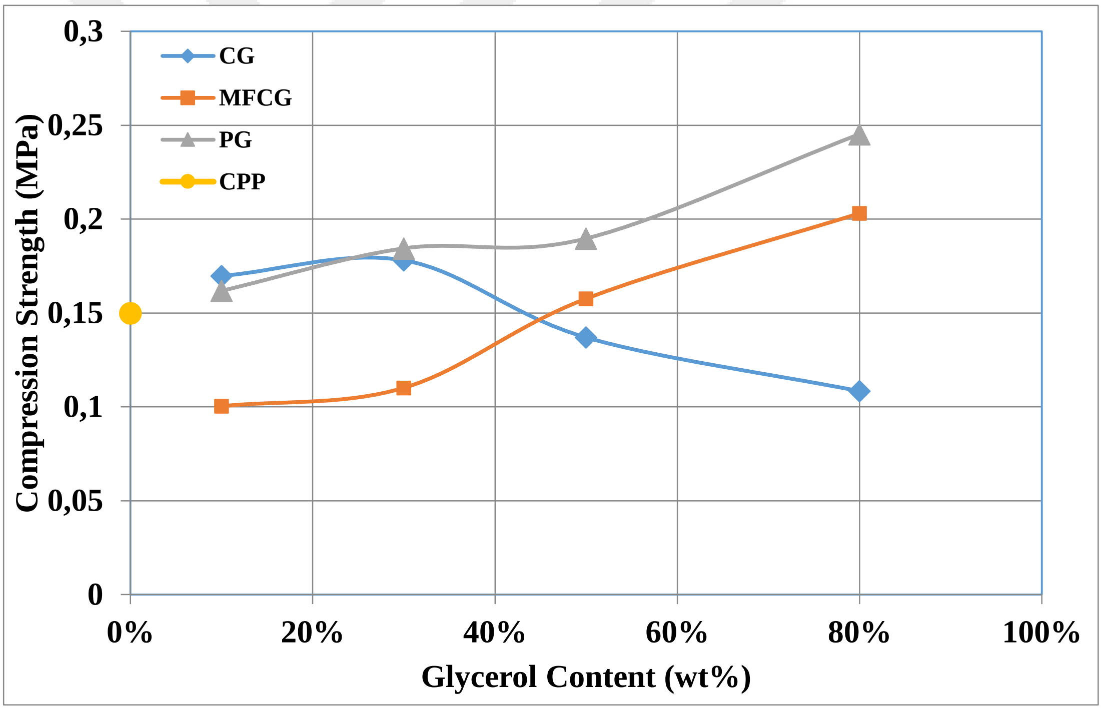


Figure 3.7 The compression test results of all samples

The compressive strength values are increased with increasing glycerol content for both PG and MFCG samples because of the purity of glycerol and the number of closed cell increase. However, compression values are decreased with increasing glycerol content until CG-30, according to FTIR results (**Figure 3.4**), urethane vibration is maximum. Due to irregular cells which are shown SEM photos (**Figure 3.12**), higher CO_2 and gas formation while preparing PUF, CG samples are more nondurable than the others. Compared to the pure PUF whose compressive strength is drawn in **Figure 3.7** from 0,1 to 0,15 W/m.K. For all samples, compressive strength, rigidity of foams is increased with purity of glycerol. This results are very important so the use of glycerol, pure glycerol (PG) and methanol-free crude glycerol (MFCG).

Zlatanic *et al.* (2004) synthesized the polyols based on midoleic sunflower, canola, soybean, sunflower, corn, and linseed oils [50].They determined that the mechanical strength increased with the hydroxyl number of the polyols. In this study, the hydroxyl number also increases with the purity of glycerol. Therefore, the compressive strength is increased.

Luo X. *et al.* (2013) researched the rigid polyurethane foams from biopolyols which was prepared with crude glycerol (22,9% glycerol, 10,9% methanol) [49]. The compressive strength of PUF was determined as 0,1845 MPa, it is higher than the commercial PUF. On the other hand, this value is less than PG-50 and PG-80 and MFCG-80. In addition, the compression value is higher than all samples with CG, so the methanol content is 16,5% and crude glycerol was reacted with sulfuric acid in the biopolyols production. As a result of this, the compressive strength of the rigid polyurethane foam, is produce from biopolyols with MFCG, will be higher.

3.4 Thermal Conductivity

Thermal conductivity is one of the most important properties for the insulation materials. Best insulation materials have the lowest thermal conductivity. Dry stagnant gas is one of the best insulating materials. The insulating properties of commercially available insulating materials are determined by the amount of gas held inside the material and the number of gas pockets. Therefore, the higher the number of cells and the smaller size, the lower thermal conductivity of such insulating material. These cells should not be interlinked, as this will allow convection of heat.

PUF is effective as an insulator because it has a high proportion (nearly 90%) of non-connected closed microcells, filled with inert gas. In this project, inert gas is carbon dioxide. Thermal conductivity values are measured with the device which uses a one-sided, interfacial, heat reflectance sensor that applies a momentary, constant heat source to the sample.

The cell structures in **Figure 3.12**, **Figure 3.13**, and **Figure 3.14**, for all types of glycerol, mixing ratio at 10%, are similar as the commercial one. The number of undamaged, closed cells are increased with the purity, so the unexpected gas formation decreases. As a result of these, the thermal conductivity decreases with the high number of cells and smaller cell size.

In the **Figure 3.8**, thermal conductivity values are shown for all samples. PG-10 has the minimum value is 0,028 W/m.K, SEM photos are supported that kind of PUF is close the commercial one. Secondly, thermal conductivity of CG-30 is 0,029 W/m.K. These two types of PUF are close the commercial one. Finally, four other samples are same thermal conductivity value with the commercial polyurethane foam, 0,030 W/m.K, MFCG-10 and MFCG-50, CG-10 and PG-30.

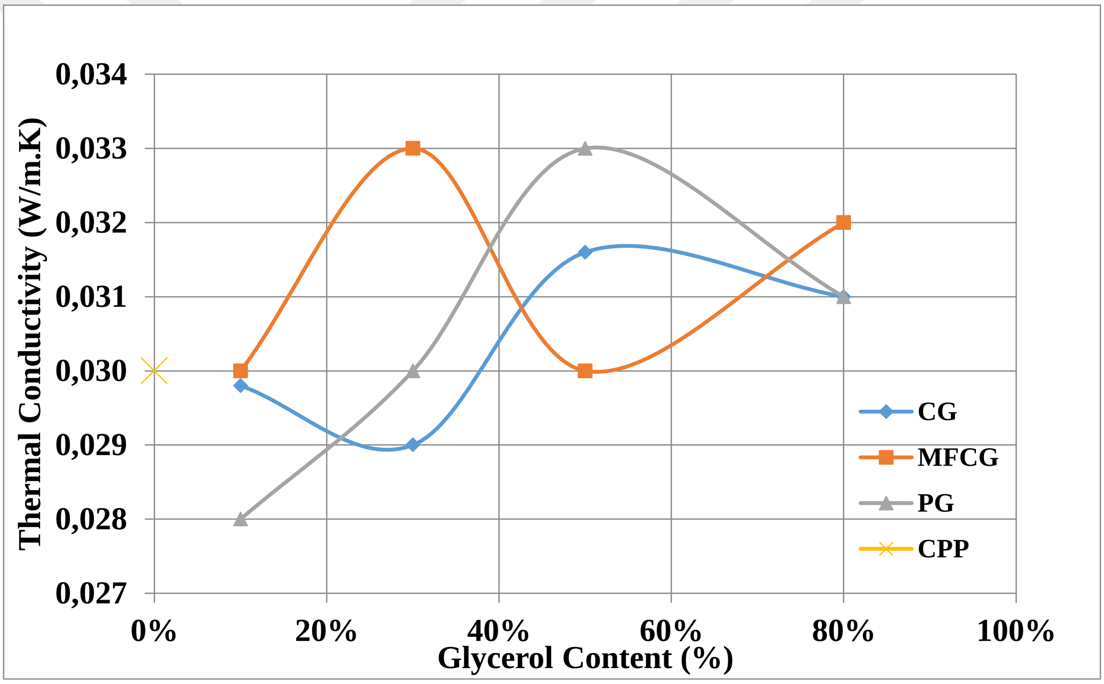


Figure 3.8 Thermal conductivity values for all PUF samples (*PUF with commercial polyether polyol: 0,030 W/m.K)

3.5 Thermogravimetric Analysis (TGA)

Figure 3.9, **Figure 3.10** and **Figure 3.11** show that the combination of TGA results of the PUF formed with crude glycerol, methanol-free crude glycerol and pure glycerol, with respectively. All samples of TGA/DTG curves are shown in Appendix Part.

For CG samples, thermal stabilities and residues left after heating are different from commercial PUF, because of their structures and gas formation. On the other hand, thermal stabilities of PUF with preparation MFCG samples are similar to CPP. In addition, the graph of MFCG-10 is the same with CPP. The thermal stabilities of PG samples did not change much, except PG-80. The graph of PG-10 is also the same with CPP, and lines are overlapping. Comparison of the solid content left, CG, MFCG and PG values are 25-35%, 29-35%, 33-42%, respectively.

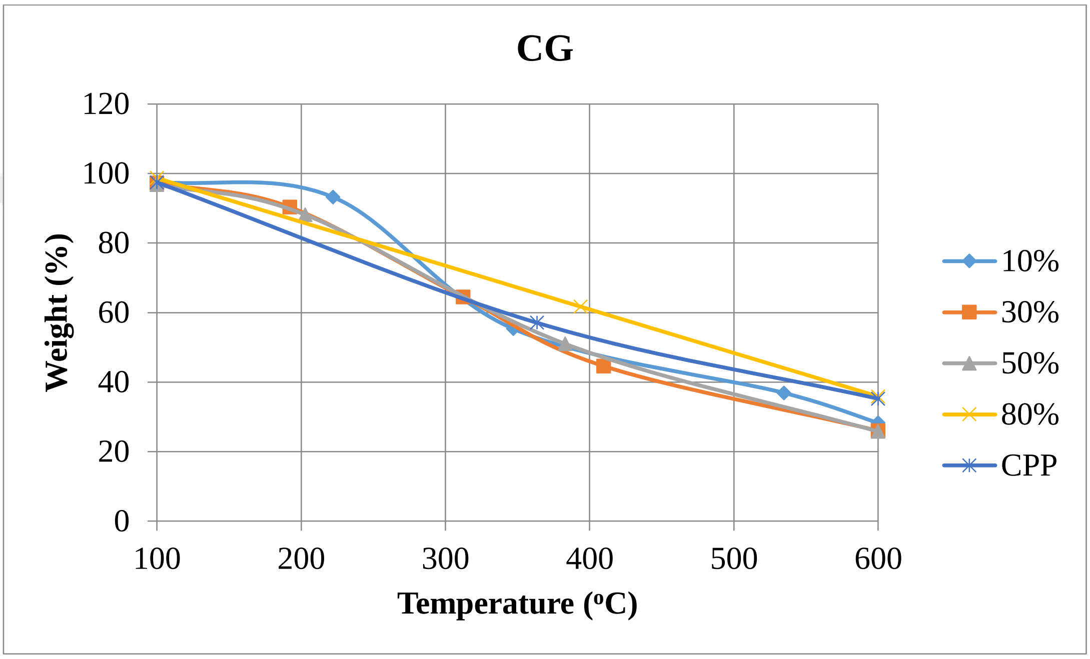


Figure 3.9 TGA results for all PUF samples with Crude Glycerol

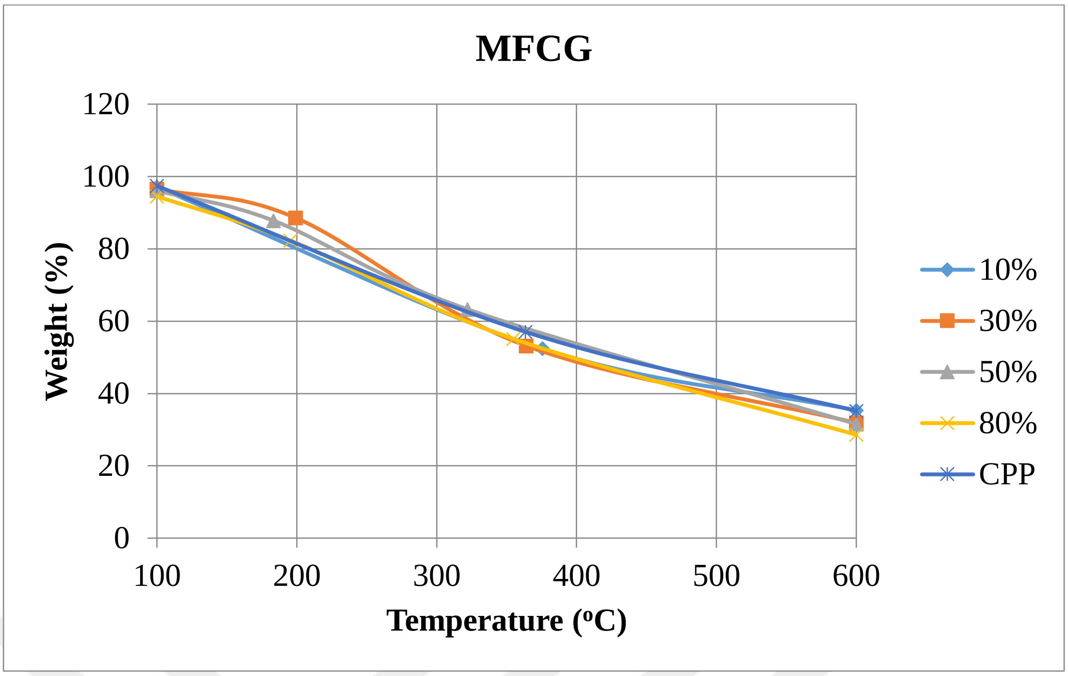


Figure 3.10 TGA results for all PUF samples with Methanol-free Crude Glycerol

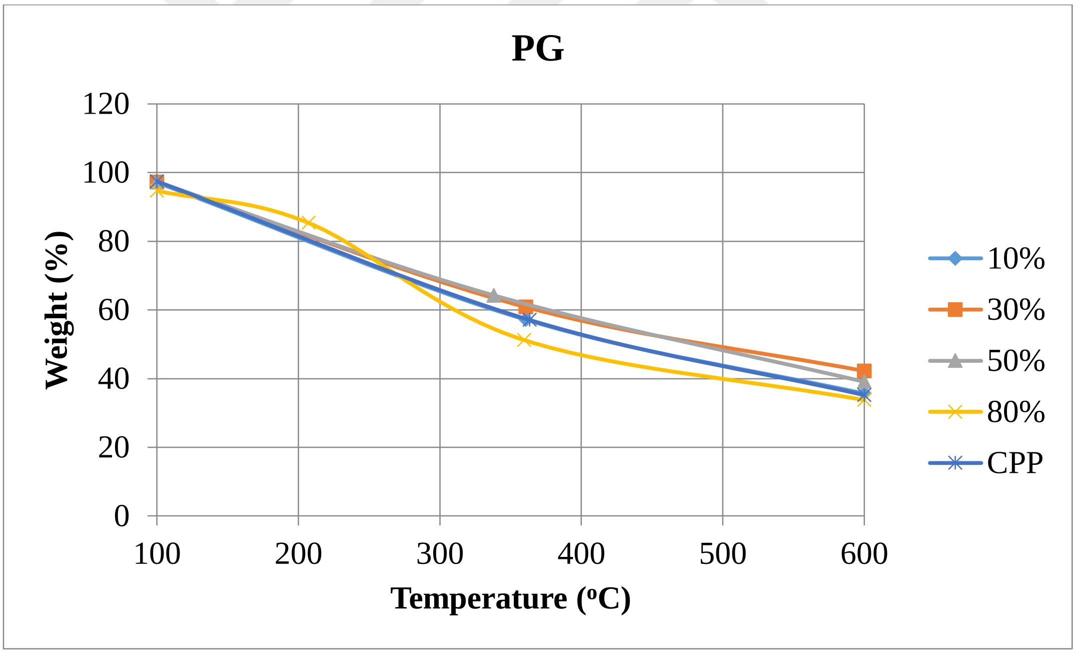


Figure 3.11 TGA results for all PUF samples with Pure Glycerol

3.6 Scanning Electron Microscopy (SEM)

The photomicrographs show the sizes and shapes of cell foams. The close cell structure is confirmed by the morphological analysis performed by SEM in **Figure 3.12**, **Figure 3.13** and **Figure 3.14** with enlargements of 50, 250 and 500 times, respectively. The structure of CPP is compact and complete. For samples with CG, PUF has lots of fragment and the inner structure was heavily damaged, and their cell size scale about 125 μm to 290 μm. For samples with MFCG, cell sizes are measured between 125 μm and 300 μm. In addition, for samples with PG, cell sizes are between 85 μm and 200 μm. According to CPP, whose cell size are between 180 μm to 375 μm, all samples are better for insulation. However, for all types of glycerol, it can be observed that the close cell structure is damaged with increasing glycerol content in commercial polyether polyol.

