EFFECTS OF TITANATE COUPLING AGENTS ON LOW DENSITY POLYETHYLENE AND POLYPROPYLENE BLENDS AND COMPOSITES

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

NOVEMBER 2008

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ABSTRACT

EFFECTS OF TITANATE COUPLING AGENTS ON LOW DENSITY POLYETHYLENE AND POLYPROPYLENE BLENDS AND COMPOSITES

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November 2008, 104 pages

The objective of this study is to investigate the effects of titanate coupling agents on low density polyethylene (LDPE) and polypropylene (PP) blends and composites in terms of their mechanical and morphological properties. PP and LDPE composites were produced separately in a Brabender internal mixer, and $CaCO_3$ was used as inorganic filler with compositions of 20, 40 and 60 %. PP/LDPE blends were produced in a twin-screw extruder with ratios of 75/25, 50/50 and 25/75. Their composites were prepared with addition of untreated and titanate-treated $CaCO_3$ at 20% filler content.

Titanate coupling agent which is appropriate for LDPE, PP and $CaCO_3$ was used to improve the mechanical properties of the blends and composites. For this purpose, “Lica 12” which is a kind of neoalkoxy organotitanate was used. Two forms of Lica 12 were used: powder form (Capow L12) and pellet form (Caps L12).

Samples with and without titanate were prepared and then they were injection molded to make specimens for tensile and impact tests. Tensile fracture surfaces of samples were examined by scanning electron microscopy (SEM). Their mechanical and morphological properties were compared with each other to determine the effects of Lica 12.

This study showed that Capow L12 improved strain at break and impact strength of PP/$CaCO_3$ composites and PP/LDPE blends containing 75% and 50% PP. The strain at break value of of PP75 composite with 20% titanate-treated filler increased significantly up to 509% which is the highest value among all blends and composites in this study. Capow L12 exhibited its functions in PP matrix much more effectively than in LDPE matrix.

Keywords: Titanate coupling agent, Lica 12, Polypropylene, Low density polyethylene, Calcium carbonate.

ÖZ

TİTANAT BAZLI BAĞLAYICILARIN ALÇAK YOĞUNLUKLU POLİETİLEN VE POLİPROPİLEN KARIŞIMLARI VE KOMPOZİTLERİ ÜZERİNDEKİ ETKİLERİ

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Kasım 2008, 104 sayfa

Bu çalışmanın amacı titanat bazlı bağlayıcıların, alçak yoğunluklu polietilen ve polipropilen karışımlarının ve kompozitlerinin üzerindeki etkilerini mekanik ve morfolojik özellikler bakımından araştırmaktır. PP ve LDPE kompozitleri, bir içsel karıştırıcı türü olan Brabender'da üretilmişlerdir. Bu işlemlerde inorganik dolgu olarak $CaCO_3$ 20, 40 ve 60 yüzdelerinde kompozitlere katılmıştır. PP/LDPE karışımları 75/25, 50/50 ve 25/75 oranlarında çift vidalı ekstruder'de üretilmişlerdir. Bu karışımlara %20 oranında titanatla muamele edilmiş ve edilmemiş $CaCO_3$ katılarak kompozitler hazırlanmıştır.

PP ve LDPE için uygun olan titanat bazlı bağlayıcı, kompozit ve karışımların mekanik özelliklerinin geliştirilmesi için kullanılmıştır. Bu amaçla bir neoalkoksi organotitanat türü olan "Lica 12" kullanılmıştır. Lica 12'nin iki farklı fiziksel haldeki yapıları kullanılmıştır: toz hali (Capow L12) ve granül hali (Caps L12).

Titanat içeren ve içermeyen örnekler hazırlanmıştır ve daha sonra bu örnekler enjeksiyonlu kalıplama yöntemiyle, çekme ve darbe testlerinde kullanılmak üzere test çubuğu şekline getirilmişlerdir. Çekme testinde kopan yüzeyler, taramalı electron mikroskop (SEM) yöntemiyle incelenmiştir. Lica 12'nin etkilerini belirlemek için bu örneklerin mekanik ve morfolojik özellikleri birbirleriyle karşılaştırılmıştır.

Bu çalışma göstermiştir ki PP/$CaCO_3$ kompozitleri ile 75% ve 50% PP içeren PP/LDPE karışımlarında Capow L12, kopmadaki uzamayı ve darbe dayanımını geliştirmiştir. %20 oranında titanatla işlenmiş dolgu içeren PP75 kompozitinde kopma uzaması önemli derecede yükselerek %509' a kadar gelmiştir. Bu değer, çalışmadaki bütün karışım ve kompozitlerde elde edilen kopma uzaması değerlerinin en yükseğidir. Capow L12, işlevlerini PP matriks içinde LDPE matriks içindekine göre daha etkili göstermiştir.

