ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

EFFECTS OF CALCIUM CARBONATE ($CaCO_3$) AND MALEIC ANHYDRITE ADDITION ON FATIGUE PROPERTIES OF POLYPROPYLENE

M. Sc. Thesis by

Fatih KOTAN, B.Sc.

515041019

Date of submission : 26.02.2007

Date of defence examination: 30.01.2008

Supervisor: Prof. Dr. İ. Ersin SERHATLI

Members of the Examining Committee: Prof. Dr. İ. Ersin SERHATLI

Prof. Dr. A. Sezai SARAÇ

Prof. Dr. Atilla GÜNGÖR (MÜ)

JANUARY 2008

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to Prof. Dr. İ. Ersin SERHATLI for his supervision, support and suggestions throughout my studies since undergraduate.

I sincerely thank to Dr. Osman G. Ersoy, for his invaluable help and support and I extend my thanks to all members of the Material Technologies Department in the name of Sibel Odabaş.

My very special thanks are to Mehmet Ali ORAL, Turgay Gönül, Seyhan Çağıl, Hatice Yılmaz and Sevinç MERT for their contribution in this thesis in almost every possible way.

Last but definitely not least, I thank to my parents Şükriye and Ali KOTAN, my sisters Hatice BALCI, Aysun KOTAN and Füsun KOTAN, my friends and my lovely wife İlke KOCA KOTAN who supported and encouraged me all my life.

December, 2007 Fatih KOTAN

TABLE OF CONTENT **PAGE NUMBER**

ABBREVIATIONS

$CaCO_3$	: Calcium Carbonate
SEM	: Scanning electron microscope
PP	: Polypropylene
MA-g-PP	: Maleic anhydride grafted polypropylene
PPS	: Poly(phenylene sulfide)
XNBR	: Carboxylated Acrylonitrile-Butadiene rubber
PEO	: Poly(ethylene oxide)
PPO	: Poly(propylene oxide)
CIP	: Crack initiation and propagation

LIST OF TABLES

LIST OF FIGURES

EFFECTS OF CALCIUM CARBONATE ($CaCO_3$) AND MALEIC ANHYDRITE ADDITION ON FATIGUE PROPERTIES OF POLYPROPYLENE

SUMMARY

Polymeric composites became one of the mostly used materials today because of their superior characteristics compared to the traditional materials. By the help of the fillers and the additives; all characteristics of polymeric materials can be changed and creating an appropriate polymeric composite for all applications is almost possible. Use of polymeric composites in structural applications has increased in last years and many load bearing part is designed by using polymeric composites. One of the most important design criteria for load bearing parts is fatigue resistance. A polymeric composite part can be strong enough for the moment but the most important thing for the part's durability is the composite's fatigue resistance. The main reason of failure for all materials is the cyclic loading on materials, in other words fatigue

The aim of this thesis is to investigate the effects of calcium carbonate ($CaCO_3$) and maleic anhydrite addition on fatigue properties of polypropylene. Different cyclic loads are applied to an isotactic homopolymer polypropylene, and the load limits are detected for ten million cycles. Then 40 % calcium carbonate filled homopolymer polypropylene composite was prepared in a twin screw co-rotating extruder and by the injection molding, dumbbell shaped tensile test specimens were produced and calcium carbonate distribution were investigated by SEM from fracture surface. Produced composite's tensile and fatigue tests were carried out and the load limits for ten million cycles and failure temperature during the cyclic loading is detected with a thermal camera. Comparison of filled and neat PP test results showed that, by the addition of hydrophilic calcite particles into the hydrophobic PP matrix increased elastic modulus value but it drastically reduced the tensile strength and fatigue resistance.

In order to improve PP/$CaCO_3$ interface interactions, 2% maleic anhydride grafted polypropylene was introduced into the PP/$CaCO_3$ matrix. A dry blend of 2% MA-g-PP and 98% PP is introduced into the twin-screw co-rotating extruder and 40% $CaCO_3$ filled PP-MA-g-PP composite was prepared. Injection molded test specimens were subjected to the tensile and fatigue tests. According to the test results; it can be explained as addition of MA-g-PP into the PP/$CaCO_3$ matrix caused the interface interaction as seen in SEM micrographs and has a positive effect in tensile and fatigue properties of PP/$CaCO_3$ composite but decreased the elongation value of the material. Addition of MA-g-PP into the PP/$CaCO_3$ matrix also decreased the failure

temperature during the cyclic temperature and changed the failure mechanism from heat generation failure to crack initiation and propagation

The first part of this thesis is a general introduction to polymeric composites. The second part is the objectives of this thesis and third, fourth and fifth parts of the thesis consists of a literature survey about effects of filler on the polymeric composites, the filler polymer interface and improvement methods and fatigue ad failure mechanisms.

The sixth part of the thesis explains the experimental work from composite production to applied mechanical and fatigue tests. In the seventh part, test results are given.

KALSİYUM KARBONAT VE MALEİK ANHİDRİT İLAVESİNİN POLİPROPİLEN MALZEMENİN YORULMA ÖZELLİKLERİNE ETKİSİNİN İNCELENMESİ

ÖZET

Polimerik kompozitler, geleneksel malzemelere kıyasla üstün özellikleri sayesinde sıklıkla kullanılan malzemeler haline gelmişlerdir. Dolgu malzemeleri ve katkılar sayesinde polimerlerin tüm karakteristikleri değiştirilebilmekte hemen her tür ihtiyaca cevap verebilecek polimer kompozitleri üretilebilmektedir. Yapısal uygulamalarda polimerik kompozitlerin kullanımları giderek artmakta ve bu kompozitler kullanılarak değişik yüklere maruz kalan parçalar tasarlanmaktadır. Yüke maruz kalan parçaların tasarımında dikkate alınması gereken en önemli kriterlerden biri de yorulma dayanımıdır. Bir polimerik kompozitin mukavemeti uygulama alanı için yeterli olsa dahi parçanın ömrünü belirleyen faktör polimerik kompozitin yorulma dayanımı olmaktadır. Tüm malzemelerin hasarlanmasının altında yatan en önemli neden çevrimsel yüklemeler, diğer bir deyişle yorulmadır.

Bu çalışmanın amacı; polipropilen malzeme içerisine eklenen kalsiyum karbonat ve maleik anhidritin polipropilen malzemenin yorulma özelliklerine etkilerinin incelenmesidir. İzotaktik homopolimer polipropilen malzemeye farklı çevrimsel yükler uygulanmış malzemenin on milyon çevrimi tamamlayabildiği yükler tespit edilmiştir. Daha sonra %40 kalsiyum karbonat($CaCO_3$) dolgulu homopolimer polipropilen çift vidalı ekstruder ile hazırlanmış ve plastik enjeksiyon ile kalıplanarak üretilen dambıl şekilli test numuneleri üretilmiş ve kalsiyum karbonatın matris içerisindeki dağılımı taramalı elektron mikroskobu (SEM) ile incelenmiştir. Üretilen kompozitin çekme ve yorulma testleri yapılmış ve on milyon çevrimi hasarsız tamamladığı yük değerleri ve çevrimsel yükleme ve hasarlanma anındaki malzeme sıcaklıkları termal kamera ile tespit edilmiştir. Dolgulu ve dolgusuz polipropilen için elde edilen test sonuçlarında elastik modül değerinin artışının yanında özellikle yapıya kalsitin girmesiyle çekme mukavemetinde ve yorulma dayanımında ciddi düşüş gözlenmiştir. Bunun nedeni olarak ise hidrofobik polipropilen ile hidrofilik kalsitin uyumlu bir yapı oluşturmamasıdır.

Kalsit ile polipropilen arasında etkileşimi arttırmak için ağırlıkça %2 oranında maleik anhidrit aşılanmış polipropilen (MA-g-PP) PP/$CaCO_3$ matrisi içerisine ilave edilmiştir. Ağırlıkça %2 oranında MA-g-PP ile %98 oranında homopolimer PP karıştırılarak çift vidalı ekstruder ile %40 $CaCO_3$ dolgulu PP/MA-g-PP kompoziti üretilmiştir. Plastik enjeksiyon ile test numuneleri üretilmiş ve bu numunelere çekme ve yorulma testleri uygulanmıştır.. Elde edilen test sonuçlarına göre yapıya ilave edilen MA-g-PP sayesinde kalsit ile polipropilen arasında kimyasal bağlanmanın meydana geldiği taramalı elektron mikroskobu incelemeleri ile tespit edilmiştir.

Ayrıca MA-g-PP ilavesinin malzemenin çekme ve yorulma özelliklerine pozitif etkisinin olduğu, malzemenin kopmada uzama değerini ve hasarlanma anındaki sıcaklığı düşürdüğü ve malzemenin hasarlanma mekanizmasını ısıl hasarlanma tipinden çatlak oluşumu ve ilerlemesi tipine dönüştürdüğü tespit edilmiştir.

Çalışmanın ilk bölümünde polimerik kompozitler ile ilgili genel bilgiler verilmektedir. Tezin ikinci bölümünde amaçlar açıklanmakta, 3. , 4. ve 5. bölümlerinde ise sırasıyla; dolgu maddelerinin polimerlere etkileri, dolgu polimer arayüzey etkileşimi ve bu etkileşimi geliştirme yöntemleri ve yorulma ve hasarlanma mekanizmaları anlatılmaktadır.

Çalışmanın 6. bölümünde ise tez çalışması sürecinde kompozitin üretiminden test aşamalarına kadar uygulanan yöntem, proses ve tekniklerin açıklamaları yapılmıştır. 7. bölümde ise uygulanan testlerin sonuçları verilmiş ve elde edilen sonuçlar irdelenmiştir.

1. INTRODUCTION

Polymers are materials consisting of small repeating structural units; called mer, combined to give a very large, linear structure. Polymeric materials are more often used day by day because of their superior properties and ease of production. Nowadays; it is possible to find a suitable polymeric material for almost every application. With the addition of fillers and blending different polymers; creating polymeric composites is also possible. A composite can be described as "a heterogeneous substance consisting of two or more materials, which does not lose the characteristics of each component". Synthetically created polymeric composites are produced to improve properties or to reduce costs. Growing up of the use of polymer matrix composites continue increasingly and find new using areas and replaces other materials in various applications, because of unique properties of polymeric matrix composites

Polypropylene is one of the mostly used polymers in modern life. Because of its superior properties such as low density, resistance to chemicals, tensile strength, impact strength and ease of production compared to traditional materials, polypropylene became very advantageous for structural applications. But, some properties of polypropylene are not good enough for structural applications. For example, its low elastic modulus is one of the major problems for load bearing applications. The cost of the polypropylene is another disadvantage when increasing petroleum prices are considered. Introducing fillers, especially calcium carbonate is one of the solutions for low modulus and high cost problem. But introducing $CaCO_3$ causes other problems such as lowering tensile and impact strength.

Different fillers have totally different effects on polymeric composites and its properties [1-7]. The effects of filler on the composite properties depend on the particle shape, particle size, volume fraction in the matrix and compatibility with matrix. Composites with high strength fillers such as glass fibers usually have strength to weight ratios that exceed better values compared to metals and their alloys [6]. This property makes polymer matrix composites ideal for structural applications. The most important thing during creating polymeric composites with

fillers is the polymer-filler interaction/interface. By increasing the interaction between the matrix and the filler; most of the mechanical properties can be improved [7].

2. OBJECTIVE OF STUDY

The aim of this study is to determine the fatigue characteristics and failure mechanisms of PP homopolymer material, to investigate the effects of $CaCO_3$ addition on polypropylene matrix and effects of polypropylene/$CaCO_3$ interface improvements by using maleic anhydrite on fatigue and fracture behavior of calcite filled polypropylene composite.

3. POLYMER COMPOSITES

Composite materials are engineered materials made from two or more constituent materials with significantly different physical or chemical properties and which remain separate and distinct on a macroscopic level within the finished structure. There are two categories of constituent materials: matrix and reinforcement. The matrix material surrounds and supports the reinforcement materials by maintaining their relative positions. The reinforcements impart their special mechanical and physical properties to enhance the matrix properties. A synergism produces material properties unavailable from the individual constituent materials, while the wide variety of matrix and strengthening materials allows the designer of the product or structure to choose an optimum combination.

In order to lower cost or to enhance properties**;** polymeric materials started to fill with inorganic or organic materials and the most important reason of adding filler in a polymeric matrix was the cost reduction [8]. In ASTMD1566-95a filler is described as "A solid compounding material, usually in a finely divided form, which may be added in relatively large proportions to a polymer for technical or economic reasons" [9]. There are many types of fillers which can be used to make a polymeric composite.

3.1. Fillers and Filler Characteristics.

There are lots of fillers used in the plastics industry. Some of these fillers are used to enhance the properties of the matrix but a significant number of these fillers are used to reduce the cost of the final product.

Mostly used fillers in producing polymeric composites are;

1. Calcium carbonate
2. Talc
3. Mica
4. Silica
5. Clays
6. Barium sulfate
7. Magnesium hydroxide
8. Aluminum trihydroxide
9. Carbon black
10. Titanium dioxide
11. Metal powders

Fillers are identified with their properties such as;

1. Physical state
    a) Solid
    b) Predispersed state
2. Chemical composition
    a) Inorganic
    b) Organic
3. Particle shape
    a) Spherical
    b) Cubical
    c) Irregular
    d) Block
    e) Plate
    f) Flake

g) Fiber

h) Mixture of different shapes

4. Particle size

    a) Nano

    b) Micro

    c) Macro

5. Aspect ratio (length/width = 1 (spherical or cubical) to 1,600 (fibers))

6. Particle size distribution

    a) Monodisperse

    b) Designed mixture of sizes

    c) Gaussian distribution

    d) Irregular distribution

7. Particle internal structure

8. Color

9. Thermal properties

    a) Thermal expansion coefficient

    b) Thermal conductivity

10. Electrical properties

    a) Non-conductive

    b) Conductive

11. Magnetic properties

    a) Magnetic

    b) Non-magnetic

Additionally; to produce a successful polymer composite, the properties given below must have taken into consideration, because the final polymer composite's critical properties are belong to these properties;

- Particle size and distribution
- Aspect ratio
- Chemical composition of surface
- Mechanical properties of filler particles

3.2. Effects of Fillers on Tensile and Fatigue Properties of Polymeric Materials

Filers can be used for modifying or changing the desired properties of polymers such as Young Modulus, density, fire retardancy etc… Some researchers have tried to formulate these effects of fillers [10].