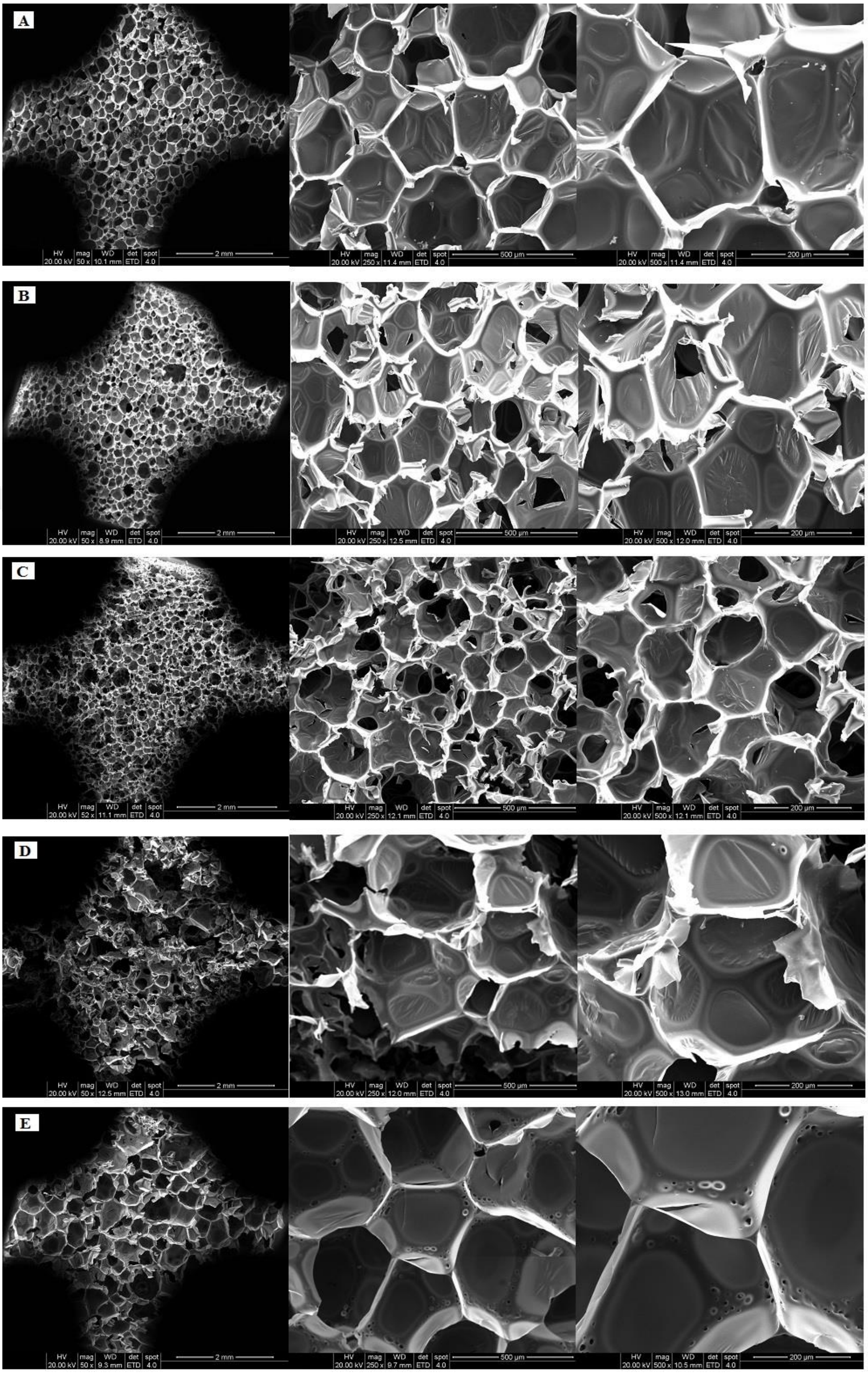


Figure 3.12 SEM photos of CG samples (A:10%, B:30%, C:50%, D:80% and E:CPP)

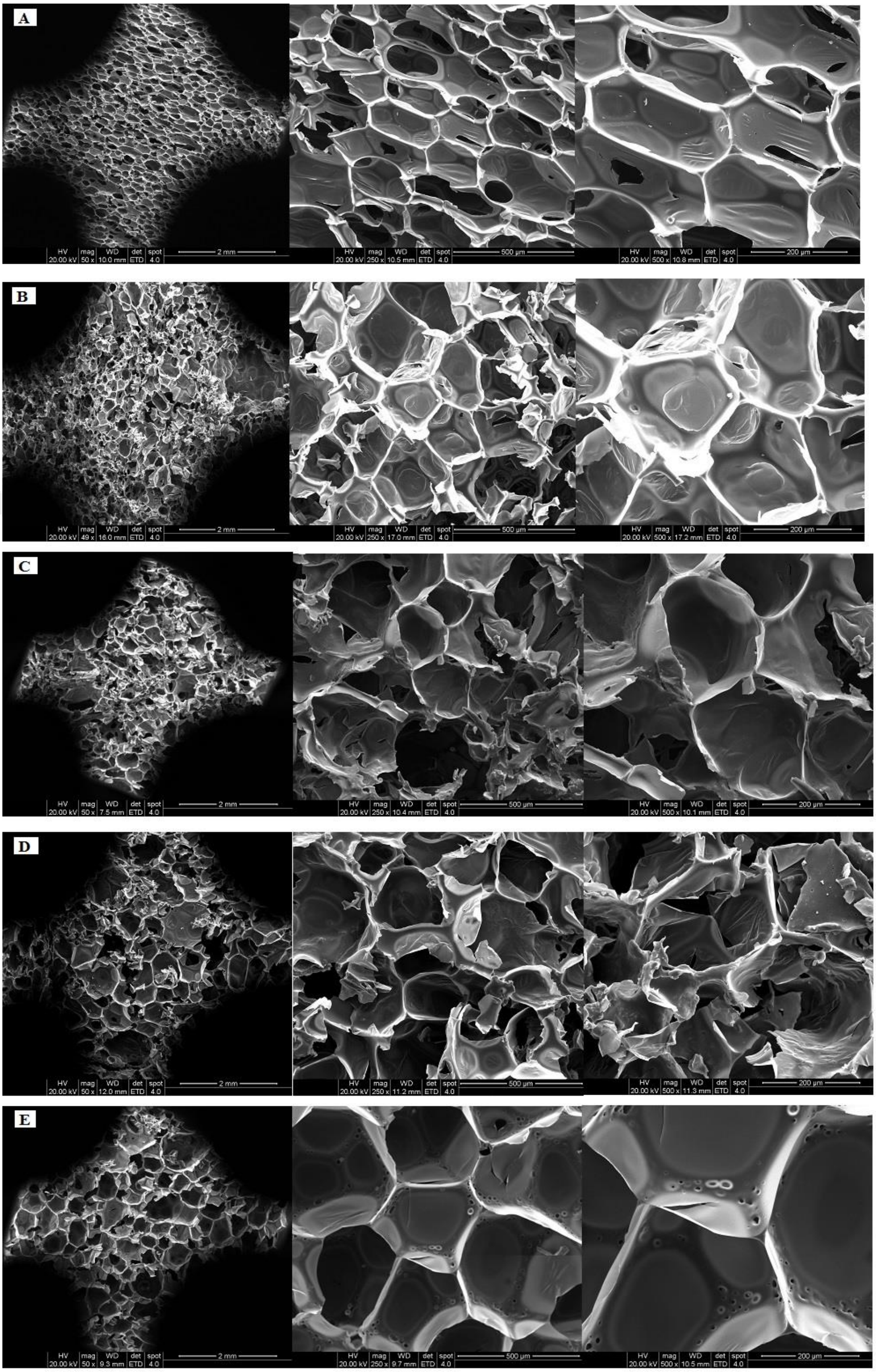


Figure 3.13 SEM photos of MFCG samples (A:10%, B:30%, C:50%, D:80% and E:CPP)

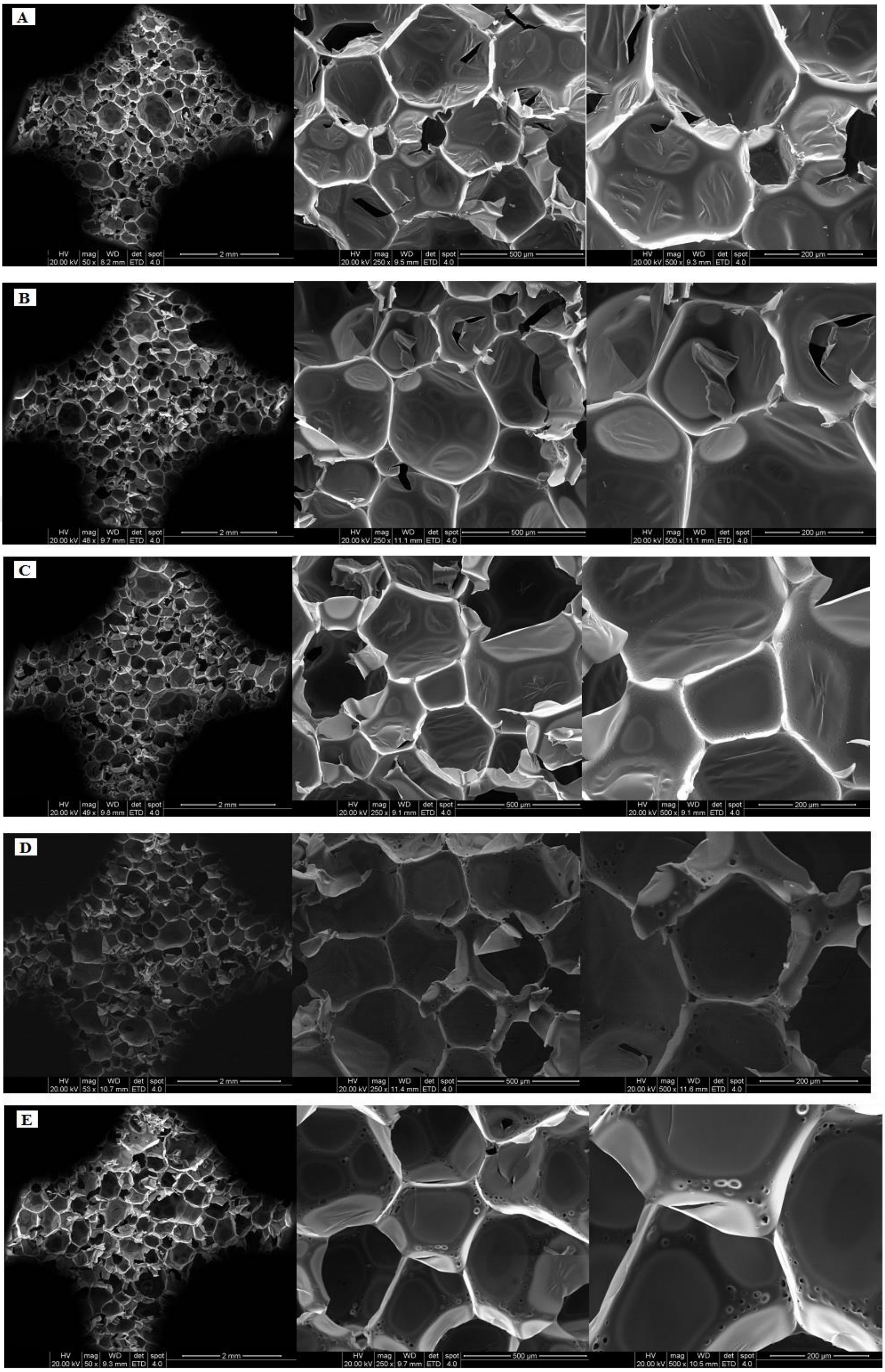


Figure 3.14 SEM photos of PG samples (A:10%, B:30%, C:50%, D:80% and E:CPP)

4. CONCLUSION

It is concluded from the results of this research that the glycerol is used for PUF production as a polyol. The mechanical and thermal properties of PUF has increased with the purity of glycerol. However, these properties has decreased with the glycerol content in polyol mixture increase. For all types of glycerol, 10% of glycerol-polyol mixture is similar as the commercial polyol. 30% mixing ratio has also acceptable results for MFCG and PG, except CG because of methanol content. PUF reaction is exothermic so the methanol is evaporated, and then it is effected the cell structure. The cell structure is one of the most important characteristic for the PUF which is used as thermal insulator.

In the previous studies of other researchers, crude glycerol was used to preparing the polyol. As a result of this study, MFCG will be used to produce biopolyols, comparison the mechanical and thermal values of CG and MFCG.

This study identifies the critical aspects of polyurethane foam production by new uses of crude glycerol and methanol-free crude glycerol which are by-products from biodiesel industry. And then, these by-products are value-added with this study.

5. FURTHER STUDIES

In this study, cup foaming method was used. The cup foaming method is basic, other methods should be used to getting more details.

In addition, only tertiary amine catalyst and its co-catalyst were used to preparation. If tin catalyst is also used to reaction between polyols and diisocyanate, so FTIR results will be different.

According to SEM results, for CG and MFCG, the amounts of surfactant should be higher than 2% to organize the cell structure, exactly.

In the previous study of another researchers, crude glycerol was used to preparing the polyol. As a result of this study, MFCG will be used to produce biopolyols, comparison the mechanical and thermal values of CG and MFCG, MFCG is more effective than CG.

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CURRICULUM VITAE

I was born in İzmir on 13.06.1987. I studied at Menemen Anatolian High School between 2001 and 2005. In addition, I graduated from Ege University, Chemical Engineering Department in 2010. During my education (2005-2010), I studied on polymers, and I took related lessons, like The Structured and Properties of Polymers, Recycling and Reuse of Plastics, Processes in Polymer Technology. My diploma project was Halogen-Free Fire Retardants for Polymeric Cable Sheat. I started to study in Master Degree in İzmir Katip Çelebi University, Material Science and Engineering Department on October, 2012. In master education, I took some elective courses, such as Surface Analysis Techniques, Biomedical Materials, Nanocomposites, Polymeric Composites, Biopolymers & Biocomposites.

Between February-2014 and May-2015, I worked in Doğa Gıda Co. Inc., where seed oils (sunflower, soybean and canola) and their oilcake are produced, as an Utilities Engineer. In 2011, I worked in detergent company as a Production Engineer.

I am advanced in Computer; Office Programmes (Word, Excel, Powerpoint), Programming (Visual Basic), and good at Drawing Programme (Autocad) and using ERP Programme.

Finally, I studied in some projects; design of a household refrigerator prototype, production of soap from vegetable oils, design of a house heating system using natural gas, reactor design for production of biodiesel from vegetable oil, design of a compact heat exchanger in heat recovery from stack gas, design of a continuous distillation column for a multi-component mixture, design of a methanol production plant.

