

MODIFICATION OF CALCIUM CARBONATE SURFACES IN NATURAL
GAS PLASMA FOR THEIR USE IN POLYPROPYLENE COMPOSITE
SYSTEMS

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

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IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
POLYMER SCIENCE AND TECHNOLOGY

DECEMBER 2006

Approval of the Graduate School of Nature and Applied Science

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ABSTRACT

MODIFICATION OF CALCIUM CARBONATE SURFACES IN NATURAL GAS PLASMA FOR THEIR USE IN POLYPROPYLENE COMPOSITE SYSTEMS

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December 2006, 73 pages

In this study calcium carbonate (CaCO_3) particles are surface modified by using plasma polymerized natural gas and effects of surface modification of CaCO_3 filler on mechanical properties of CaCO_3 -PP composites are investigated. Different combination of plasma factors; RF power, natural gas flow rate, and plasma discharge durations, are investigated. Mechanical properties such as tensile strength and Young's Modulus are measured by tensile testing machine. Storage modulus and loss modulus measurements are done by DMA. Some information about structures generated by natural gas plasma surface modification is obtained by FTIR tests. The tensile fracture surfaces of prepared composites are investigated by using SEM micrographs.

It is concluded that, despite some enhancement obtained in the moduli; the technique of natural gas plasma surface modification of CaCO_3 particles did not introduce significant improvement in mechanical properties of composite as expected. This result may partially be attributed to selected plasma parameters (i.e., flow rate, RF power, and discharge duration).

Keywords: Plasma Surface Modification, Filler, Calcium Carbonate, Polypropylene, Mechanical Properties.

ÖZ

POLİPROPİLEN KOMPOZİT SİSTEMLERİNDE KULLANILMA AMACIYLA KALSİYUM KARBONAT YÜZEYLERİNİN DOĞAL GAZ PLAZMASIYLA YÜZEY DEĞİŞİKLİĞİ

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Tez Yöneticisi: Prof. Dr. Güneri AKOVALI

Aralık 2006, 73 sayfa

Bu çalışmada kalsiyum karbonat (CaCO_3) taneciklerinin yüzey değişikliği plazmada polimerleşmiş doğal gaz kullanılarak gerçekleştirildi ve CaCO_3 dolgu yüzey değişikliğinin CaCO_3 -PP kompozitlerinin mekanik özelliklerine etkisi araştırıldı. Farklı plazma değişkenleri; RF gücü, doğal gaz akış hızı, ve plazma süresi'nin etkileri araştırıldı. Gerilme dayanımı ve Young katsayısı gibi mekanik özellikler gerilme testi cihazı ile ölçüldü. Elastik katsayı ve sönüm katsayı değerleri DMA ile test edildi. FTIR incelemeleri ile doğal gaz plazması sonucu oluşan yapı hakkında bilgi edinildi. Hazırlanmış örneklerin gerilme dayanımı testi kopma yüzeyleri taramalı elektron mikroskop'u ile incelendi.

Sonuç olarak; dayanım katsayısı değerlerindeki bazı artışlara rağmen, CaCO_3 parçacıklarının doğal gaz plazma ile yüzey değişimi beklendiği üzere mekanik özelliklerde önemli bir artış sağlayamadı. Bu sonuç belli bir oranda seçilen plazma parametrelerine (akış hızı, RF gücü, ve plazma süresi) bağlanabilir.

Anahtar Kelimeler: Plazma Yüzey Değişikliği, Dolgu, Kalsiyum Karbonat, Polipropilen, Mekanik Özellikler.

To My Family
and
To You

ACKNOWLEDGMENTS

I would like to express my deepest gratitude to my supervisor Prof. Dr. Güneri AKOVALI for his guidance, advice, criticism, encouragements and insight throughout the research.

I would also like to thank Alper ÜNVER for his suggestions and comments throughout the research. Without his valuable support, this work would be much more difficult.

I want to express my gratitude to Mikrons and Petkim for samples supplied.

I would like to thank to Prof. Dr. Teoman TİNÇER for his guidance and suggestions during the mechanical tests.

I would like to thank to Dr. Agnes SAFRANY from Hungarian Academy of Sciences Isotopes and Surface Chemistry Institute for SEM studies. Additionally, I would like to thank to Sevim ULUPINAR for DSC, DMA analyses and Seha TİRKEŞ for FTIR analyses.

And finally, I wish to express my sincere appreciation to my family for their endless support, encouragement, and love that they gave me in every moment of my life.

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ABBREVIATIONS

| | |
|-------------------|---|
| PP | Polypropylene |
| CaCO ₃ | Calcium Carbonate |
| E' | Elastic (Storage) Modulus |
| E'' | Loss Modulus |
| T _g | Glass Transition Temperature |
| T _m | Melting Temperature |
| tanδ | Damping |
| SEM | Scanning Electron Microscopy |
| FTIR | Fourier Transform Infrared Spectroscopy |
| DMA | Dynamic Mechanical Analysis |
| DSC | Differential Scanning Calorimetry |
| sccm | Standard Cubic Centimeters per Minute |
| RF | Radio Frequency |
| wt% | weight percent |

CHAPTER I

INTRODUCTION

Generally, polymers are not used alone as a final product. Depending on how the final product will be used, various additives can be compounded with the virgin polymers. Fillers are special additives in various forms of particulates that are commonly added to plastics and rubbers. With the combination of fillers, composite materials with enhanced mechanical properties can be achieved. According to their functions, fillers can be classified as reinforcing and non-reinforcing. Reinforcing fillers are used to improve the mechanical and physical properties of polymers, while non-reinforcing fillers are used mostly to reduce the cost of the final products.

Properties of filled composites are affected by the properties of the components, by the shape of the filler phase, by the morphology of the system, and by the extent of the polymer-filler interfacial interactions [1]. As for particulate-filled systems, there are multiple interactions with particles and polymer, at interfaces/interphases, where the matrix and particulates are in contact, which have great importance considering properties of the final product. In order to get better properties, proper surface treatment of particulate fillers is usually performed to get better adhesion between the matrix and the filler.

Amongst the particulate fillers, calcium carbonate (CaCO_3) has a wide application area in thermoplastic and thermoset materials. Relatively low cost of CaCO_3 is the main driving force for its wide usage. Additionally, it may improve modulus, heat resistance, hardness, processibility, shrinkage, and color fastness [2]. As an inorganic filler, however, CaCO_3 particles have polar, hydrophilic, and high free

energy surfaces. Therefore, they are intrinsically incompatible with most polymer surfaces with non-polar, hydrophobic, and with low energies. Polypropylene (PP) can be an example of these polymers that can not wet CaCO_3 surfaces properly. Poor dispersion and agglomeration that are the reasons of this incompatibility may result in voids and cavities at filler-matrix interface which can cause deterioration of mechanical properties, such as toughness [3]. Up to certain levels of loading these negative effects may be compensated, however, at higher levels, decline of the properties are inevitable. Additionally, existence of CaCO_3 in semi-crystalline polymers such as PP can reduce the stability of matrix during processing or during usage. Furthermore, due to polar nature of its surface, CaCO_3 can interact with the polar stabilizer molecules by interfering with hydroxy, ester, or amine groups of stabilizers and so protective capacity of antioxidants and light stabilizers can be reduced. Moreover, some CaCO_3 particles originally may contain impurities such as iron and manganese ions, which can help to catalyze the autoxidation reactions [4,5].

Compatibility of polar fillers with non-polar matrices can be achieved by proper surface modification of the filler. Plasma surface modification is one of the powerful techniques that can be used for surface modification. Previously, surface modification of CaCO_3 by plasma surface modification technique was studied for the first time by Akman [6]. In this study, which gave us the inspiration to pursue this work, acetylene was used as monomer for plasma polymerization. It was found that plasma can alter the CaCO_3 surfaces favorably. Some enhancement in elongation was also achieved.

In this study, CaCO_3 particles are surface modified by plasma technique and effects of surface modification on mechanical properties of PP- CaCO_3 composites are investigated. Natural gas is used as the monomer for proper surface modification of CaCO_3 . In our study, it is aimed to get better adhesion between CaCO_3 particulates and PP matrix by creating thin mostly hydrophobic plasma polymerized films of natural gas onto the surfaces of CaCO_3 . As both CaCO_3 and natural gas are readily available and economical, production of composite systems

with higher levels of filler loadings, possessing at least similar mechanical properties at the end, as compared to systems with much less filler content is targeted. By this way, it is proposed to lower the costs of the production of PP-CaCO₃ composite systems.

This thesis consists of four chapters. First chapter contains some brief information about polymeric composites, fillers, interfaces/interphases, plasma and plasma surface modification. The second chapter presents experimental details of this thesis work, while in the third chapter, results are presented with related discussion. In the fourth chapter this work is concluded.

1.1 Polymeric Composites

Composite materials can be defined as a macroscopic combination of two or more distinct materials, having a recognizable interface between them. These heterogeneous systems obtained by artificial combination of different materials in order to get better mechanical properties than the individual components by themselves cannot attain.

Concerning the mechanical properties of final composite product, polymers usually mixed with materials that have high strength/stiffness properties. Thus, the definition can be narrowed to systems that contain reinforcing material and a matrix that surrounds and supports the reinforcing material. Hence, it would be concluded that composites generally have a discontinuous phase, which can be fibers or particles, stiffer and stronger than the continuous matrix phase and physical or mechanical properties of composites are generally derived from that phase.

Composite systems can be classified in many ways, such as, by categorizing according to the geometry or according to the matrix material. Fibrous, laminated, and particulate fillers are the classes of geometrical categorization. Particulate fillers which cover a wide range of different materials are often spherical, or at least have dimensions of similar order in all directions (isometric). The particle characteristics can be classified as spheres, cubes, blocks, rods, flakes, and any other shapes of roughly equal axes. Common fillers used in polymeric composites are glass (spheres), CaCO_3 (cube and block), kaolin, mica, talc (flakes), and wood flour (flakes) [7]. Generally, particulate fillers improve some of the properties while degrading others, such as improving the strength and stiffness but reducing the impact strength. These composites are considered as particulate composites. Besides some filler can only be used for extending rather than reinforcing, as these filler particles are employed for the main purpose of cost reduction and these composites are generally referred as filled systems.

1.2 Fillers

Polymers are always used in combination with other ingredients. The term filler is usually used for solid additives added to polymers in order to reduce the costs of final product because of their relative low cost as compared to polymers. However, this addition can only be done up to certain loading levels, as the cost reduction comes with a decline in many mechanical properties.

Fillers can be classified as particulate fillers, rubbery fillers, fibrous fillers, etc. In general, particulate fillers are used in composites to reduce costs and/or to impart specific mechanical or physical properties [8]. They may be classified as mineral, natural or synthetic, inorganic or organic fillers. Mineral fillers include CaCO_3 , clay, talc, alumina tri-hydrate, natural silicas and mica [9].

The term extender is used for fillers that are added primarily to increase the bulk of the material, and to reduce the amount of the expensive polymer required for the application. Some particulate filler only serve as extenders. On the other hand, reinforcing fillers provide a substantial improvement in mechanical properties of the composite system, such as tensile strength, rigidity, durability, hardness and heat distortion temperature.

The incorporation of fillers such as mica, kaolin, CaCO_3 , and talc into thermoplastics is a common practice in the plastics industry. Depending on the application that the composite will be used, filler percent usually changes between 10 and 20 wt% [10]. Although higher loadings are also used, exceeding certain level of filler may adversely affect the processability, ductility, or strength of the composites.

Inevitably, all matrix properties are affected by added materials. From that point of view, effects on matrix properties are dependent on the aspect ratio of filler, size of the particle, the particle size distribution of the filler, filler surface modification, and degree of dispersion of fillers in the polymer [11]. Smaller particles (with large surface areas) provide better adhesion to the polymers. Coarse and fine particles together result in better packing, which also influences the optical properties of the matrix.

1.3 Interfaces and Interphases

The properties of all heterogeneous materials are determined by the characteristics of the components, composition, structure and interfacial interactions [12]. Similarly, in reinforced composites; interfaces play an important role in determining the final properties of the composite. However, in polymeric composites it would be very difficult to state an area with only two dimensions for

matrix and filler. On the other hand, an area having a thickness and surrounding the particle surface, having local properties different from those of the bulk matrix can be stated. This dynamic area called as interphase where momentum, mass and energy transfer occur. Such an interphase forms by the adsorption of the polymer on the surface of the filler in composite systems [12]. Its definition is schematically illustrated in Fig. 1.1. The size and type of interphase varies strongly with the nature of the particle and with the type of polymer matrix.

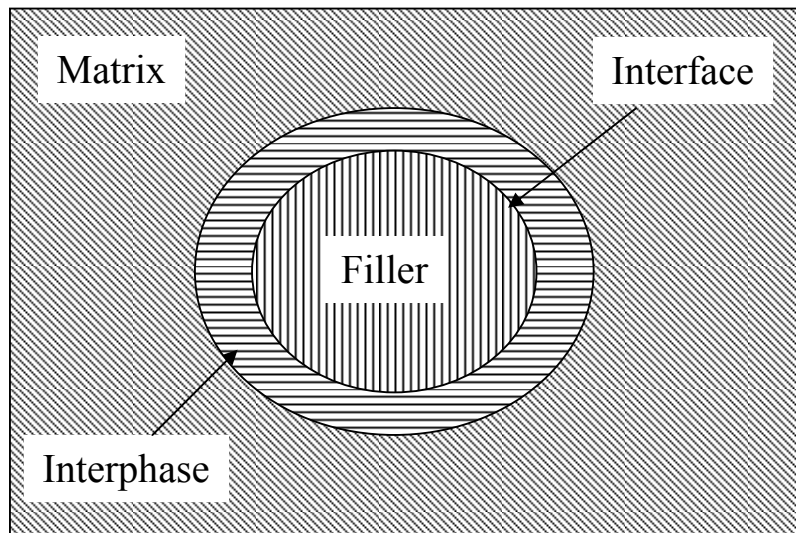


Figure 1.1 Conceptual drawing of interface and interphase in particulate filled composites.

Control methods of the interfacial properties may be summarized as follows;

- Mechanical modification: Thermal conditioning, simple washes and abrasion treatment of material surfaces.
- Physical Modification: Surface deposition and modification techniques using plasma and corona discharges.
- Chemical Modification: Modifying or coupling agents.

1.4 Surface Modification of Fillers

Polymer-filler interface is the key factor for the control of composite properties. High performance is achievable only with a strong interfacial adhesion. Natural surfaces of particulate fillers, however, are less than optimum for good interactions with polymers. Fillers are usually hydrophilic and do not easily combine with most polymeric materials which are usually hydrophobic. Therefore, fillers are often modified to provide a hydrophobic surface to increase the adhesion of hydrophobic polymers. Several approaches can be used for modifying filler surfaces. Increasing the number of active sites on the filler surface can be a solution. This would be performed either by physical treatments or by acid treatments. Another solution can be altering the chemical composition of existing active groups on the filler surface. Acetic treatment, isocyanation, grafting, addition of other low molecular weight substances, and silane modifications fall into this category.

With the aid of these methods, fillers then can interact with chemical groups present in the matrix material. Enhancement in mechanical properties is one of the results of such modification. Additionally, better rheological properties, hindered agglomeration are also achievable with increased interactions between filler and polymer.

1.5 Plasma

Plasma is a mixture of electrons, negatively and positively charged particles, and neutral atoms and molecules [13]. Taking into consideration the energy of the particles constituting it, plasma is energetically the fourth state of the matter, apart

from the solid, liquid, and gas states [14]. Figure 1.2 presents graphically the transitions between each of the four forms of matter occur in nature.

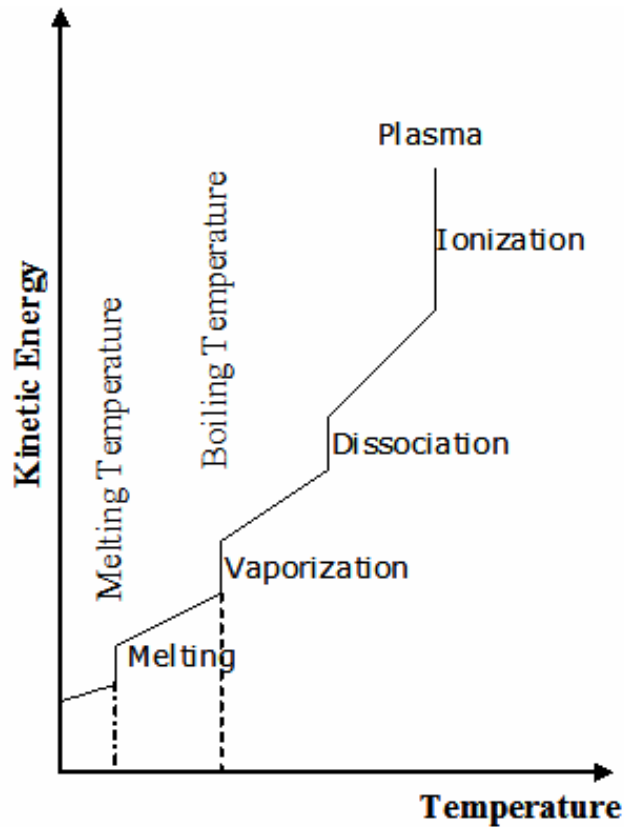


Figure 1.2 Transition states of matters [13]

Plasmas are generally categorized on the basis of electron densities and electron energies. However, it may also be categorized as equilibrium and non-equilibrium plasmas. Low temperature plasmas (glow discharge) that are suitable for the applications of polymeric materials are of the non-equilibrium type. In glow discharge plasma, the temperature of the ions and molecules are often ambient whereas that of electrons is higher by a factor almost up to 100. Thus plasmas produced by glow discharges are called non-equilibrium plasmas because the

electron temperature is not in equilibrium with the gas temperature. Other types of plasmas known are interstellar plasma, alkaline vapor plasma and hot plasma, which are often used for controlled fusion.