Tensile strength is one of the most important properties between the mechanical properties. The most general equation is describes the effect of volume fraction of filler (ϕ_f) on the tensile strength of composite (σ_c) [11]:

$$\sigma_c = \sigma_p * (1 - a\,\phi_f^b + c\,\phi_f^d) \qquad (3.1.)$$

In order to predict if tensile strength of the composite increases or decreases as the volume fraction of the filler increase, the values of these coefficients (a, b, c, d) must be known. These constants are selected to describe certain features of the filler's behavior such as, constant “a” is usually related to stress concentration, constants “c” and “d” are related to the effect of particle size. The constant “b” is usually assigned the arbitrary value of 0.67. In case of smaller the particle size, the values of these constants are increasing [11]. To explain experimental data many modifications of the above equation or its parameters (constants) are used.

For low volume fraction of filler, the Einstein equation (equation 3.3) usually fits experimental data:

$$\sigma_c = \sigma_p * (1 + a\,\phi_f^b) \qquad (3.2.)$$

In the equation, b = 1 for spherical particles and “a” depends on the adhesion between the matrix and the filler The Einstein equation predicts the addition of filler increases tensile strength but it is not acceptable for all case; so other researchers such as Nicolais and Narkis modified the equation [12] .

The Nicolais and Narkis equation (equation 3.4.) is a common modified the Einstein equation in which a=1.21 and b=2/3 [12]

$$\sigma_c = \sigma_p \frac{(1-\phi_f)}{1+2{,}5\phi_f} \exp(B\phi_f) \tag{3.3.}$$

In this equation, to characterize the interaction between filler and polymer, parameter "B" is used. [12] Also some other researchers developed equations. One of them is Piggot and Leinder [13] equation:

$$\sigma_c = \lambda\sigma_p - \chi\phi_f \tag{3.4.}$$

Table 3.1: Effect of different fillers on Tensile Strength [14]

Filler	Polymer	Concentration % wt	Change in Tensile Strength	Note	Ref.
Alumino-silicate	PVAc	10,50%	0% or +35%	decreases with interaction increasing	[22]
$CaCO_3$	PE	2 – 25%	+10% or +50%	phosphate modified	[23]
	PE	2 – 25%	-10% or -50%	not modified	[23]
	PP	5 – 30%	-30% or -40%	Elongation decreases	[24]
Glass beads	epoxy	10 – 40%	-25% or -60%	no adhesion	[25]
	epoxy	10 – 40%	no effect	good adhesion	[25]
	PP	10 – 50%	-11% or -45%	debonding stress; no treatment	[28]
Nanoparticle	epoxy	2 – 24%	+60% or +180%	montmorillonite; layered composite	[26]
Fumed Silica	PDMS	30 – 50%	+5% or +40%	increases as particle size decreases	[27]
Talc	PP	5 – 30%	0% or + 80%	depending on phosphate coating	[29]
Glass fiber	PP	30%	+50%	depending on aspect ratio	[30]
	PP	30%	+90%		[31]
	PA66	30%	+100%	elongation reduced	[30]
	PSU	30%	+67%	surface treated	[30]

As shown the data in the Table 3.1. Tensile strength of a filled material is strongly affected by;

- Particle size: small particles increase the tensile strength; for example; nanoparticles and fumed silica
- Particle shape: fillers with higher aspect ratio can improve the tensile strength.
- Interaction with the matrix: surface modified (treated) fillers can improve the tensile strength when compared to the untreated fillers, such as untreated calcium carbonate in PE decreases tensile strength but after phosphate modification tensile strength increases
- Concentration: fillers can increase the tensile strength to a critical concentration level, further increase in filler's concentration after the critical level decreases tensile strength

Composites' stiffness is measured by the elastic (Young) modulus, obtained from flexural test. Fillers increase the stiffness significantly. Einstein equation is used to predict composites' modulus, at high filler concentrations the change of elastic modulus deviates from that predicted by the Einstein's viscosity equation modified by Guth and Gold predicts [15];

$$E = E_0(1 + 2{,}5\phi + 14{,}1\phi^2) \qquad (3.5.)$$

Gingrich et al, worked on the effect of volume fraction of different fillers on Young Modulus of composite as given in the Figure 3.3[16].

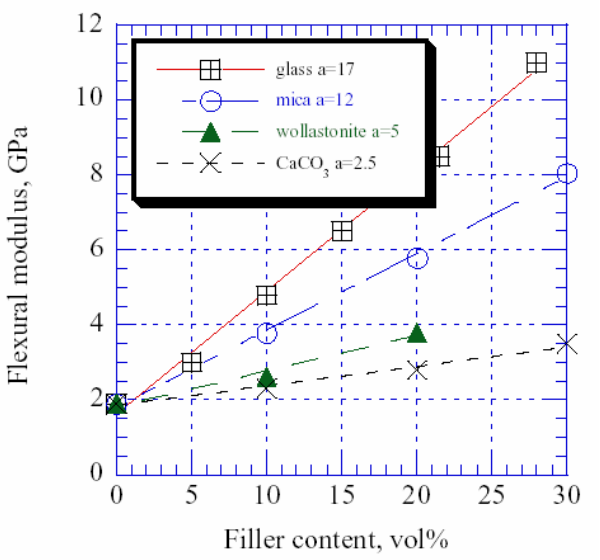

Figure 3.1. Flexural modulus of polyketone with different fillers. [16]

As a result of these Modulus value of composite depends on;

- Particle modulus
- Particle shape
- Particle size
- Aspect ratio
- Concentration

Elongation is mostly inversely proportional to tensile strength, which means, an increase in the tensile strength of a filled material usually causes a decrease in elongation [11] but small\nano particle size fillers when used at low concentrations, can cause an increase in elongation by acting as an internal lubricant [19]

Another critical property of a polymer composite, impact property; is strongly affected by;

- Particle size of the filler
- Particle shape of the filler
    - fiber like fillers increase the impact properties because of their high aspect ratio

- Particle rigidity
    - hollow particles and fillers having low hardness substantially decrease the impact strength
- Interaction with the matrix
    - if there is no interaction between the filler and the matrix; crack initiation and propagation will occur on the filler surface
- Concentration
    - increase in the concentration of the filler causes an increase on the impact strength till the maximum packing value.
- Nucleation
    - some fillers act as a nucleating agent which contribute to an increase in the impact strength because of increasing crystallinity

Fatigue resistance is one of the most important material characteristics when the subject is useful life and failure of materials. Polymeric composites generally fail with the mechanism of crack initiation and propagation [18-20], when the frequency of cyclic loading is low and they fail with the mechanism of hysteretic heating [21] when the cyclic loading frequency is high.

Effects of fillers on fatigue properties of polymers are parallel to the effect of fillers on tensile properties. Generally; fatigue resistance of a polymer is affected same way as its tensile strength when a filler is introduced to the polymer matrix and this phenomena is strongly related to the aspect ratio of the filler and the filler matrix interaction [22,23].

4. INTERACTION BETWEEN FILLER AND MATRIX IN POLYMER COMPOSITES

When the subject is mechanical properties; one of the most important phenomena in polymeric composites is the interaction between fillers and polymer matrix [24]. The interaction determines polymeric composites' mechanical properties [11]. Generally, a better interfacial bonding will impart better properties to a polymer composite, such as high modulus, tensile strength, and hardness as well as resistance to tear, fatigue, cracking, and corrosion [19].

To form an interaction between the fillers and the polymeric matrix; a pretreatment can be applied to the filler surface. These pretreatments increase the adhesion between the filler and the matrix.

4.1. Theories of the Adhesion between the Filler and Polymer

Adhesion between the filler and the polymer is a key issue when the subject is the final mechanical properties of a polymer composite.

There are five kinds of adhesion mechanisms used for explaining the adhesion between polymer and filler or reinforcing material;

a) Mechanical adhesion

b) Chemical adhesion

c) Electrostatic adhesion

d) Adhesion through diffusion

e) Thermodynamic absorption

4.1.1. Mechanical Adhesion

The theory of mechanical adhesion can be explained as penetration of the adhesive polymeric material in the rough surface of filler. This mechanical adhesion can be improved by increasing the porosity and surface roughness of fillers or reinforcing materials.

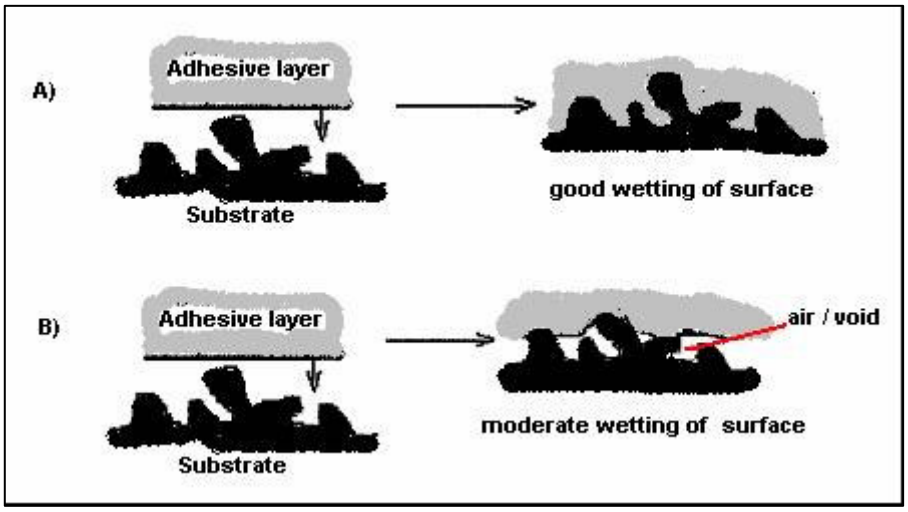

Figure 4.1. Mechanical Adhesion model a) a Good wetting of surface b) moderate wetting of surface [25]

As shown in the Figure 4.1., mechanical adhesion model is valid for macro sized fillers which have high surface roughness such as wood, paper or textiles. If wettability of the filler by the polymer is poor the interaction will be very poor and there will be voids or air bubbles on the surface of the fillers. These voids and air bubbles are possible weak zones which can be possible crack growth zones. [25].

4.1.2. Chemical Adhesion

Chemical adhesion is the strongest adhesion type of all. Adhesives that are used in daily life works this way. Chemical adhesion can take place with ionic bonding, covalent bonding or the weakest of all; hydrogen bonding.

Chemical adhesion is more resistant to water and temperature. As an example of this theory; silane coupled filler or reinforcing materials' surface form primary bonds with the matrix [26].

4.1.3. Electrostatic Adhesion

Some conducting materials may pass electrons to form a difference in electrical charge at the join. This results in a structure similar to a capacitor and creates an attractive electrostatic force between the materials. The electrostatic adhesion theory is proposed by Deriagin and Krotova [27]. Deriagin and Krotova observed electrical effects while separation through the detachment of reinforcing materials from the matrix. According to the theory; when an electrical discharge is produced; separation energy is 10-1000 times higher than the energy necessary for breaking the intermolecular links. The electrostatic adhesion can be simulated like a condenser; the adhesion energy is equivalent to the mechanical work needed for the separation of two sides of a flat condenser [25].

4.1.4. Adhesion through Diffusion

Voyutski [28] is defining adhesion through diffusion as the adhesion between two identical polymers. When two polymeric materials are in a direct contact and they are thermodynamically compatible, interdiffusion occurs between the two species. It is possible by the molecular motions of polymeric chains but not too low temperatures [11].

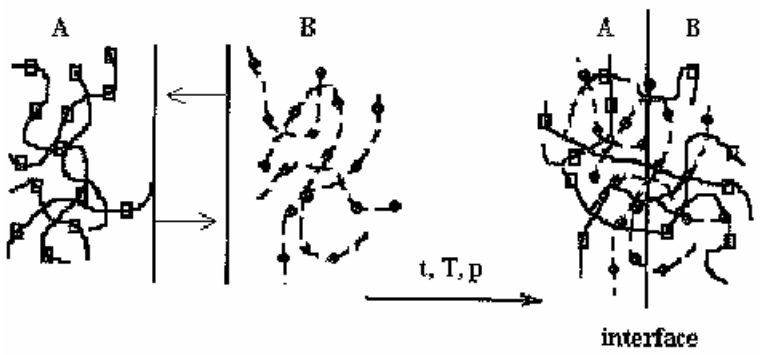

Figure 4.2. Graphical representation of adhesion through diffusion t: time T: temperature p: pressure [25]

In figure 4.2. ;only one polymeric material is responsible for the diffusion. Adhesion level depends on time, temperature and pressure.