APPENDIX

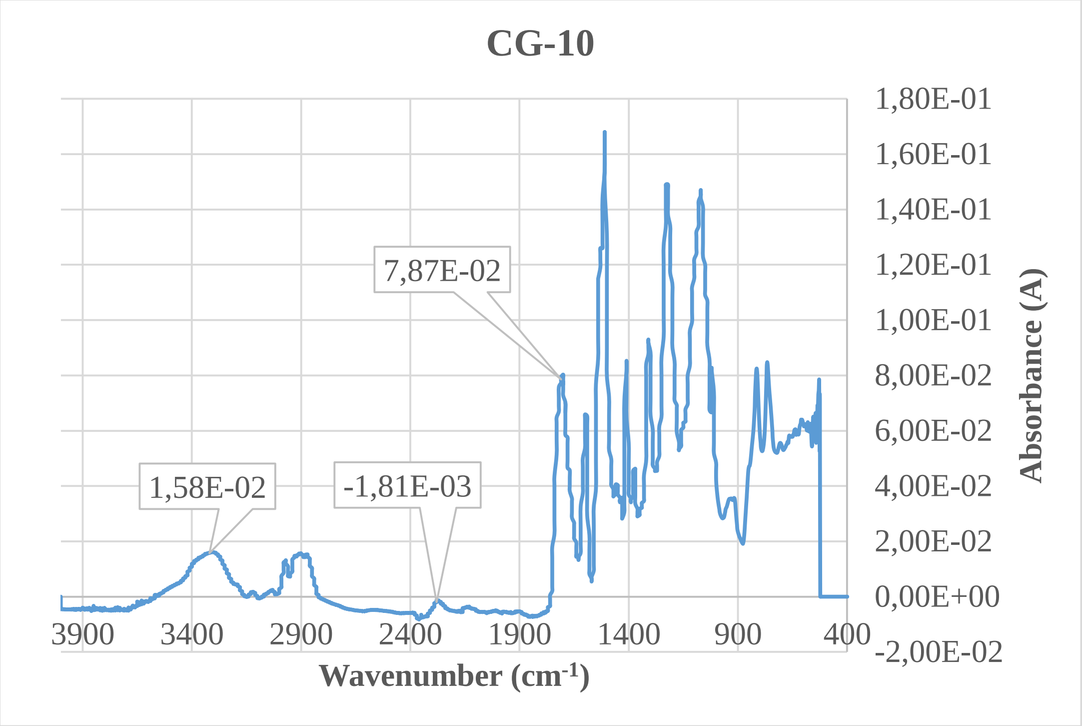

Figure 6.1 FTIR spectrum of CG-10

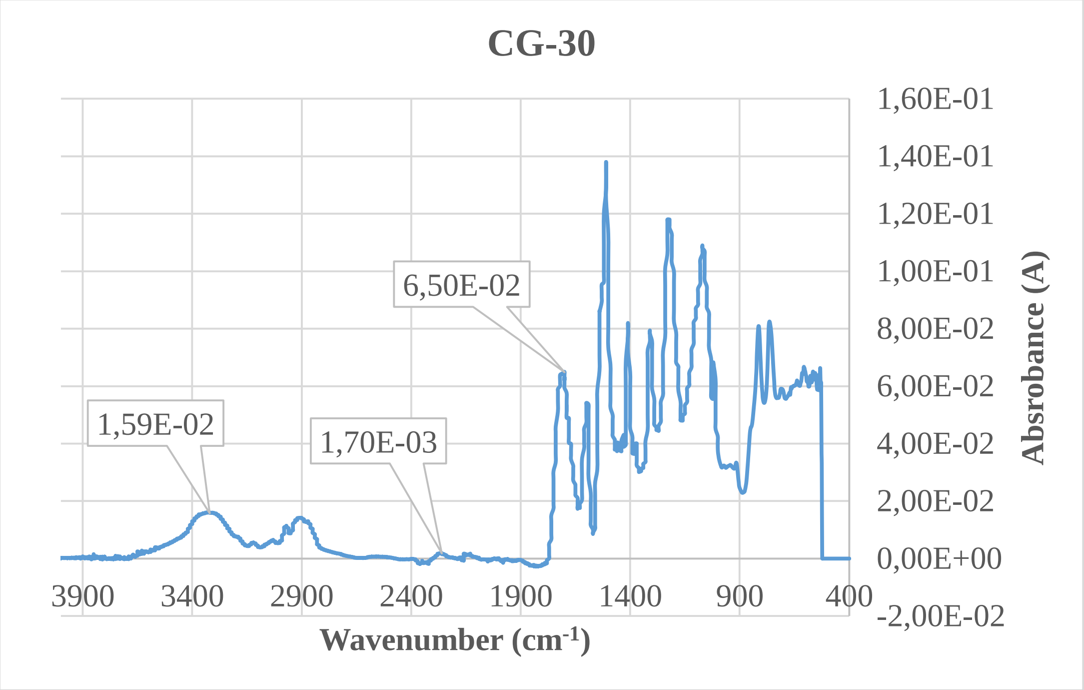

Figure 6.2 FTIR spectrum of CG-30

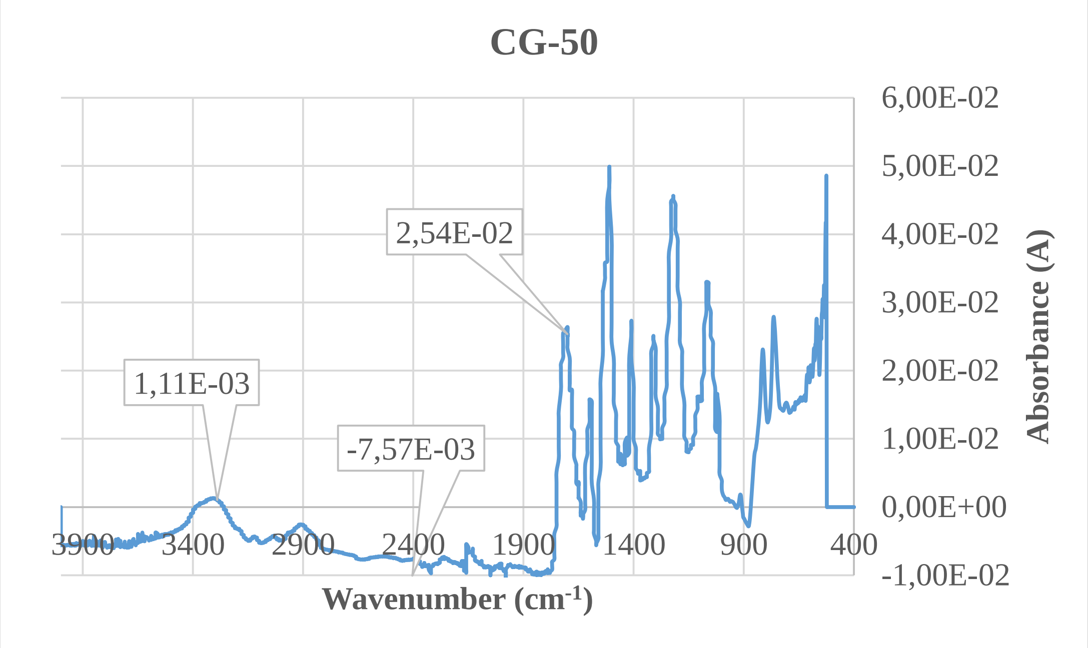

Figure 6.3 FTIR spectrum of CG-50

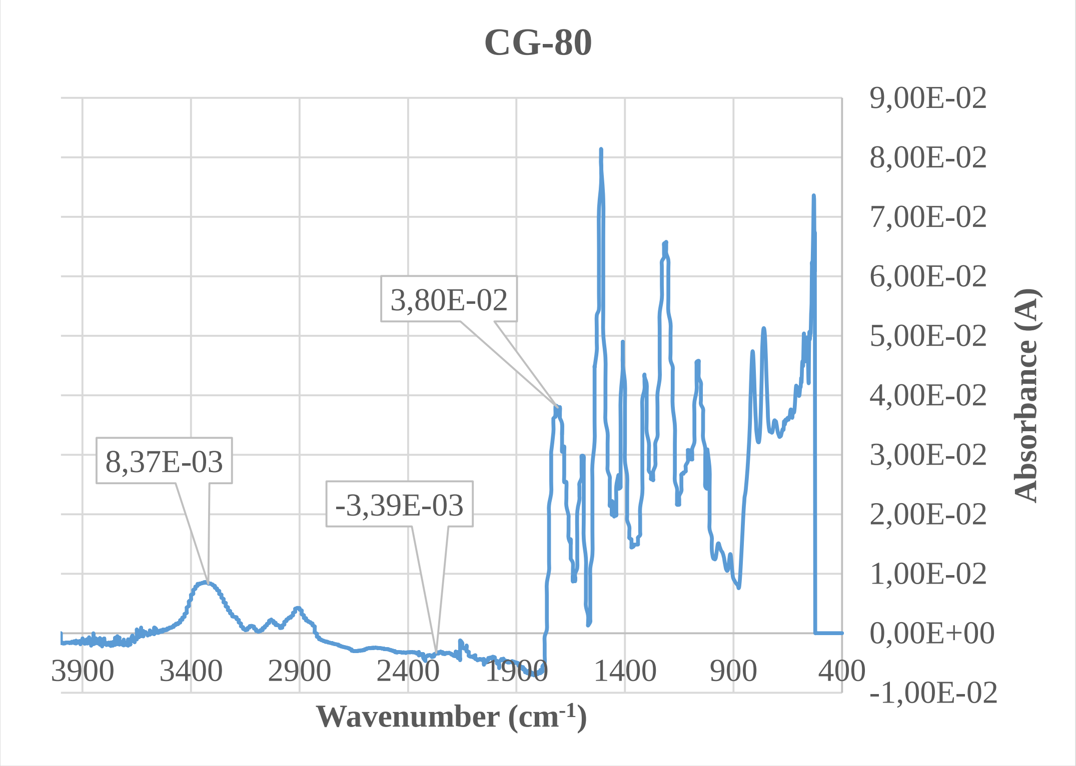

Figure 6.4 FTIR spectrum of CG-80

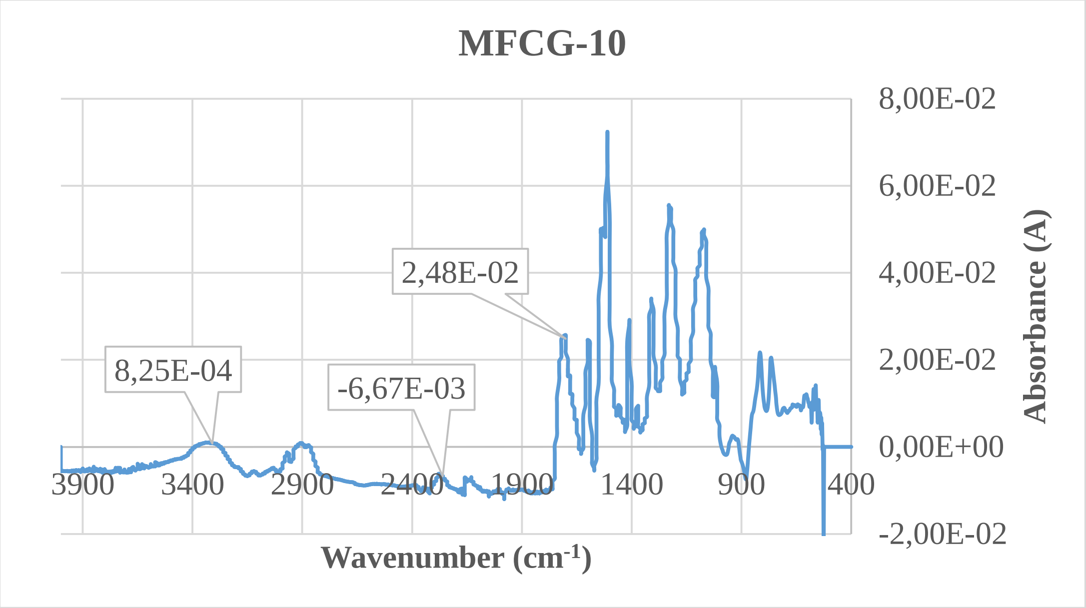

Figure 6.5 FTIR spectrum of MFCG-10

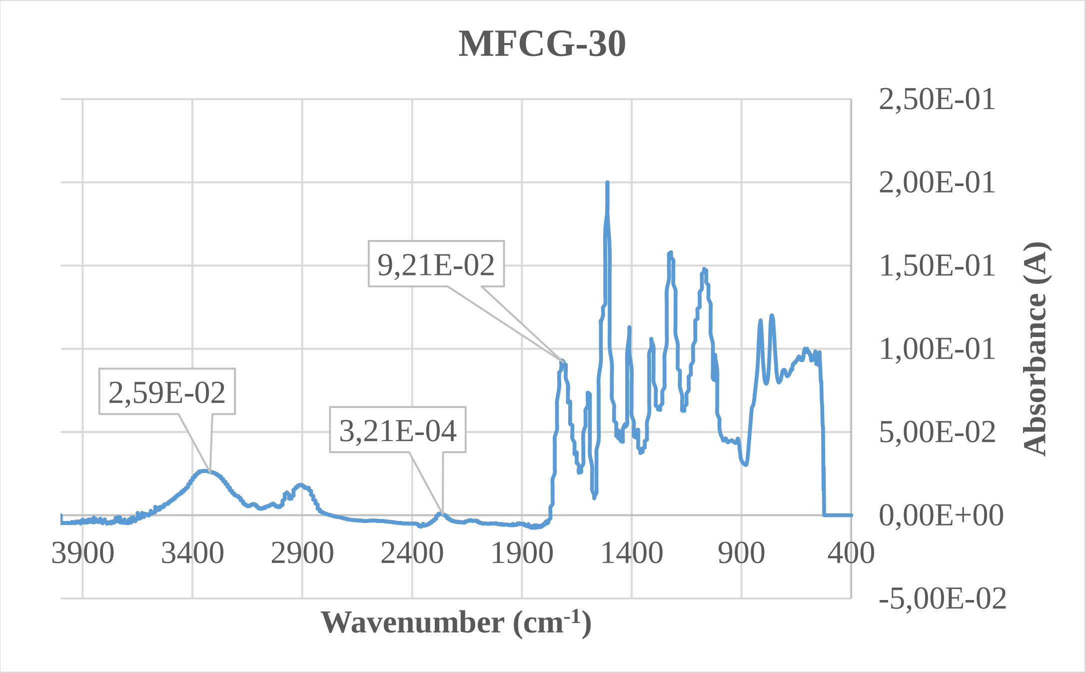

Figure 6.6 FTIR spectrum of MFCG-30

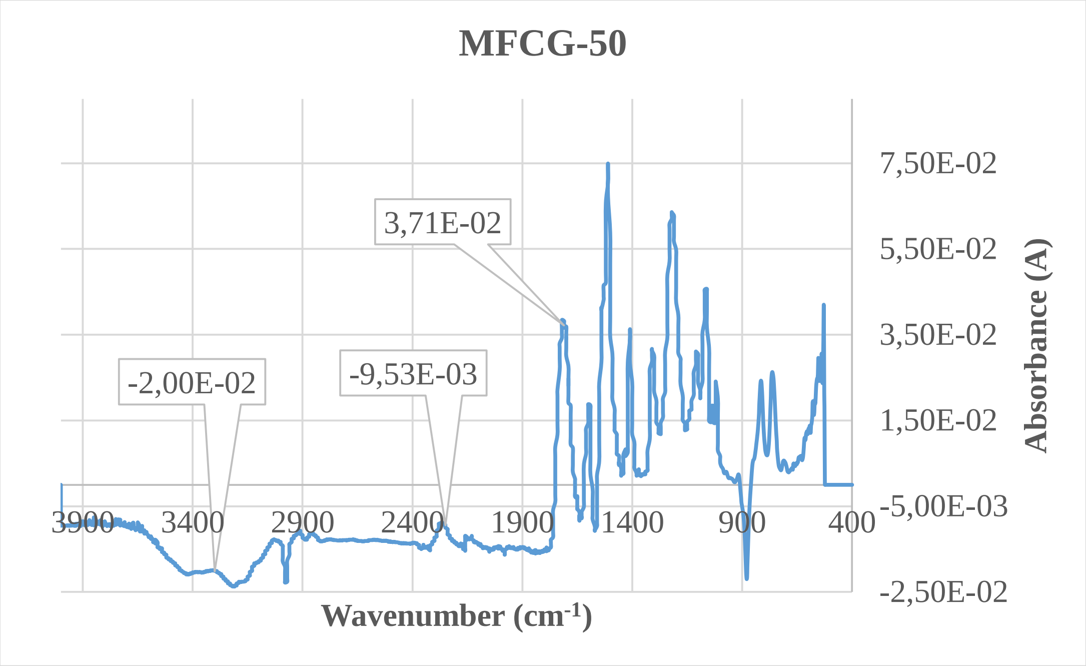

Figure 6.7 FTIR spectrum of MFCG-50

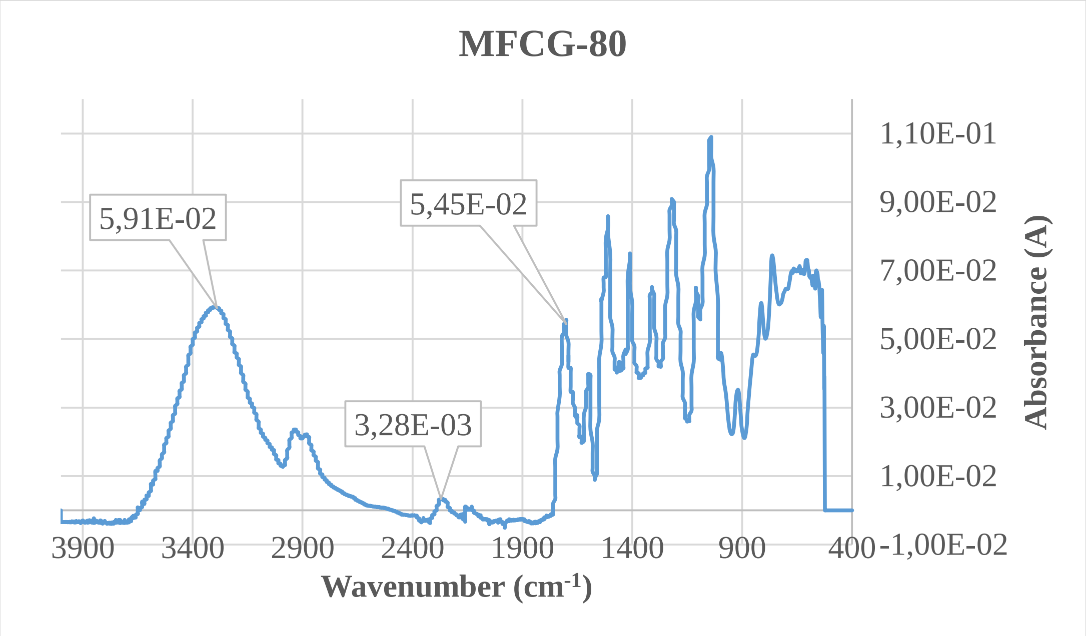

Figure 6.8 FTIR spectrum of MFCG-80

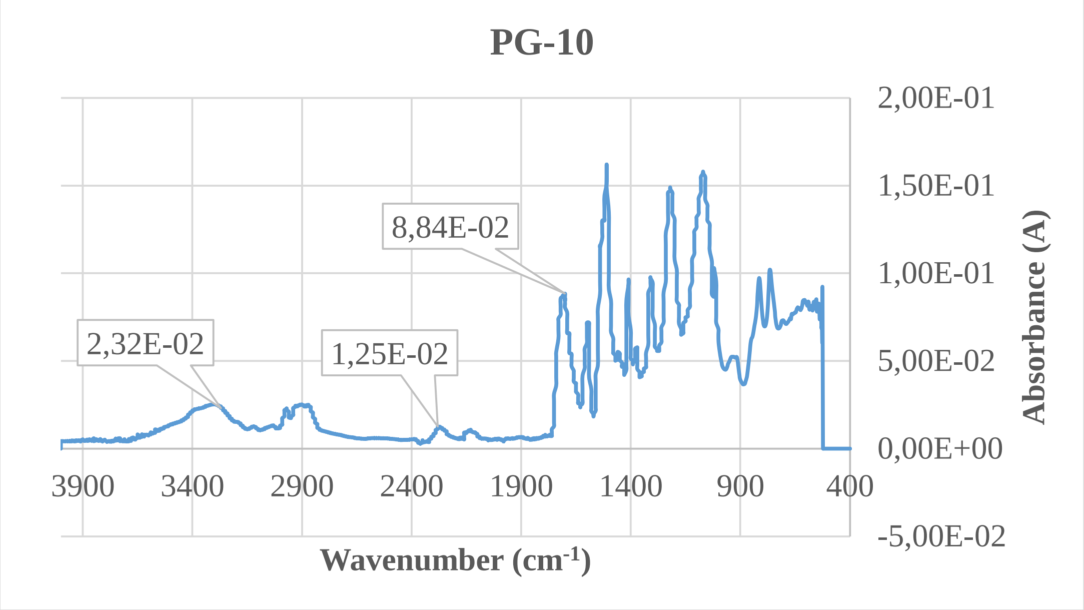

Figure 6.9 FTIR spectrum of PG-10

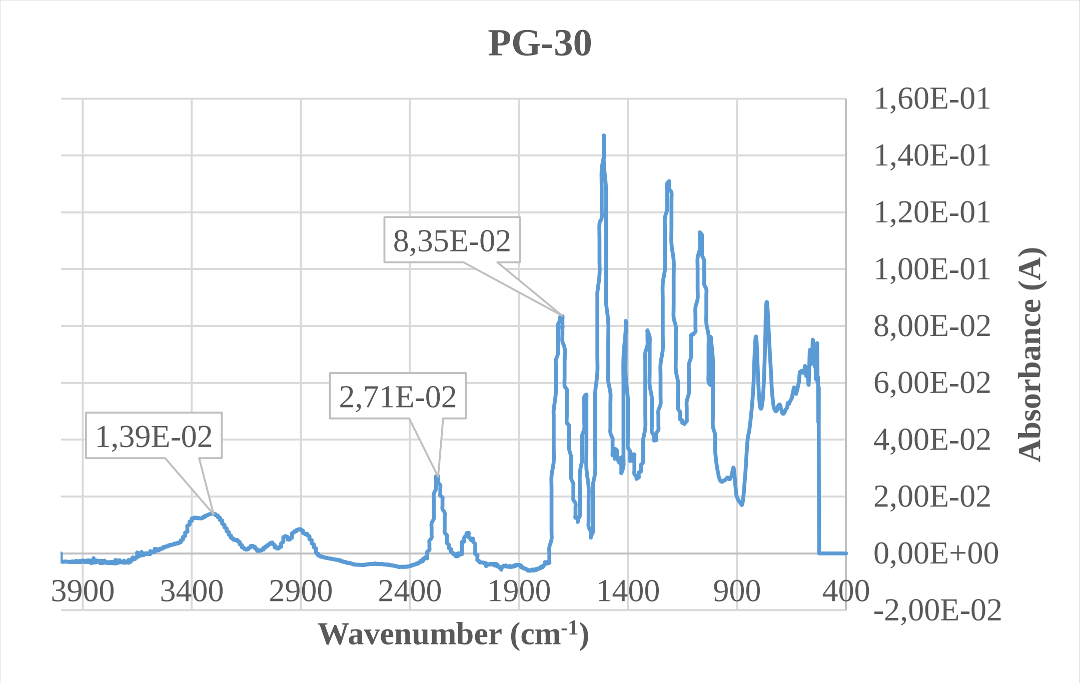

Figure 6.10 FTIR spectrum of PG-30

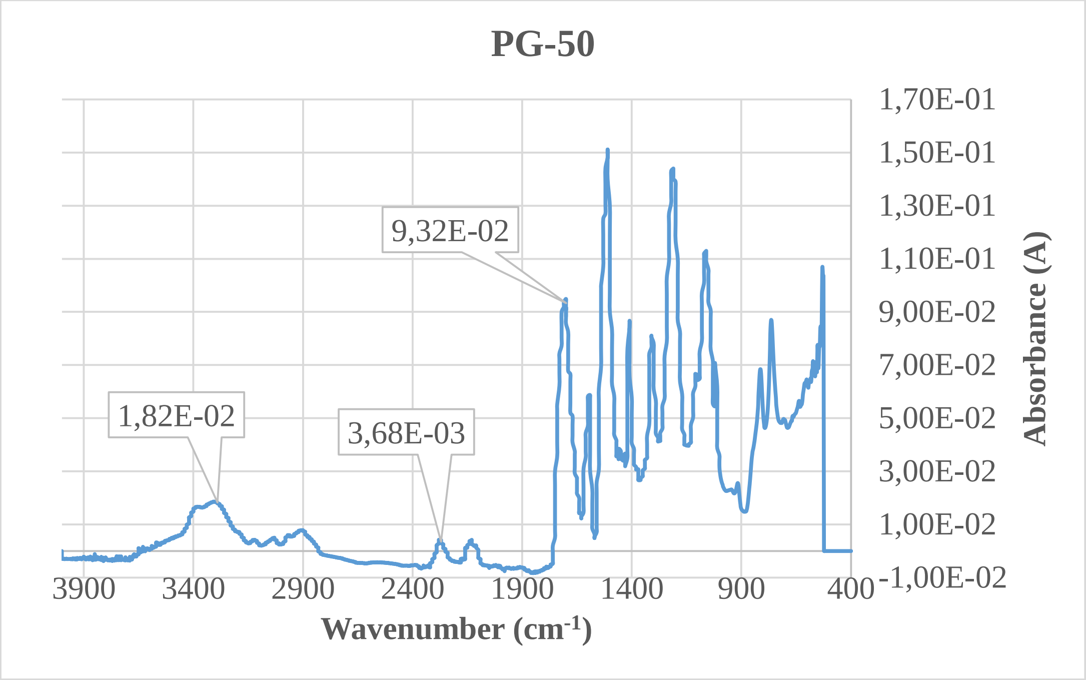

Figure 6.11 FTIR spectrum of PG-50

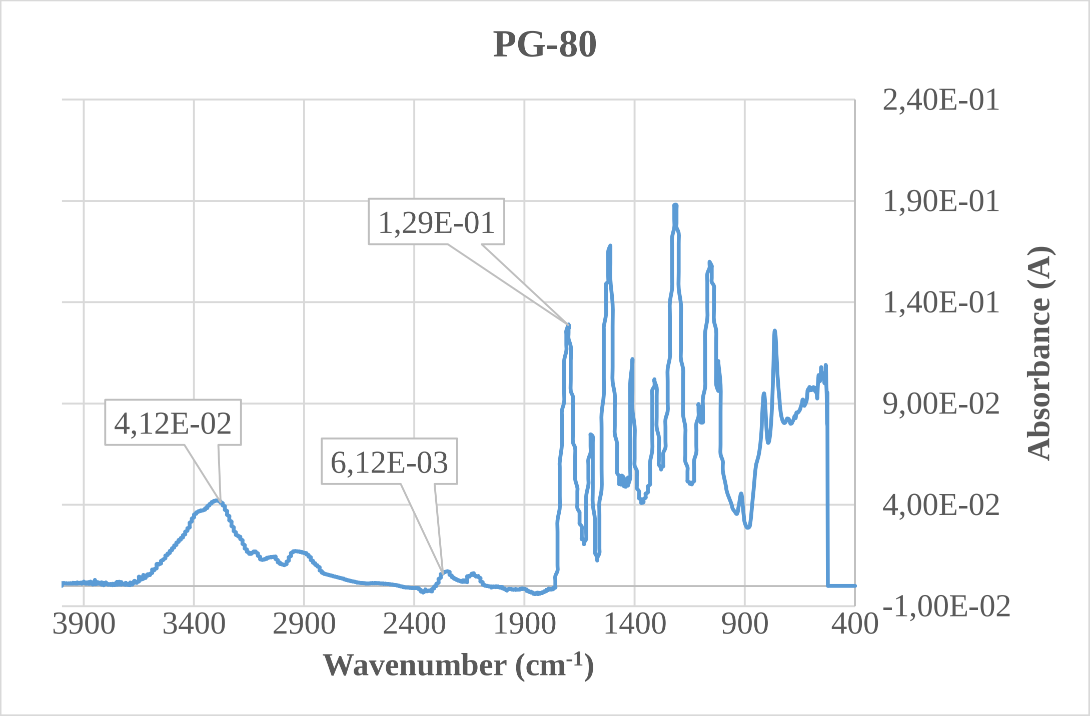

Figure 6.12 FTIR spectrum of PG-80

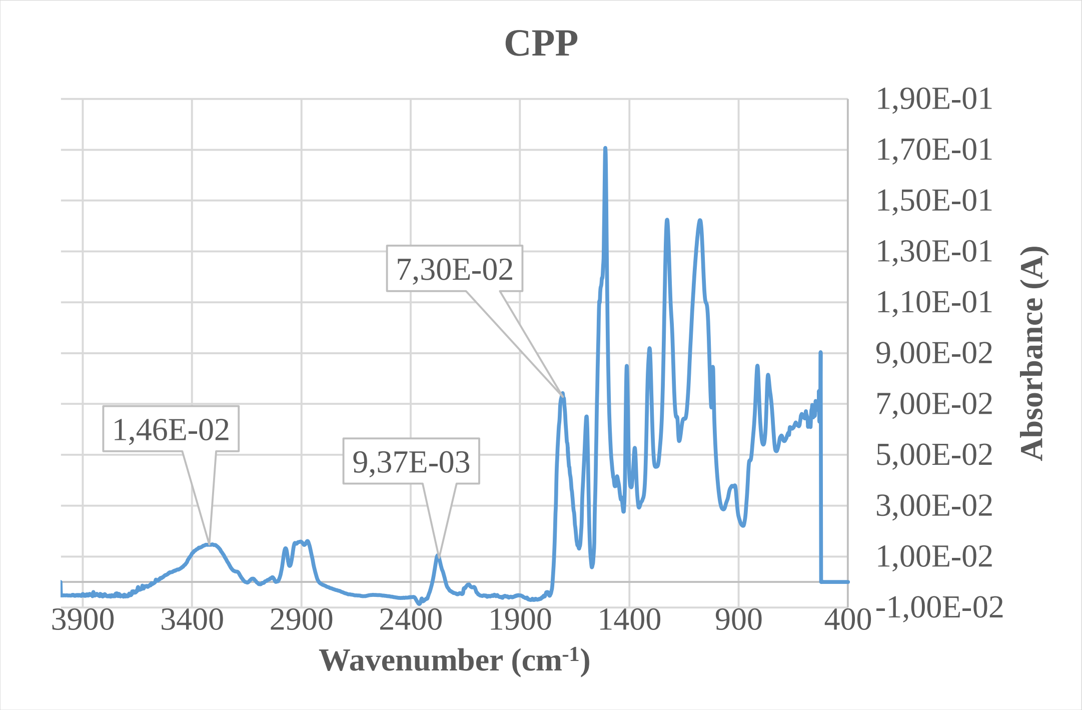

Figure 6.13 FTIR spectrum of CPP

Table 6.1 Compression values of PUF samples

PUF Samples	Compression Strength [MPa]
CPP	0,150
CG-10	0,169
CG-30	0,178
CG-50	0,136
CG-80	0,108
MFCG-10	0,100
MFCG-30	0,110
MFCG-50	0,157
MFCG-80	0,203
PG-10	0,161
PG-30	0,184
PG-50	0,189
PG-80	0,245