To reach the plasma state of atoms and molecules, energy for the ionization must be input into the system including atoms and molecules from an external energy source. Further, the plasma state does not sustain at atmospheric pressure, but at lower pressures. In summary, in order to get low temperature plasma medium in laboratory conditions, an external energy source, a vacuum system and a reaction chamber are required.

In general, due to its availability, electric energy is used for plasma ignition and maintaining the plasma state. Electric field can be produced either by an alternating current or by a direct current supply. The different alternating current frequencies employed for the excitations are 100 kHz, 13.56 MHz in the radio frequency range and 2.45 GHz in the microwave range. Frequencies in the range 10–20 MHz are most commonly used for industrial applications.

Amongst the excitation sources, the setup for RF is one of the simplest ones. In the case of RF discharge, two electrodes are mounted into (or around of) a vacuum chamber. Generally, a process gas at a pressure of several torrs is introduced. When the RF voltage exceeds a certain value in the range of some hundred volts depending on the type of the gas, pressure, and reactor geometry, the discharge ignites. The major drawbacks of RF discharges are the need of electrodes and the relatively low degree of ionization. A block diagram of RF cold plasma system used for material processing is presented in Fig. 1.3. Generally, it consists of a reactor, a power supply unit, a matching network, vacuum system, and controllers.

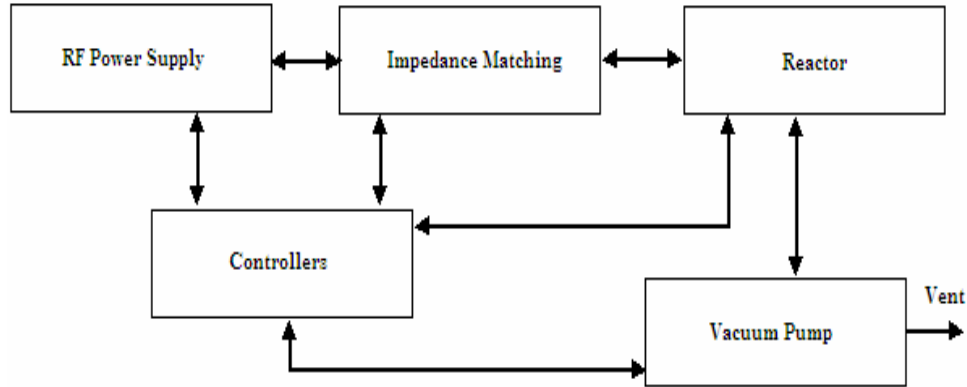
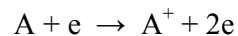


Figure 1.3 Block diagram of a typical RF plasma system

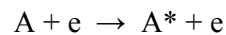
Inside the reactor, ionization takes place due to externally applied electric field. When sufficient energy supplied to an atom or a molecule, it produces electrons while leaving positive ions behind. Further ionization can be achieved by further collisions of accelerated ions and electrons by the external electric field. This excited state sustain for a very short period of time (<100 ns) and falls to a lower energy level (or ground state) by radiative decay. This relaxation process is known as glow discharge [15].

The general ionization mechanism that going on in plasma reactor can be summarized as follows [15]:

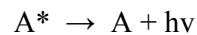
Ionization of an atom starts with the supply of sufficient energy from an external source:



Atoms can be promoted from ground state to excited state by electron impact as well;

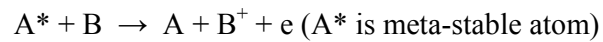


Radiative decay occurs when atom falls from excited state to lower energy level:

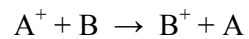


This relaxation produces a glow discharge.

Similarly, ionization of neutral atoms can be achieved if a neutral atom collides with a meta-stable atom (energy-rich chemical reagent with a longer radiative time) which is at an energy level higher than the ionization energy of the neutral atom:



or



Other than these, reactions like electron impact dissociation, secondary ionization, symmetrical resonant transfer, asymmetrical charge transfer, electron-ion recombination and ion-ion recombination can take place under the influence of the plasma conditions.

1.6 Plasma Parameters

A comprehensive list of the process parameters that can affect the finishing properties of plasma process is given in Table 1.1. However, parameters can also be categorized as follows:

a) When a polymer is introduced into plasma medium, interactions and reactions are governed by internal plasma parameters [16], which are;

- type of species present in the plasma
- spatial distributions
- energy distributions
- directional distributions

b) Internal plasma parameters are determined in a complex way by external plasma (process) parameters [16], such as;

- reactor geometry
- type of excitation
- applied power
- type process gas
- gas pressure
- gas flow rate

Table 1.1 Cold Plasma Parameters for Materials Processing [14]

| Kinetic (gas system) | Electrical (plasma system) | Surface (substrate system) |
|---|--|--|
| 1. Precursor gases 2. Carrier gases 3. Mass flow rates 4. Pressure 5. Gas delivery location | 1. Frequency (DC and RF) <ul style="list-style-type: none"> • Free fall • Mobility • Diffusion 2. Electrode geometry <ul style="list-style-type: none"> • Electrodeless • Electrode 3. Discharge power <ul style="list-style-type: none"> • Field strength • Current density • Particle energy • Active neutrals • VIS to UV radiation 4. Electrode material | 1. Material <ul style="list-style-type: none"> • Conducting • Insulating 2. Temperature 3. Position |

1.7 Plasma Surface Modification

In non-equilibrium plasmas, high energy electrons can be used to dissociate and ionize the molecules of gas to form chemically reactive radicals and ions. In such conditions, reaction can be promoted at low temperatures as thermal energy is not needed to break chemical bonds. With non-equilibrium plasma, it is possible to process substrates that do not have thermal stability necessary to withstand processing at high temperatures. Therefore, nowadays, on a laboratory scale, plasma modification is the most accepted technique for the surface modification of polymers. It is a clean and solvent-free technique for achieving surface modification. However, high investment and operating cost are the main deficits of plasma techniques.

CHAPTER II

EXPERIMENTAL

2.1 Materials

2.1.1 Calcium Carbonate

Calcium carbonate (CaCO_3) is one of the most abundant white mineral (15%) in the earth's sedimentary crust [17]. It is called with a number of different names such as marble, limestone, calcite, and chalk. CaCO_3 exists in three crystalline formations (calcite, aragonite, vaterite), but only calcite has practical importance [18]. It is found in the form of marble, limestone and chalk. There is an abundant supply of this mineral filler and it is commercially available in a wide range of particle sizes. Generally, natural resources consist high percent (>98%) of CaCO_3 , with trace amounts of magnesium carbonate, iron oxide, and aluminum silicates. Having Mohs hardness of 3, all types are relatively soft minerals, with a specific gravity of 2.71 at 23 °C. It is non-toxic, nonirritating, nonabrasive, odorless, and white in color with low refractive index.

Due to its low cost, CaCO_3 is one of the most widely used filler (or extender) in the plastics industry. Its price varies with the grade. In many polypropylene (PP) applications it competes with talc. Its main advantages are being non-toxic, having low cost, low moisture with bright white colors (which is valuable for coloring purpose). It is generally used as an extender at high loadings; however, it can also improve impact strength and stiffness with surface properties of high brightness

and high gloss. The same with other particulate fillers, its use reduces shrinkage during molding [19]. Surface treated or fine grades of CaCO_3 have better dispersions in PP than uncoated or coarse grades. Nevertheless, it brings some disadvantages such as: lowered tensile and compressive strengths, reduced elongation, poor corrosion resistance, and increase in part weight (having density of 2.7 g/cm^3), that restricts its wide usage.

Calcium carbonates are available in different grades: dry processed, wet or water ground, beneficiated ground, precipitated, and surface-treated. For many applications, the filler is manufactured by merely crushing the mineral, followed by pulverizing and air classification into the desired particle size. Precipitated grade is a synthetic form produced by carbonization and is available in very fine particle. This material is usually used for food contact applications due to its available high purity grades. Nonetheless, higher production cost than the ground mineral products, restricts its usage in other applications that do not require high purity.

In order to improve the compatibility with, and dispersion in, polymers, fatty or other organic acids, and especially stearic acid surface treatments are widely performed. More hydrophobic surfaces, increase in oxidation resistance and reduction in wear during processing, are other achievable properties with such coatings.

In beneficiated ground, which is the most widely used grade, iron and silica are usually removed to minimize catalyzation of resin degradation, and the mineral is finely ground, with median particle sizes of 1–10 μm . Different manufacturing methods produce different size distributions of the particulate fillers (i.e. largest particle size ($>12 \mu\text{m}$) is obtained with dry processed grades; coarse particles are removed in wet ground grades, with a median particle size of $<3 \mu\text{m}$).

As a filler, CaCO_3 properties can be summarized as follows [20]:

- It is the most abundant white material in the earth's crust.

- It is also known as marble, limestone, calcite, chalk, aragonite, coral, shell, whiting, and dolomite.
- It is the largest volume mineral filler used in the plastics, sealants, rubbers, paper, coating, adhesive, and textile industries.
- Its wide utility is due to its whiteness, low abrasion, broad particle-size range, and low cost.
- Commercial grades are coarse ground, fine ground, and precipitated.

For the present study, CaCO_3 is provided from Mikron's A.Ş Niğde. Product specifications and particle size distribution can be seen in Fig. 2.1 and Table 2.1 [21].

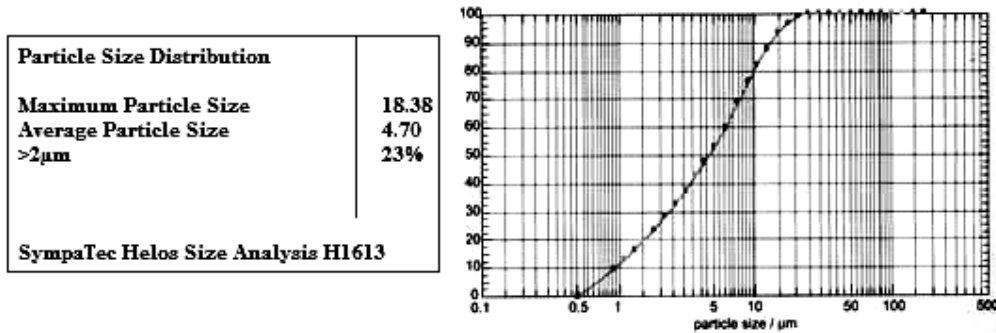


Figure 2.1 Particle size distribution of CaCO_3

Table 2.1 CaCO₃ specification

| | |
|--------------------------------|-----------------------------|
| Name of the product | TC 5 |
| Product specifications | High purity and whiteness |
| Source | Mikron's Kalsit Ocağı-Niğde |
| Chemical Specifications | |
| CaCO ₃ | >99.5% |
| MgCO ₃ | <0.20% |
| Fe ₂ O ₃ | <0.01% |
| SiO ₂ | <0.01% |
| Al ₂ O ₃ | <0.02% |
| Amount insoluble in HCL | <0.01% |
| Physical Specifications | |
| Density | 2.7 gr/cm ³ |
| Hardness | 3 Mohs |
| Whiteness (L=) | 98.5% |

2.1.2 Polypropylene

PP, which has a wide range of application areas, is one of the versatile polymers. It is used in daily life as films, fibers, and extruded or molded goods. It is one of the fastest growing classes of thermoplastics, following the Polyethylene and Polyvinyl Chloride [11].

Its low cost and favorable mechanical properties are the driving force for its high growth rate in use. Among the thermoplastics, PP is one of the lightest polymers (0.9g/cc) with high strength to weight ratio. It also has a high melting temperature (160–170°C) and has better heat resistance than other low cost thermoplastics [11].

PP is often compounded with fillers in order to reduce costs and get better mechanical strength and enhanced thermal resistance. However, in such composites, rigid filler addition usually results in lowered toughness and impact resistance (especially at low temperatures). CaCO₃ is one of the most widely used

particulate fillers in PP composites. It increases not only the economical efficiency of the final product but also some mechanical properties. However, the filler content usually does not exceed 10–20wt% [10], because highly filled systems show insufficient mechanical properties like low tensile strength.

PP is used in components of automobiles, large or small appliances, packaging films, containers, medical devices, and textiles. Its key properties are as follows [22, 23];

- Relatively low density than other plastics.
- Easiness in processability
- High chemical inertia
- High environmental stress-cracking resistance
- Good water barrier
- Non-toxic, odorless, tasteless
- High dielectric properties
- Transparency, especially with random copolymers
- High tensile strength
- Suitable to dry coloring
- Long shelf life.
- Recyclable

For this thesis, PP used is provided from PETKİM. Product is marketed under the trade name of Petoplen MH 418. Its specifications are given in Table 2.2 [23].

Table 2.2 Specifications of PP used for composite preparations

| | |
|----------------|-----------------|
| Material | Isotactic PP |
| Supplier | Petkim |
| Trade name | Petoplen MH 418 |
| MFI | 4–6g/10 min |
| T _m | 166°C |
| Shape | Pellet |

2.1.3 Natural Gas

Natural Gas is used directly from the city gas line. It is known as a gas mixture consisting methane, ethane, propane, butane, pentane, and hexane with the compositions given in Table 2.3.

Table 2.3 Natural Gas Content [24]

| | Mole percent |
|--|--------------|
| Methane CH ₄ | 0,90 |
| Ethane C ₂ H ₆ | 0,05 |
| Propane C ₃ H ₈ | 0,03 |
| Butane C ₄ H ₁₀ | 0,01 |
| Pentane C ₅ H ₁₂ | 0,01 |
| Hexane C ₆ H ₁₄ | 0,01 |

2.2 Apparatus

2.2.1 Plasma System

Plasma system used in our discharge experiments consists of a vacuum pump, liquid nitrogen trap, Pyrex Reactor (18cm in length, 4.5cm in diameter), two external electrodes (15cmX6.5cm and 15cmX5.5cm)), mass flow meter and its controller unit (MKS-247 4 channel), capacitance manometer (MKS 10-10⁻¹torr), RF generator and matching unit (0-50W RF, 13.56 MHz, Tegal Corporation). Image of the reactor and schematic representation of the system are given in Fig. 2.2 and Fig. 2.3, respectively.

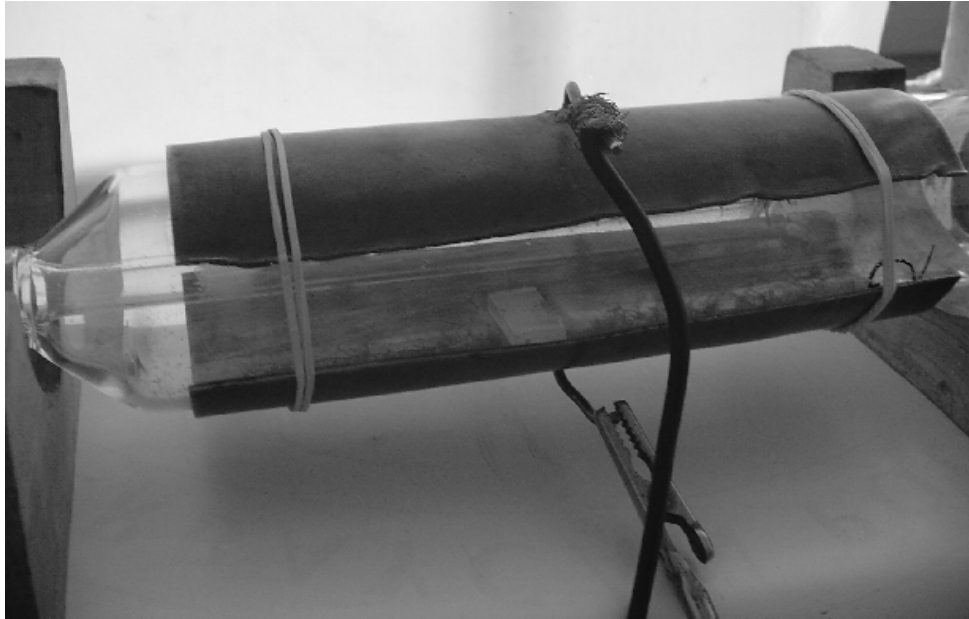


Figure 2.2 Image of the reactor during plasma application

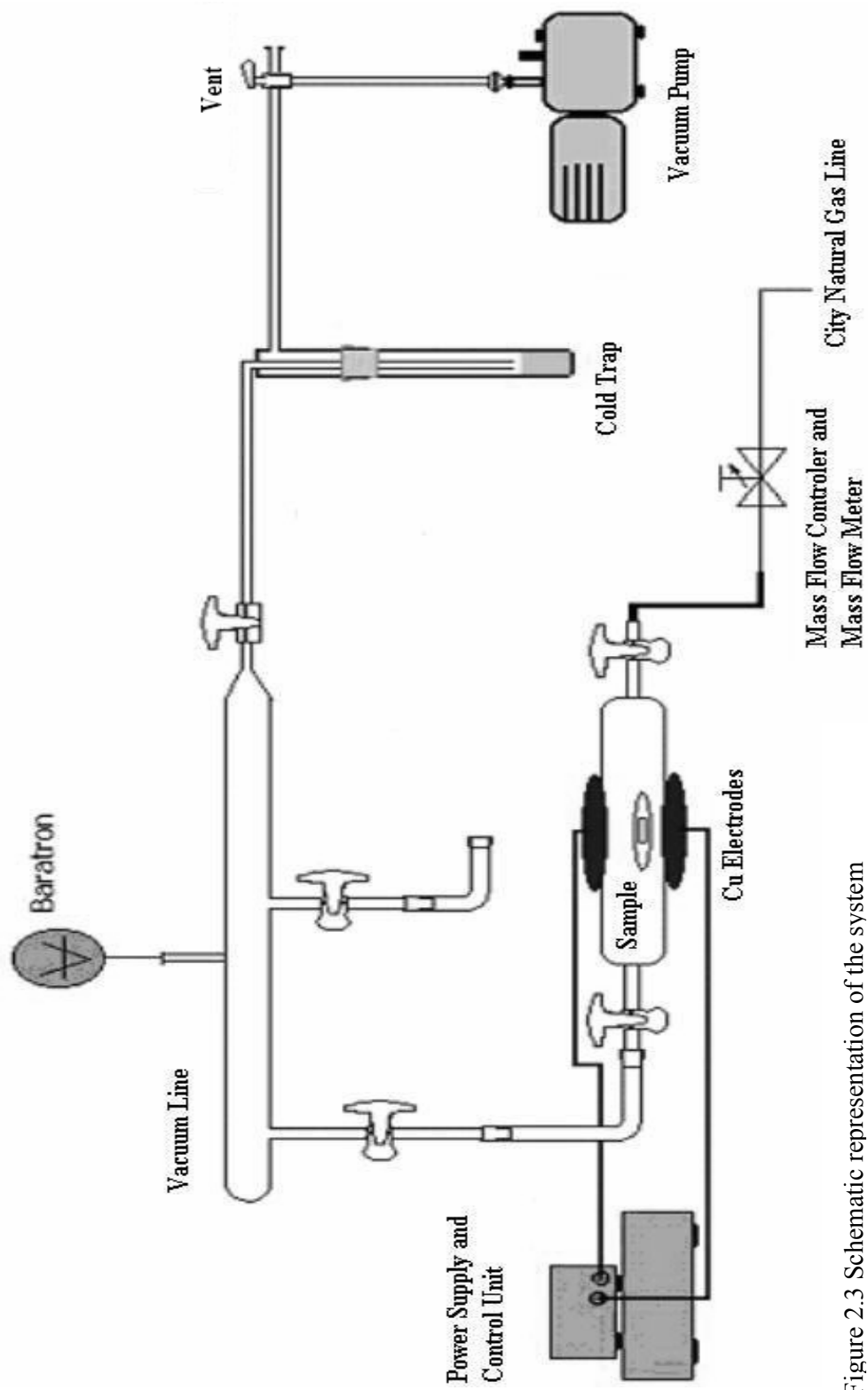


Figure 2.3 Schematic representation of the system

2.2.1.1 Power Supply

Power generator unit is used to initiate and sustain plasma inside the reactor. In this study commercial RF plasma system is operated at specific frequency of 13.56 MHz established by international agreements. The RF generator is designed to operate at a constant impedance of 50 ohm. As the impedance of glow discharge is much higher and varies with the process parameters, it is necessary to use an impedance matching network unit between reactor and power supply to match the impedance of the plasma to the output impedance of the generator. These can be done either manually or automatic devices. Otherwise most of the power will reflect to the power supply instead of being absorbed by the plasma medium [14].