4.1.5. Thermodynamic Absorption (Wetting)

When one or both of the components of the composite is in liquid state and there is a very good contact between these components, physical or chemical bond formation

can be possible [25]. A thermodynamic adhesion model which was proposed by Sharpe and Schonhorn [29], based on thermodynamic considerations resulting from Young's equation and as well as from Durpe's equation. The form of Durpe' equation;

Durpe's equation:

$$W_0 = \gamma_A + \gamma B - \gamma_{AB} \quad (4.1.)$$

W_0 means thermodynamically reversible adhesion energy, γ_A means free surface energy of compound A, γ_B means free surface energy of compound B and γ_{AB} represents recovered interfacial energy.

In Young equation, contact angle is estimated and θ measured by drop deposited on a solid surface. Young's equation;

$$\gamma_S = \gamma_{SL} + \gamma_L \cos \theta \quad (4.2.)$$

γ_S - free surface energy of solid

γ_{SL} - solid/liquid interfacial energy

γ_L - free surface energy of liquid

θ - contact angle

4.2. Filler Treatments for Improved Adhesion

In a polymeric composite between the filler and matrix there might be physical interaction, chemical interaction or both of them as shown in the Figure 4.3. Interactions depend on the nature of polymeric matrices and the nature of filler.

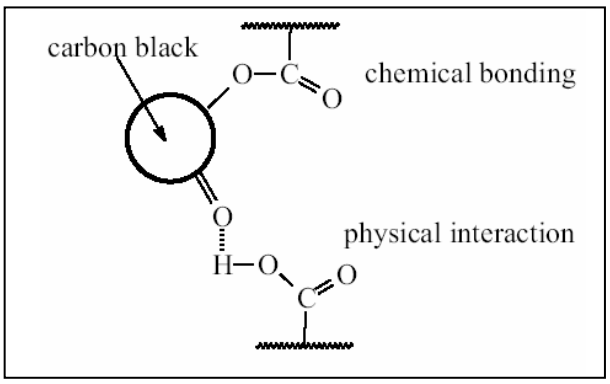

Figure 4.3.Interaction between XNBR rubber and Carbon Black [30]

There are different methods improving the adhesion between polymer and filler or reinforcing materials but one of the most important things is choosing the right method considering nature of polymeric matrices and the nature of filler. There are four different methods used for improving adhesion between the filler and the matrix.

1) Chemical treatment with low molecular weight compounds
    - surface of inorganic or organic filler is treated with low molecular weight compounds in order to decrease surface free energy
    - possibility of wetting increases
2) Chemical treatment with macromolecular compounds
    - Van der Waals bonds or acid-base interactions are present
    - Macromolecules are adsorbed on the filler surface

4.3 Use of Maleic Anhydride as a Coupling Agent

The main reason for poor adhesion between the filler and the matrix is thermodynamic incompatibility. When the surface energy of the filler is high, wettability of the filler by the matrix polymer is low. For this reason; surface treatment on fillers or use of coupling agents is necessary to improve the adhesion.

There are lots of coupling agents and filler surface treatment methods used for improving the filler-matrix interaction. Mostly used coupling agents are:

- Silanes
- Phosphorus based compounds
- Stearic acid
- Peroxides
- Acrylamides

And there are some surface modification techniques used:

- Oxidation
- Ozone (corona) treatment
- Acid treatment

Generally, silane coupling agents are used as adhesion promoters between fillers, especially glass fibers and thermosets or polar polymers such as polyamides. Because of their low polarity and lack of reactive groups these coupling agents have, however, limited interaction with the polymer matrix in the case of polyolefins [31].

When working with a low polar molecule like polypropylene, and calcium carbonate it is difficult to achieve a strong interaction between calcium carbonate and PP and there are only a few techniques can be applied to increase the adhesion. These are:

- Treating with HDPE oligomer
- treating with a copolymer based ethylene oxide and propylene oxide (PEO\PPO)
- treating with a diblock poly(butadiene-b-acrylic acid) copolymer
- coating with modified PP which has the rests of maleic acid on the ends of macromolecular chain

Treating the surface of calcium carbonate with modified polypropylene having maleic acid or anhydride at the end of the chain is a method of improving the adhesion and so the treated material is well dispersed, becoming compatible with the PP matrix [24]. In figure 4.4; possible interfacial bonding after maleic anhydride modification is shown.

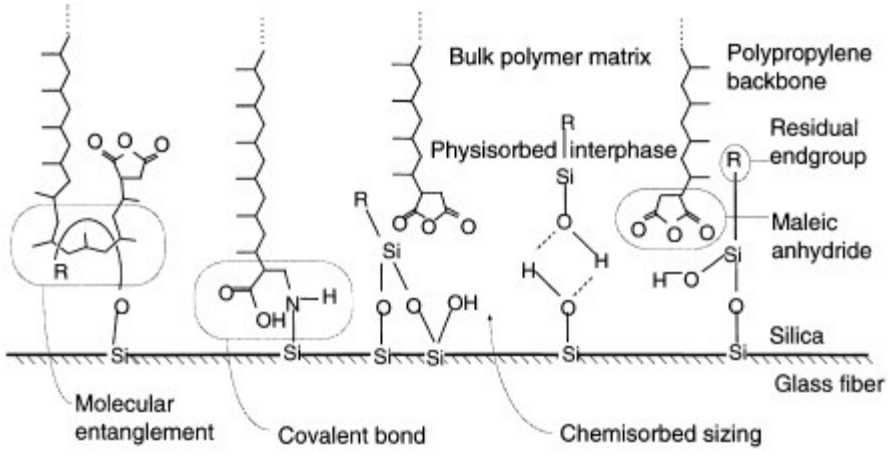

Figure 4.4. Possible interfacial bonding after maleic anhydride modification. [32]

The mechanism of adhesion by MA-g-PP is shown in the Figure 4.5. is given below. The single C-O bond of the maleic anhydride breaks at 200-240^0 C and free electrons interacts with the Ca^{+2} ions of the calcium carbonate. [14]

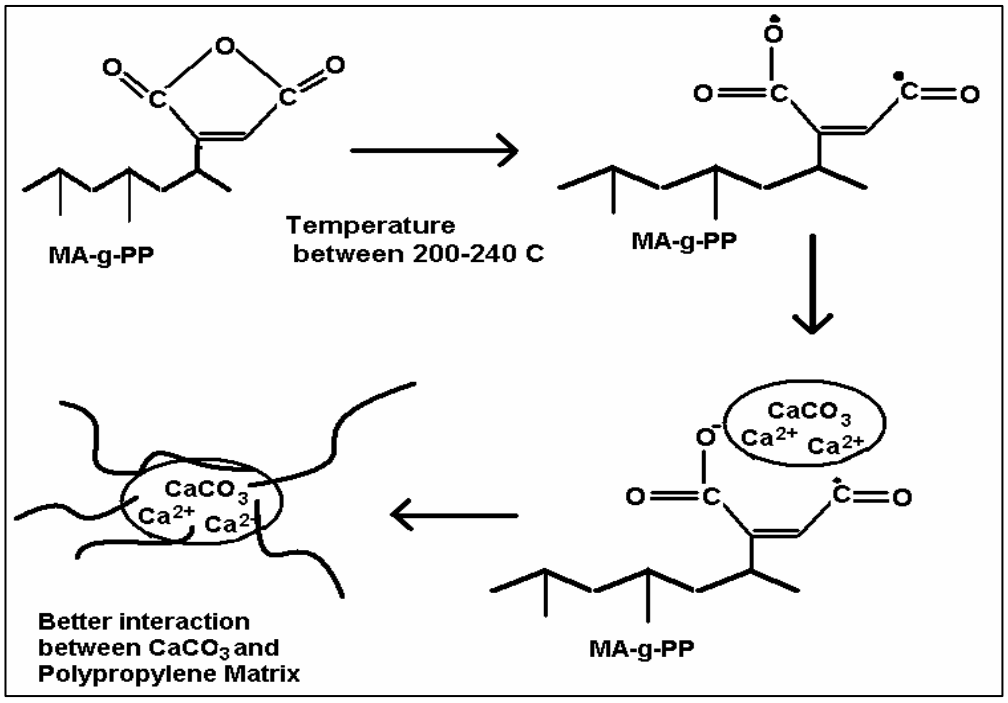

Figure 4.5. Mechanism of adhesion by MA-g-PP

5. FATIGUE AND FRACTURE MECHANISMS IN POLYMERIC MATERIALS

Fatigue is one of the most often seen failure reason of all. Fatigue is the progressive and localised structural damage that occurs when a material is subjected to cyclic loading. During the cyclic loading, the maximum stress values are less than the ultimate tensile stress limit, and may be below the yield stress limit of the material.

In cyclic loading, there are some critical parameters which affect the fatigue life of a material. In figure 5.1., the representation of a typical tensile-compression and tensile-tensile type cyclic loading graphics are given.

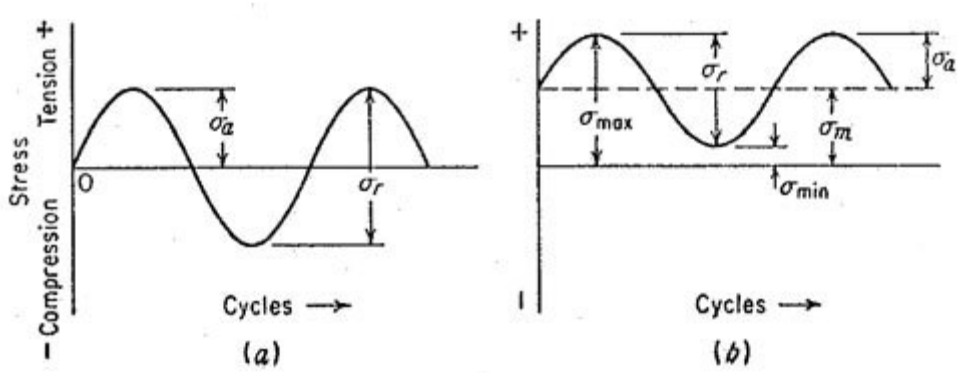

Figure 5.1. Cyclic loading types. a) tensile-compression type cyclic loading, b) tensile-tensile type cyclic loading.

The critical parameters of a cyclic loading are;

1) σ_{max} = maximum stress
2) σ_{min} = minimum stress
3) σ_m = mean stress
4) σ_r = amplitude of the load
5) Frequency

In high-cycle fatigue situations, materials performance is commonly characterised by an *S-N curve*, also known as a *Wöhler curve*. This is a graph of the magnitude of a

cyclical stress (*S*) against the logarithmic scale of cycles to failure (*N*). (Figure 5.2) [18].

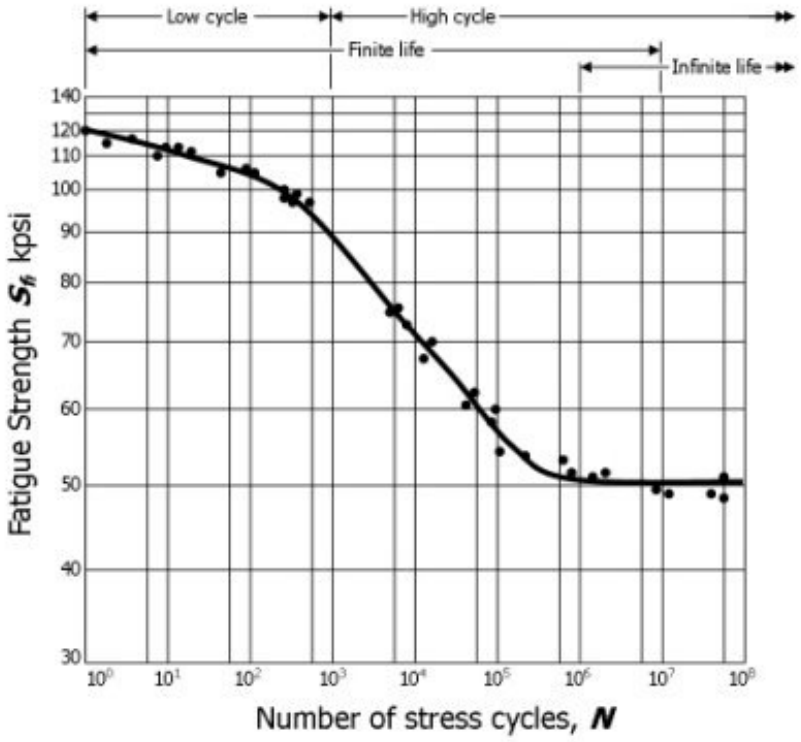

Figure 5.2. S-N (Wöhler) curve

There are mainly two fatigue failure mechanisms in polymeric materials. These are:

1) Crack initiation and propagation
2) Cyclic softening

5.1. Crack Initiation and Propagation

At low frequencies of cyclic loading or when the generated heat is not high; the failure mechanism of the polymeric materials is CIP. In CIP, failure occurs in four phases [18]. These are;

1) Crack nucleation: Occurs at the defect zones, especially on the filler surface in polymeric composites.
2) Stage 1 crack growth
3) Stage 2 crack growth
4) Ultimate ductile fracture

A schematical expression of CIP is shown in Figure 5.3.