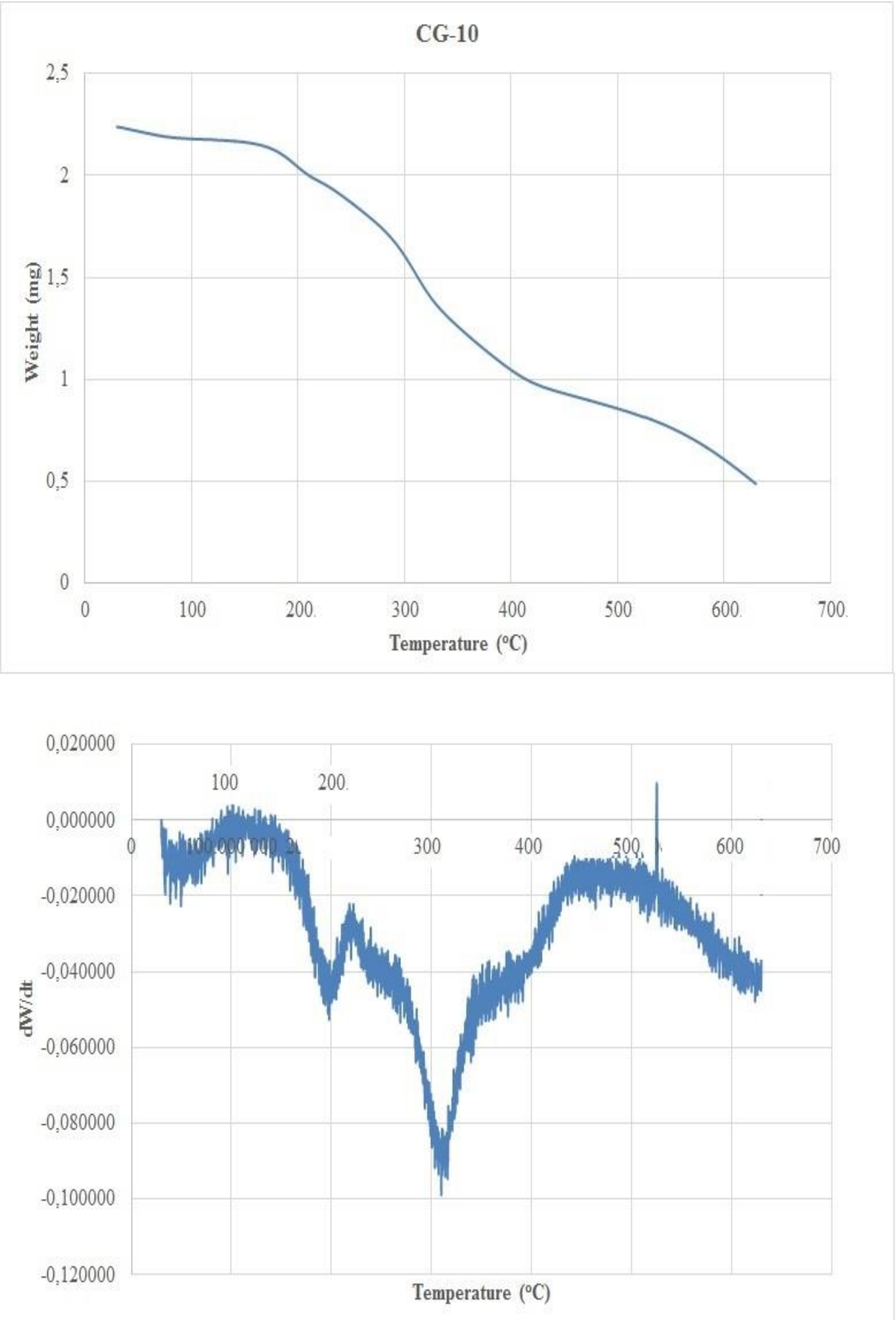

Figure 6.14 TGA/DTG graphs of CG-10

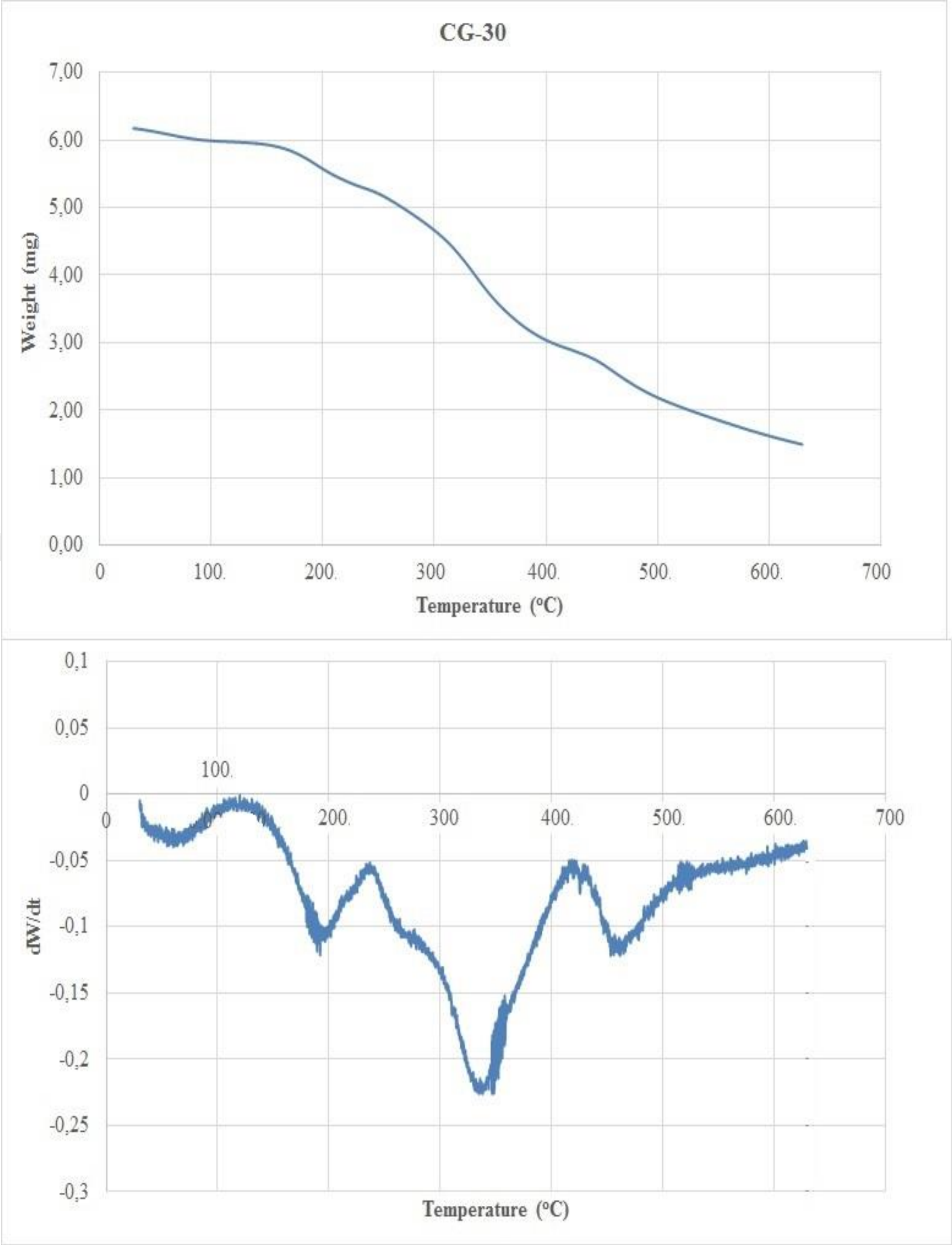

Figure 6.15 TGA/DTG graphs of CG-30

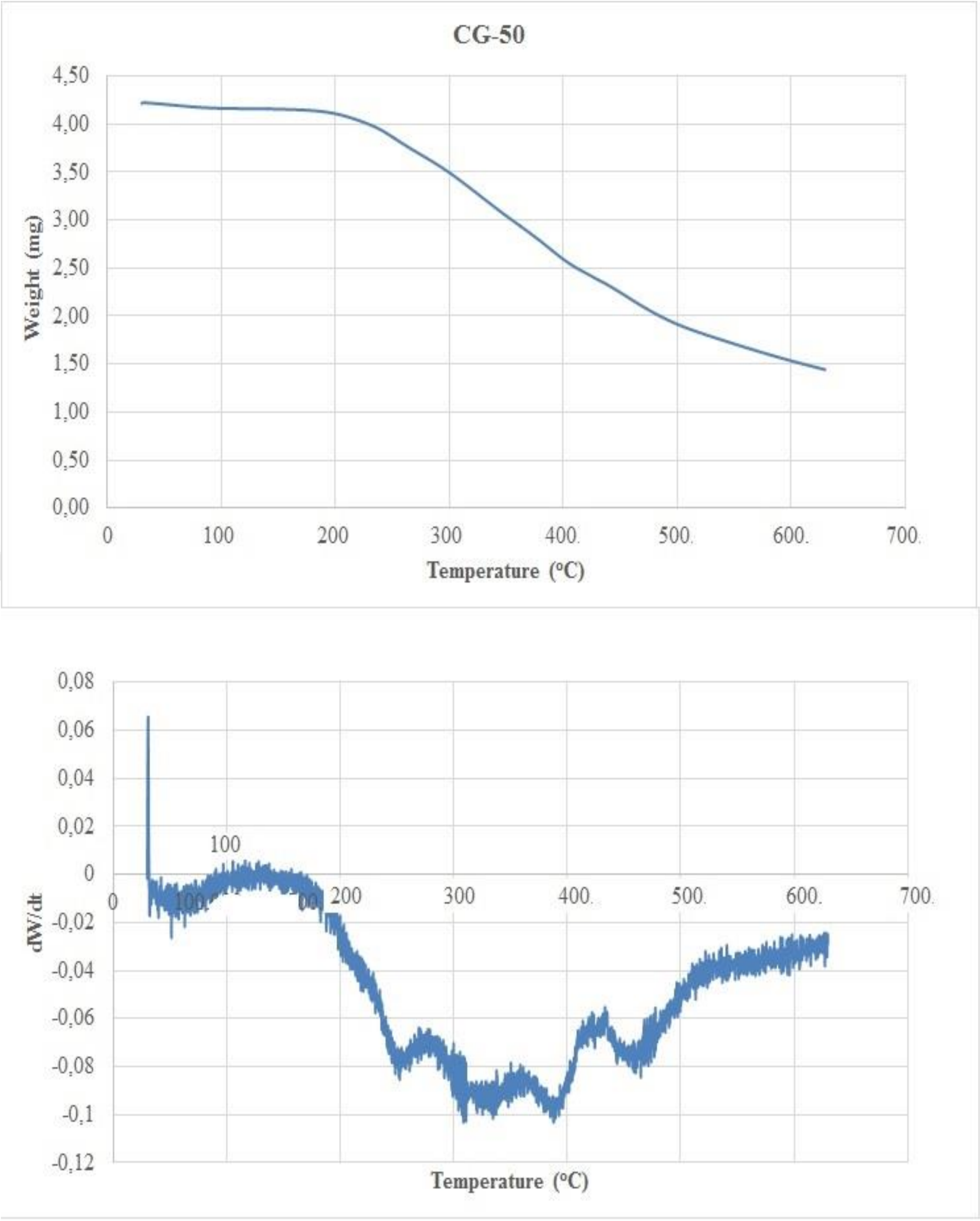

Figure 6.16 TGA/DTG graphs of CG-50

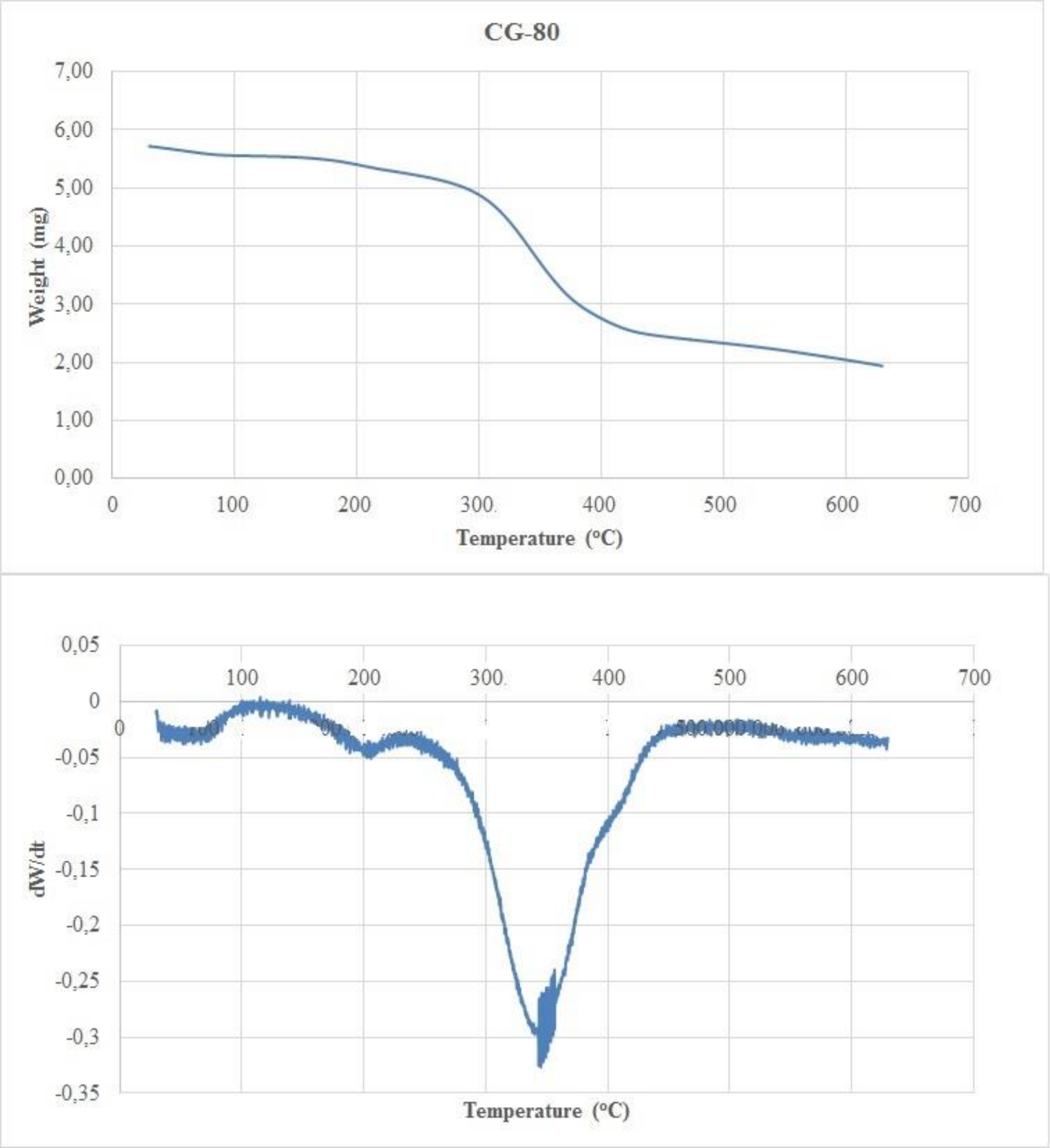

Figure 6.17 TGA/DTG graphs of CG-80

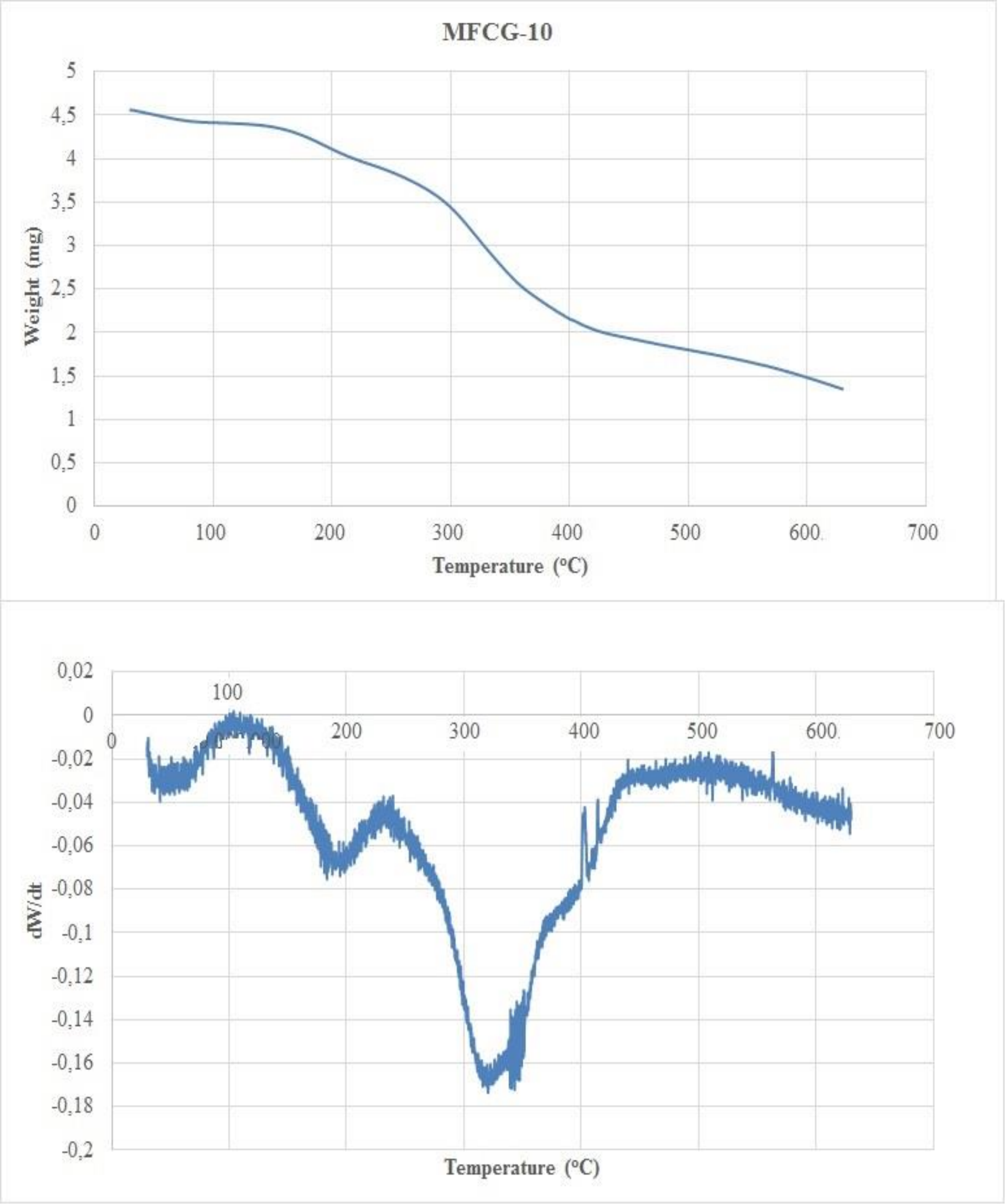

Figure 6.18 TGA/DTG graphs of MFCG-10

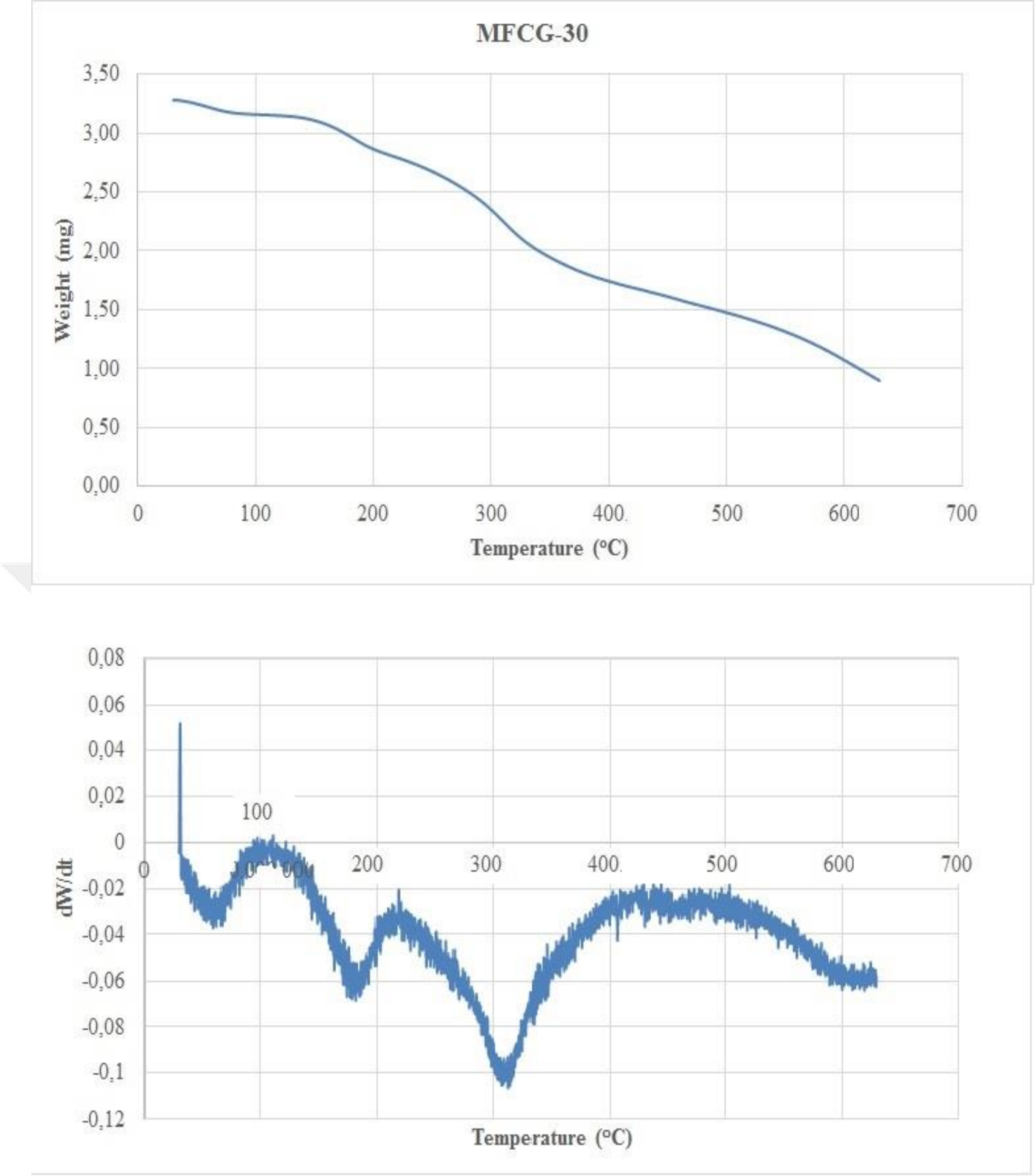