2.2.1.2 Matching Network

The impedance of the plasma can vary from a few ohms to several thousand ohms. Therefore, an impedance match is necessary to prevent excessive reflected power from damaging the generator, and to know how much power is being delivered into the plasma media actually.

Impedance matching network is usually an adjustable transformer that transforms the impedance of the plasma to the required output impedance of the generator. The matching unit is placed physically as close as possible to the powered electrode. In parallel plate reactors the matching unit is usually mounted onto the flange supporting the powered electrode.

When the power impedance match is achieved, the reflected power is usually less than 1% of the forward power and most of the electrical energy is being absorbed by the plasma discharge media.

2.2.1.3 Vacuum System

In order to get glow discharge plasma at room temperatures, low pressure of $1-10^{-2}$ torr with a continuous gas flow into the reactor is needed. Therefore, vacuum system must maintain this pressure/flow regime. In vacuum process combination of several pump systems is used to reach the system lower base pressures quickly. Depending on the desired pressure inside the system rotary pump would also be sufficient alone. However, there always exists remaining gases inside of the system, such as air, and water vapor. Remaining gases may also be consumed in chemical reactions under plasma conditions.

2.2.1.4 Controller

As controller is a kind of brain of the plasma system, it should control all the process variables; pressure, gas flow rate, power level, and processing time. Depending on the operation to be controlled it may be a simple relay or a timer, a needle valve, a microprocessor with sophisticated displays, a fully automated process control terminal with multi-process capabilities, electronic data-outputs, and alarm systems. In our system, natural gas is controlled with a mass flow controller unit (MKS-247 4 channel).

2.2.2 Brabender Plasticorder

A Brabender Plasticorder Model PLV 151 processibility tester is used to mix the materials. Processing temperature is 210°C for 4 minutes at a mixing rate of 60 rpm.

2.2.3 Platen Press and Molds

A PHI platen press is used to press the samples. In order to prevent melt adhesion to the steel molds, polyester films are placed to the inner side of the molds. Processing temperature is 210°C for 10 minutes.

2.2.4 Tensile Tester

LLoyd Model LS 500 computer controlled tensile testing machine is used for mechanical test of the samples. The sample sizes are kept at following values, gage length: 3.1 cm, width of the sample: 2.87×10^{-1} cm, and thickness of the sample: 9.4×10^{-2} cm (see Fig. 2.4). The rate of the elongation is 0.31 cm/min. The number of specimens tested for each measurement is 9-10.

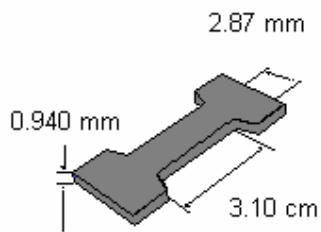


Figure 2.4 Dimensions of the specimens used for tensile tests

2.2.5 Scanning Electron Microscopy

JEOL-JSM LV 5600 scanning electron microscope is used to investigate the tensile fracture surfaces of selected composite samples that are prepared with treated and untreated CaCO₃ fillers.

2.2.6 FTIR Spectrometer

BRUKER Vertex 70 FTIR spectrometer is used to get information about the chemical structure of the new surfaces obtained after surface modification with natural gas plasma. With this aim, natural gas plasma is re-applied to sodium chloride optical crystals for the selected plasma conditions.

2.2.7 Dynamic Mechanical Relaxation Spectra

Dupont Thermal Analyst 2000 dynamic mechanical analyzer (DMA) is used to determine the mechanical property changes of the samples over a wide temperature range. Thermal scanning is performed from -80 °C to 80 °C with a heating rate of 5°C under resonance mode. Samples with dimensions of 3 cm X 1 cm X 0.9 mm are cut from plates prepared for tensile tests.

2.2.8 Differential Scanning Calorimeter

Thermal transition of selected composites are examined by using Dupont Thermal Analyst 2000 Differential Scanning Calorimeter 910S. Thermograms are taken in

the temperature range of -100 °C to 200 °C. Samples are heated with the uniform rate of 5 °C/min. Average sample weight used is 7.8 mg.

2.3 Sample Preparation

As it may contain great amount of moisture [25], CaCO₃ particles are first dried in vacuum oven at 80 °C for 12 hours. Then, they are kept in the desiccator until their surface modifications performed.

Surface modification by natural gas plasma is performed by means of the system shown in Figure 2.2. Firstly, particles are placed inside the reactor then they are spread out by mild shaking in order to get maximum filler surface area for plasma interactions. After lowering the system pressure to base pressure of 0.302 torr with the rotary vane pump, natural gas supplied into system at a certain rate with the help of mass flow meter and mass flow controller units. When system pressure reached to a stable value, plasma glow discharge is ignited. For all treatments, just after ignition, system pressure showed a little decrease. Surface modification by natural gas plasma is applied under different power, time and gas flow rate combinations (see Table 2.4).

Plasma durations are chosen considering the previous study [6]. The three different determined discharge periods are 0.5, 1, and 2 hours. Power supply unit of the system can operate between 0-60 watts. However stable plasma glow discharge can only be reached between 10 and 50 watts. These two power values are used as boundary values throughout the experiments so as to observe the actual difference possibly resulted in surface modifications of CaCO₃ particles by different powers applied. Gas flow rates are chosen according to the flow meter's capability which is in between 0 and 7.14 sccm for natural gas. Like discharge power, the effect of gas flow rate is also investigated at three different flow rate values, which are 1, 3

and 7 sccm. However, natural gas flow rate is kept constant at 7 sccm while investigating the effects of other plasma parameters, i.e. power and time.

Reactor is filled up to a certain value where the height of CaCO_3 is reached nearly to 0.5 cm (see Fig. 2.2), at the bottom. The reactor is designed to be separated from system without vacuum breakage. This make possible to remove the reactor from the system and than regenerate the surface at the bottom by a little shaking in order to modify the surface of the particles from sub layers. At every one sixth of the total plasma process period (see Table 2.4), glow discharge is turned off and reactor, which is under vacuum, is separated from the system and particle surface is refreshed 6 times. Afterwards, reactor is connected to the system prior to pressure equalization between the system and the reactor. After pressure equivalence monomer flow is re-initiated and glow discharge is ignited again as the system became stable.

Composite plates are prepared from virgin PP or PP filled with untreated and surface enhanced CaCO_3 . For mixing of polymer melt and filler a Brabender Plasticorder is used. In mixing process, first PP pellets are introduced into the Brabender working at a rate of 60 rpm at 210 °C in 1 minute period. Brabender's mixing rate is chosen to be the same as the Akman's study [6]. Then CaCO_3 (treated or untreated) is introduced and both matrix and filler are mixed for 3 more minutes. The output of Brabender is then pre-molded at 210°C and cut into small pieces and molded again at 210 °C for 10 minutes under a pressure of 10 atm. Obtained composite plates are sized to 20 cm X 10 cm X 0.94 cm.

As it is known that very rapid cooling can suppress crystallization [11], hot mold taken out from platen press at 210 °C is allowed to cool at room temperature for 5 minutes and then rapid cooling is achieved with cold water bath. Surfaces of plates taken out from platen press are became more rigid inside between two molds in that 5 minutes period and better surface finishes are obtained from final rapid cooling. Subsequently, specimens are cut out for tensile test by using the dump-bell shaped die (see Fig. 2.4). For every pre-determined conditions, except sample

#9 and #13 (see Table 2.1), two plates are prepared and 9-10 specimens are cropped from each plates.

In order to get same thermal history with other plates prepared, plates of 100% pure PP are also mixed in Brabender, then pre-molded, cut in to small pieces, re-molded, cooled, and cut out for mechanical tests.

Table 2.4 Plates prepared during study

| Sample No | CaCO₃ (wt %) | Power (W) | Gas Flow Rate (sccm) | Time (hour) |
|------------------|--------------------------------|------------------|-----------------------------|--------------------|
| 1 | 30 | 10 | 1 | 0.5 |
| 2 | 30 | 10 | 3 | 0.5 |
| 3 | 30 | 10 | 7 | 0.5 |
| 4 | 30 | 10 | 7 | 1 |
| 5 | 30 | 10 | 7 | 2 |
| 6 | 30 | 50 | 7 | 0.5 |
| 7 | 30 | 50 | 7 | 1 |
| 8 | 30 | 50 | 7 | 2 |
| 9* | 30 | 50 | 7 | 2 |
| 10 | 0 | - | - | - |
| 11 | 30 | - | - | - |
| 12 | 50 | - | - | - |
| 13 | 50 | 50 | 7 | 2 |

* Plate prepared from powders kept under atmospheric condition for one month after plasma modification.

For all applied plasma surface modifications, the deposition of plasma polymerized natural gas is observed in different forms. As the total energy given into the system by applied plasma increased, white color of the CaCO₃ became darker. Color changes of CaCO₃ are observed visually.

Apart from tensile tests, DSC and DMA specimens for certain conditions are also cut and their mechanical in response to changing temperature are observed.

Detailed chemical changes onto the surface of CaCO_3 are tried to be observed with re-applying the same plasma conditions on sodium chloride crystals and taking FTIR spectrum of them. SEM pictures are used to examine the fracture surfaces of the composite samples selected from treated and untreated filler containing specimens.

CHAPTER III

RESULTS AND DISCUSSION

Interphases/interfaces, where the matrix and fillers are in contact, have a great influence on the mechanical properties of the final product. As a mineral filler, CaCO_3 particles have mostly polar, hydrophilic, and high free energy surfaces. Thus, it is expected to be incompatible with the non-polar, more hydrophobic, and low free energy polymer matrices. So far several methods are conducted to make this filler compatible with non-polar matrices (especially with polypropylene (PP)) [26-31], as incompatibility is the reason for agglomeration and poor dispersion, which results in deterioration of the mechanical properties of the final product. Generally, CaCO_3 particles surface are modified with covered organic materials and silicate minerals. Amongst those methods, surface modification with stearic acid has been used for many years. Even though, it is not as wide spread as its counterparts, plasma polymerization can also be regarded as one of the powerful method for surface modification. It is a clean, solvent-free technique that can modify almost any surface with a great uniformity. It is capable of varying surface properties of the substrate without changing the bulk properties of plastic. Additionally, unlike other polymerization methods, monomer does not have to have an active double bond or functional group. Plasma polymerized methane and ethane can be example of this [32-34].

Previously, surface modification of CaCO_3 by plasma surface modification technique was studied by Akman [6]. In that study, acetylene was used as the monomer. For two different steady plasma conditions selected, mechanical property changes of 10, 20 and 30wt% loaded PP- CaCO_3 composites are compared in the study. It was demonstrated for the first time that plasma can be

used for surface modification of CaCO_3 particles. DSC analyses showed that surface modification of CaCO_3 did not affect the percent crystallinity of PP in the composites prepared. With tensile tests, it was seen that for both modified and unmodified systems toughness, yield strength, and elongation at break values of PP- CaCO_3 composites decreased with the increase of filler percent. On the other hand, one of the applied plasma conditions showed more than 50% increase for elongation at break values of each loading level.

As Akman showed that modified CaCO_3 particles when used in PP composite systems may yield better mechanical properties than untreated ones, plasma surface modification of CaCO_3 is further studied under different plasma conditions with a different monomer. Since it is readily available and economical, natural gas was chosen as monomer. Additionally, natural gas is mostly composed of methane whose plasma polymer would be expected to give a PE-like structure, which probably will produce proper surfaces on CaCO_3 filler to be compatible with the PP.

In this study, CaCO_3 particles are surface modified by depositing thin plasma polymerized natural gas on particle surfaces and effects of surface modification on mechanical properties of PP- CaCO_3 composites are investigated.

3.1 Fourier Transform Infrared Spectroscopy

To have some understanding of the nature of the deposited plasma polymeric material onto the surfaces of CaCO_3 particles; Fourier Transform Infrared Spectroscopy (FTIR) spectra of films obtained at selected plasma conditions on NaCl optic crystal surfaces are checked. For this purpose, being parallel with the plasma conditions used for the samples tested mechanically, six plasma conditions are selected and applied. Since CaCO_3 particles would not allow one to take proper IR spectra to check it experimentally, combinations of selected sample plasma

treatments are re-applied onto NaCl crystals, which are placed inside of the reactor. Like it is done for the treated CaCO₃, FTIR spectra of all crystals are taken immediately after plasma treatment, in order to prevent the possible complicating effects of oxygen on to the structure.

As it is stated in the experimental section, natural gas consists of simple hydrocarbons. Nearly 90% of natural gas is methane. Other 10% of it is propane, butane, and so on. Hence, one can expect to find the absorption bands of C-H and C-C bonds in the FTIR spectra. Besides, it is known that, it is nearly impossible to avoid traces of oxygen incorporation to the system, either of water vapor origin or from atmospheric oxygen. Therefore, O-H, C-O or C=O bands may also present in the spectra. Spectra of plasma polymerized natural gas which are obtained at the conditions of 2h and 0.5h of 50W-7sccm, 0.5h, 1h, and 2h of 10W-7sccm, and 10W-3sccm-0.5h are given in Fig.s 3.1-3.

As it is expected from natural gas plasma, when the spectra of all samples are investigated, it is seen that methyl group's (-CH₃) asymmetric and symmetric stretches are present at 2960 and 2872 cm⁻¹, respectively. Additionally, even though, for some samples they are not pointed with proper wave numbers, all spectra have the peaks at 2927 or 2931 cm⁻¹ indicating the asymmetric methylene stretching. With the presence of these peaks, it can be stated that there exists a saturated aliphatic structure for the plasma polymer of natural gas, which can be assumed that the same type of coat is being produced on the CaCO₃ particles after natural gas plasma application.

In general, branching that occurs in hydrocarbons shows skeletal stretching vibrations and methyl bending vibration below 1500 cm⁻¹ in their spectra. For every spectrum, peaks at around 1460 cm⁻¹ are indications of these branches. As it can be seen from spectra, however, it would not be wrong to expect to have different degree of branching for each plasma condition. In other words, small variations in the heights of peaks for different plasma conditions can be the reason of different branching degree of structure obtained. Comparing the bands of

methyl bending vibrations at 1460 cm^{-1} of the plasma conditions 10W-3sccm-0.5h and 10W-7sccm-0.5h (see Fig. 3.1), the difference between two peaks can clearly be seen as the plasma condition with the monomer flow rate of 7sccm has a really strong band. This increase in height may suggest that flow rate would be a factor that can affect branching degree. Conversely, similar effect can not be seen for plasma duration. Fig. 3.2 shows the spectra of three 10W-7sccm conditions with plasma durations of 0.5, 1, and 2 hours. Again, 10W-7sccm-0.5h spectrum has the longest peak of methyl bending vibration. As 1h plasma has the shortest peak, it would not be possible to reach a consistent conclusion for the effect of plasma duration on branching. Fig. 3.3 shows the spectra of two 50W-7sccm conditions with plasma durations of 0.5h and 2h. Comparing two figures, it is seen that RF power increase from 10W to 50W decreases the branching for 0.5h and does not change the peak height for 2h.

The symmetrical bending vibration, which involves the in-phase bending of C-H bond, generally, occurs near 1375 cm^{-1} . This absorption band becomes very stable when methyl group is attached to another carbon atom. Since every single spectrum has this band at exactly 1376 cm^{-1} or 1373 cm^{-1} , it would not be wrong to state that plasma polymerized natural gas, which mainly consists of methane, results in a polymeric film with a saturated and branched PE-like hydrocarbon structure.