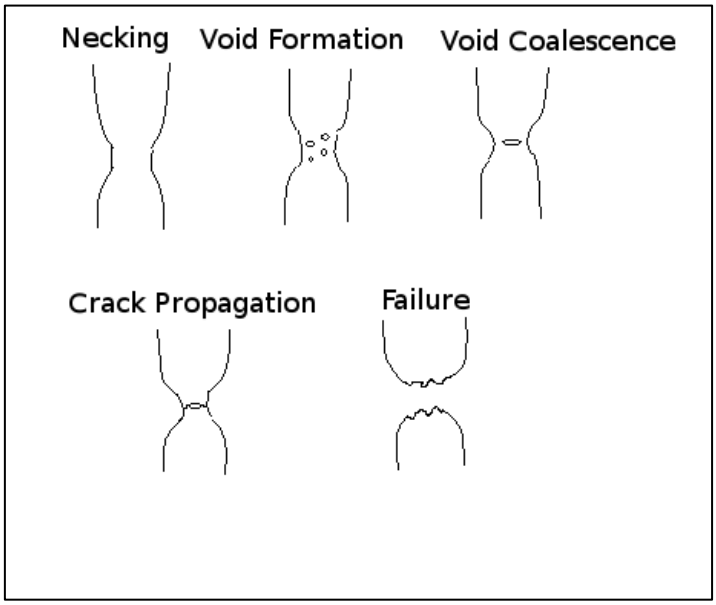

Figure 5.3. Crack initiation and propagation

5.2. Cyclic Softening

At high frequencies of loading at polymeric materials, heat is generated during the cyclic loading. Generated heat can be expressed as the area between the cyclic stress-strain curves. (Figure 5.4.)

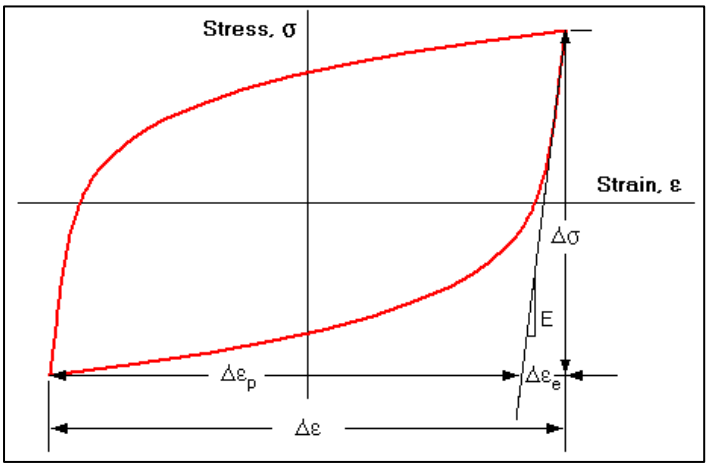

Figure 5.4. Cyclic stress-strain curve.

If the generated heat is more than the materials heat transfer capacity; material begins to heat. Increase of the heat causes polymeric materials to soften and polymeric materials' tensile strength and elastic modulus decrease [33]. With the decreasing

tensile strength; the strain during the loading increases and this causes more heat generation. The significant decrease at the slope and shifts of hysteresis loops are a god indicator for cyclic softening [18] which is shown in Figure 5.5. and 5.6.

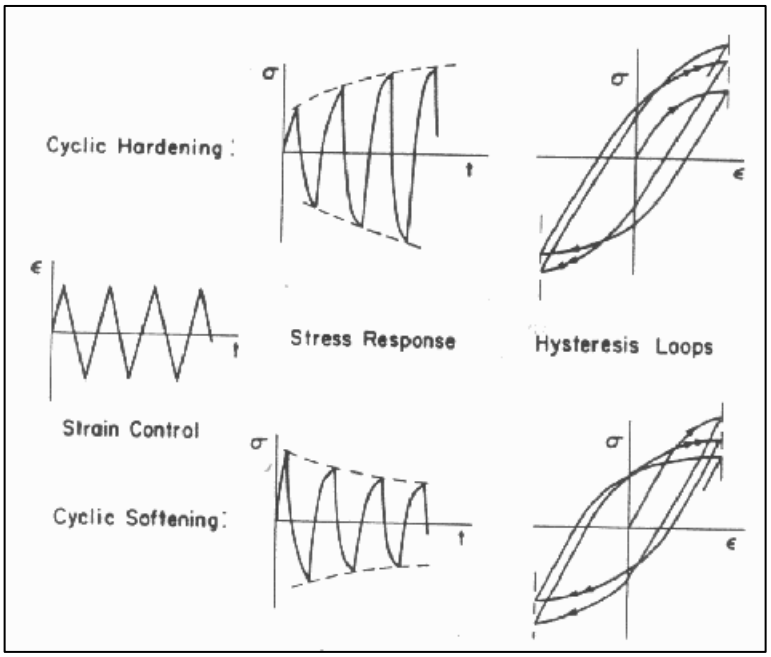

Figure 5.5. Cyclic hardening and softening behavior of materials

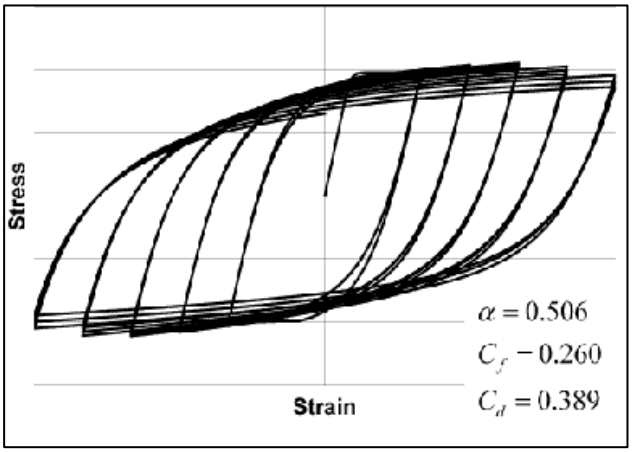

Figure 5.6. Shift of hysteresis loop and decrease in the slope of the loop.

When the temperature of the material increases to a critical limit, material softens and fails because polymeric materials can not bear load after their softening point.

6. EXPERIMENTAL WORK

6.1. Materials Selection

In this study; an isotactic homopolymer polypropylene (PP) is used, from the producer Borealis/Austria, grade HE125MO with the MFI value of 12 g/10min. The physical properties of the material are given in the table below.

Table 6.1: Borealis HE125MO physical properties

PHYSICAL PROPERTIES		Typical Value	Unit	Test Method
Density		908	kg/m^3	ISO 1183
Melt Flow Rate	230 C/2.16 kg	12	g/10 min	ISO 1133
Tensile Stress at Yield	50 mm/min	34.5	MPa	ISO 527-2
Tensile Strain at Yield	50 mm/min	9	%	ISO 527-2
Tensile Modulus	1 mm/min	1550	MPa	ISO 527-2
Charpy Impact Strength, notched	+23 C	03.May	kJ/m^2	ISO 179/1eA
Hardness, Rockwell		100	R-scale	ISO 2039-2
Heat Deflection Temperature	0.45 N/mm^2	88	C	ISO 75-2

Calcium carbonate ($CaCO_3$) is supplied from Omya Madencilik/Turkey, grade OmyaCarb 3Xtra-KA, without surface treatment and average particle size of 5,5 microns.

The coupling agent; Maleic Anhyride grafted polypropylene (MA-g-PP), is supplied from Uniroyal Chemical/Middlebury, grade Polybond 3200 with 1% Maleic anhydride (MA) grafted. The physical properties of the material are given in the table below.

Table 6.2: Polybond 3200 physical properties

PHYSICAL PROPERTIES		Typical Value	Unit	Test Method
Melt Flow Rate	190 C/2.16 kg	12	g/10 min	ASTM D-1238
Density	+23 C	0.91	g/cc	ASTM D-792
Melting Point		160-170	C	DSC
Maleic Anhydride Level		1	%	

6.2. Compounding

In this study; level of 40%wt calcium carbonate and 2%wt of MA-g-PP is selected because; 40% $CaCO_3$ and 2% MA-g-PP is the best choice when considering the optimum point of price vs. performance for the polymeric compound according to the tests carried out before. Polymeric compounds are produced with an intermeshing, co-rotating twin screw extruder.

The twin-screw extruder which was used in this work is a PRISM TSE24 IIC, with the screw diameter 24mm and L/D ratio 28:1(shaft length/screw diameter). Data about the PRISM TSE24 IIC extruder is given in Table 6.1.

PRISM TSE24 IIC extruder, which is shown in figure 6.1, has 7 heat controlled modular barrel segments with length of 96 mm or (4 x screw diameter) and a die with three 3 mm strand holes. The machine's critical parameters such as heating zone temperatures, motor speed, shaft torque and melt temperature is controlled by a computer mounted on the machine.

Table 6.3: Prism TSE 24 Twin screw extruder data sheet

	Units	PRISM TSE24
Screw diameter	Mm	24
Maximum screw speed	Rpm	1000
L/D (shaft length/screw diameter)	-	28:1
Channel depth	Mm	5.15
Screw diameter/channel depth	-	5.15
Screw/barrel clearance	Mm	0.2
Shaft center line distance	Mm	18.75
Shaft center line/radius ratio	-	1.5625
Total Area	cm^2	8.5
Screw area	cm^2	4.7
Free area	cm^2	3.8
Total volume	cm^3	511
Free volume	cm^3	228
Barrel peripheral surface area	cm^2	830
Surface area/total volume	m^2/litre	0.14
Surface area/Free volume	m^2/litre	0.31
Max. channel shear rate @ 1000 rpm	s^{-1}	244
Max. power	kW	9
Max. torque/shaft	Nm	43
Max. torque/Free volume	Nm/ cm^3	0.16

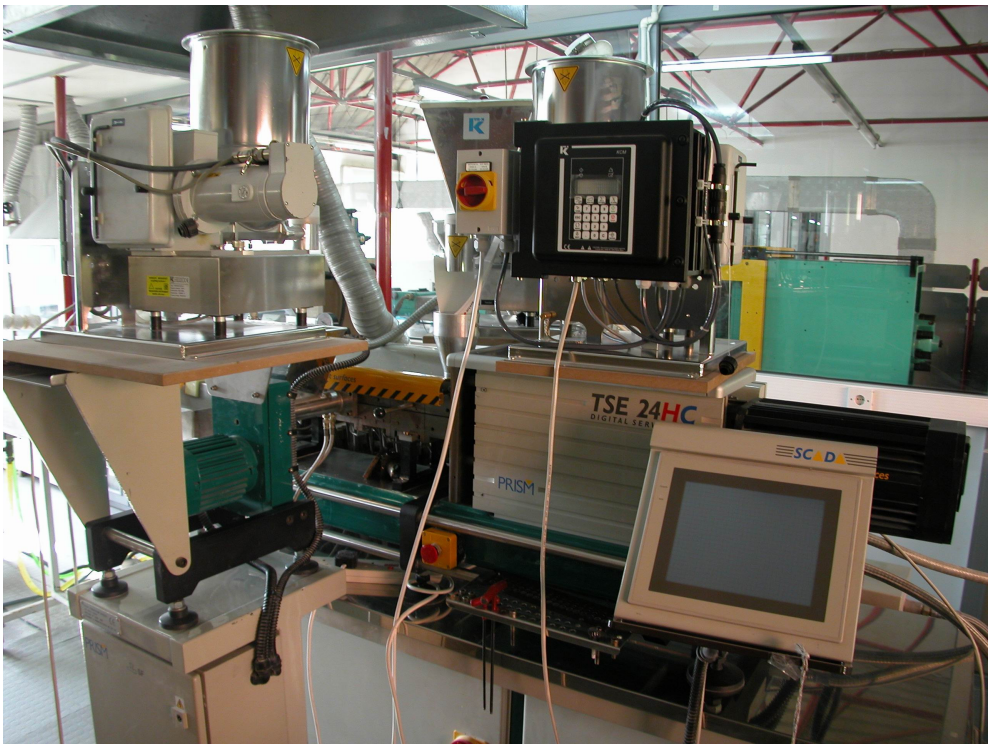

Figure 6.1. PRISM TSE24 IIC extruder with K-Tron gravimetric feeders.

As shown in Figure 6.2., the barrel can be split in the middle for easy screw removal and cleaning. A pressure sensor is connected to the die barrel to measure the melt pressure generated by movement of the screws [34].

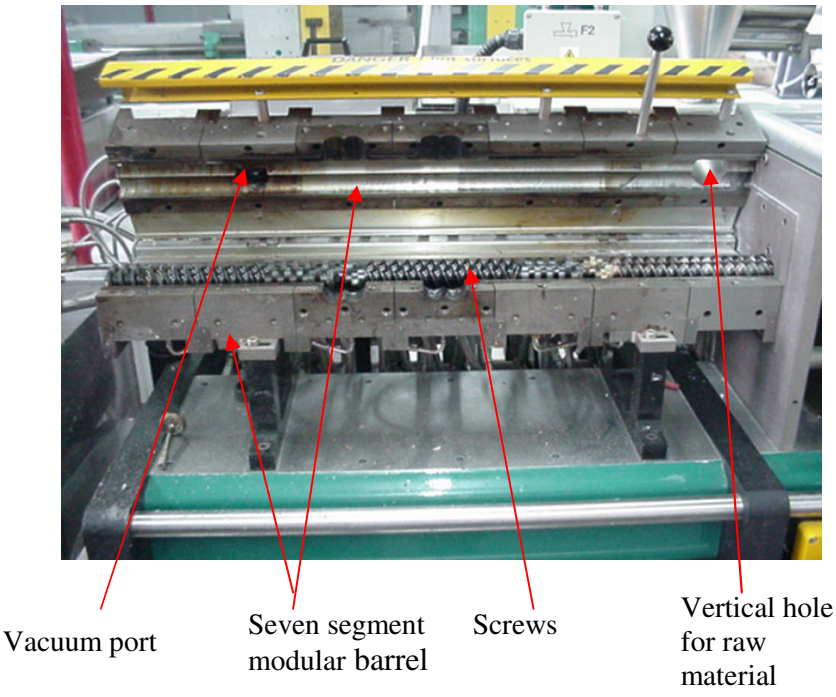

Figure 6.2 Prism Twin Screw Extruder Barrels and Screws

The extruder is equipped with two K-Tron gravimetric feeders and one Brabender side feeder. All components of the compound is fed into the extruder with the gravimetric feeders and produced spaghetti like compound is cut into granules with the granulating unit shown in the figure 6.3.