Figure 6.19 TGA/DTG graphs of MFCG-30

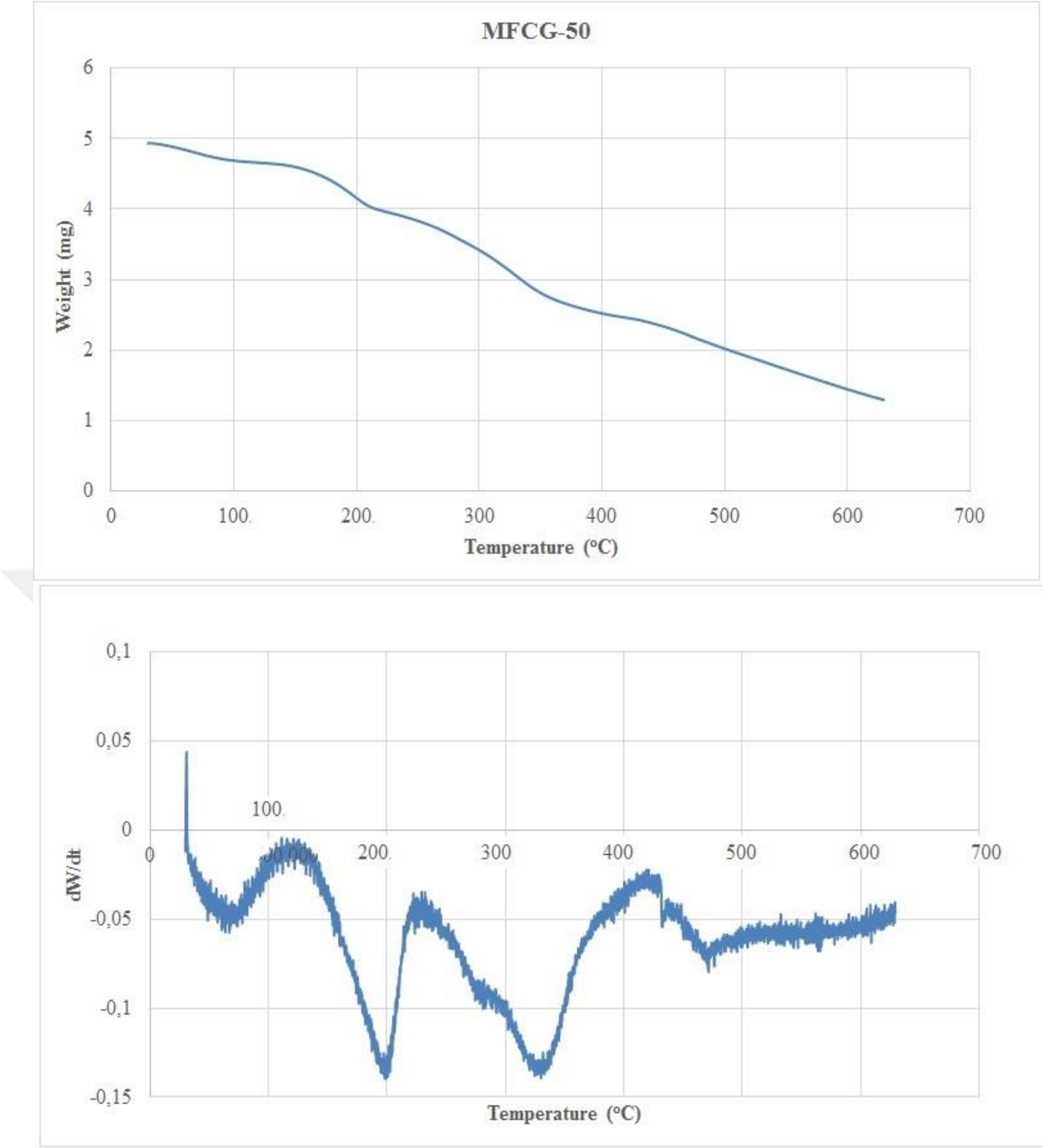

Figure 6.20 TGA/DTG graphs of MFCG-50

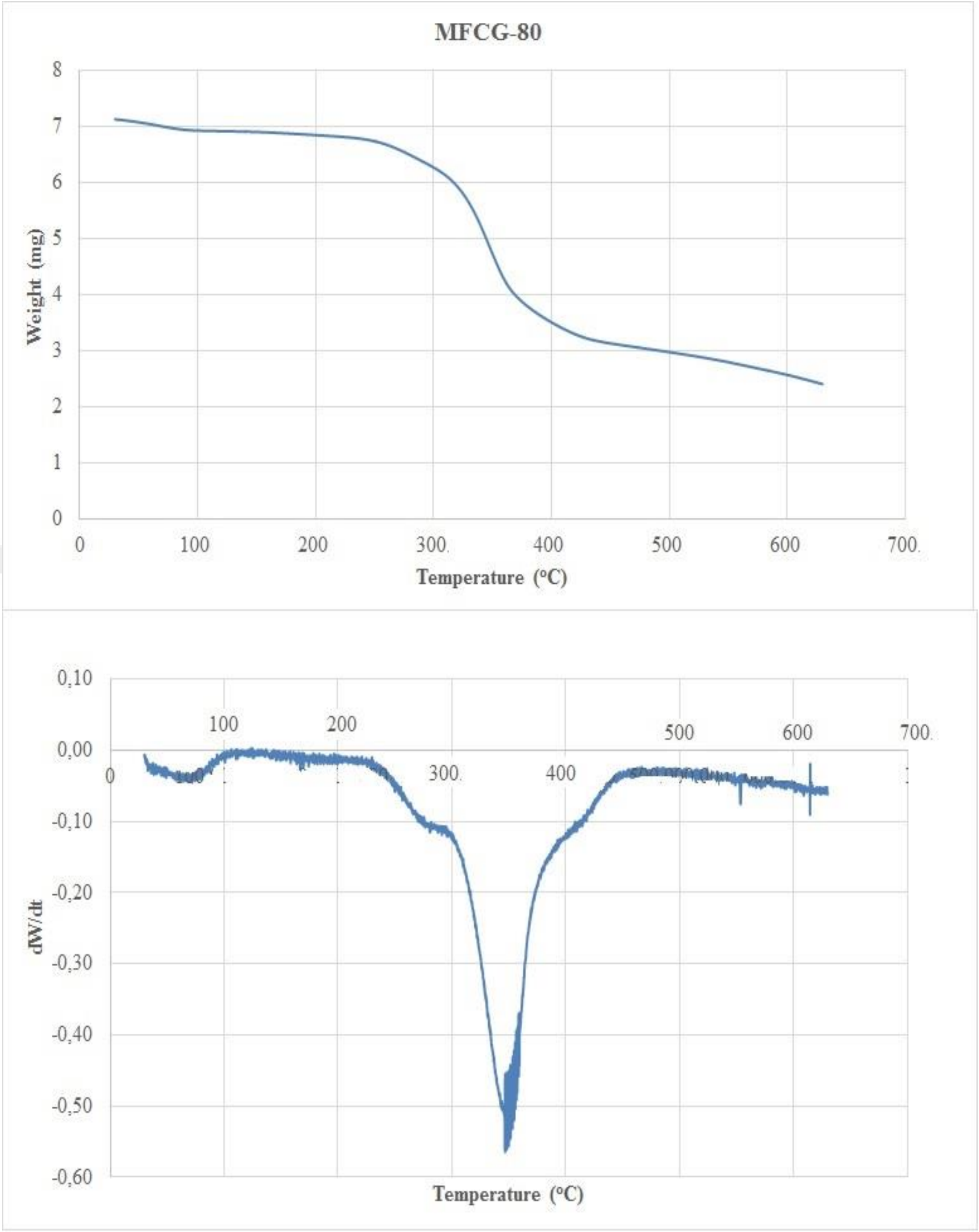

Figure 6.21 TGA/DTG graphs of MFCG-80

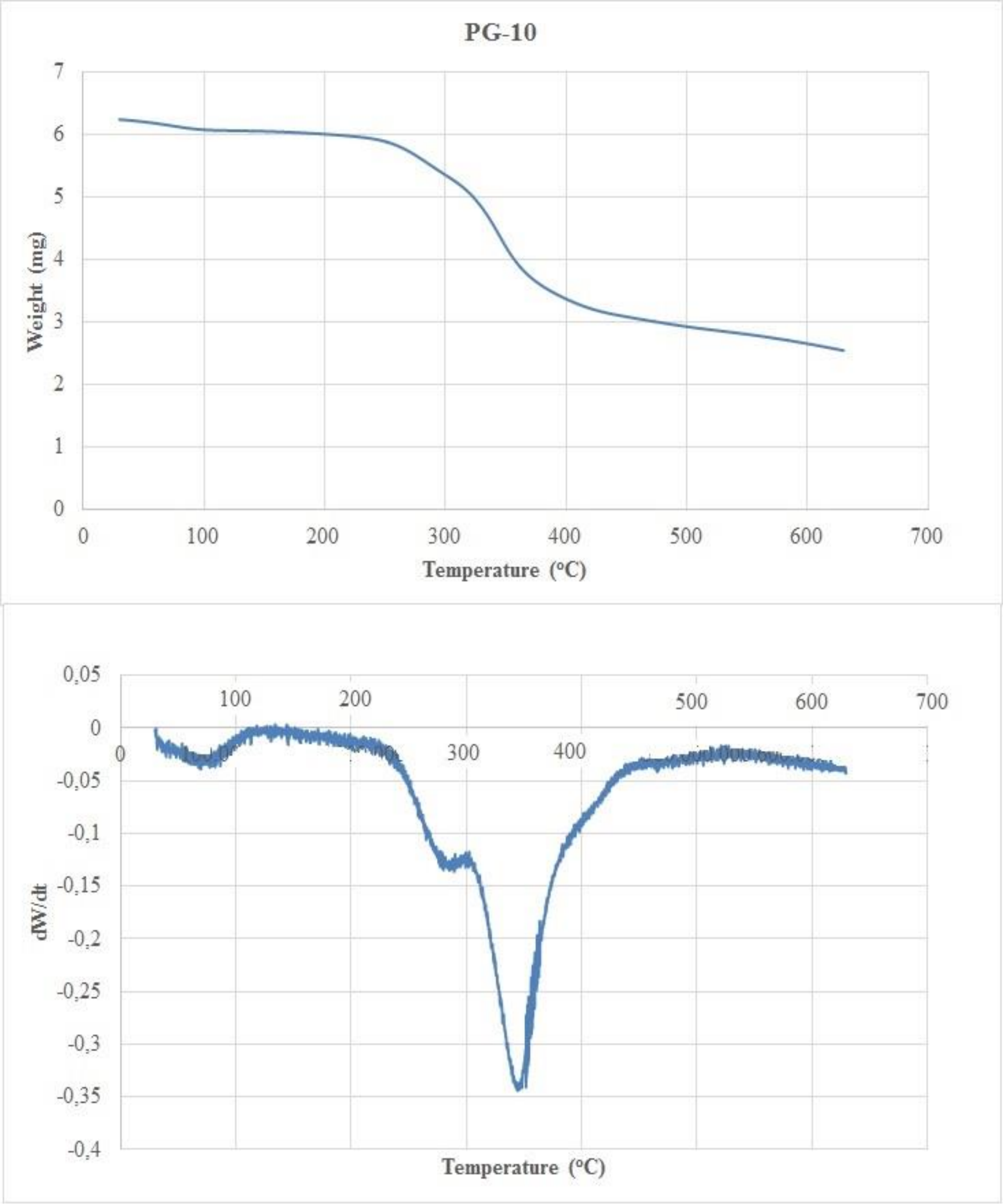

Figure 6.22 TGA/DTG graphs of PG-10

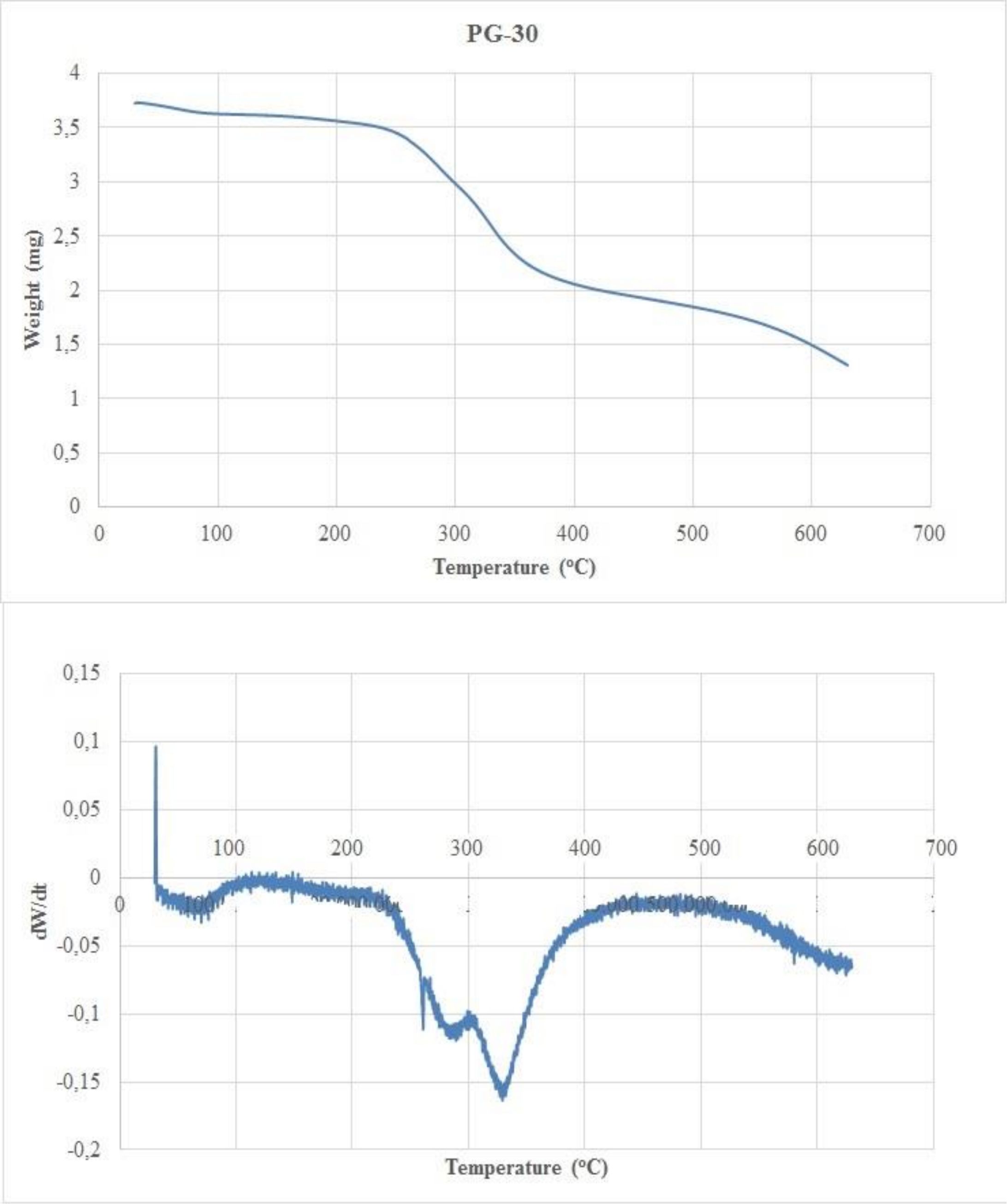

Figure 6.23 TGA/DTG graphs of PG-30

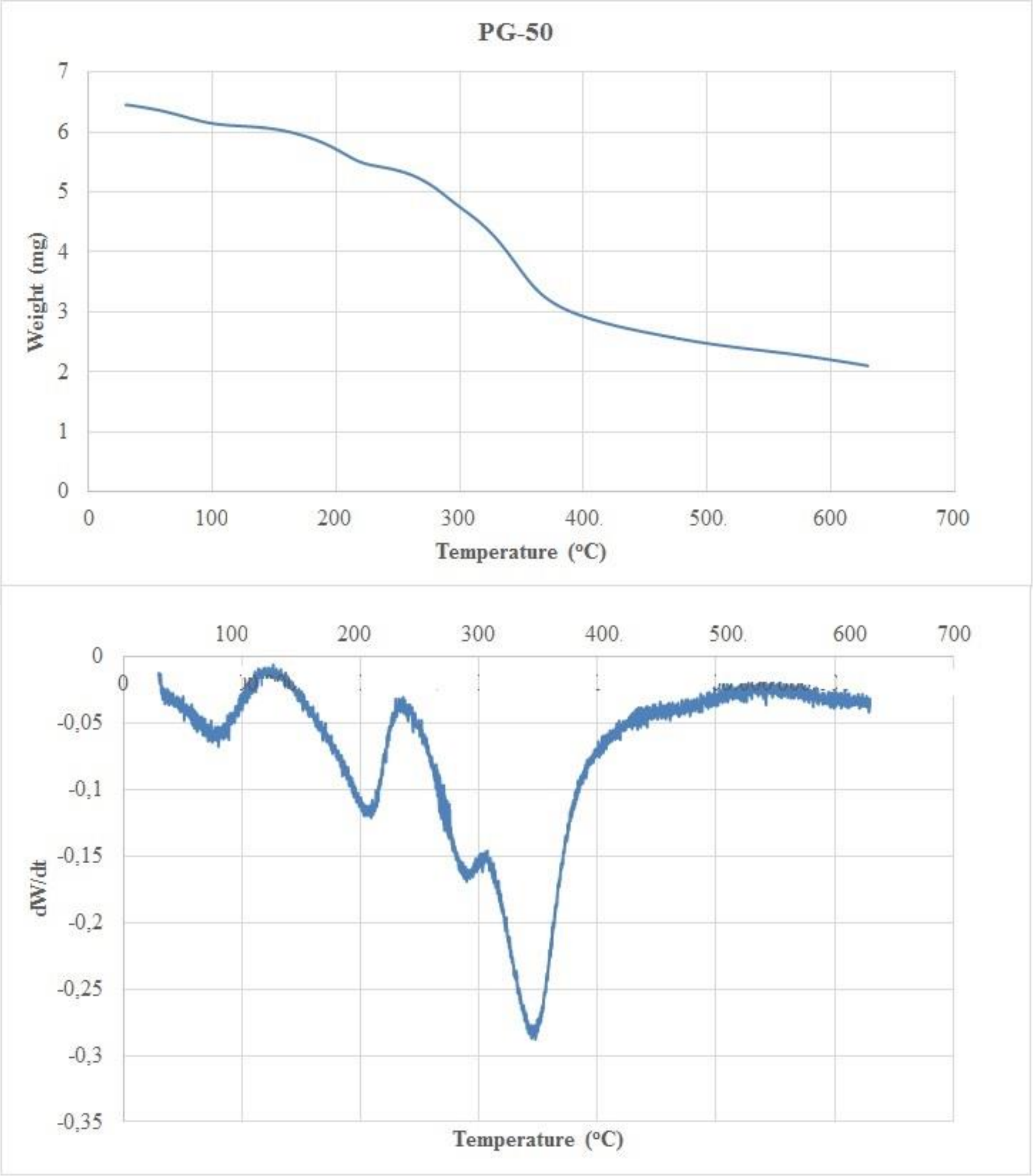