It is known that C=O stretching vibrations show strong bands in the large region of $1870\text{-}1540\text{ cm}^{-1}$ for different chemical structures. For example, normal aliphatic ketones absorb at 1715 cm^{-1} or aliphatic aldehydes absorb near $1740\text{-}1720\text{ cm}^{-1}$. In the spectra there exist peaks around 1700, which suggests the C=O stretching vibrations. Besides, there are some peaks between 3450 cm^{-1} and 4000 cm^{-1} which indicates O-H stretching. This proves the oxygen incorporation with the radicals generated by plasma whether by atmospheric oxygen or water vapor present in the reactor.

Table 3.1 shows the peak assignments of spectra of applied natural gas plasmas on sodium chloride crystals.

Table 3.1 Peak assignments of FTIR spectra

| Wave Number | Assignment |
|---------------------------|--|
| 2960cm ⁻¹ | -CH ₃ asymmetric stretch |
| 2872cm ⁻¹ | -CH ₃ symmetric stretch |
| 2930cm ⁻¹ | Methylene asymmetric stretch |
| 1460cm ⁻¹ | Methyl bending vibrations |
| 1373cm ⁻¹ | C-H inphase symmetrical bending vibrations |
| 1715cm ⁻¹ | C=O stretches |
| 3450-4000cm ⁻¹ | O-H stretches |

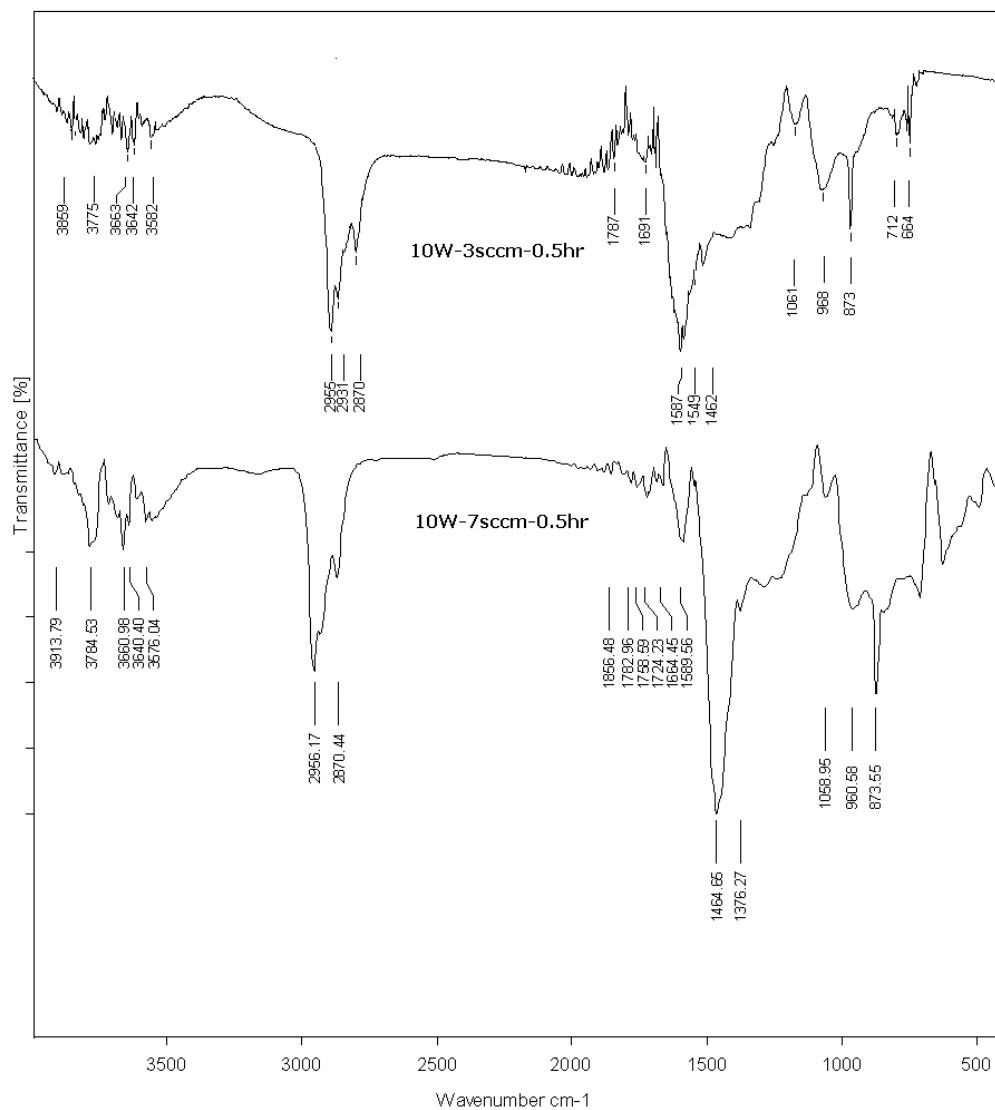


Figure 3.1 FTIR spectra of sodium chloride crystals natural gas plasma surface treated under conditions of 10W-3sccm-0.5h and 10W-7sccm-0.5h

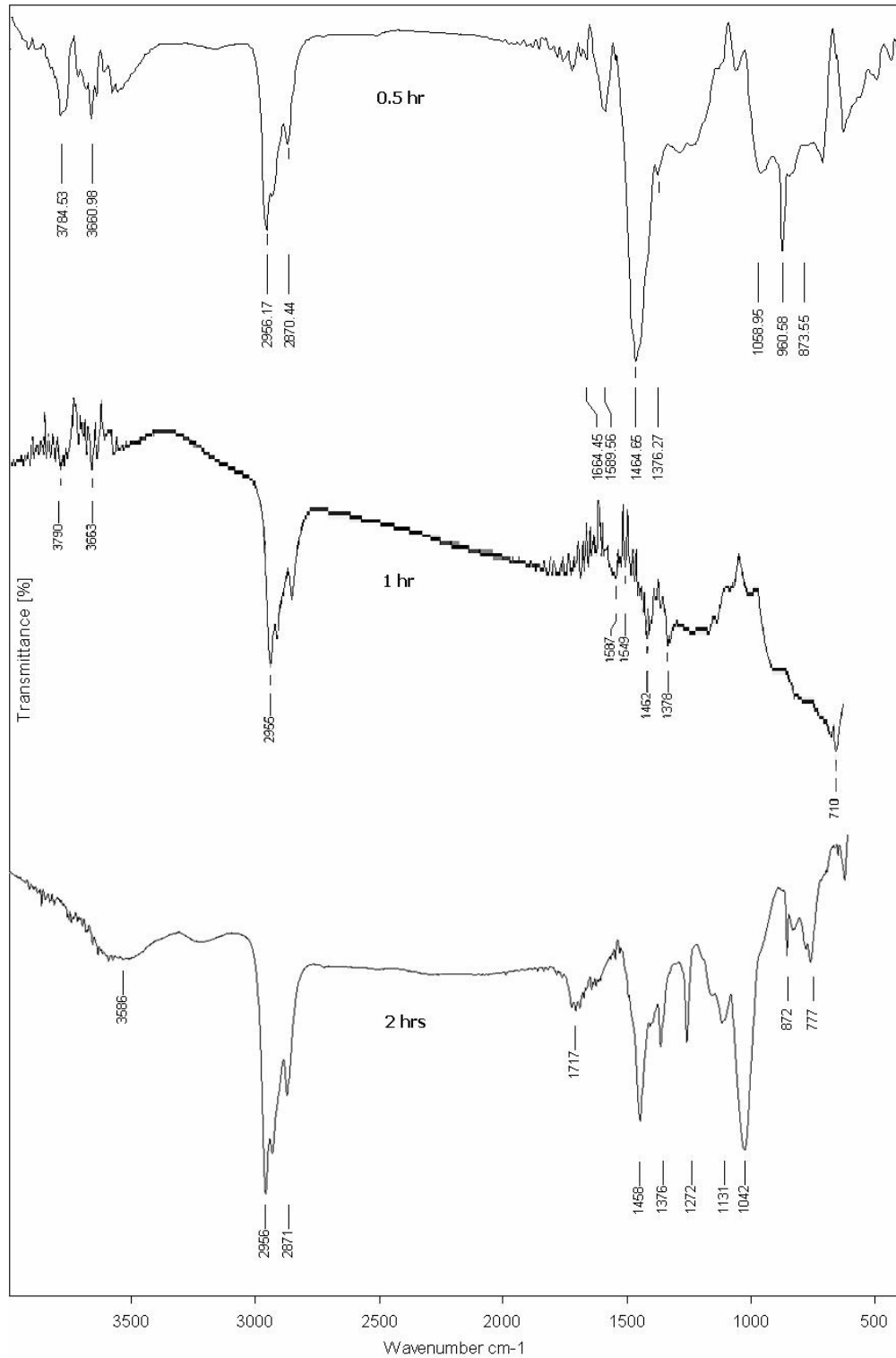


Figure 3.2 FTIR spectra of sodium chloride crystals natural gas plasma surface treated under conditions of 10W-7sccm-0.5h, 10W-7sccm-1h, and 10W-7sccm-2h

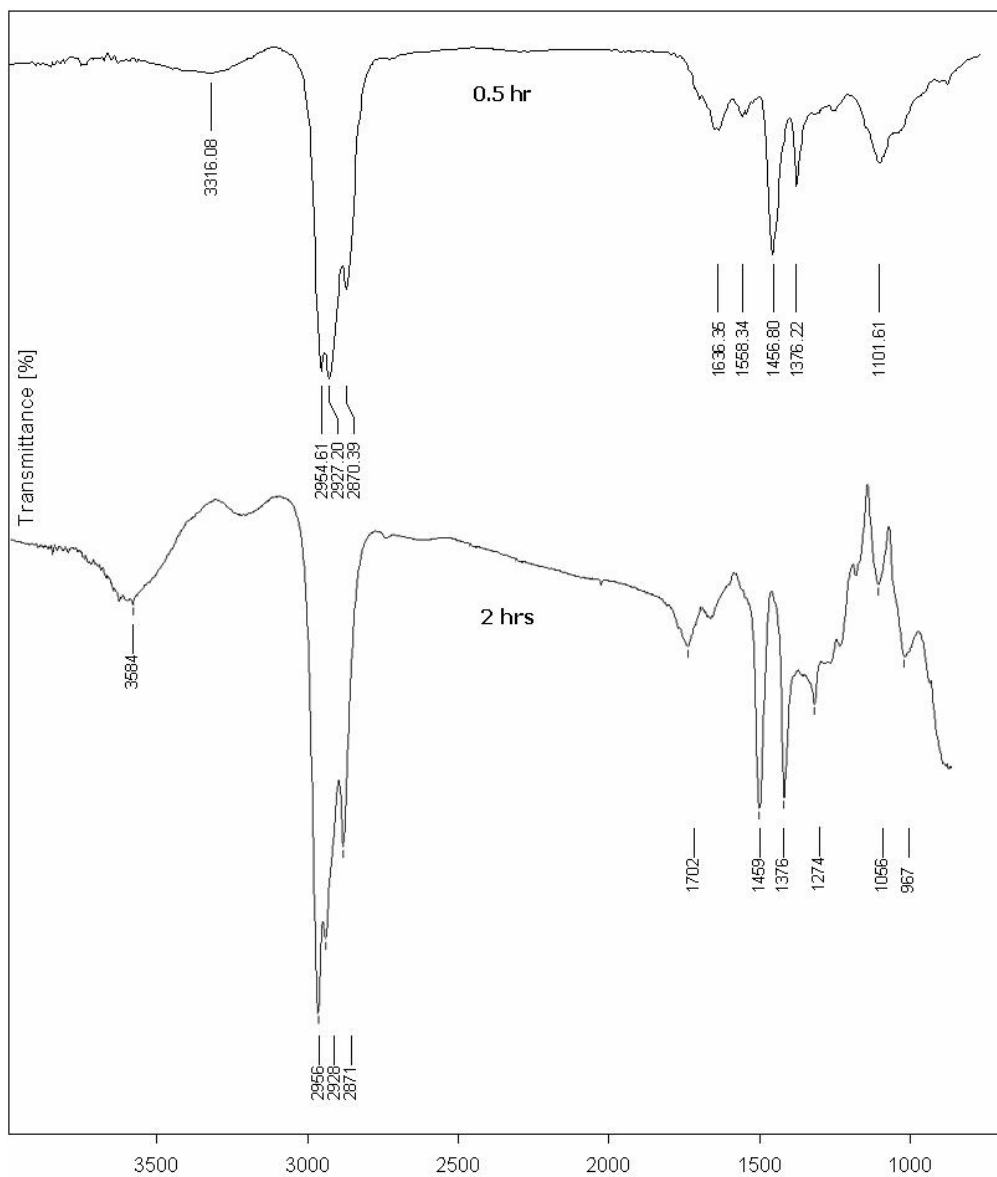


Figure 3.3 FTIR spectra of sodium chloride crystals natural gas plasma surface treated under conditions of 50W-7sccm-0.5h and 50W-7sccm-2h

3.2 Differential Scanning Calorimetry

In order to investigate the effects of CaCO₃ loadings and plasma surface modification of CaCO₃ particles on degree of crystallinity of the matrix, Differential Scanning Calorimetry (DSC) experiments are performed. The crystallization behavior of the composites is studied in the temperature range of -100 to 200°C under nitrogen atmosphere with a heating rate of 5°C/min. Unlike T_m, legible T_g values of samples cannot be attained by DSC. Obviously crystallinities and high filler loadings are blocking appearance of T_g in the DSC curves.

Table 3.2 shows the test results along with the calculated percent crystallinities.

Table 3.2 DSC Temperature of Fusion and Heat of Fusion values

| Sample Name | Melting Temperature (°C) | Heat of Fusion (J/g) | Percent Crystallinity (%) * |
|--------------------------|--------------------------|----------------------|-----------------------------|
| PP (pellet) | 164.0 | 67.4 | 35.5 |
| PP (plate) | 165.0 | 81.5 | 42.9 |
| 30% PP-CaCO ₃ | 164.9 | 58.4 | 30.7 |
| 30% 10W-3sccm-0.5h-1 | 164.9 | 59.2 | 31.2 |
| 30% 10W-3sccm-0.5h-2 | 165.0 | 63.8 | 33.6 |
| 30% 10W-7sccm-0.5h-1 | 165.2 | 60.6 | 31.9 |
| 30% 10W-7sccm-0.5h-2 | 164.9 | 60.3 | 31.7 |
| 30% 10W-7sccm-2h | 165.2 | 60.2 | 31.7 |
| 30% 50W-7sccm-0.5h-1 | 164.9 | 61.1 | 32.2 |
| 30% 50W-7sccm-0.5h-2 | 165.0 | 59.9 | 31.5 |
| 30% 50W-7sccm-2h | 165.8 | 58.3 | 30.7 |
| 30% 50W-7sccm-2h** | 165.3 | 61.0 | 32.1 |
| 50% 50W-7sccm-2h | 164.8 | 43.9 | 23.1 |

*Percent Crystallinity=(Sample Melting Enthalpy)/(100% Crystalline Polymer's Melting Enthalpy(190 J/g)) [35]

** Sample prepared from plasma treated CaCO₃ kept under atmospheric condition for one month after plasma modification

Theoretical melting point of perfectly isotactic PP is about 171°C. On the other hand, commercial isotactic polymers may have melting points in range 160–166°C due to atactic material and non-crystalline regions [11]. In our system, variation of melting temperatures for samples remained between 164.0 °C and 165.8 °C. The constancy of T_m most probably shows that plasma polymer coats created on filler particle surfaces are intact enough and did not release any oligomers, and hence did not interfere with the crystals of the matrix. On the other hand, heat of fusion values, which are obtained by automatic integration of the area over melting peak, showed a great decrease for the samples containing CaCO₃. This can easily be seen by comparing the calculated heat of fusion values of pellet or virgin processed, and 30wt% unmodified CaCO₃ loaded samples, which are 67.4 J/g, 81.5 J/g, and 58.3 J/g respectively. These differences should be attributed to different amount of crystalline parts that polymers have. Figure 3.4 a, b, and c show the DSC traces of selected samples. Fig. 3.5 represents the DSC curve of composite system that is loaded with 50wt% CaCO₃ which is surface modified under the condition 50W-7sccm-2hours. As a result, percent crystallinities are changed only by use of the fillers, as expected, being independent of the existence or non existence of plasma polymer coats created on their surfaces.

It is known that heat of fusion of semi-crystalline polymers can be related with their percent crystallinity [6]. Crystalline fraction can be calculated by using the equation;

$$\chi = H_f / H_{cc}$$

where χ is polymer's crystalline fraction, H_f is melting enthalpy of polymer, and H_{cc} is the melting enthalpy of a completely crystalline polymer which is 190 J/g for PP [35]. As it can be interpreted from the formula, calculated results showed the same trend with enthalpy values. Results are given in Table 3.2.