Figure 6.3. Prism Granulating Unit

In order to achieve good melting and mixing of polymers by high shear, high residence time in the reaction zones, and venting close to the outlet of the extruder, a screw is designed which is shown schematically in the Figure 6.4. Six different zones of this screw can be explained like:

- raw material intake and solid conveying zone
- plasticizing zone (first kneading block)
- melt conveying zone
- further homogenization zone (second kneading block)
- degassing zone
- pressure built up zone

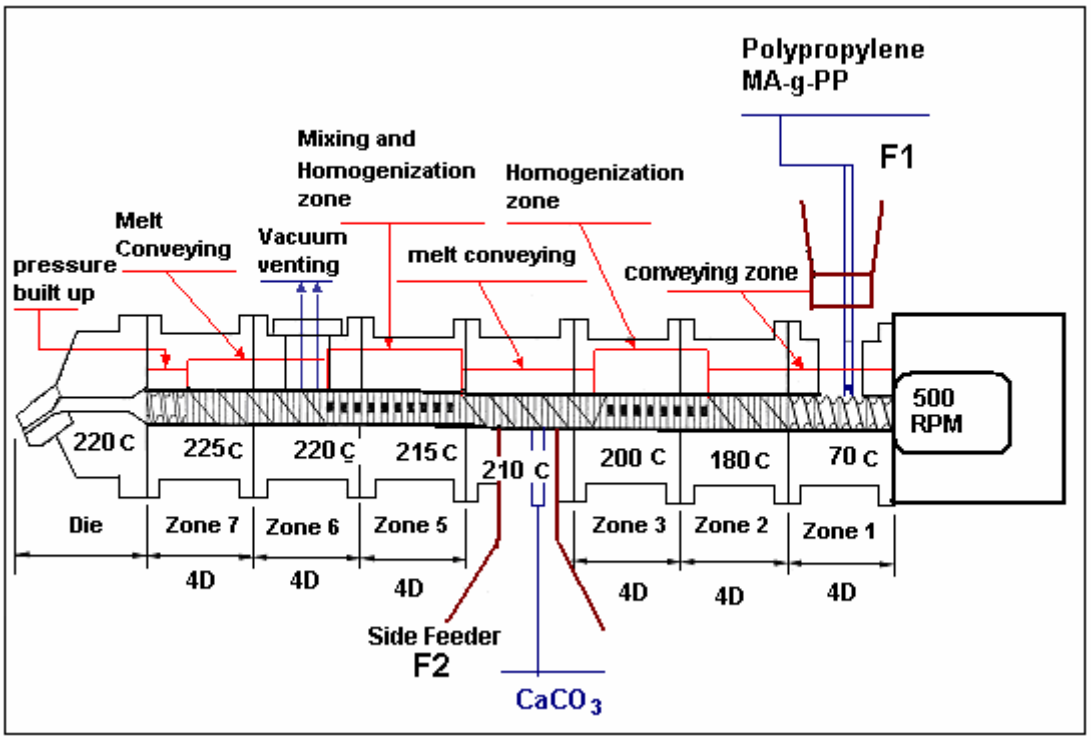

Figure 6.4 Extruder screw design

6.3. Specimen Production with Injection Molding

In this study; ISO R527 type standard specimens were produced with an Arburg Allrounder 320C fully hydraulic plastic injection machine. (Figure 6.5)

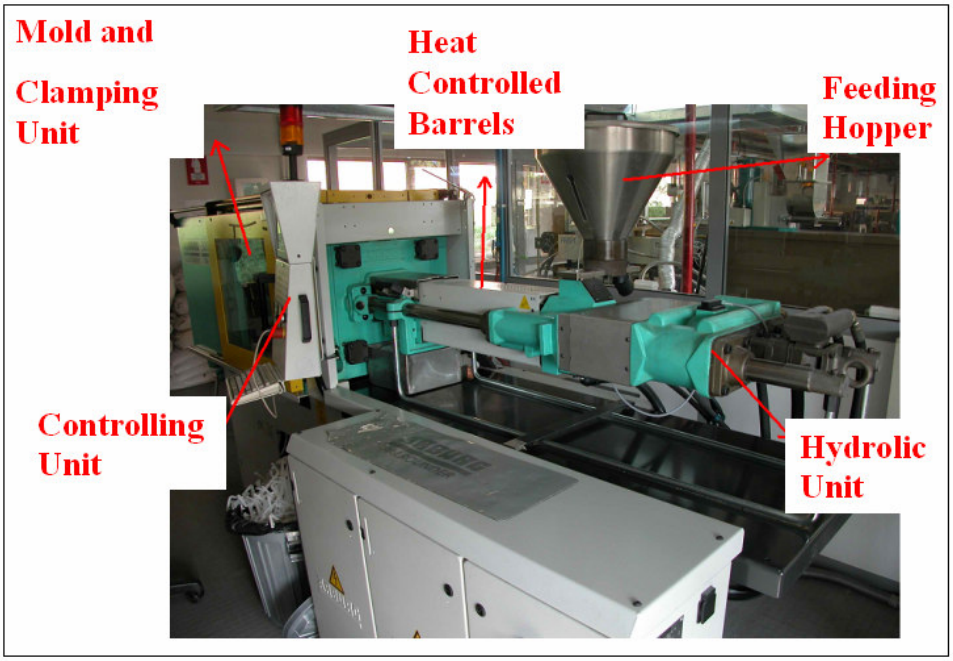

Figure 6.5.Arburg Allrounder 320C Injection Machine

A plastic injection machine consists of mainly two parts, injection unit and clamping unit. Plastic granules are fed into the barrel from a feeding hopper. In the barrel, there is a reciprocating screw which can make rotational and linear movements together. In the barrel, plastic is melted and with the linear movement of the screw, it is injected into the mold. After injection, a holding pressure is applied in order to control the shrinkage and maintain the dimensional stability. After holding pressure, the mold is kept close for cooling of the injected part. A schematical illustration of an injection machine is given in Figure 6.6.

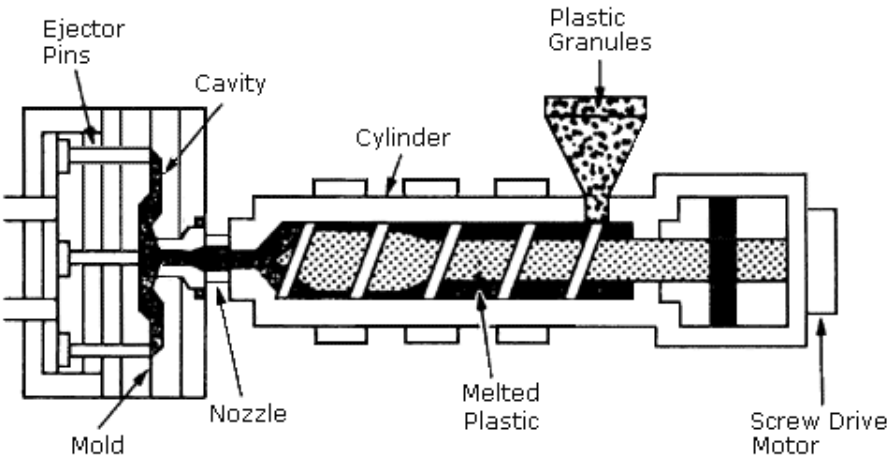

Figure 6.6. Injection Molding Machine illustration

The Arburg injection machine's specifications are given below in Table 6.2.

Table 6.4: Arburg Allrounder 320C Injection machine specifications.

	unit	Arburg Allrounder 320C
Screw diameter	mm	30
Max. injection pressure	bar	2000
Max. volumetric displacement	cm^3	144
Hydraulic motor power	W	1500
Max. clamping force	tons	50
Max. screw speed	rpm	154
Screw back pressure	bar	350

The molds are shown in Figures 6.7. and 6.8.

Figure 6.7. Tensile specimens mold ISO R 527[35].

Figure 6.8. Impact test specimens mold ISO 178[36].

6.4. Morphology Investigation

Examination of the morphology of the polymeric composite is done by a scanning electron microscope (Jeol JSM 6400). To investigate the interface between polymer and the inorganic filler and filler dispersion in the matrix, injection molded impact test specimens are immersed in liquid nitrogen for 2 hours and broken with a sudden impact. Before the SEM investigation, to provide electro conductivity the fractured surfaces were coated with gold by sputter. Gold-coated fracture surfaces are investigated with different magnifying values.

6.5. Tensile Test

Zwick universal tensile testing machine Z020 equipped with 20 kN load cell as load indicator and a mechanical long stroke extensometer as extension indicator is used to measure tensile properties of samples.

Tensile specimens, injection molded according to ISO R527 [59] specimens are left in a heat controlled room for at least 48 hours to eliminate the effects of post crystallization or physical aging. Testing speed is set to 50 mm/min and gauge length (L_o) is set to 70 mm as shown in the Figure 6.9. The test is performed at standard condition, i.e., 23 ± 2^0C and 50 % humidity.

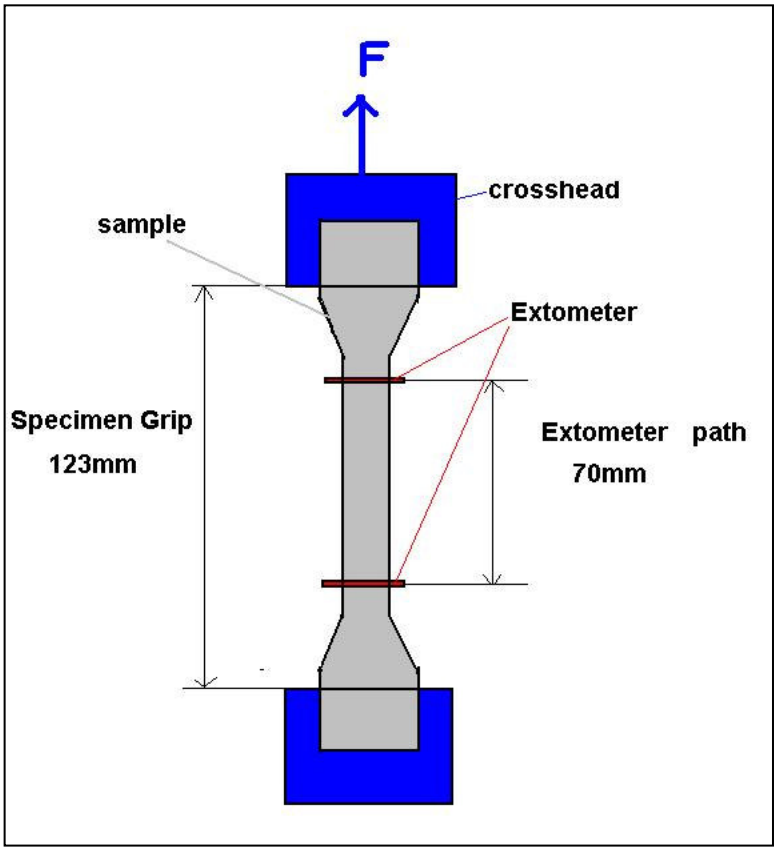

Figure 6.9. Tensile test illustration.

Following tensile properties were measured:

- Tensile stress or yield stress shown as σ_y (tensile load per unit area of original cross section within the narrow parallel portion). Tensile stress expressed in MPa means Newton per square millimeter (N/mm^2) is the first top point on the load / extension curve at which an increase occurs in the elongation but without an increase in load.

- Tensile strain or percentage elongation at yield shown as ε_y (per cent increase in the distance of extensometer path). Tensile strain is the percentage elongation corresponding to tensile stress point.
- Elastic modulus or Young modulus is calculated according to the stress values at %0,1 and %0,25 elongation by regression method.

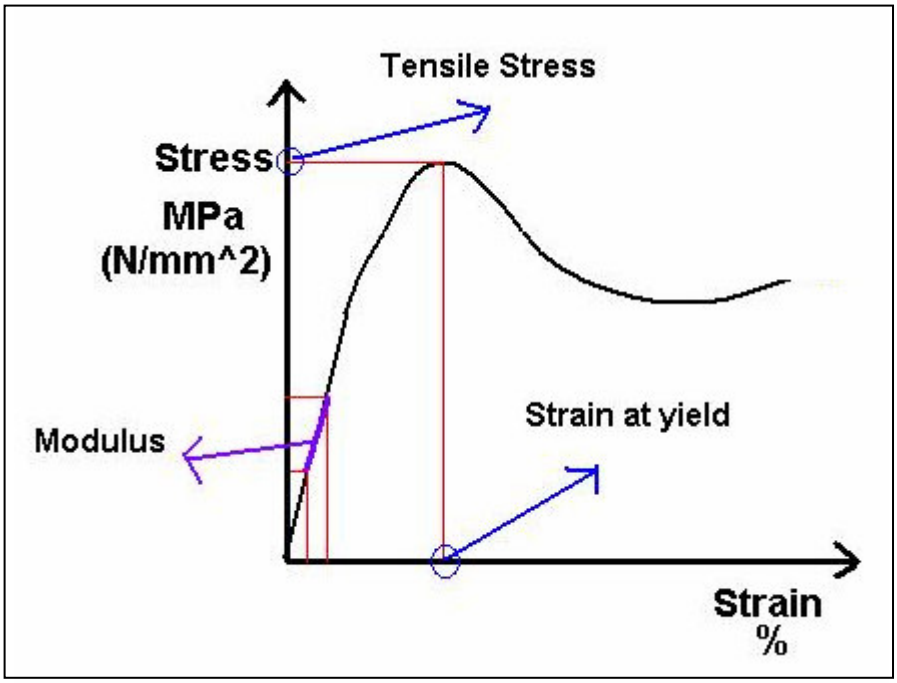

Figure 6.10. Considered points in the stress-strain graph of specimens

6.6. Izod Impact Test

According to ISO 180 standard [68], Izod impact tests are carried out. The test specimen and the notch are defined in the ISO standard as type 1A. The testing machine is Ceast Impact Tester equipped with 2.75 J pendulum(Figure 6.11.). The Izod impact strength, in kilojoules per square meter (KJ/m^2), is calculated as follows:

$$\text{Izod Impact Strength} = A_k / (X \times Y_k) \times 10^3 \qquad (6.6)$$

where A_k is the impact energy, in joules, absorbed by the test specimens and it is corrected for frictional losses. X is the thickness, in millimeters, of specimen. Y_k is the difference of width and notch depth, in millimeters.