Figure 6.24 TGA/DTG graphs of PG-50

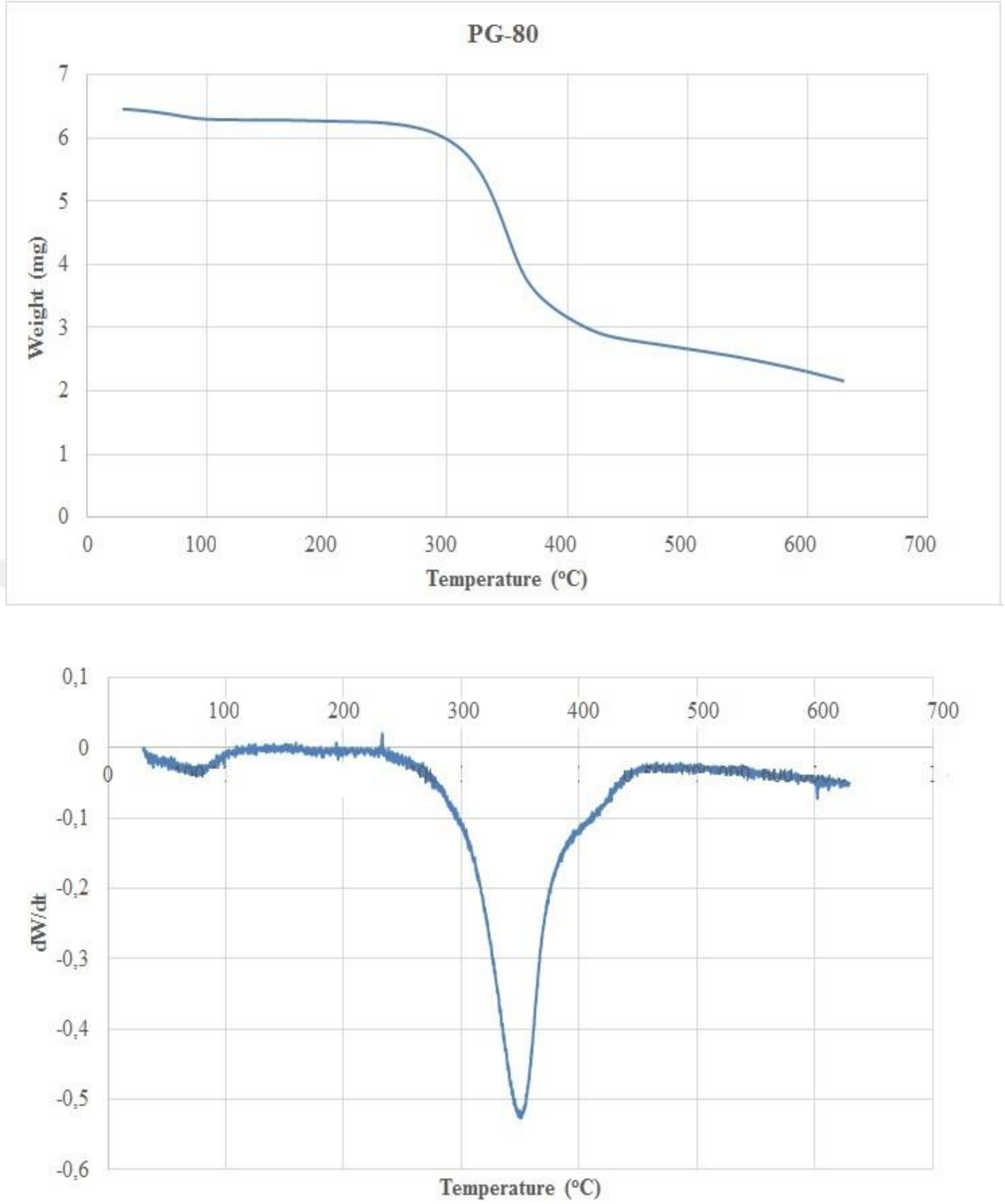

Figure 6.25 TGA/DTG graphs of PG-80

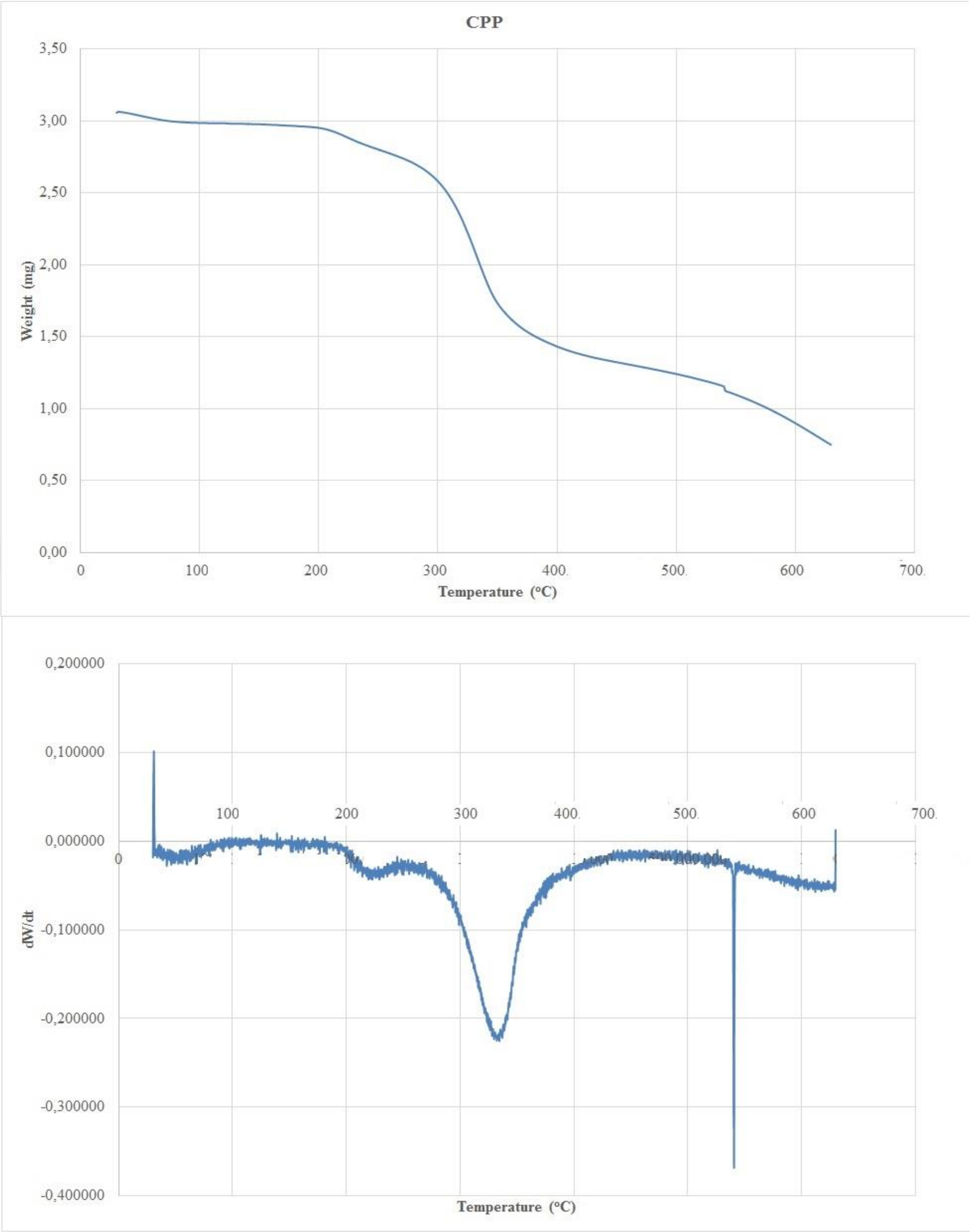

Figure 6.26 TGA/DTG graphs of CPP

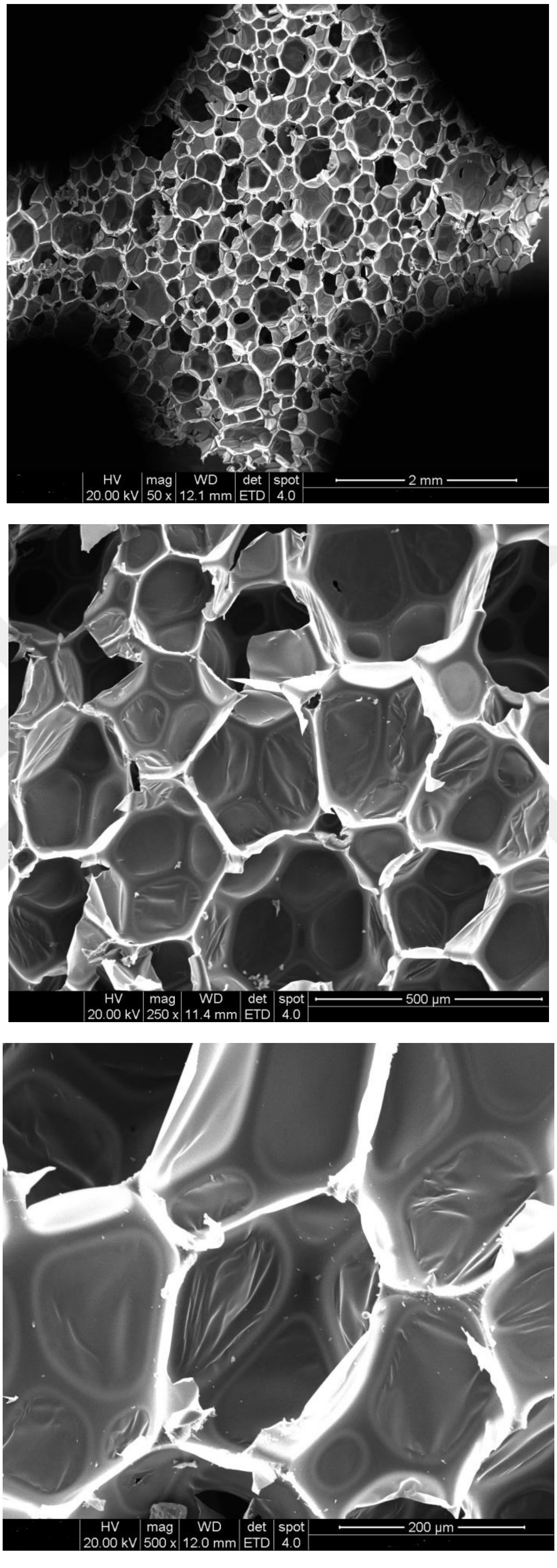

Figure 6.27 SEM photos of CG-10 (50x, 250x, 500x)

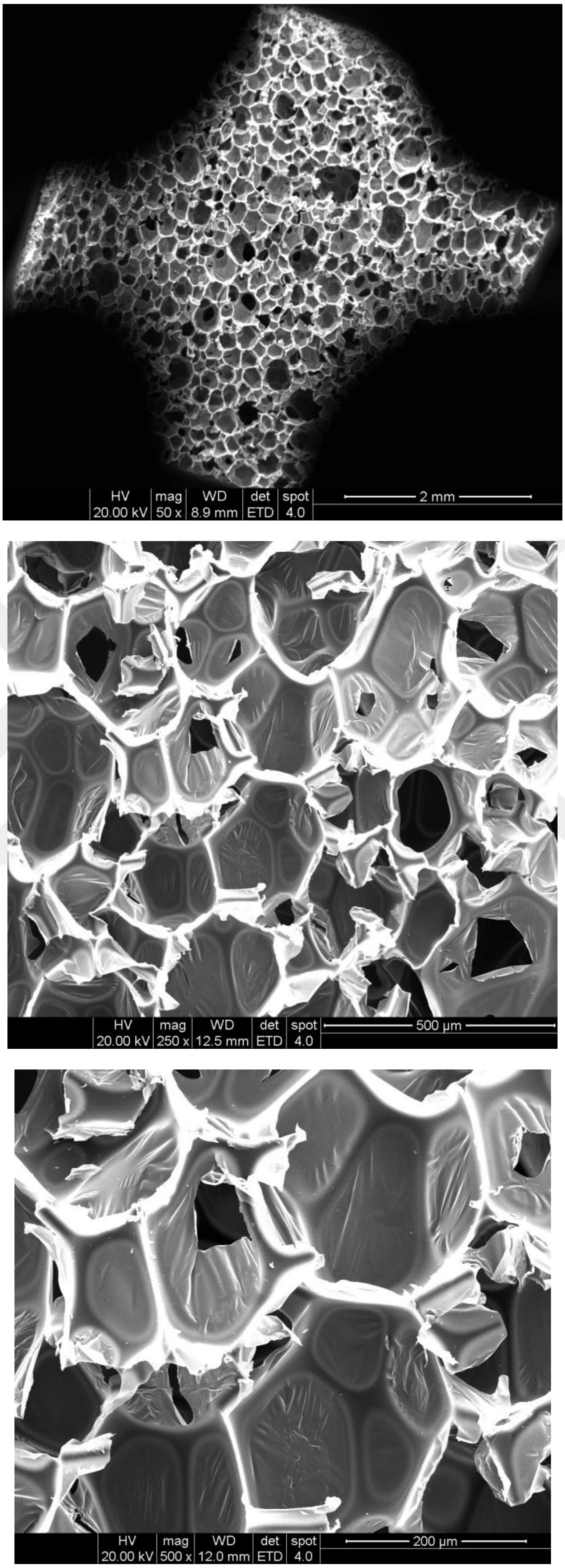

Figure 6.28 SEM photos of CG-30 (50x, 250x, 500x)

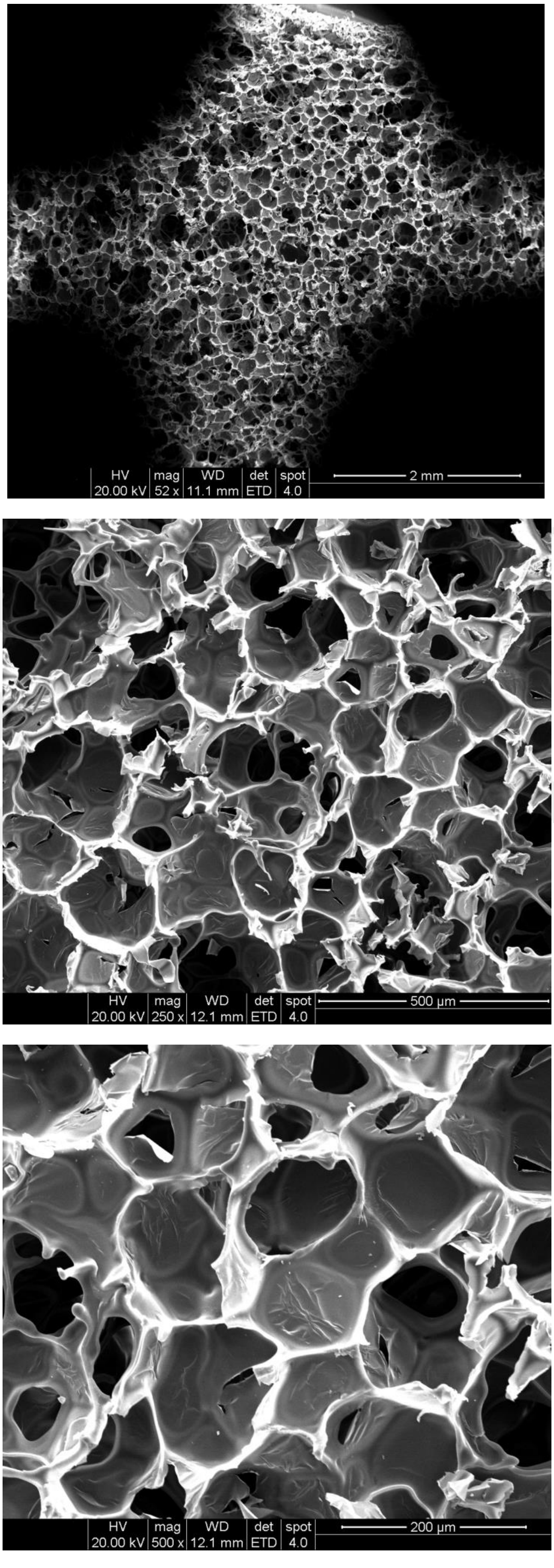