Anahtar Sözcükler: Titanat bazlı bağlayıcılar, Lica 12, Polipropilen, Alçak yoğunluklu polietilen, Kalsiyum karbonat.

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To my parents and my dear grandmother

ACKNOWLEDGEMENTS

I would like to express my deepest gratitude to my thesis supervisor Prof. Dr. Erdal Bayramlı for his guidance, understanding, kind support and encouraging advices throughout my thesis.

I am greatly indebted to my thesis co-supervisor Dr. A. Bedii Erdemir for his guidance, essential advices, criticism and precious discussions throughout my thesis.

Special thanks go to Osman Yaslıtaş from Department of Chemistry for his technical support and unforgotten helps during my study in laboratory.

I especially thank to my sweetie Ayşe Kırcalı for her patient love and for not leaving me alone in my stressful days.

I would sincerely thank to H. Onur Bektaş and M. Alper Fakılı as my faithful comrades for their endless friendship, being always right beside me and making my life at METU happy and memorable.

I express my special thanks to my labmates Mehmet Doğan and Ümit Tayfun for sparing their time and all helps during my experiments and study. I wish to thank my friends; B. Fuat Çankaya, Selahattin Erdoğan, Yasin Kanbur, Cenk Konuk, Erkan Biber and especially Murat Erdoğan for cooperation and friendship with their all kind of supports.

I dedicate this dissertation to my parents Vildan-Özcan Yılmaz, my brother Orçun Yılmaz and specially my grandmother Yüksel Bıçkıcı. They always offered their love, care and support during my whole education life. My family's absolute unquestionable belief in me, have been a constant source of encouragement to achieve my goals.

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INTRODUCTION

Plastics have become quite important and widely used materials in daily life and industry for the last forty years. One of the reasons for the great popularity of plastics in a wide variety of industrial applications is due to the tremendous range of properties exhibited by plastics and their ease of processing. Plastic properties can be tailored to meet specific needs by blending with other plastics and through modification with an enormous range of additives (fillers, fibers, plasticizers, stabilizers) [1].

Polymer composites are mixtures of polymers with inorganic additives having certain geometries (fibers, flakes, spheres, particulates). Thus, they consist of two or more components and two or more phases. Modification of organic polymers through the incorporation of additives yields, with few exceptions, multiphase systems containing the additive embedded in a continuous polymeric matrix. The resulting mixtures are characterized by unique microstructures or macrostructures that are responsible for their properties. The primary reasons for using additives are: property modification or enhancement; overall cost reduction; improving and controlling of processing characteristics [2].

There is considerable interest in polymer blends. This is driven by consideration of the difficulty in developing new polymeric materials from monomers. In many cases it can be more cost effective to tailor the properties of a material through the blending of existing materials. One of the most basic questions in blends is whether or not the two polymers are miscible or exist as a single phase. Although miscible blends of polymers exist, most blends of high molecular weight polymers exist as two-phase materials. The morphology of the phases is of great importance in this manner. A variety of morphologies exist such as dispersed spheres of one polymer in another, lamellar structures, and co-continuous phases [3].

Coupling agents are molecular bridges at the interface between two substrates, an inorganic filler and organic polymer matrix. Titanium derived coupling agents are unique in that their reaction with the protons at the inorganic interface results in the formation of organic monomolecular layers on the inorganic surface. Titanate-treated inorganic fillers are hydrophobic, organophilic and organofunctional. When incorporated into polymer systems, they often promote adhesion, improve dispersion, improve impact strength and thus reduce embrittlement, make inorganic loadings even though at high filler content, prevent phase separations [4].

This study aims to investigate effects of titanate coupling agents on polypropylene and low-density polyethylene blends and composites in terms of mechanical and morphological properties. As titanate coupling agent, a kind of neoalkoxy organo-titanate having a trade name of “Lica 12” is selected. Its powder and pellet forms are used where their trade names are “Capow L12” and “Caps L12”, respectively. Composites of PP/$CaCO_3$ and LDPE/$CaCO_3$ with varying filler content are prepared by internal mixing in Brabender. PP/LDPE blends and their composites containing $CaCO_3$ are produced in twin-screw extruder.

All samples are injection molded in order to obtain standard test specimens for mechanical characterization. Tensile test is performed to investigate tensile strength, percentage strain at break and Young’s modulus of all samples. Besides that, impact strength values are obtained by charpy impact test. As morphological analysis tensile fracture surfaces are examined by scanning electron microscopy (SEM). Tensile test data and SEM data is found to be in agreement with offered discussion as regards the treated and untreated filler inclusions.