Figure 6.11. Ceast impact tester

6.7. Fatigue Tests

Fatigue tests are carried out with a MTS hydraulic testing machine shown in figure 6.12. MTS system is actually a tensile tester but it works with a hydraulic system and this difference gives the system ability of loading the specimens at high frequencies.

Figure 6.12. MTS fatigue testing system

The system is equipped with hydraulic specimen grippers as shown in the Figure 6.13.

Figure 6.13. Hydraulic grippers of MTS fatigue testing system

With the testing system, tensile-tensile type fatigue tests were carried out at 10 MPa mean stress. Maximum stress and amplitude is decreased until the specimen stands for 10^6 cycles without failure. With the acquired test results S-N diagrams are created.

During the fatigue tests; because of the high frequency of loading, a hat generates and in this work, a thermal camera is used to determine the specimen temperature. (Figure 6.14.)

Figure 6.14. FLIR ThermaCAM PM695 thermal camera

7. RESULTS AND DISCUSSION

7.1. Tensile Test Results

Tensile properties of filled polymeric composites strongly depended on polymer filler interaction but because of having a weak interaction such as mechanical adhesion of polymeric materials to the surface of filler the tensile stress are drastically decreased but modulus value is increased. After introducing the MA-g-PP into the matrix, tensile strength increases to the level of neat PP. With the addition of calcium carbonate and MA-g-PP, strain value decreased and elastic modulus increased as shown in the Table 7.1.

Specimen	Tensile Stress	strain at yield	E-Modulus
PP neat	33,998	8,380	1710,452
PP+40% CaCO3	21,346	4,184	2613,226
PP+40% CaCO3+2%MA-g-PP	32,4	3,438	2959,8

Table 7.1: Tensile test results

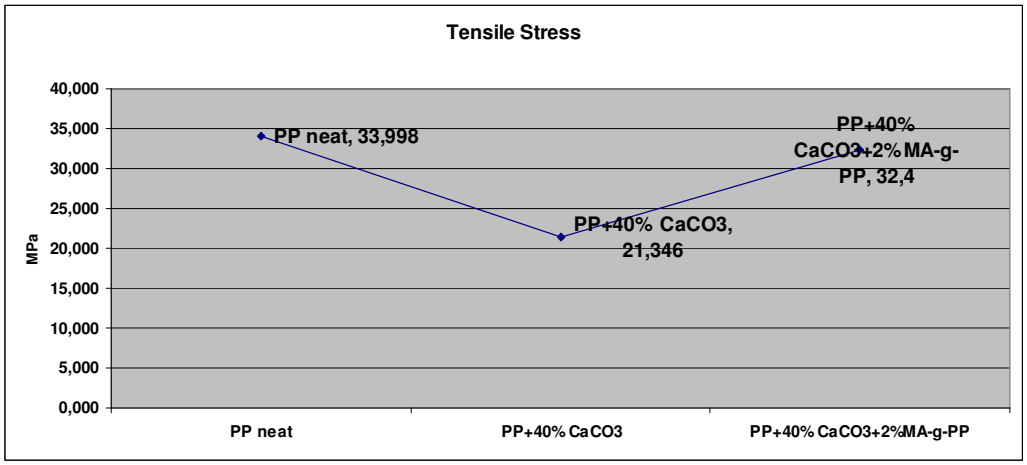

Figure 7.1: Tensile test results

7.2. Impact Test Results

After introducing calsite into the matrix impact strength of the PP is decreased from Izod notched test results are given in Table 7.2. and Figure 7.2.

Specimen	Impact KJ/m^2
PP neat	3,400
PP+40% CaCO3	3,050
PP+40% CaCO3+2%MA-g-PP	3,2

Table 7.2: Izod notched impact test results

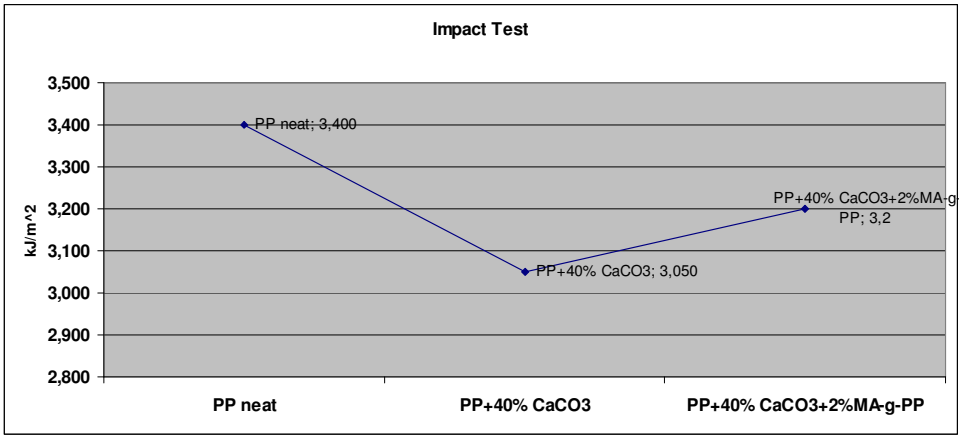

Figure 7.2: Izod notched impact test results

7.3. Morphology Investigation

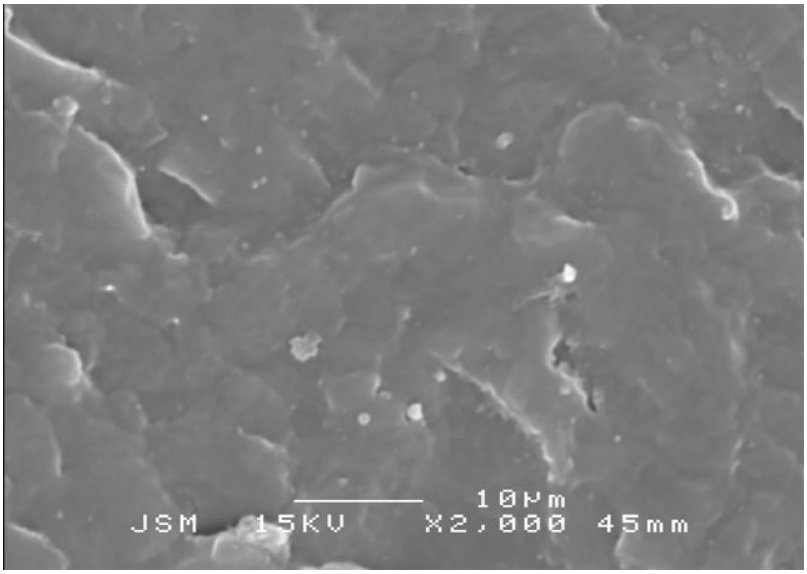

Figure 7.3. SEM micrograph of neat polypropylene

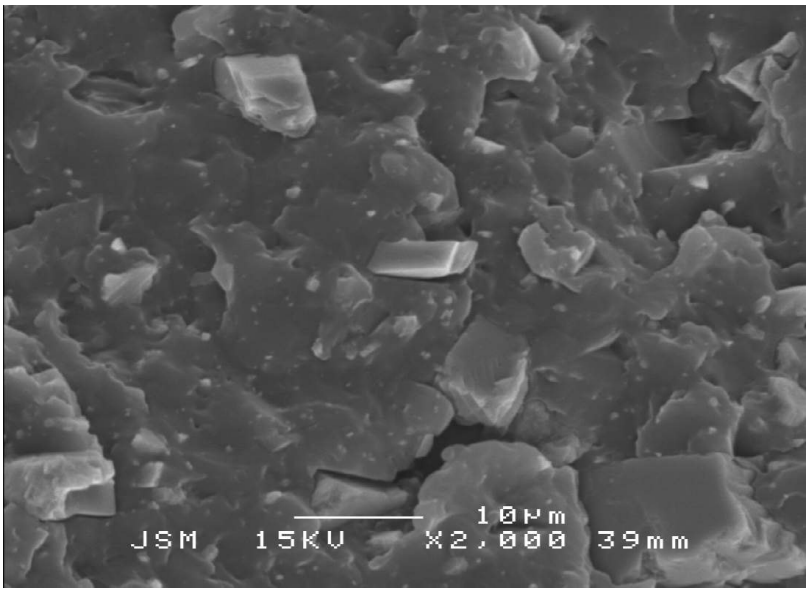

Figure 7.4. SEM micrograph of 40 % $CaCO_3$ filled polypropylene

SEM micrographs show that, during extrusion process the calcite particles are well dispersed and there is no interaction between calcite and polypropylene except mechanical adhesion between filler and polymeric materials (Figure 7.3-7.4).

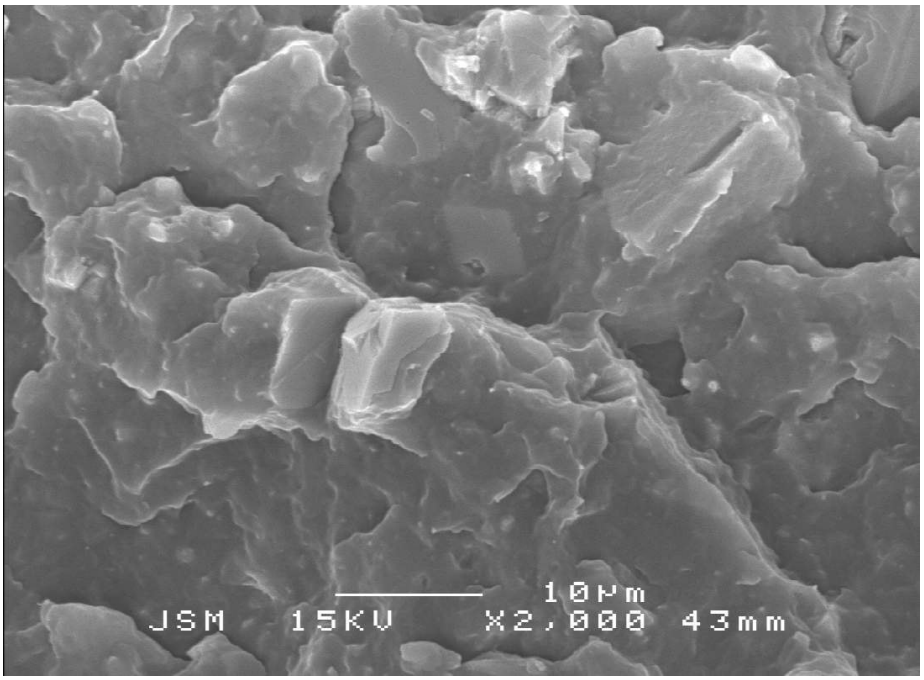

Figure 7.5. SEM micrograph of 2 % MA-g-PP + 40 % $CaCO_3$ filled PP

SEM micrographs comparison according to the % MA-g-PP content, show that;

- In Figure 7.4., the calcite surface is clear, there is no significant filler matrix interaction
- With the loading of 2% MA-g-PP, filler surface are completely wetted by the polymeric matrix. Surface of the calcite particles are not clearly observed in Figure 7.5.

7.4. Fatigue Test Results

In this study; neat PP, 40% $CaCO_3$ + PP and 40% $CaCO_3$ + 2% MA-g-PP + PP compounds are subjected to fatigue testing and their S-N curves are plotted. The aim of the fatigue testing was to determine the maximum stress level which the materials can withstand 10^6 cycles without failure.

Neat PP material reach 10^6 cycles at the maximum stress of 16 MPa. Test data for neat PP is given at the Table 7.3. and S-N curve for neat PP is given in Figure 7.6.

	Segments	Cycles(N)	log(N)	Max. stress (Mpa)
1		1	0	33,50
2		1	0	33,50
3		1	0	33,50
4	15336	7668	3,884682104	18,00
5	34626	17313	4,238372329	17,00
6	31110	15555	4,191870015	17,00
7	33192	16596	4,220003426	17,00
8	93612	46806	4,670301528	16,50
9	80966	40483	4,607272688	16,50
10	20000000	10000000	7	16,00

Table 7.3: Fatigue test results for neat PP

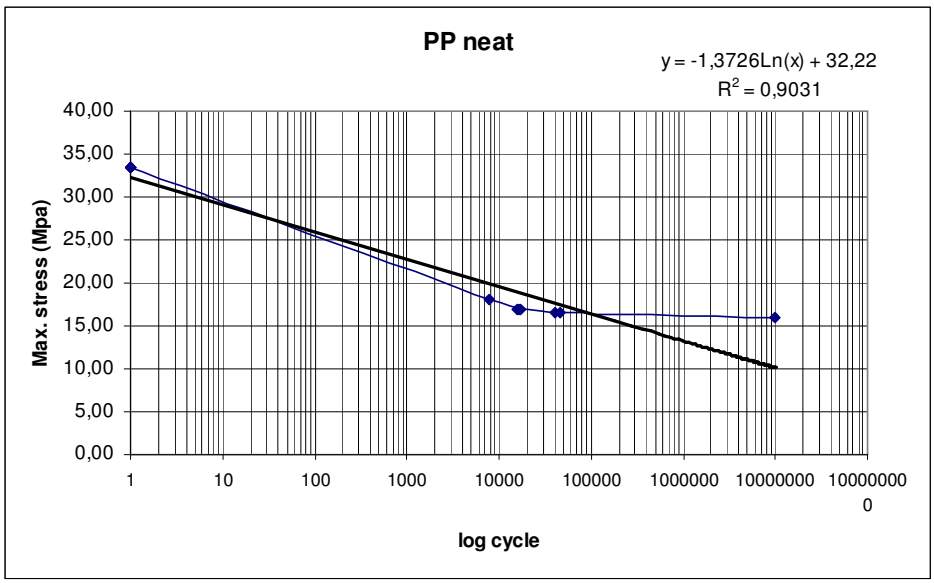

Figure 7.6: S-N curve of neat PP

According to the test results; neat PP material can withstand a max stress of 16 MPa and an amplitude of 12 MPa for lifetime.