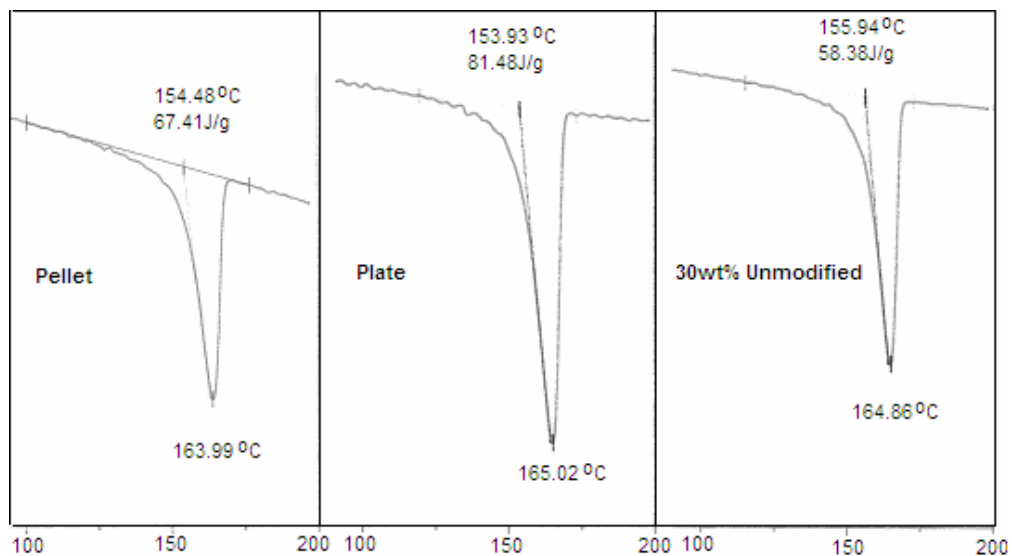


Figure 3.4 – a) DSC traces of selected samples for the calculation of crystalline fractions; PP (pellet), PP (Plate), and PP composite prepared with 30wt% unmodified CaCO₃

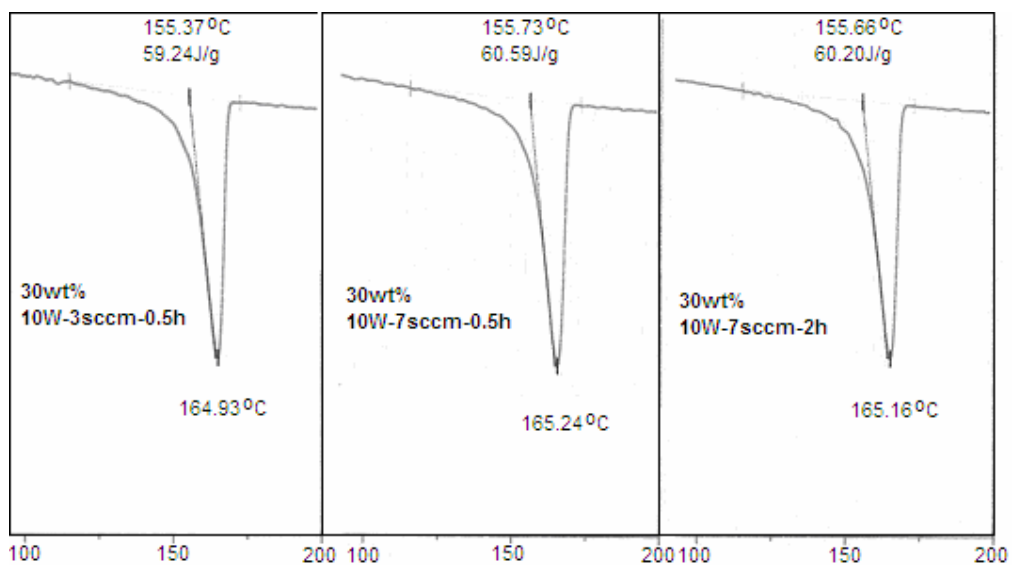


Figure 3.4 – b) DSC traces of selected samples for the calculation of crystalline fractions; PP composites prepared with 30wt% modified CaCO₃ under plasma conditions of 10W-3sccm-0.5h, 10W-7sccm-0.5h, and 10W-7sccm-2h

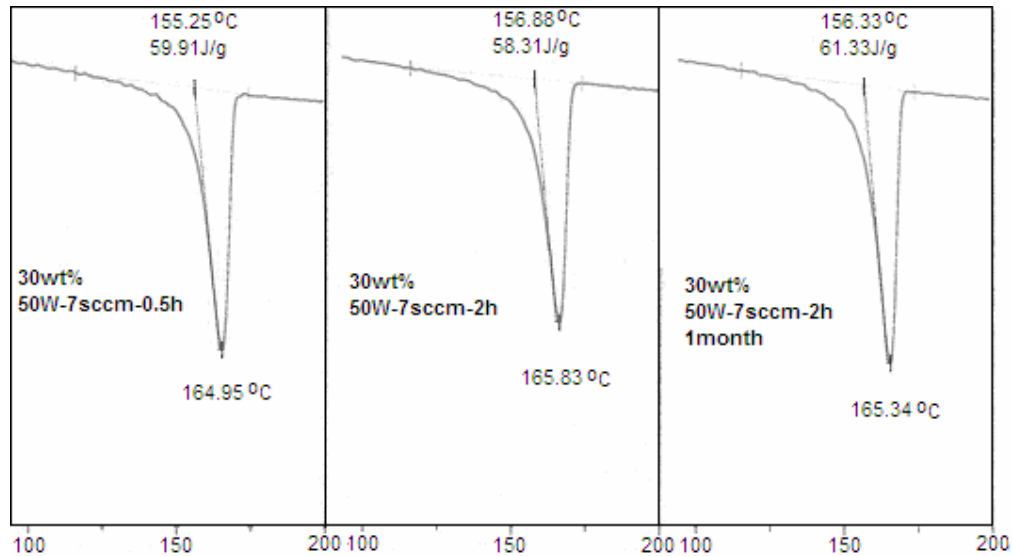


Figure 3.4 – c) DSC traces of selected samples for the calculation of crystalline fractions; PP composites prepared with 30wt% modified CaCO₃ under plasma conditions of 50W-3sccm-0.5h, 50W-7sccm-2h, and 50W-7sccm-2h but kept one month under atmospheric conditions before compounding

Hence, it can be concluded that incorporation of the CaCO₃ added to PP matrix has a negative effect on the melting enthalpy or in other words on the crystallinity of the PP. Although, obtained enthalpy values are quite lower than available data in literature [6,11], reduction of crystalline percent with the addition of reinforcement is in accordance with previous findings.

At this point, it is worth to point out the differences obtained between two unfilled PP samples that are prepared either from the pellet and the other from the processed PP. This difference maybe ascribed to different thermal history of polymers. Besides, processing, i.e. mixing, molding, and cooling, can have great influence on crystallinity of samples. As described in the experimental section of this work, plates are prepared by rapid cooling in order to suppress crystallinity. However, for better surface finishes, plates are kept at room temperature for 5 minutes just before rapid cooling. During that duration, PP chains could have been

ordered to form crystallite parts and that may have resulted in an increase of heat of fusion of virgin PP.

Even though there are slight differences between unmodified and modified samples, it would not be possible to converse about the effects of plasma surface modification on crystallinity. However, like the trend obtained from unfilled and unmodified filled samples, comparison of 50W-7sccm-2h modified 30wt% and 50wt% filled systems, which are 58.3 J/g and 43.9 J/g, respectively (see Figure 3.4c and Fig. 3.5), showed a reduction in heat of fusion. Again, this also proves the same negative effect of CaCO₃ addition to PP matrix. Besides, composite prepared from CaCO₃ that is modified but kept under atmospheric condition for one month, does not show a significant difference, which may indicate that oxygen functionalities on radicals generated by plasma also does not have any effect on crystallinity.

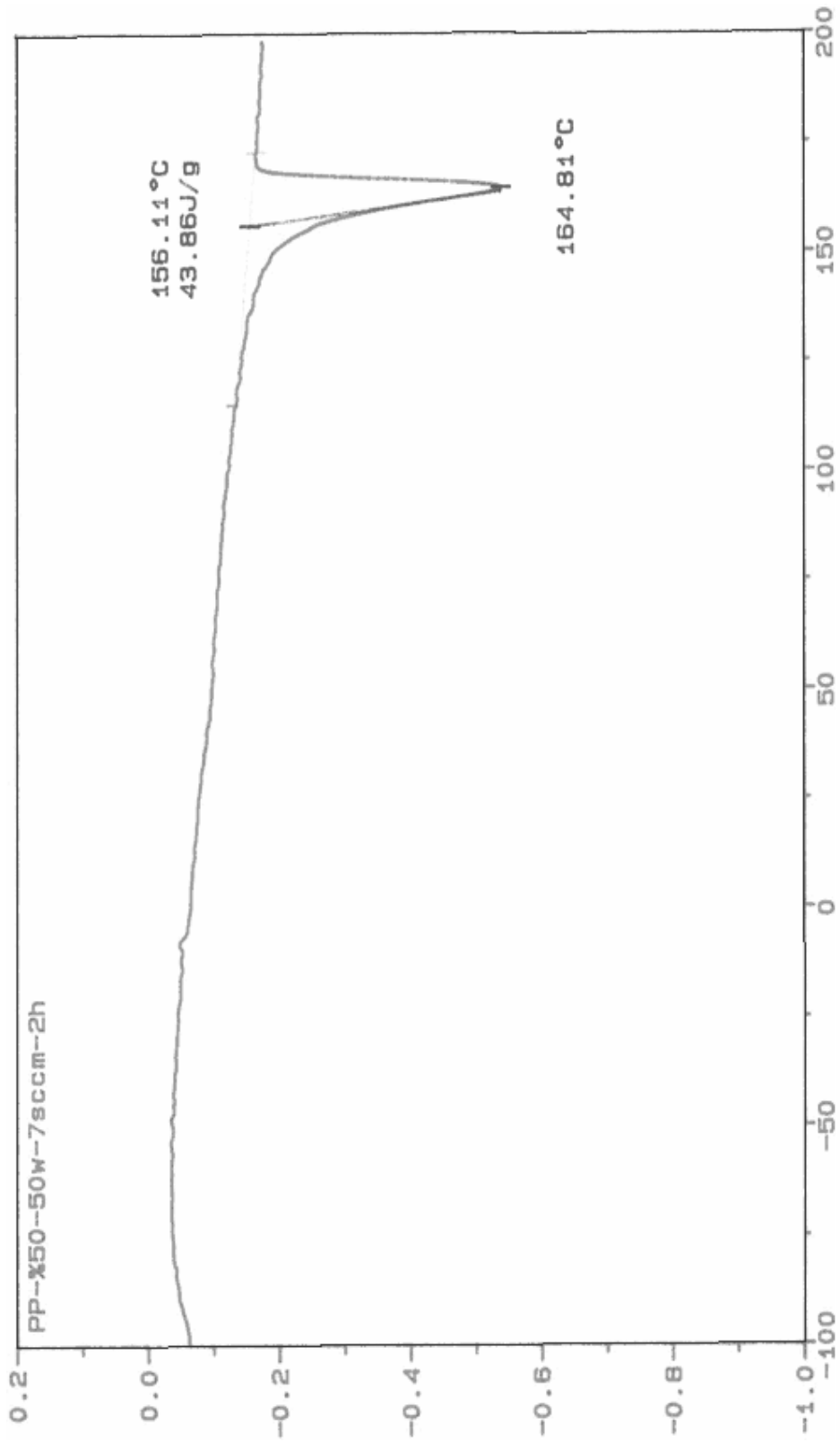


Figure 3.5 DSC curve of composite system loaded with 50wt% CaCO₃ modified by the conditions 50W-7sccm-2hours (heating rate of 10 °C/min)

3.3 Tensile Tests

The effects of surface modification of CaCO_3 particles by natural gas plasma on mechanical properties of PP- CaCO_3 composites are investigated with Lloyd tensile tester. Before the tests, prepared plates are cut into dog bone shape with size shown in Fig. 2.4. The rate of the elongation is chosen to be 0.31cm/min and the number of test specimens prepared for each measurement is 9-10. Except the plates prepared with 50wt% non-treated and treated CaCO_3 and 30wt% treated CaCO_3 which is aged for one month under atmospheric condition before mixing, two plates are prepared for every pre-determined conditions and average of the values from each plates are used while making the final calculations. Figs 3.6-10 show sample stress-percent strain curves of virgin PP, 30wt% containing non-treated and treated filler and 50wt% containing non-treated and treated filler, successively. Table 3.3 shows the actual and relative values of tensile strength, Young's modulus, and stress at yield.

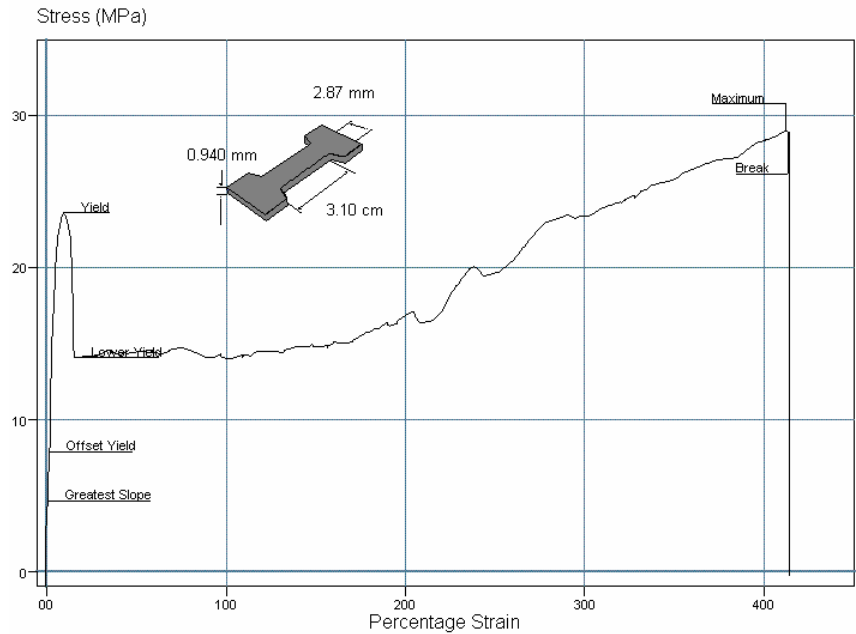


Figure 3.6 Stress-Percent Strain curve of virgin PP obtained at a cross-head speed of 0.31 cm/min

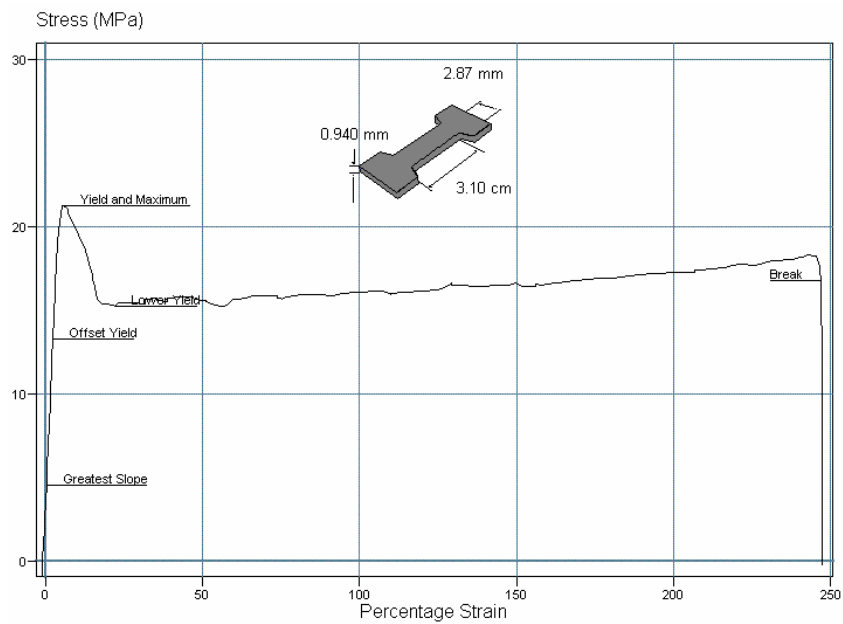


Figure 3.7 Stress-Percent Strain curve of 30wt% of non-treated CaCO₃ loaded PP obtained at a cross-head speed of 0.31 cm/min.

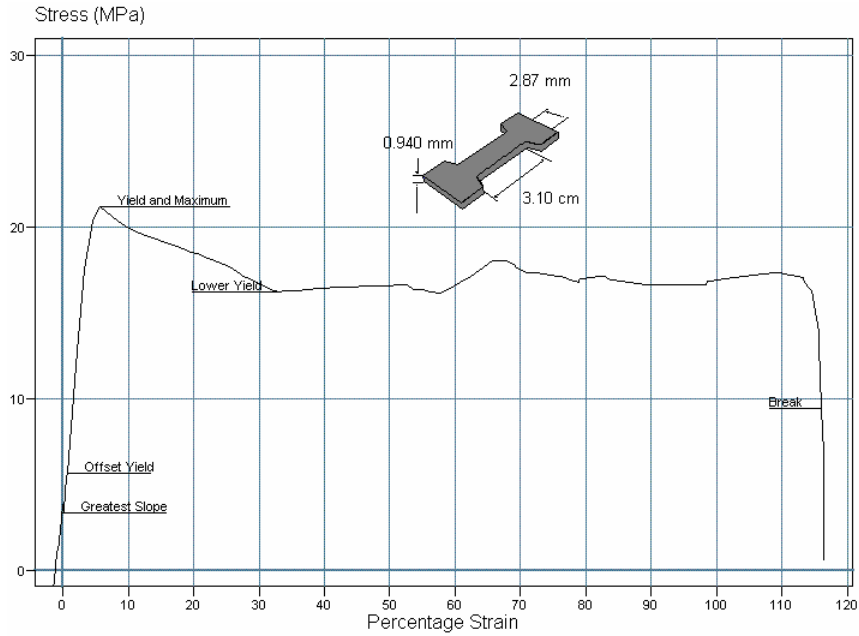


Figure 3.8 Stress-Percent Strain curve of 30wt% 10W-3sccm-0.5h sample obtained at a cross-head speed of 0.31 cm/min

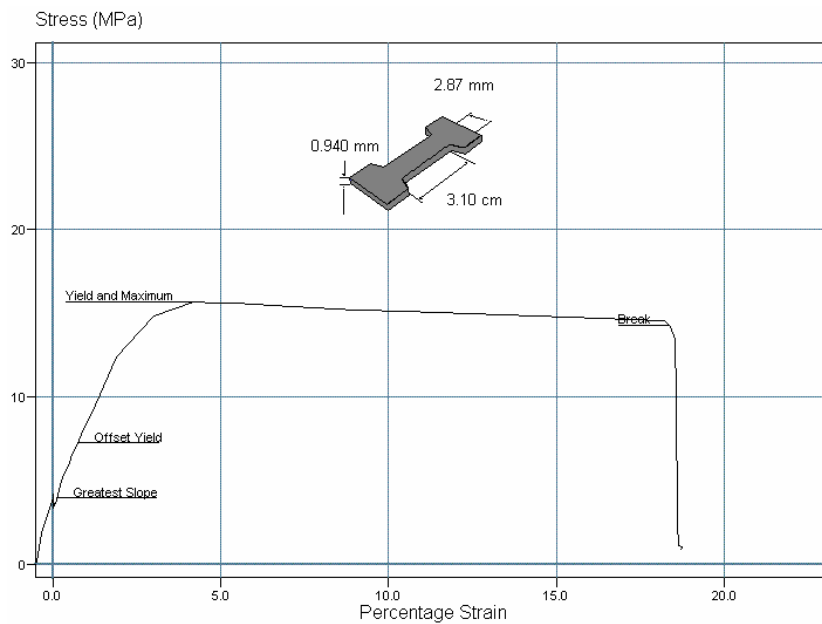


Figure 3.9 Stress-Percent Strain curve of 50wt% of non-treated CaCO₃ loaded PP obtained at a cross-head speed of 0.31 cm/min.