Figure 6.29 SEM photos of CG-50 (50x, 250x, 500x)

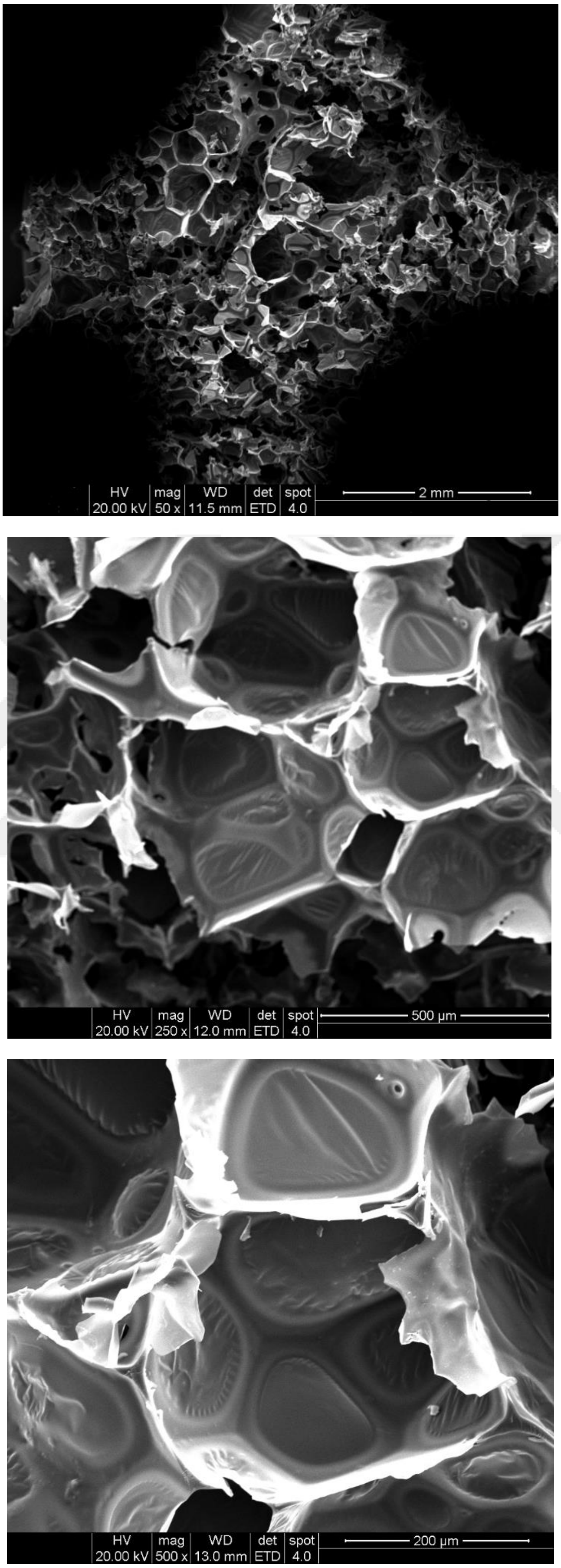

Figure 6.30 SEM photos of CG-80 (50x, 250x, 500x)

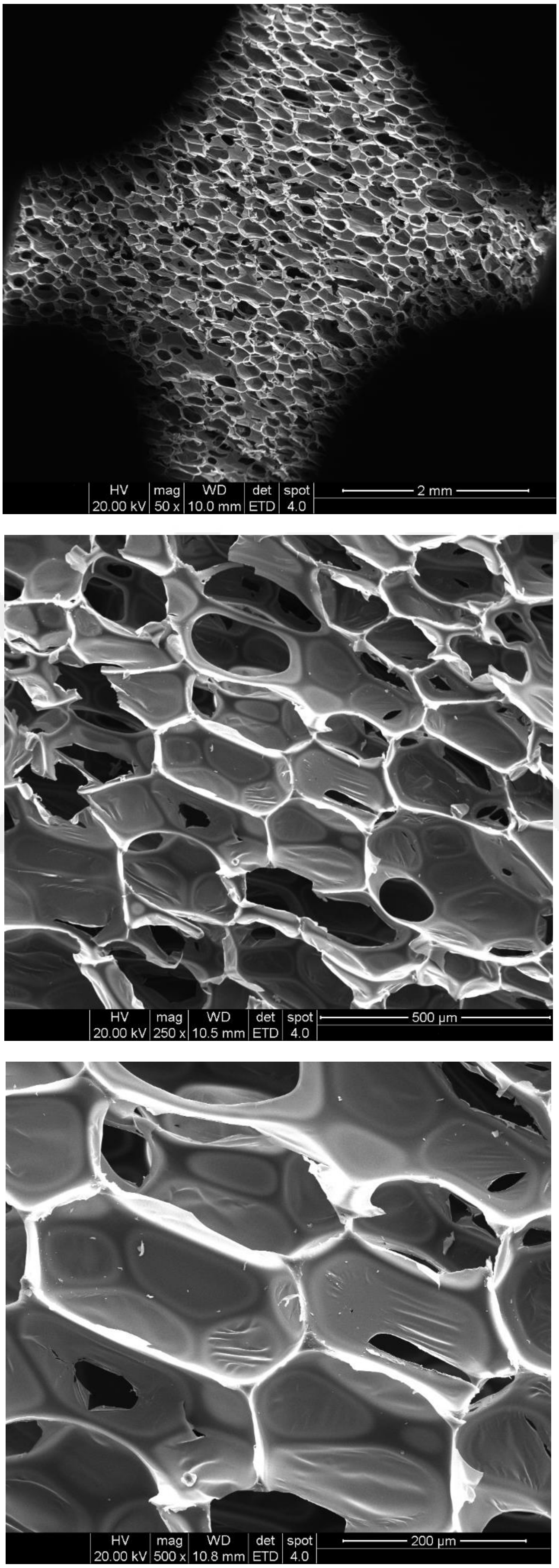

Figure 6.31 SEM photos of MFCG-10 (50x, 250x, 500x)

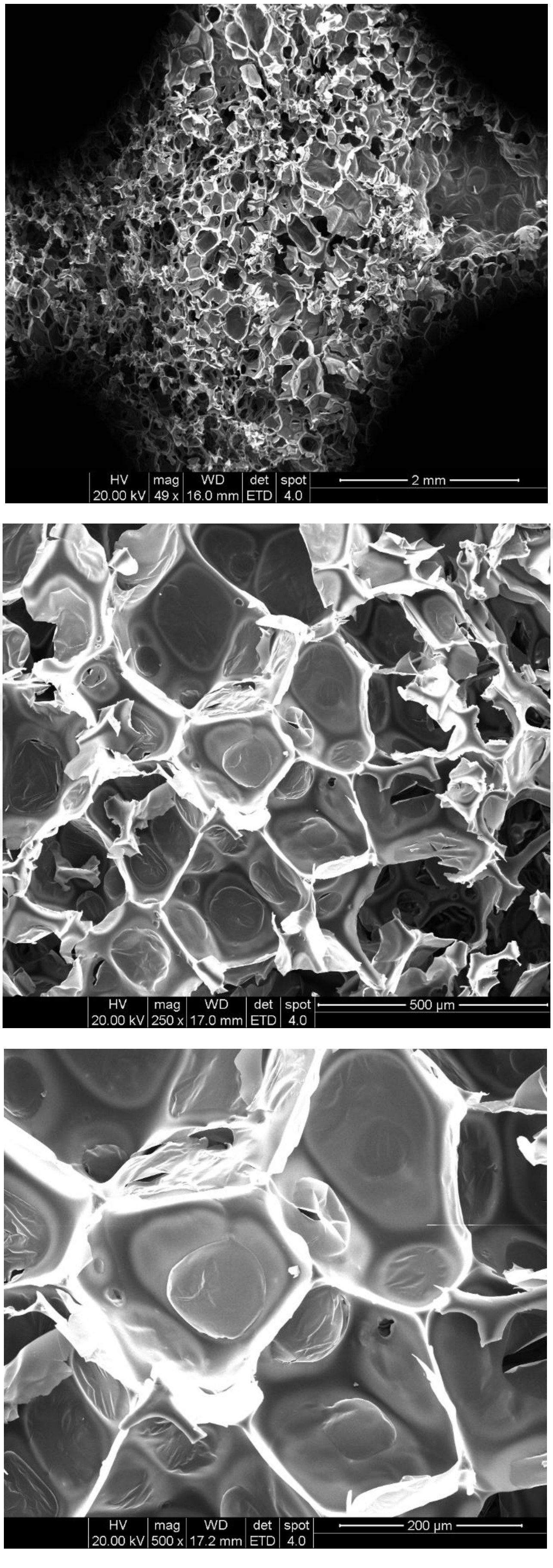

Figure 6.32 SEM photos of MFCG-30 (50x, 250x, 500x)

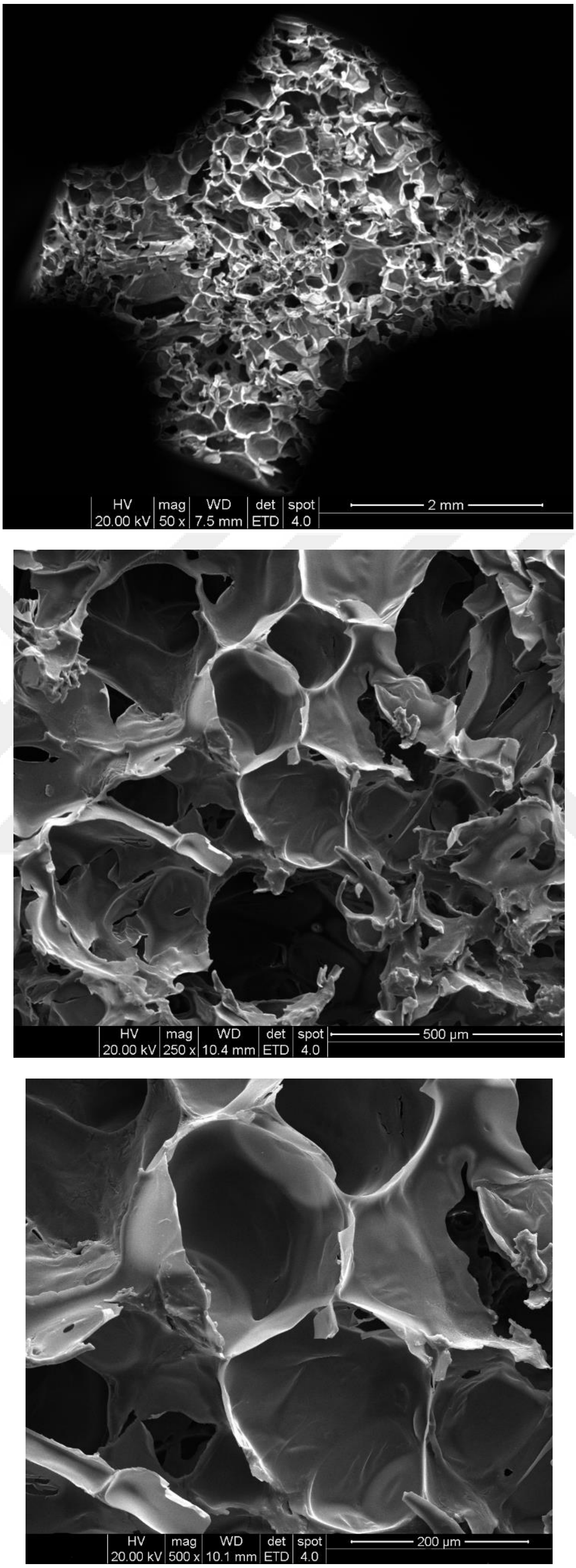

Figure 6.33 SEM photos of MFCG-50 (50x, 250x, 500x)