When 40% $CaCO_3$ is introduced into the matrix; the maximum stress value that material withstand decreases to 13 MPa at an amplitude of 6 MPa. Test results of 40%$CaCO_3$ + PP composite is given in the Table 7.4. and S-N curve is given in Figure 7.7.

	Segments	Cycles(N)	log(N)	Max. stress (Mpa)
1		1	0	20,50
2		1	0	20,50
3		1	0	20,50
4	10952	5476	3,738463439	17,00
5	11570	5785	3,762303363	17,00
6	30730	15365	4,186532565	16,00
7	35092	17546	4,244178125	16,00
8	160832	80416	4,905342467	15,00
9	91798	45899	4,661803224	15,00
10	90158	45079	4,653974273	15,00
11	7599790	3799895	6,579771596	14,00
12	4847970	2423985	6,384529928	14,00
13	20000000	10000000	7	13,00

Table 7.4: Fatigue test results for 40%$CaCO_3$ + PP composite

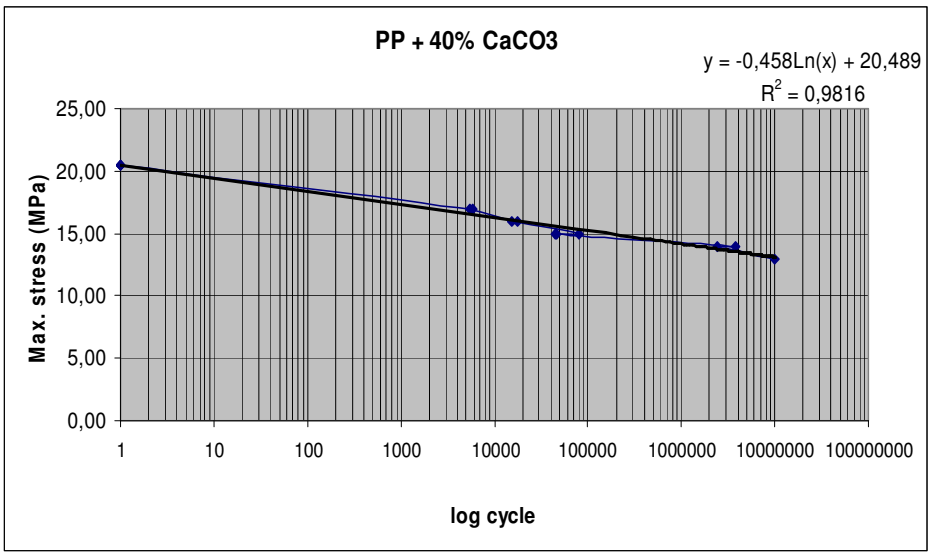

Figure 7.7: S-N curve of 40%$CaCO_3$ + PP composite

The curve in the S-N diagram for 40%$CaCO_3$ + PP composite is still linear; which means the composite didn't reach the lifetime no-failure guarantee.

When 2% MA-g-PP is introduced to the 40%$CaCO_3$ + PP composite matrix, maximum stress is raised to 17 MPa, which is higher than the neat PP at an amplitude of 14 MPa. Test results of 40%$CaCO_3$ 2% MA-g-PP + PP composite is given in the Table 7.5. and S-N curve is given in Figure 7.8.

	Segments	Cycles(N)	log(N)	Max. stress (Mpa)
1		1	0	32,50
2		1	0	32,50
3		1	0	32,50
4	70401	35200,5	4,547	18,50
5	119045	59522,5	4,775	18,50
6	578038	289019	5,461	18,00
7	681285	340642,5	5,532	18,00
8	1124641	562320,5	5,75	17,50
9	20000000	10000000	7	17,00
10	20000000	10000000	7	17,00

Table 7.5: Fatigue test results for 40%$CaCO_3$ + 2% MA-g-PP+ PP composite

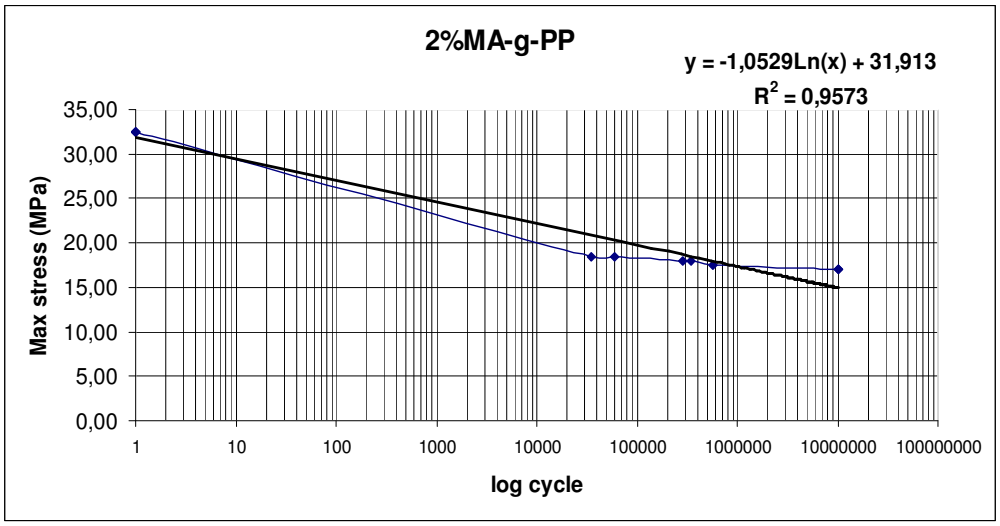

Figure 7.8: S-N curve of 40%$CaCO_3$ + 2% MA-g-PP+ PP composite

According to the fatigue test results MA-g-PP introduction to the matrix increased the fatigue resistance of the system and the test results showed that the composite is more resistant to fatigue than the neat PP.

7.5. Heat Generation during the Fatigue Testing and Failure Mechanisms of Materials

During the fatigue testing, temperatures of the specimens are detected with a thermal camera continuously.

The thermal camera images of neat PP during the cyclic loading are given in Figures 7.9.-7.11.

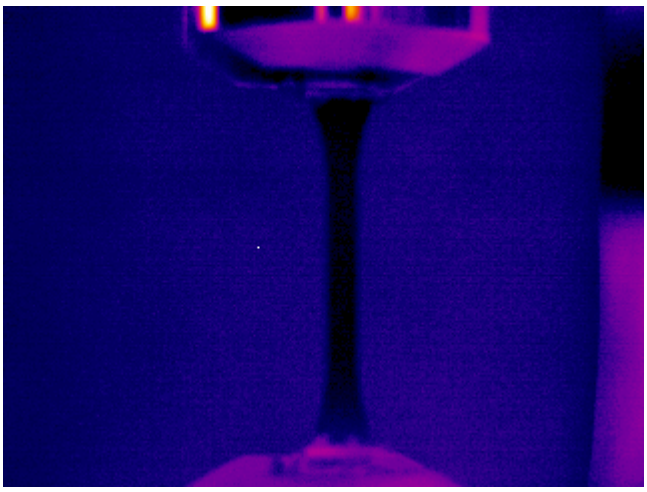

Figure 7.9. Thermal camera image of Neat PP at 0 cycles. Temperature of the specimen is 26,9^{0}C

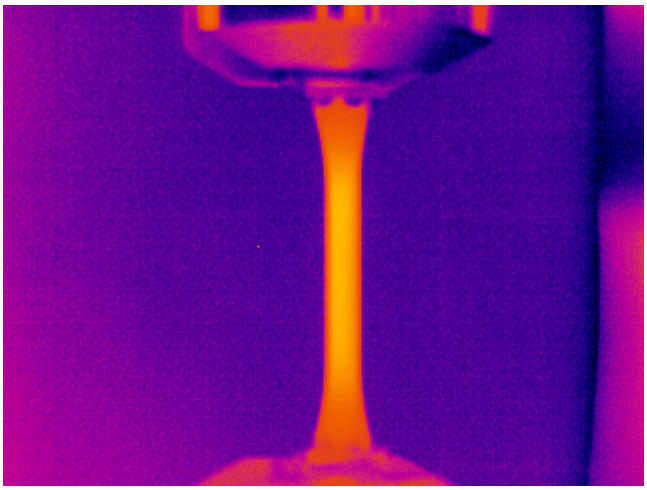

Figure 7.10. Thermal camera image of Neat PP at 5100 cycles. Temperature of the specimen is 45^0C

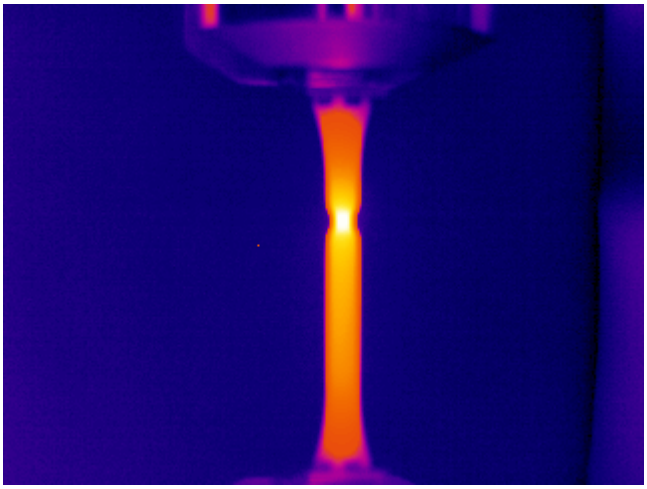

Figure 7.11. Thermal camera image of Neat PP at 9450 cycles (failure). Temperature of the specimen is $91,8^0$C

When 40% $CaCO_3$ is introduced, heat generation of the material at 16 MPa maximum stress increases because of the internal friction and generated heat is at the same level of neat PP at the maximum stress of 18 MPa.

The thermal camera images of 40%$CaCO_3$ + PP composite during the cyclic loading are given in Figures 7.12.-7.14.

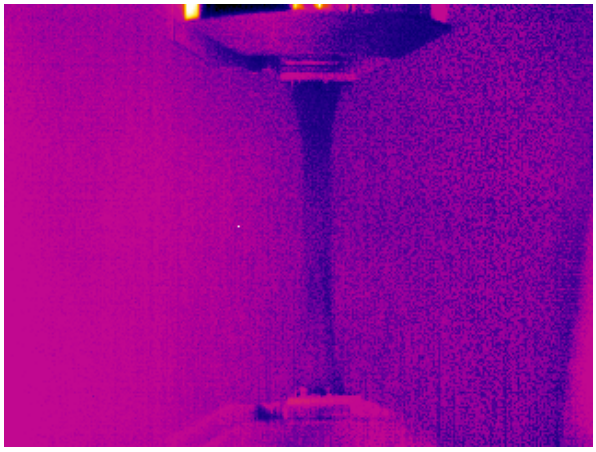

Figure 7.12. Thermal camera image of 40% $CaCO_3$ + PP composite at 0 cycles. Temperature of the specimen is 25^0C

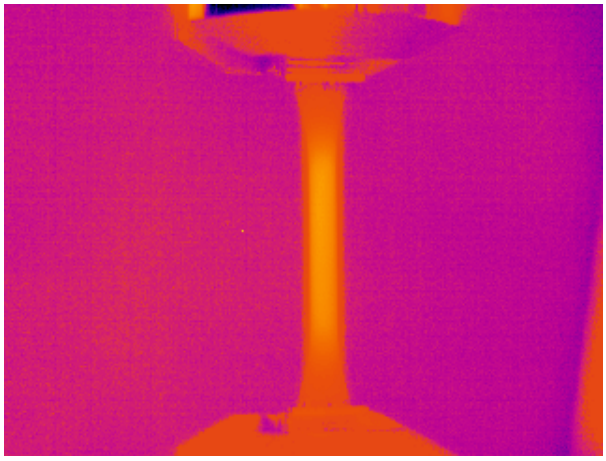

Figure 7.13. Thermal camera image of 40% $CaCO_3$ + PP composite at 2880 cycles. Temperature of the specimen is $35,7^0$C

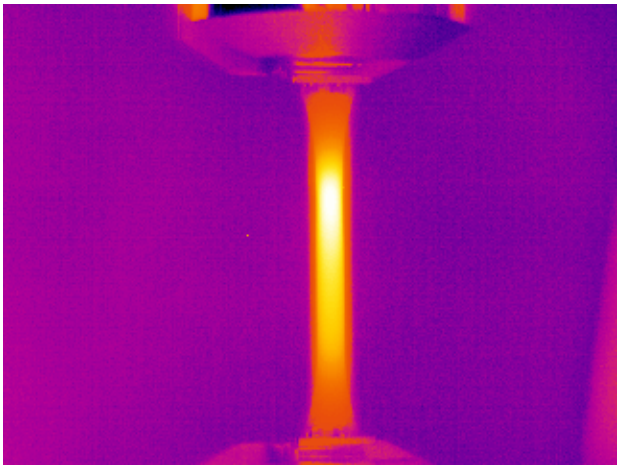

Figure 7.12. Thermal camera image of 40% $CaCO_3$ + PP composite at 5850 cycles (failure). Temperature of the specimen is $68,3^0$C

When 2% of MA-g-PP is introduced into the 40%$CaCO_3$ + PP composite, generated heat decreases because of decreasing strain during cyclic loading and internal friction.