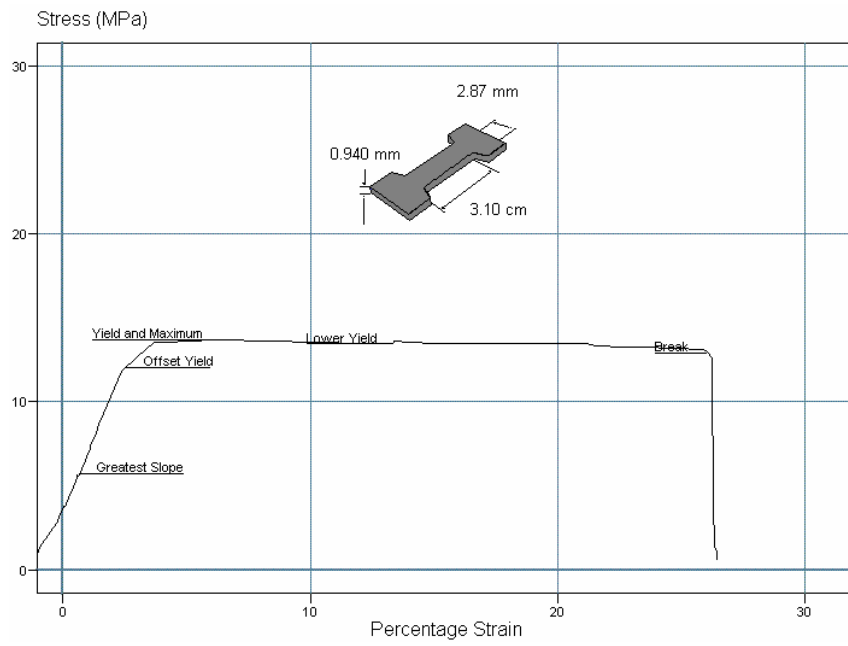


Figure 3.10 Stress-Percent Strain curve of 50wt% 50W-7sccm-2h sample obtained at a cross-head speed of 0.31 cm/min

Table 3.3 Tensile test results obtained with a cross-head speed of 0.31cm/min

| Sample Name | Tensile Strength (MPa) | | Young's Modulus (MPa) | | Stress at Yield (MPa) | |
|--------------------------|------------------------|------|-----------------------|------|-----------------------|------|
| | AC* | RL** | AC | RL | AC | RL |
| Virgin PP | 31 ±4.6 | 1.00 | 424 ±42 | 1.00 | 23 ±1.74 | 1.00 |
| 30% PP-CaCO ₃ | 23 ±1.7 | 0.74 | 517 ±29 | 1.22 | 22 ±1.03 | 0.96 |
| 50% PP-CaCO ₃ | 14 ±0.6 | 0.45 | 385 ±33 | 0.91 | 14 ±0.57 | 0.61 |
| 30% 10W-1sccm-0.5h | 20 ±0.7 | 0.65 | 505 ±40 | 1.19 | 20 ±0.59 | 0.87 |
| 30% 10W-3sccm-0.5h | 23 ±1.8 | 0.74 | 543 ±44 | 1.28 | 23 ±1.75 | 1.00 |
| 30% 10W-7sccm-0.5h | 21 ±1.3 | 0.68 | 566 ±40 | 1.33 | 21 ±1.31 | 0.91 |
| 30% 10W-7sccm-1h | 20 ±1.7 | 0.65 | 491 ±31 | 1.16 | 16 ±2.23 | 0.70 |
| 30% 10W-7sccm-2h | 21 ±0.9 | 0.68 | 505 ±33 | 1.19 | 20 ±0.94 | 0.87 |
| 30% 50W-7sccm-0.5h | 21 ±0.5 | 0.68 | 507 ±54 | 1.20 | 21 ±0.44 | 0.91 |
| 30% 50W-7sccm-1hr | 21 ±0.7 | 0.68 | 501 ±39 | 1.18 | 21 ±0.64 | 0.91 |
| 30% 50W-7sccm-2h | 21 ±0.5 | 0.68 | 508 ±35 | 1.20 | 19 ±1.91 | 0.83 |
| 30% 50W-7sccm-2h*** | 22 ±1.1 | 0.71 | 530 ±23 | 1.25 | 22 ±1.08 | 0.96 |
| 50% 50W-7sccm-2h | 15 ±1.3 | 0.48 | 620 ±44 | 1.46 | 15 ±1.27 | 0.65 |

*AC corresponds to observed values (Actual)

**RL stands for relative, meaning ratio with respect to that of virgin PP

***Sample prepared from treated CaCO₃ kept under atmospheric condition for one month after plasma modification

As it is expected, tensile strength values obtained from PP-CaCO₃ composites, decreased gradually by increasing percent CaCO₃ loadings. Virgin PP showed the highest tensile strength values with 31±4.6 MPa. With the incorporation of CaCO₃, these values decreased to 23±1.7 MPa and 14±0.6 MPa for 30wt% and 50wt% loadings. These decreases correspond to values from 1.00 (PP) to 0.74 and 0.45, relatively. This is plausible due to poor interfacial adhesion between the matrix and the filler. However, plasma surface modification which is performed to increase these interactions would not yield any promising result. Under nine different conditions, all 30wt% treated CaCO₃ filled samples gave lower or equal tensile strength values comparing with sample containing 30wt% non-treated CaCO₃. Test results remained in the range 20-23 MPa for 30wt% loaded samples. Despite the aim of the study, any positive or consistent effect of surface modification of filler by natural gas plasma onto the tensile strength of samples can not be observed.

In the same way, monotonic decrease with the addition of CaCO₃ is also valid for stress at yield values. This can be seen easily by comparing 30wt% and 50wt% unmodified or modified CaCO₃ filled samples. Further increase of percent CaCO₃ results in decrease in yield stress from 22±1.03 MPa to 14±0.57 MPa for unmodified CaCO₃ filled samples and from 19±1.91 MPa to 15±1.27 MPa for modified CaCO₃ filled (50W-7sccm-2h) samples. For 30wt% plasma surface treated CaCO₃ loaded samples, however, it is seen that yield stress values ranged between 19-21 MPa which indicates the inefficiency of surface modification. On the other hand, different from other 30wt% loaded samples, the sample 10W-3sccm-0.5h has same yield stress value with virgin PP. Oppositely the sample 10W-7sccm-1h has nearly same yield value with sample loaded 50wt%. Besides, it is observed that the plate prepared with CaCO₃ particles that are modified and kept for one month under atmospheric conditions, has higher yield value than plate prepared from CaCO₃ particles that are treated under same conditions but processed immediately. These differences indicate the complexity of the effect of plasma surface modification.

It can be stated that up to a certain level of loadings, particulate fillers increase the tensile modulus of PP. However, increasing filler content increases the extent of aggregation; and modulus starts to decrease [36]. Our experimental results are also proved that. Young's modulus of virgin PP plate is improved from 424 MPa to 517 MPa by the addition of 30wt% CaCO₃. Further increase of CaCO₃ loading (i.e., 50%), however, resulted in reduction of the modulus (487 MPa). It is known that agglomerates are one of the reasons for the mechanical strength reduction in particulate filled composite systems and is also known that CaCO₃ particles tend to form agglomerates. Hence, this decrease in tensile modulus can be attributed to increased fraction of CaCO₃ that quite probably agglomerated. However, it can also be stated that uniform distribution of particles may not result in promoted mechanical properties, as the filler-matrix interaction is also important. Fig. 3.11 shows the changes in Young's modulus of PP with the addition of CaCO₃.

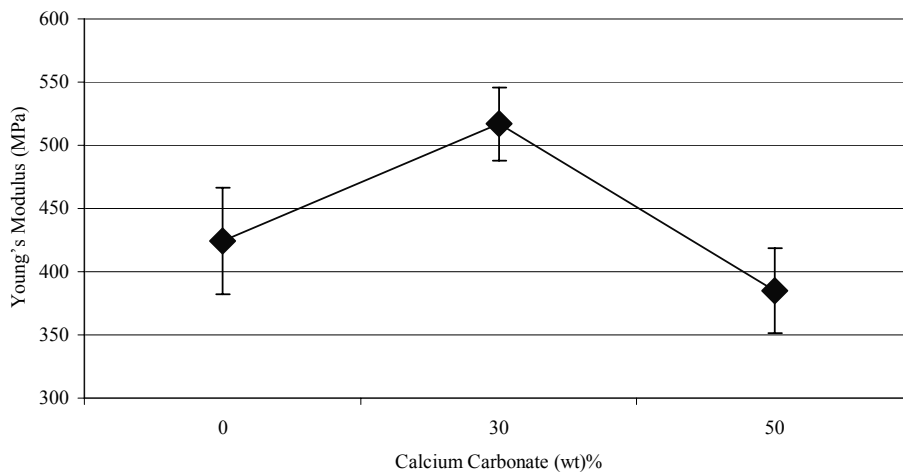


Figure 3.11 Changes in Young's modulus of PP with the addition of CaCO₃

With the surface modification of CaCO₃, some significant enhancements in modulus are observed. Within the first three experiments, it is aimed to see the effect of gas flow rate on mechanical properties of composites. Plasma conditions are 10W-0.5h and 1, 3, or 7sccm. Surface modification with natural gas flow rate of 3 and 7sccm caused enhancement in modulus values of composites, however the lowest flow rate, i.e. 1sccm, gave lower modulus than the sample prepared with unmodified CaCO₃. Figure 3.12 shows the monomer flow rate dependency of modulus values of PP-CaCO₃ composites. As it is seen, modulus increase nearly linear with gas flow rate. This can be attributed to the better surface deposition obtained at higher monomer flow rates as there should be enough activated species under vacuum conditions for plasma polymerization. On the other hand, it is also known that high flow rates would also decrease the deposition degree as species may not find enough time to be activated or activated species may be taken away with the flow. Linear increase in Young's modulus suggests that both flow rates (3 and 7sccm) are sufficient for plasma, however, higher flow rates should be investigated in order to find the optimum monomer rate for maximum deposition.

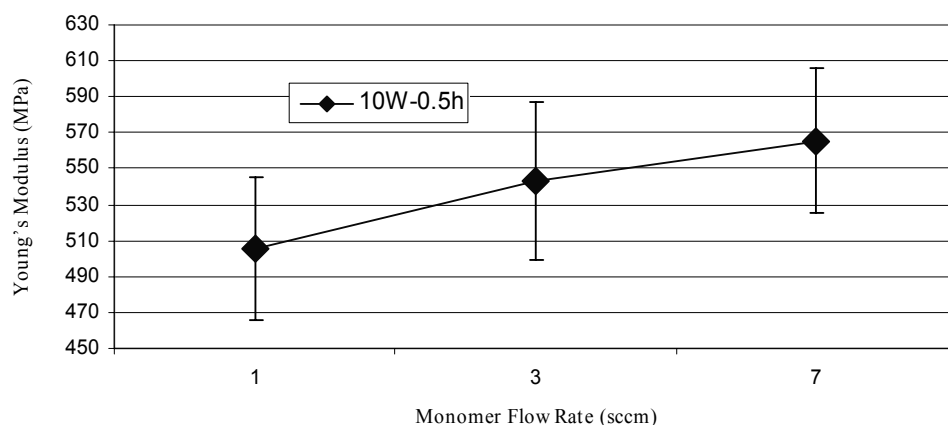


Figure 3.12 Changes in Young's modulus values of PP filled 30wt% CaCO₃ surface modified at 10W-0.5h with three different monomer flow rates

As an another plasma polymerization factor, duration of applied plasma is investigated under the fixed RF power of 10W and fixed natural gas flow rate of 7sccm. Three different plasma discharge periods, 0.5, 1, and 2h, are applied. According to tests, Young's modulus value firstly decreased from 566 ±40 MPa to 491 ±31 MPa, which is even lower than unmodified CaCO₃ loaded samples. Making the total plasma duration 2 hours, modulus increased to 505 ±33 MPa as shown in Fig. 3.13., though. Similarly, in modifications performed at the RF power of 50W and natural gas flow rate of 7sccm, Young's modulus values firstly decreased from 507 ±54 MPa to 501 ±39 MPa when the duration is doubled to 1 hour, then returned to 508 ±35 MPa as the duration became 2 hours. Fig. 3.13 shows the modulus changes with respect to plasma duration for two different RF power values. Great decrease that is seen for the first condition (at lower power), is not that much for the second condition (at higher power). Besides, modulus values for the second condition are very close to each other, (max difference is lower than 2% of the min value). All 50W treated samples have modulus values lower than unmodified CaCO₃ loaded sample. From these results, apart from other plasma factor, one may reach to the conclusion that Young's modulus value strongly

depends on applied power and if the power reaches to a certain value other effects become negligible.

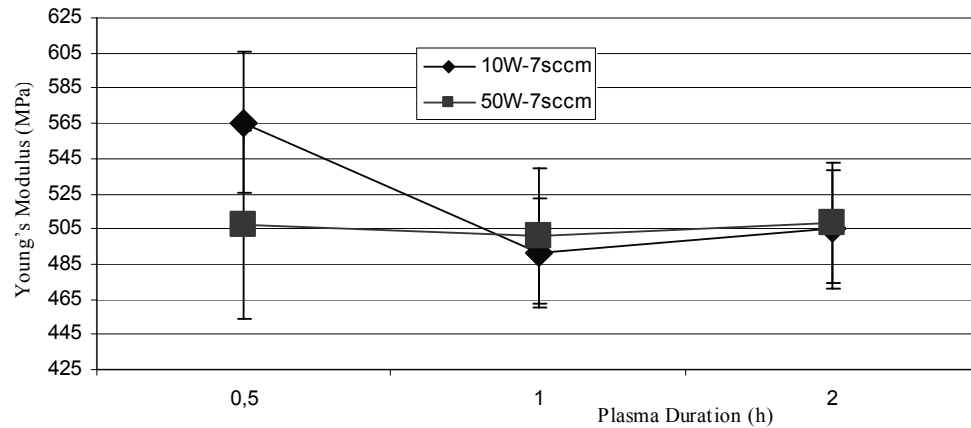


Figure 3.13 Changes in Young's modulus values of PP filled 30wt% CaCO₃ surface modified at 10 and 50W with changing plasma duration.

However, this conclusion may be deficient if other factors are not taken into consideration. Therefore, plasma control parameter $W*t/(F*M)$ (where W is the supplied power in watts, F is the molar flow rate of monomer in mol/min, M is the molecular weight of monomer in kg/mol, and t is the time of treatment in minutes) [37], which includes all probable factor effecting the polymer deposition rate, would provide trustworthy explanation. According to this parameter, it may be stated that as plasma duration or RF power increases, the value of control parameter increases, contrarily as the flow rate increases that value decreases. Table 3.4 gives the calculated values of the control parameter used in the experiments.

Table 3.4 Control parameters of applied plasma surface modifications

| Sample Name | W*t/(F*M) |
|-----------------------------------|------------------|
| 30% 10W-1sccm-0.5hour | $10*30/1 = 300$ |
| 30% 10W-3sccm-0.5hour | $10*30/3 = 100$ |
| 30% 10W-7sccm-0.5hour | $10*30/7 = 43$ |
| 30% 10W-7sccm-1hours | $10*60/7 = 86$ |
| 30% 10W-7sccm-2hours | $10*120/7 = 171$ |
| 30% 50W-7sccm-0.5hour | $50*30/7 = 214$ |
| 30% 50W-7sccm-1hour | $50*60/7 = 429$ |
| 30% 50W-7sccm-2hours | $50*120/7 = 857$ |
| 30% 50W-7sccm-2hours ¹ | $50*120/7 = 857$ |
| 50% 50W-7sccm-2hours | $50*120/7 = 857$ |

¹Plate prepared from powders kept 1month under atmospheric condition before compounding

In order to reach a conclusion, one has to realize the system's response to the applied energy. In our system mechanical properties, i.e. Young's modulus can be assumed as the above mentioned response. From Fig. 3.12, it is seen that as flow rate increases Young's modulus also increases. On the other hand, from Fig. 3.13, it is seen that at the RF power of 10W, as plasma duration increases Young's modulus decreases. For the case of 50W, however, no significant changes occurred as plasma duration increased.