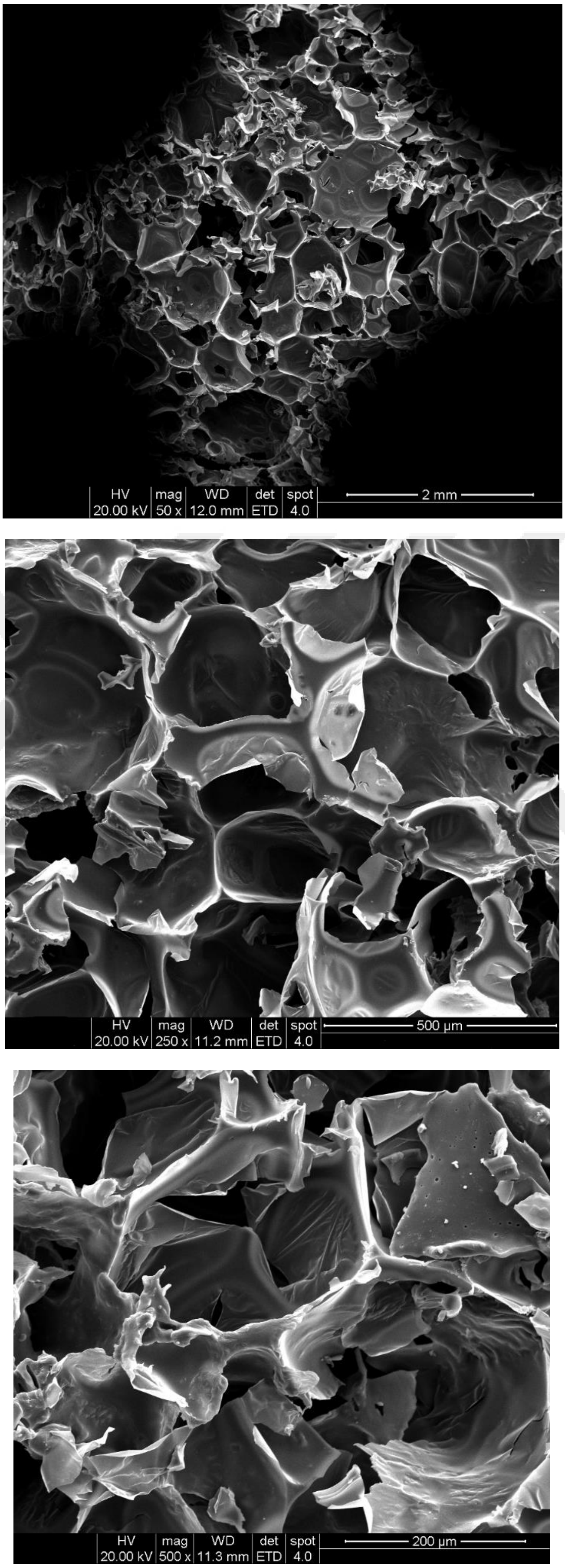

Figure 6.34 SEM photos of MFCG-80 (50x, 250x, 500x)

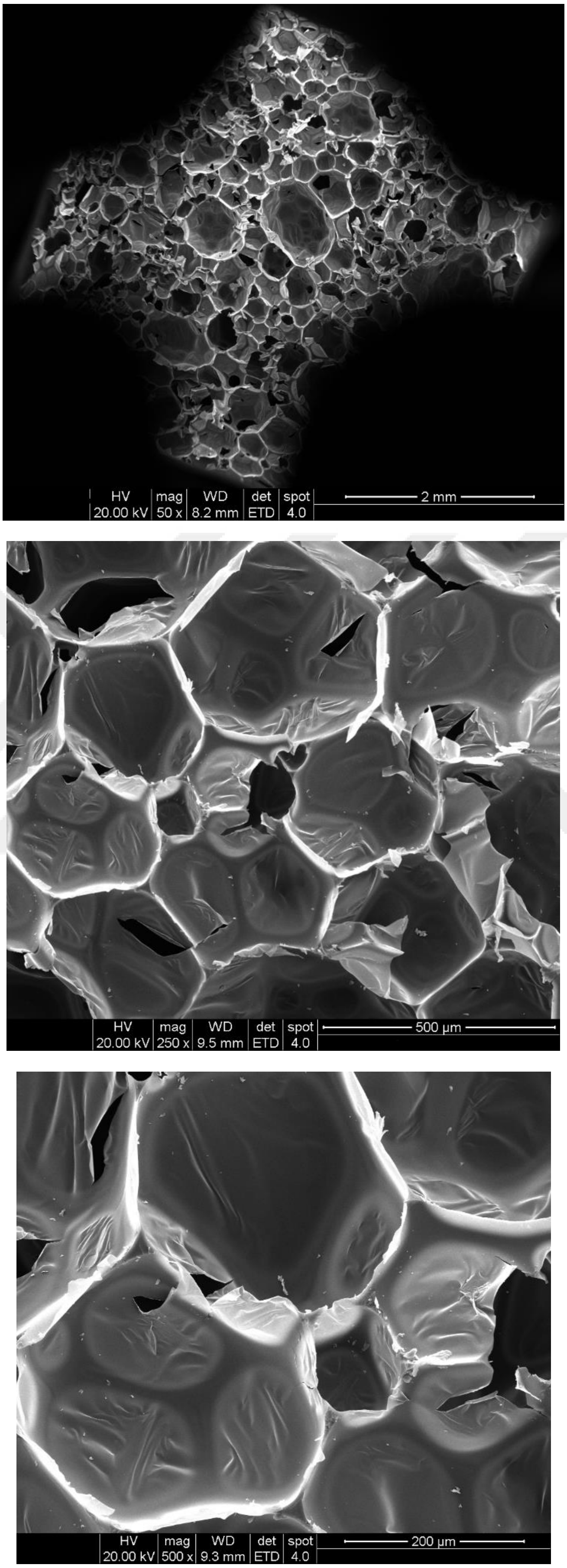

Figure 6.35 SEM photos of PG-10 (50x, 250x, 500x)

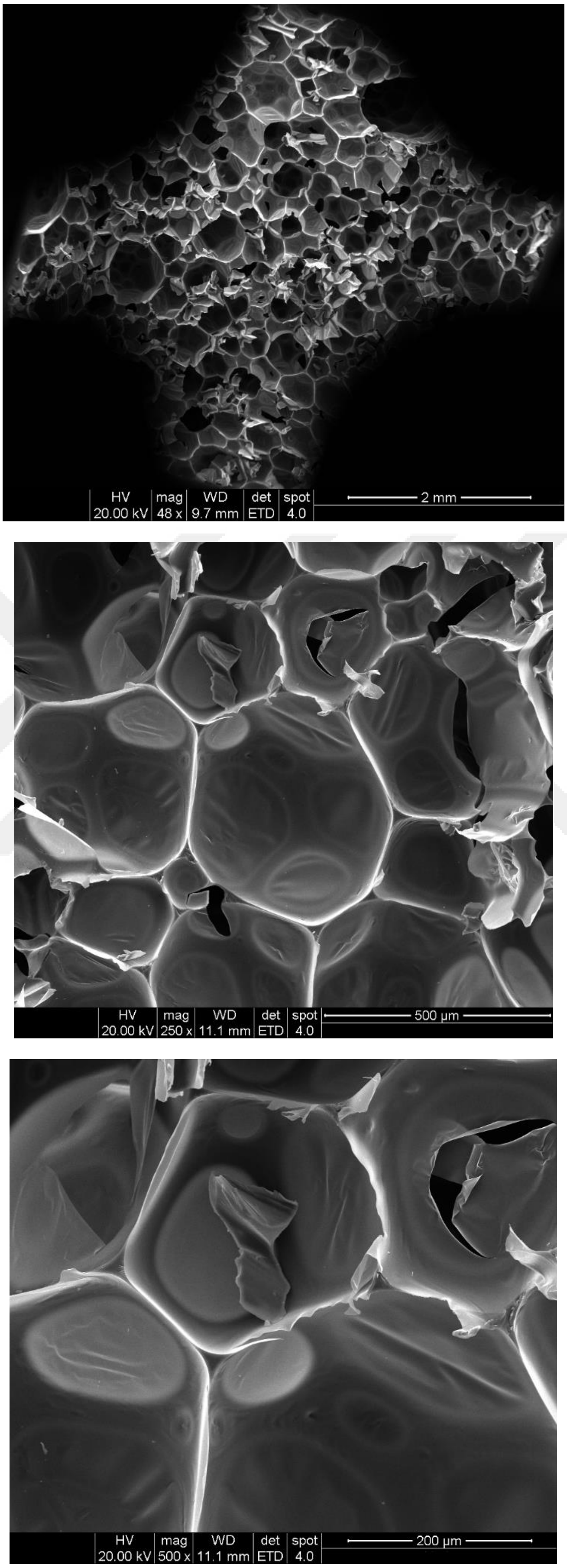

Figure 6.36 SEM photos of PG-30 (50x, 250x, 500x)

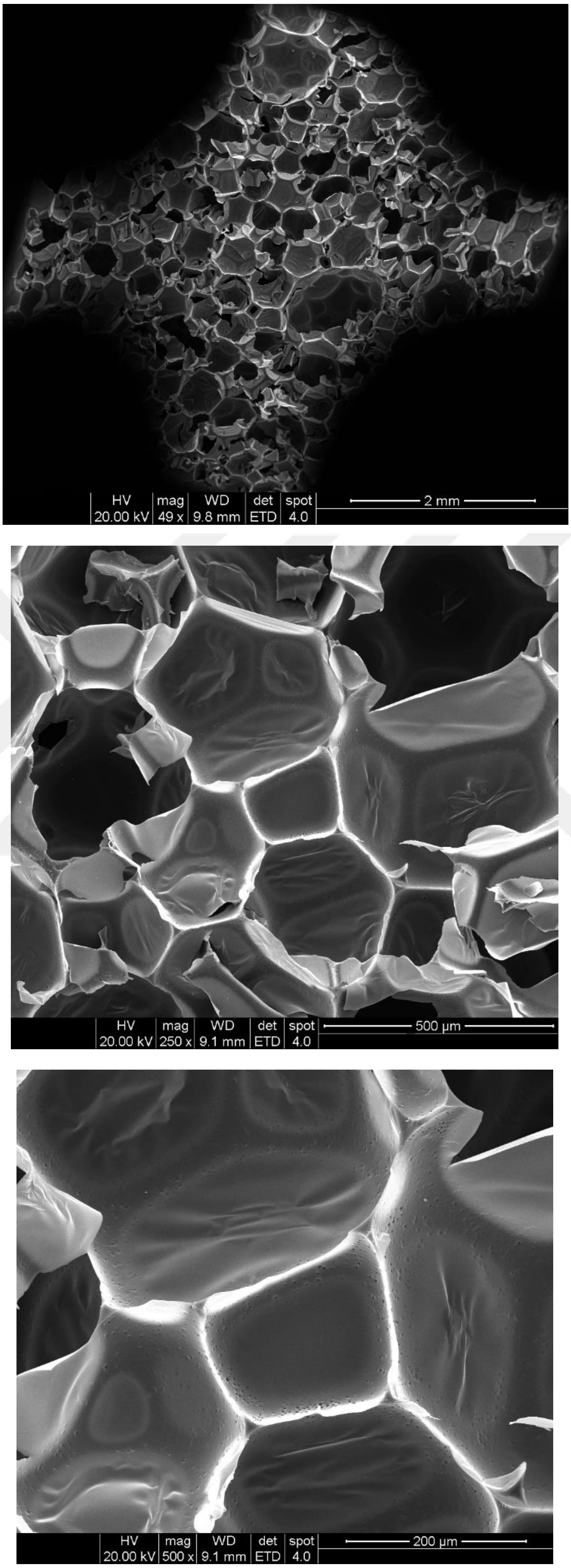

Figure 6.37 SEM photos of PG-50 (50x, 250x, 500x)

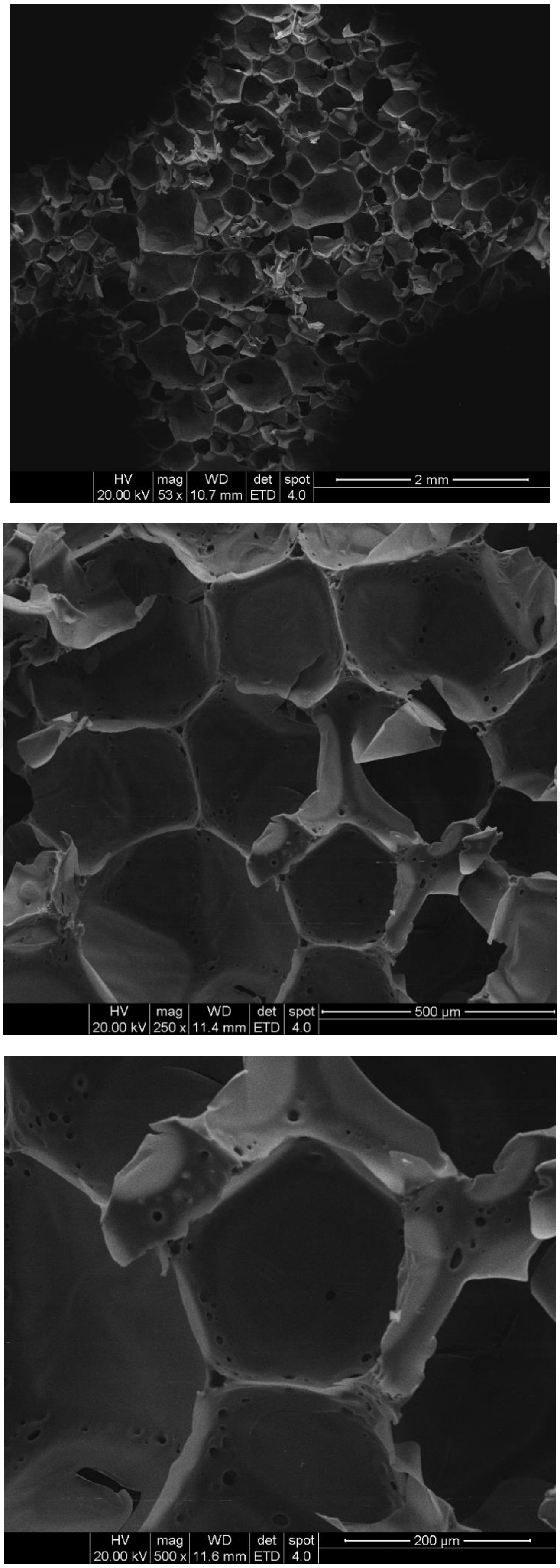

Figure 6.38 SEM photos of PG-80 (50x, 250x, 500x)

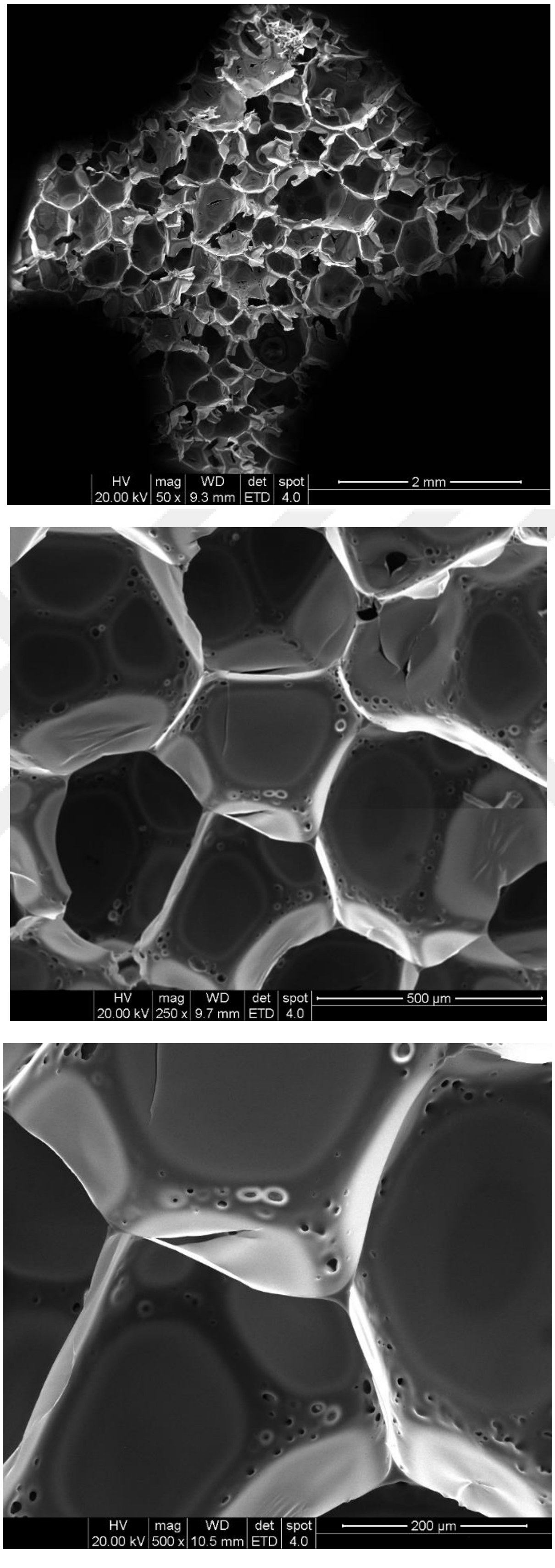

Figure 6.39 SEM photos of CPP (50x, 250x, 500x)