The thermal camera images of 40%$CaCO_3$ + 2% MA-g-PP + PP composite during the cyclic loading are given in Figures 7.15.-7.17.

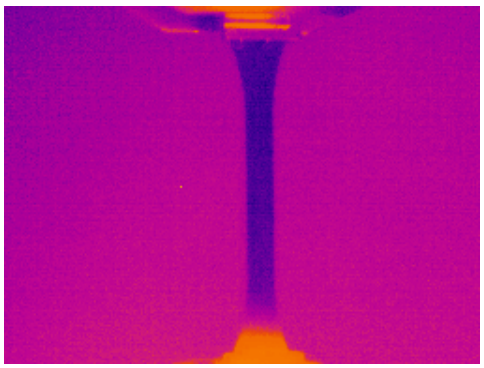

Figure 7.15. Thermal camera image of 40% $CaCO_3$ + 2% MA-g-PP + PP composite at 0 cycles. Temperature of the specimen is 26,3^{0}C

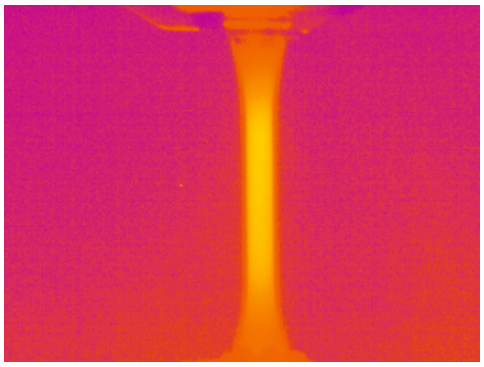

Figure 7.16. Thermal camera image of 40% $CaCO_3$ + 2% MA-g-PP + PP composite at 14400 cycles. Temperature of the specimen is 45,7^{0}C

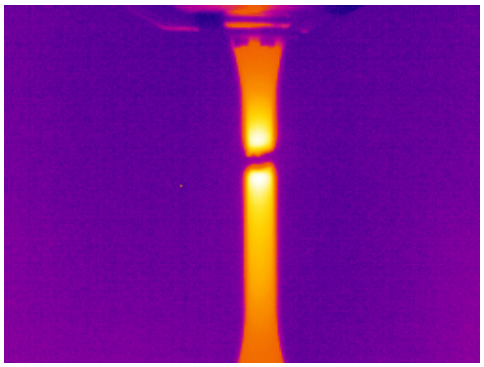

Figure 7.17. Thermal camera image of 40% $CaCO_3$ + 2% MA-g-PP + PP composite at 27900 cycles. Temperature of the specimen is 81,7^{0}C

According to the test results; CaCO3 introduction increases the heat generation in the matrix but when MA-g-PP introduced, heat generation decreases.

Comparison of the heat generation levels are shown in the Figure 7.18.

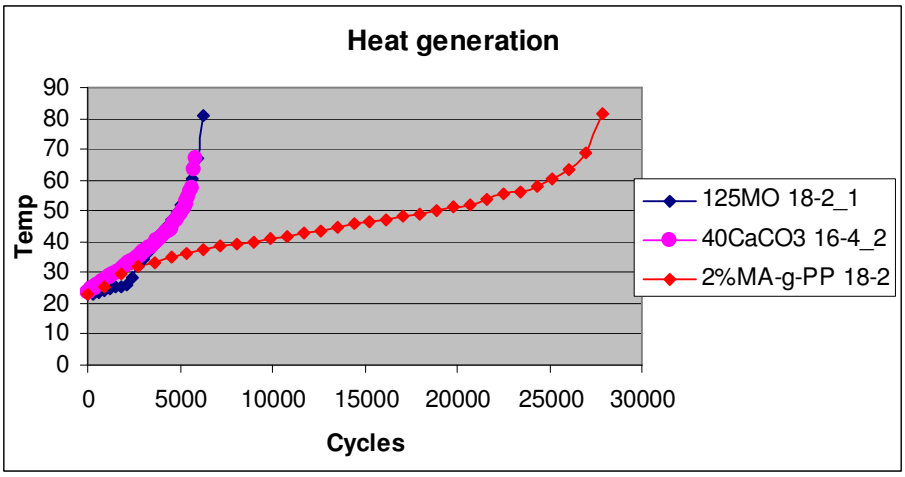

Figure 7.18. Comparison of heat generated during cyclic loading

MA-g-PP introduction also changes the failure mechanism from cyclic softening to crack initiation and propagation. The pictures of the specimens of all materials are given in Figure 7.19. It is clearly seen that neat PP and 40%$CaCO_3$ + PP show viscous failure because of the cyclic softening but 40% $CaCO_3$ + 2% MA-g-PP + PP composite shows brittle failure.

Figure 7.19. Fatigue test specimens after cyclic loading

8. CONCLUSION

In this study**,** the effects of $CaCO_3$ on polypropylene and the effects of interface improvements on fatigue properties by modifying the interface interaction were investigated.

It is observed that, when calcite is introduced to the PP matrix; tensile strength, impact strength and fatigue resistance decreases; elastic modulus and heat generation during cyclic loading increases. As a result of these changes, it can be said that 40%$CaCO_3$ filled PP is a weaker material when compared to the PP.

In case of MA-g-PP loading into 40% $CaCO_3$ PP composites, tensile strength, impact strength, elastic modulus values and fatigue resistance are significantly increased. Heat generation during cyclic loading is decreased.

As a result of this work; loading of $CaCO_3$ into the polypropylene matrix caused decrease in mechanical and fatigue properties due to lack of interface interaction between hydrophilic calcite surface and hydrophobic PP. With the addition of MA-g-PP up to optimum level (2%), these decreased mechanical properties can be improved by improving the filler surface PP matrix interaction. By the help of the MA-g-PP, it is possible to produce better PP composites at a lower cost.

REFERENCES

[1] **Almeras X. and Le Bras M.**, 2003. Effect of fillers on the fire retardancy of intumescent polypropylene compounds, *Polymer Degradation and Stability*, **82**, 325–331.

[2] **Rana A.K.,Mandal A.,Mitra B. C., Jacobson R., Rowell R., Banerjee A.N.**, 1998. Short jute fiber-reinforced polypropylene composites:Effect of compatibilizer**,** *Journal of Applied Polymer Science*, **69**, 329-338.

[3] **Coutinho F.M.B., Costa T.H.S.**, 1999. Performance of polypropylene–wood fiber composites, *Polymer Testing*, **18**, 581–587.

[4] **Attia O**.,2001. Modelling the fatigue life of polymer–matrix fibre-composite components, *Composites Science and Technology*, **61**, 2273–2283.

[5] **Zebarjad S.M**., 2004. Influence of filler particles on deformation and fracture mechanism of isotactic polypropylene, *Journal of Materials Processing Technology*, **155-15**, 1458-1472.

[6] **Thomason J. L., Vlug M. A.,** 1997. Influence of fibre length and concentration on the properties of glass fibre-reinforced polypropylene, *Composites Part A **28A**, 277-288.*

[7] **Liauw C.M., Rothon N.R., Lees G.C., Dumitru P., Iqbal Z., Khunova V. and Alex P.,** 2000. Filler Surface Modification with Organic Acids and Derivatives, Functional Effect Fillers 2000, Berlin, Germany, 13-15 September 2000.

[8] **Seymour B. R.,** 1991. Reinforced Plastics Properties & Applications, ASM International,,New York

[9] **ASTM D 1566,** 2002. Standard terminology relating to rubber. *American Society of Testing Materials.*

[10] **Rocha M.C.G., Silva A.H., Coutinho F.M.B. and Silva A.L.N.**, 2005. Study of composites based on polypropylene and calcium carbonate by experimental design*, Polymer Testing*, Article in Pres.

[11] **Wypych G.,**2000. Handbook of Fillers, Plastic Design Library, New York.

[12] **Nicolais L. and Narkis M.**, 1971. Stress strain behavior of styrene-acrylonitrile/glass-bead composites in the glassy region**.** *Polymer Engineering and Science*., **11**, 1971, 194.

[13] **Piggott M R. and Leidner J.**,1974. Strain behavior of particulate-filled composites, Journal of Applied Polymer Science*,* **18**,1619-1628.

[14] **Oral M. A.,** 2007. Effects of polymer filler interface improvements on mechanical and physical properties of $CaCO_3$ filed polypropylene composite, *MSc Thesis*, ITU Polymer Scince and Technology

[15] **Wang M-J, Wolff S, Tan E-H**,1993. Filler-Elastomer interactions. Part VIII. The role of the distance between filler aggregates in the dynamic properties of vulcanizates, *Rubber Chemistry Technology*., **66**, No.2,178-95

[16] **Gingrich R P,Machado J M, Londa M, Proctor M G**,1995. Filled and Reinforced Aliphatic Polyketone Compounds, Antec '95 Conference Proceedings, Vol. II, Boston, Ma., 7th-11th May 1995, 2345-50.

[17] **Yang K., Yang O., Li G.,Sun Y. and Feng D.**, 2006. Morphology and mechanical properties of polypropylene/calcium carbonate nanocomposites, *Materials Letters*, **60,** 805-809.

[18] **Grandt A.F.,** Fatigue for engineers, 2001 *ASME* , California

[19] **Li Y., Wang Q.F.,** 2002 A study of internal friction in polypropylene (PP) filled with nanometer-scale CaCO3 particles, *Materials Science and Engineering*, **370**, 268-272.

[20] **Ferreira J.A.M., Costa J.D.M,** 1999**,** Analysis of fatigue and damage in glass-fibre reinforced polypropylene composite materials, *Composites Science and Technology*, **59,** 1461-1467.

[21] **Rittel D.,** 2000, An investigation of the heat generated during cyclic loading of two glassy polymers. Part I: Experimental, **32,** 131-147.

[22] **El Fray M., Alstadt V.,** 2003, Fatigue behaviour of multiblock thermoplastic elastomers. 1. Stepwise increasing load testing of poly(aliphatic/aromatic-ester) copolymers, **44,** 4635-4642.

[23] **El Fray M., Alstadt V.,** 2003, Fatigue behaviour of multiblock thermoplastic elastomers. 2. Dynamic creep of poly(aliphatic/aromatic-ester) copolymers, **44,** 4643-4650.

[24] **Bhattacharya S.K.**, 1986. Interface in Polymer, Ceramic and Metal Matrix *Composites*, Marcel Decker Inc.,New York.

[25] **Kulhestra A.K., C.Vasile**,2002. Handbook of Polymer Blends and *Composites*, Rapra, Shawbury

[26] **Ahagon A. and Gent N.**,1975. Effect of interfacial bonding on the strength of adhesion, *Journal of Polymer Science*, Polymer Physics,**13**, 7,1285, quoted in ref 43.

[27] **Deryagin B. V. and Kurotova N. A.**,1948. Doklad Akademii Nauk SSSR, **61**, 849 quoted in ref 43.

[28] **Voyutskii S. S and Margolina Y. L.**, 1957. The nature of self-adhesion(tack) of polymers, *Rubber Chemistry and Technology*, **30**, 2, 531, quoted in ref 43.

[29] **Sharpe L. H. and Schonhorn H.**,1963. Surface tension of molten polypropylene, *Chemical Engineering News*, **15**, 67, quoted in ref 43

[30] **Bandyopadhyay S, De P P, Tripathy D K, De S K, Kaut. U. Gummi Kunst**.,1996. Effect of chemical interaction between surface oxidized carbon black and carboxylated nitrile rubber on dynamic properties, *Journal of Applied Polymer Science* **49**, No.2, 115-9.

[31] **Van Der Oever M., Pejis T.,** 1997, Continous glass-fibre reinforced polypropylene composites. II. Influence of maleic-anhydride modified polypropylene on fatigue behaviour. *Composites,* **29A,** 227-239.

[32] **Gamstedt E. K., Berglung L.A.,** 1999, Fatigue mechanisms in unidirectional glass-fibre reinforced polypropylene, *Composites Science and Technology,* **59,** 759-768.

[33] **Rittel D., Eliash N.,** 2003, Hysteretic heating of modified poly(mthylmethacrylate), *Polymer,* **44,** 2817-2822.

[34] **Ersoy, O.G.,** 2003. Effect of inorganic filler phase on final performance of binary immiscible polypropylene/polyamide-6 blend, *PhD Thesis*, Boğaziçi University, İstanbul

[35] **ISO R 527**, 1993. Determination of tensile properties, *International Standard Organization.*

[36] **ISO 178**, 2001. Plastics, Determination of flexural properties of rigid plastics, *International Standard Organization.*

RESUME

Fatih KOTAN was born in Eskişehir in 1980. He was graduated from Eskişehir Anatolian High School in 1998. He admitted to Istanbul Technical University, Metallurgical and Materials Engineering department and graduated as a Metallurgical and Materials Engineer in 2004.

He continued his education in Istanbul Technical University, as M.Sc. student to Polymer Science and Technology Programme of Institute of Science and Technology in 2004.

He maintained his thesis in ARÇELİK Research and Development Center, Material Technologies Department in the embrace of University-Industry co-operation