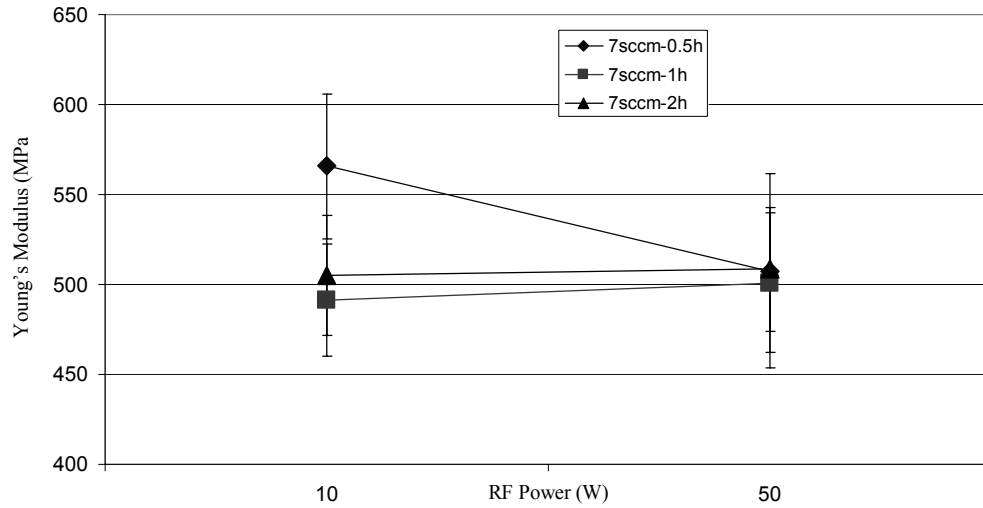


Figure 3.14 RF power effects on Young's modulus values of PP filled with 30wt% surface modified CaCO₃

For further understanding of the effect of RF power, in Fig. 3.14 the modulus changes with respect to plasma power for different plasma durations are given. As it is seen, when plasma power reaches to 50W, modulus reaches to certain value no matter what the other factors are. This observation coincides well with the effects of plasma control parameter of which is assumed that after a certain value, modulus levels off and/or starts to decrease. This is easily understood when comparing the tensile test results of samples with corresponding plasma parameters. Table 3.5 shows the modulus values with their associated control parameters.

Table 3.5 Plasma control parameter and Young's modulus values of samples prepared from plasma surface modified CaCO₃

| Sample Plate Name | Young's Modulus (MPa) | Control Parameter |
|-----------------------|-----------------------|-------------------|
| 30% 10W-1sccm-0.5hour | 505 ±40 | 300 |
| 30% 10W-3sccm-0.5hour | 543 ±44 | 100 |
| 30% 10W-7sccm-0.5hour | 566 ±40 | 43 |
| 30% 10W-7sccm-1hours | 491 ±31 | 86 |
| 30% 10W-7sccm-2hours | 505 ±33 | 171 |
| 30% 50W-7sccm-0.5hour | 507 ±54 | 214 |
| 30% 50W-7sccm-1hour | 501 ±39 | 429 |
| 30% 50W-7sccm-2hours | 508 ±35 | 857 |
| 30% 50W-7sccm-2hours* | 530 ±23 | 857 |
| 50% 50W-7sccm-2hours | 620 ±44 | 857 |

*Plate prepared from powders kept 1month under atmospheric condition before compounding

As it is seen from Table 3.5 maximum value of modulus is achieved with minimum control parameter and as it increases modulus starts to decrease and finally levels off. These results then, made it clear that when the control parameter is lower than a certain value; natural gas plasma surface treatment is an effective way to alter the Young's modulus values of PP-CaCO₃ composites. However, it should also be noted that surface modification under 10W-7sccm-1h plasma conditions which has the second minimum control parameter value has the lowest modulus value. This is contrary to the above pointed out statement.

In Table 3.4, last three rows present the modulus values of three different samples which have the same control value. As it can be understood from those rows, second sample is prepared from particles treated under the same conditions of the first sample but kept one month under atmospheric condition before compounding. Third sample, alternatively, is prepared in 50wt% CaCO₃ composition that is treated with the same conditions as the other two samples.

As it is stated above, CaCO₃ addition makes PP stiffer, which results in high modulus, however, exceeding certain loading level results in reduced modulus

values. That is proved as shown in Fig. 3.11. Nevertheless, sample prepared from 50wt% CaCO₃ that is modified at 50W-7sccm-2h condition showed the highest modulus value amongst all samples. This 61% increase (from 385 ±33 MPa to 620 ±44 MPa) is clearly contrary to the plasma parameter proposal that is given to explain the tensile test results. This astonishing increase, then, tells us that not only the plasma factor but also loading level may affected the modulus of PP-CaCO₃ composites since it has the only difference from other samples. And it may be concluded as plasma surface modification can be more effective on modulus at higher loadings.

3.4 Dynamic Mechanical Analysis

Dynamic mechanical analyses (DSC) are also performed with samples prepared from plasma treated CaCO₃ at selected plasma conditions, in order to determine the effects of CaCO₃ and its surface modification on mobility of PP. Thermal scanning is performed over a range of -80 °C to 80 °C at a heating rate of 5°C under resonance mode. Samples (3cm x 1cm x 0.9mm) are cut from the same plates prepared for tensile tests. Viscoelastic properties, which are storage modulus (E'), loss modulus (E''), and mechanical loss factor ($\tan\delta = E''/E'$) are investigated as a function of temperature. Fig. 3.15 and Fig. 3.16 show the DMA thermograms of samples prepared from virgin PP and PP filled with 30wt% surface modified CaCO₃ under the condition of 50W-7sccm-0.5h natural gas plasma.

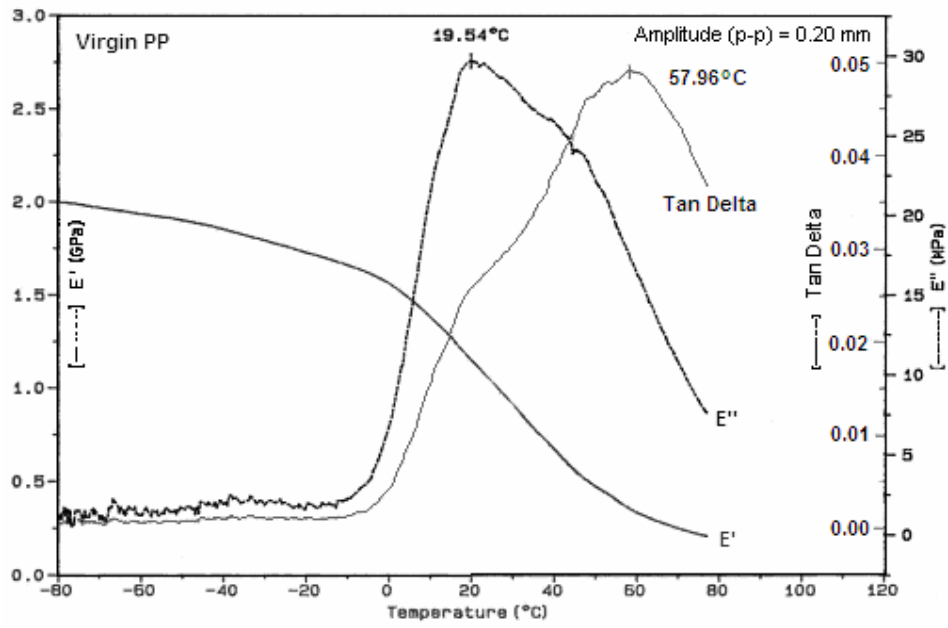


Figure 3.15 DMA thermogram of virgin PP

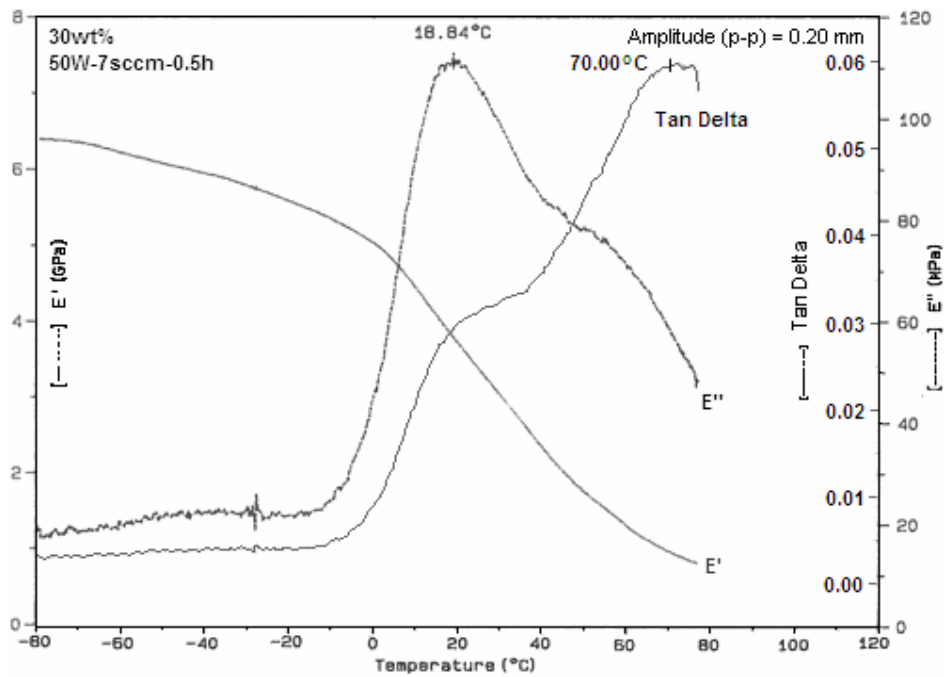


Figure 3.16 DMA thermogram of PP composite filled with 30wt% surface modified CaCO₃ with 50W-7sccm-0.5h natural gas plasma

Table 3.6 Elastic Modulus (GPa) values of samples examined with DMA (at 0°C)

| Name of the Samples | Elastic Modulus (GPa) |
|-------------------------------------|-----------------------|
| Virgin PP | 1.55 |
| 30% Unmodified PP-CaCO ₃ | 3.20 |
| 30% 10W-3sccm-0.5hour | 2.40 |
| 30% 10W-7sccm-0.5hour | 2.60 |
| 30% 10W-7sccm-2hours | 3.00 |
| 30% 50W-7sccm-0.5hour | 5.00 |
| 30% 50W-7sccm-0.5hour | 4.85 |
| 30% 50W-7sccm-2hours | 4.50 |
| 30% 50W-7sccm-2hours* | 2.75 |
| 50% 50W-7sccm-2hours | 5.00 |

*Plate prepared from powders kept 1month under atmospheric condition before compounding

Table 3.6 which gives the E' values (at 0°C) is presented to understand the effect of plasma surface modification of CaCO₃ and its loadings on storage modulus of PP matrix. According to the findings, it can be suggested that three factors have significant effects on E' of samples. These are filler percentage, time interval between plasma treatment and mixing, and RF power. It is seen that CaCO₃ presence has a positive effect on E' as it increases from 1.55 GPa to 3.20 GPa with the addition of (30wt%) CaCO₃. Additionally, further increase of percent CaCO₃ raises E' value more. These improvements can be attributed only to increased filler percent the filler; however, taking into account that all composite samples are prepared from surface modified CaCO₃, plasma treatment may also have a share on this additional improvement.

Differently, RF power has both positive and negative effect on E'. As comparing with the unmodified 30wt% CaCO₃ filled sample, it seems that 10W RF power treatment has a negative effect on E' no matter what the monomer flow rate (3 or 7 sccm) or the plasma duration is (0.5 or 2h). On the other hand, 50W RF power has a positive effect on E'. E' value of unmodified composite sample increases from 3.20 GPa to 4.90 GPa for two 50W-7sccm-0.5h samples and to 4.50 for 50W-7sccm-2h sample. That small difference between the two 50W-7sccm treatments is

probably due to different plasma durations. Hence, it wouldn't be wrong to count the plasma duration as a potential factor effecting on E' .

Lastly, sample prepared with aged CaCO_3 after plasma surface treatment has lower E' than samples prepared with CaCO_3 treated at the same conditions but not aged. As those particles are exposed to air quite longer than other samples, it may be stated that, oxygen in air may lessen the number of radicalic sites on the plasma treated surface of filler particles which possibly result in decrease of polymer filler interactions in composite.

It is known that for semi-crystalline materials like PP, T_g is the lower limit of operating temperature range. However, accurate determination of T_g can sometimes be very difficult. Even though, they may give different results that may differ in the 25°C range, several methods can be used for the determination of T_g . Certain points on the DMA thermograms, such as peaks of $\tan \delta$, E' , or E'' can be credit to T_g . Onsets of these curves may also be used [38].

In our DMA thermograms several points can be defined as T_g , such as a hump for $\tan \delta$, onsets of $\tan \delta$, E'' , and E' that are alternate in the range of -35°C and 26°C . For all samples, onset of the decline in E' curve is at about 0°C , while this value is -5 and -10°C for the onsets of $\tan \delta$ and E'' , respectively. However, for the onset values of $\tan \delta$ and E'' of the samples prepared with 30 and 50wt% CaCO_3 that are treated under the plasma conditions of 50W-7sccm-2h, deviated -5°C . In a similar way, for all samples, E'' peaks and $\tan \delta$ humps are at about 20°C , except the same aforementioned two samples, which are 14 and 16°C , respectively. Hence, one can state any of the above mentioned temperatures (i.e., -10 , -5 , 0 , or 20°C) as the T_g for investigated composites.

It is known that as polymer gets stiffer, its T_g also increases [39]. Knowing this, it would not be wrong to expect the higher the T_g values of PP- CaCO_3 composites, with further addition of the CaCO_3 . Nevertheless, whether it is -10 , -5 , 0 , or 20°C T_g of samples are nearly equal to each other with a deviation of $\pm 2^\circ\text{C}$, which

means that neither natural gas plasma surface modification nor CaCO₃ addition has any remarkable effect on T_g of PP. Hence, it would not be possible to enlarge the operating temperature range of PP beyond lower limit with the addition of unmodified or modified CaCO₃. On the other hand, some enhancements are achieved with upper temperature limit.

tan δ , which is also called damping, is an indicator of how efficiently the material loses energy due to molecular re-arrangements and internal friction. It is defined as the ratio between loss modulus and storage modulus. In the analyses, it is seen that tan δ does not changed a lot with the addition of CaCO₃ (unmodified or modified). The reason is that the loss modulus, similar to storage modulus, changes with addition of CaCO₃ whether its surface is modified or not. However, it is seen that the E'' peak, observed in virgin PP thermogram shifts towards high temperatures, yet become unseen because it lies beyond the temperature range of the thermogram (see Fig. 3.16). This peak (or sometimes a hump) is generally used for the determination of the upper limit of operating temperature range. With the addition 30wt% unmodified CaCO₃, the peak which is at 58°C for virgin PP, is lost and maximum readable temperature became 78°C. This means that operating range is at least enlarged from 58 °C to 78 °C. Other samples also present similar enlargements, however, there cannot be found any consistent result relating with surface modification.

3.5 Scanning Electron Microscopy

In order to verify the interfacial adhesion at the PP-CaCO₃ interface and determine whether natural gas plasma surface modification of CaCO₃ particles affects the dispersion in PP matrix, Scanning Electron Microscopy (SEM) is used to examine the tensile fracture surface of the selected composite samples. Figs 3.17-22 depict SEM micrographs of virgin PP, 30wt% and 50wt% unmodified CaCO₃ filled PP,

30wt% 10W-3sccm-0.5h and 10W-7sccm-1h, and 50wt% 50W-7sccm-2h modified CaCO₃ filled PP, respectively.

Plastic deformation is plausible for unfilled and maybe for 30wt% filled systems; however, further loaded systems are not expected to show plastic deformation at all. This means a much more brittle failure is foreseen for the 50wt% filled systems.

The rough surface shown in Fig. 3.17 suggests a ductile fracture, which can be expected from virgin PP. With the addition of 30wt% CaCO₃, however, it is seen that morphology changed. Polymeric fibrils can be seen easily from Fig 3.18 for 30wt% filled system. This suggests plastic deformation before fracture resulted from poor interaction of PP and CaCO₃.

For 50wt% filled system, conversely, it is not possible to see the aforementioned fibrils. Instead, most of the particles are clearly visible and they are loosely scattered at the fracture surface, with large cavities adjacent to them (see Fig. 3.19). This signifies weak bonding between the filler and matrix. Besides, with the increase of CaCO₃ amount, distribution within the matrix become more difficult and thus weakens the adhesion between the matrix and filler. This can easily be understood, comparing the number of visible particles in micrographs of 30wt% and 50wt% filled systems. This brittle fracture is also consonant with the trend obtained for the tensile tests.

Fig. 3.20 and 3.21 show tensile fracture surfaces of PP 30wt% filled with CaCO₃ treated at 10W-3sccm-0.5h and 10W-7sccm-1h, respectively. Since they did not show any fibrous formation, fracture surfaces represent a seemingly brittle failure; however presence of deep valleys may suggest different fracture. Layer pull-outs can be the reason of these valleys. Voids and cavities left behind by CaCO₃ particles. Nevertheless, CaCO₃ particles can be seen more easily in 10W-7sccm-1h micrograph than 10W-3sccm-0.5h. This indicates better dispersion at the same

mixture rates obtained with 10W-3sccm-0.5h plasma conditions which is consonant with tensile tests of samples.

SEM micrograph of tensile fracture surface of PP that is filled with 50wt% 50W-7sccm-2h treated CaCO_3 is given in Fig. 3.22. Similar to 50wt% untreated filler containing sample, agglomerates are almost not seen and brittle fracture is clearly obvious for treated sample. Both surfaces have large voids and cavities probably due to left CaCO_3 particles. Nonetheless, unlike the untreated filler containing sample, CaCO_3 particles are hardly seen in modified filler containing one's micrograph. Instead, a different morphology with better filler embedding is observed. As the only difference between these two 50wt% loaded samples is plasma surface modification, this morphology can be attributed to treatment. However, same surface morphology does not exist in other plasma treated CaCO_3 loaded composite micrograms. It seems that loading level may also important in such formation. Tensile test result can also be considered in a same way.

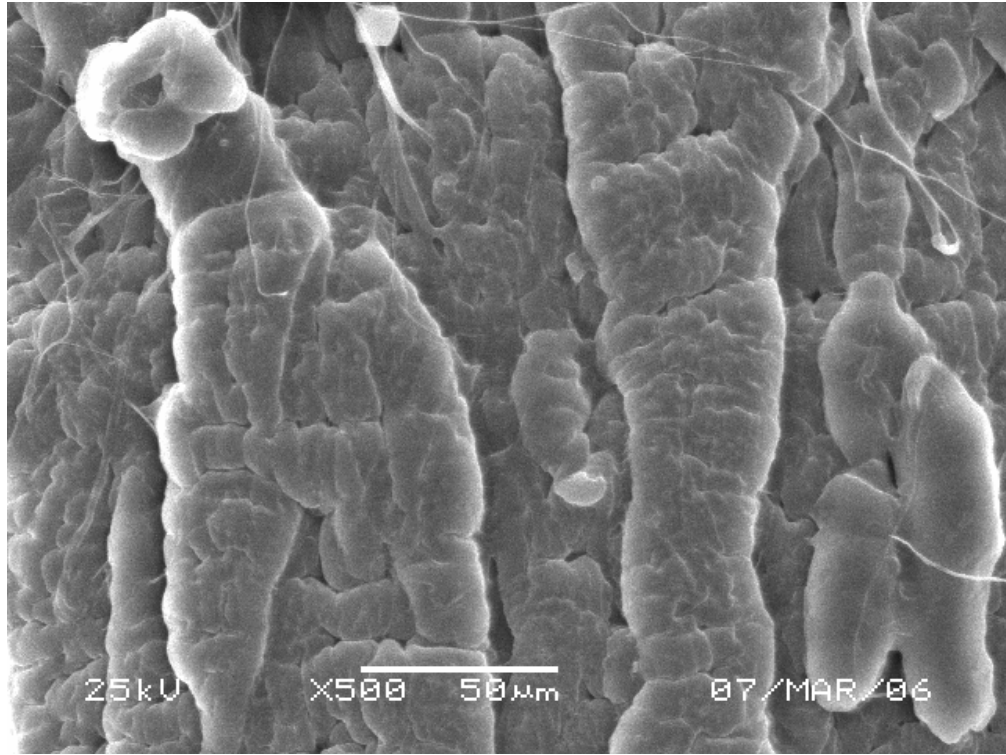


Figure 3.17 SEM micrograph of virgin PP

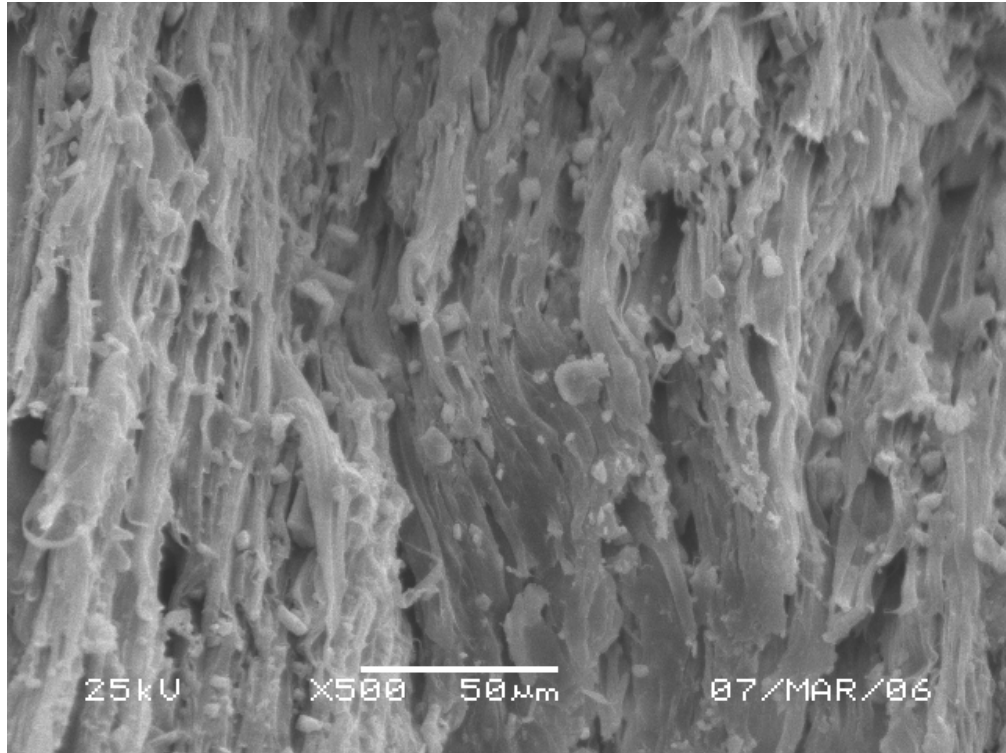


Figure 3.18 SEM micrograph of PP filled with 30wt% unmodified CaCO₃

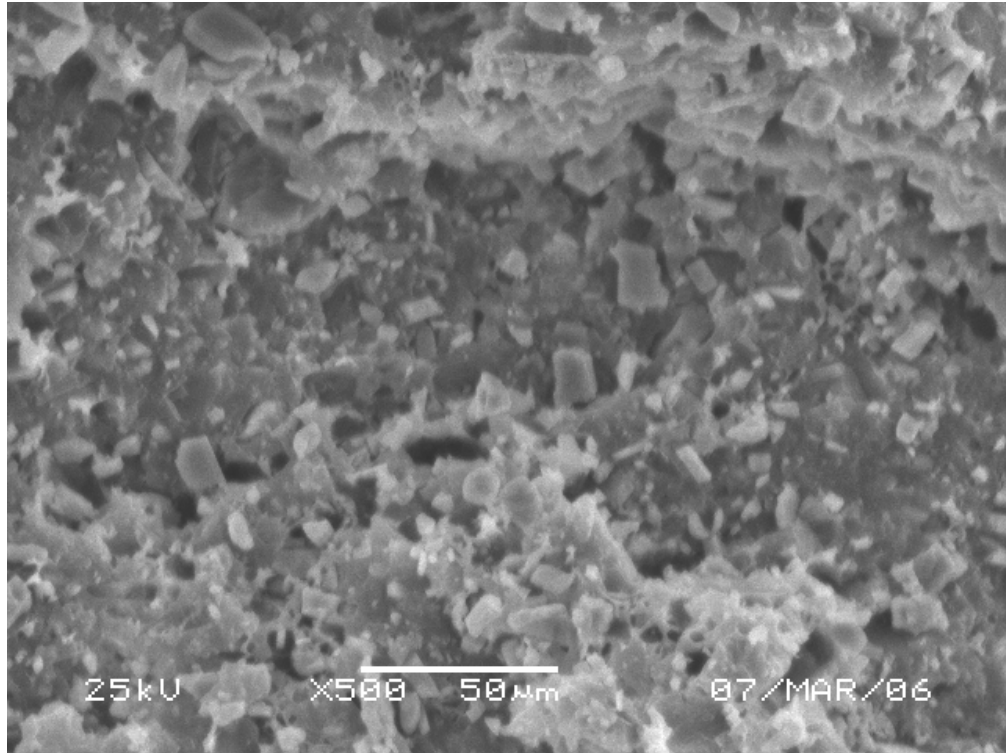


Figure 3.19 SEM micrograph of PP filled with 50wt% unmodified CaCO₃

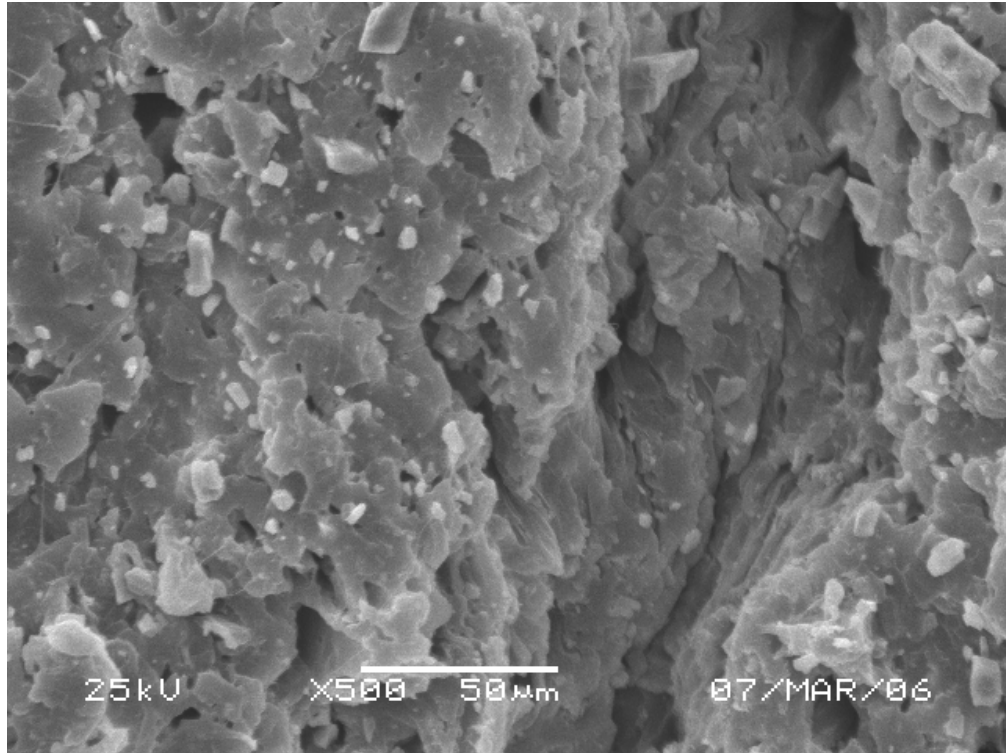


Figure 3.20 SEM micrograph of PP filled with 30wt% CaCO₃ modified at 10W-3sccm-0.5h

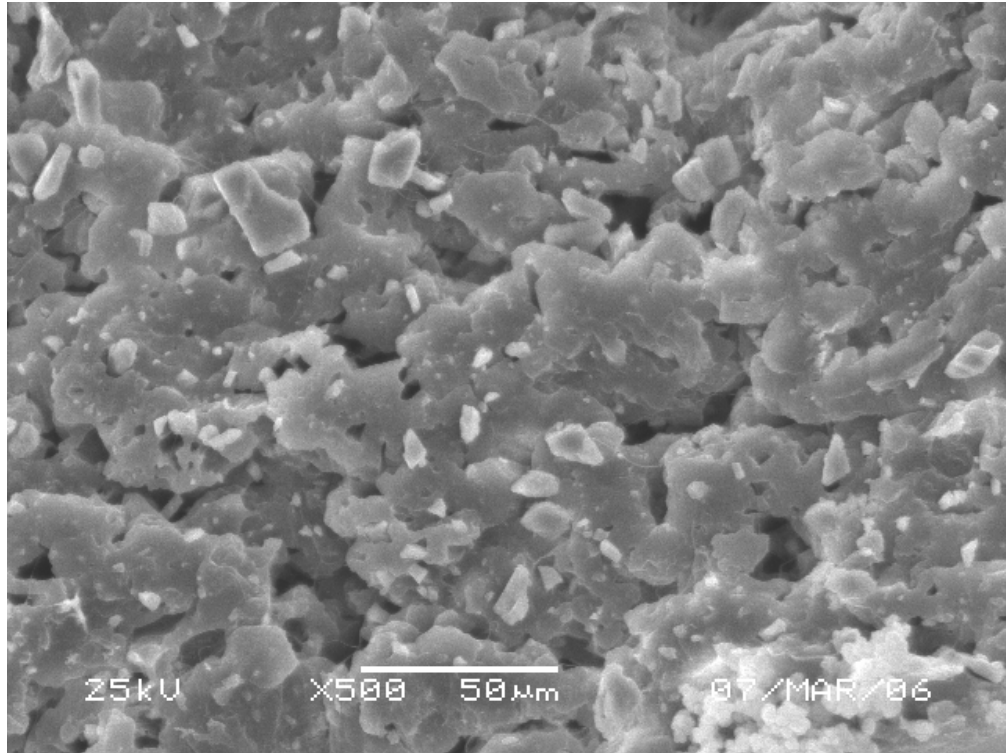


Figure 3.21 SEM micrograph of PP filled with 30wt% CaCO₃ modified at 10W-7sccm-1h

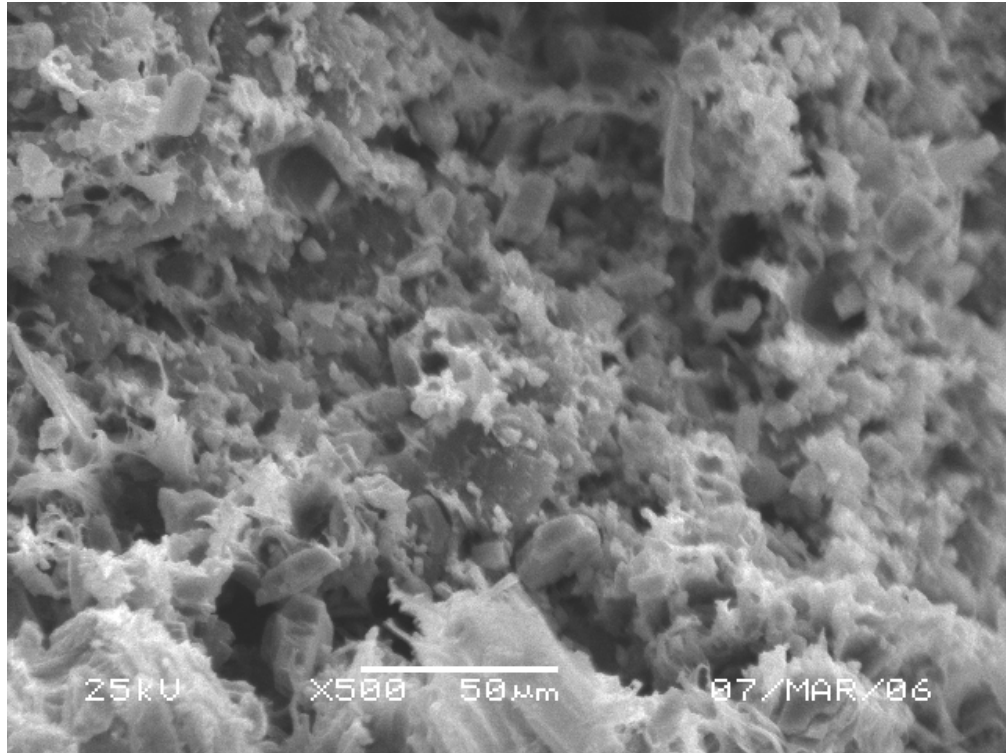


Figure 3.22 SEM micrograph of PP filled with 50wt% CaCO₃ modified at 50W-7sccm-2h

CHAPTER IV

CONCLUSION

In this study, CaCO₃ surfaces are tried to be modified by treatment with plasma technique, by using natural gas as the unconventional monomer in the plasma system. The effects of surface treatment on mechanical properties of CaCO₃-PP composites are investigated.

Different combinations of plasma factors; RF power, monomer flow rate, and plasma duration, are employed in the studies. Through out this work, 30wt% CaCO₃ is used normally for composite formation. Additionally, several 50wt% untreated and treated samples are also prepared. In order to prevent the aging effect of the plasma coat, all plasma treated particles are immediately used in composite preparation just after their plasma modification. One additional sample plate is also prepared with treated CaCO₃ particles which are kept under atmospheric conditions for one month, to investigate the aging effects.

FTIR spectra of plasma coated films on sodium chloride IR crystals provide some information about structures that are generated by natural gas plasma. It is concluded that possibly branched PE-like film structures are deposited onto the surface of crystals in plasma. Similar polymeric films are assumed to exist on the surface of CaCO₃ particles treated under similar plasma conditions.

As expected, DSC experiments showed that percent crystallinity of PP decreased with addition of CaCO₃. Plasma surface modification of CaCO₃, on the other hand, does not have any additional effect on percent crystallinity of PP composites.

For untreated CaCO₃ loaded samples, mechanical properties of PP are decreased somewhat with 30wt% CaCO₃, with the exception of Young's modulus. Further increase of filler content (50wt%), however, greatly reduced all mechanical properties.

Samples loaded with plasma treated CaCO₃, some improvements in Young's modulus are achieved. It is observed that plasma control parameter should be lower than certain value in order to get enhancement in mechanical properties. At the same time, it is seen that CaCO₃ percent may also play an important role for the enhancement of modulus as maximum modulus value achieved with 50wt% loaded sample in the scope of this study.

In DMA studies, it is observed that CaCO₃ addition and its surface modification do not affect T_g. However, storage and loss modulus values of PP are increased with the addition of CaCO₃. Additionally, operating temperature ranges of the systems enlarged from upper limit as secondary transition seen on tan δ is shifted towards higher temperatures.

SEM micrographs of tensile fracture surfaces show that CaCO₃ dispersion is uniform in all samples. With the addition of CaCO₃, fracture morphology becomes brittle. This result is in accordance with tensile test results. Surface modification, on the other hand, seems to help to disperse the particles better. Being different from other plasma treated samples the morphology of 50wt% loaded sample, that seems to have better filler dispersion, is showing that modification may be more successful at higher loadings.

In this study, it is aimed to get composite systems with higher loading levels and lower final product costs, without any significant reduction in mechanical properties of matrix. Despite some enhancement in modulus, all mechanical test results showed that natural gas plasma used for surface modification of CaCO₃ are not too successful for the plasma conditions selected to reach to the aim planned.

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