CHAPTER 2

BACKGROUND INFORMATION

2.1 Composites

A Composite is a heterogeneous material that consists of two or more phases that are insoluble in each other. At least one phase is mostly inorganic as dispersed phase. Composites are designed to have mechanical properties and performances superior than constituent materials have independently. They may have unique advantages over monolithic materials such as high strength, high stiffness, low density, high corrosion, long fatigue life, high thermal stability, insulation and conduction. Besides that they have an important advantage that is reduction in life cycle cost [5].

Composites mainly consist of two phases: matrix phase and reinforcement phase. Matrix phase is the main constituent binding the other components together in the composite. It can be metallic, ceramic or polymeric. The second constituent is reinforcement phase, which enhances and improves the mechanical properties of the matrix. Reinforcement phase is dispersed in matrix phase and properties of composite depends on properties of the constituent phases, their relative amounts and geometry of the dispersed phase (i.e., size and shape of the reinforcing component, their distribution and orientation) [6]. Reinforcing agents are filler materials which can be minerals, metallic powders, organic by products or synthetic inorganic compounds [7]. They can be also classified according to their geometry as; particles, fibers and flakes which have different properties.

The interaction of components at phase boundaries, associated with the existence of a thick interface, i.e. interphase, is also a parameter affecting the properties of polymer composites. It is often considered as a separate phase, which controls adhesion between the components, thus, it can play an important role in controlling the failure mechanisms, fracture toughness and overall stress-strain behavior of the material [5].

2.1.1 Polymer Matrix Composites

Polymers are the most common matrix materials for composites. Polymer matrix composites have found widespread applications since they have the advantage of being easily fabricated into any large complex shape [6]. Composites can have thermoplastic or thermosetting polymer matrices. Thermosetting and thermoplastic matrix composites are in many ways superior materials compared to common metals and ceramic materials. Matrix selection is performed based on chemical, thermal, electrical, flammability, environmental, cost, performance and manufacturing requirements [8].

Thermosetting materials cannot be remelted and reshaped once they are cured as they form three-dimensional molecular chains, called crosslinking. The most common thermoset polymer matrix materials are unsaturated polyesters, epoxies and polyamides [6]. Thermoplastic materials generally have high toughness values and proper damage tolerances compared thermosetting materials. They are used for a wide variety of nonstructural applications without fillers and reinforcements [6]. Thermoplastic molecules can be reshaped with heat and pressure since they do not cross-link. This provides them the property of being easily fabricated by conventional plastics processing techniques such as extrusion, injection molding and blow molding. Thermoplastic materials also provide low cost-high volume processing of composite structures [6]. The most common thermoplastic matrices are polyolefinic (polyethylene, polypropylene), vinylic polymers (polyvinyl chloride, polyamides) [6].

2.2 Polymer Blends

Mixing of two or more polymers at different chemical composition is an effective way of combining performance and economic relationships using existing materials. Fundamental issues that affect the properties of blends include interfacial behavior and equilibrium phase, physical and chemical interactions between the components, phase morphology and rheology, all of which are related to the issues of compatibility. One of the most important way of polymer blending is the incorporation of an elastomeric phase in a rigid matrix to enhance mechanical toughness [9].

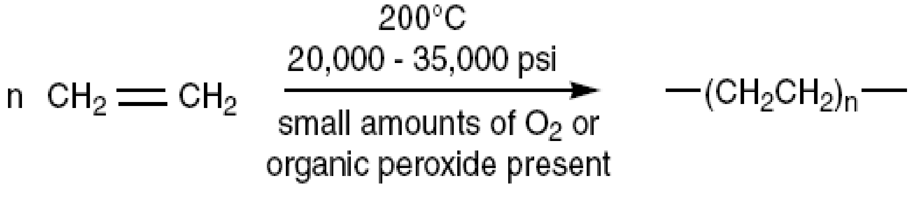
Control of the morphology of these two-phase systems is critical to achieve the desired properties. However, most of the polymer pairs are thermodynamically immiscible and technologically incompatible; hence produce a multi-phase system during processing, which may damage the performance of the materials. Fortunately, owing to the deformable nature of the dispersed phase in the immiscible blends, various morphologies can be generated in-situ such as fiber, ribbon, plate, etc. during processing some of which enhance the properties of the blends. As a result, the properties of the polymer blend depend on the type of polymers, the morphology of the blend, and the effects of processing parameters [1]. Polymer blends can be typically prepared in five techniques: melt blending, latex blending, partial block copolymerization, graft copolymerization, and synthesis of interpenetrating networks. Melt blending is a simple mechanical means of creating a well-dispersed mixture of polymers. It could be performed in twin or single screw extruder, two-roll mill, or in an intensive mixer.

The physical properties of a blend depend on the degree of miscibility between the components. Fully-miscible blends generally represent the simplest case. For amorphous polymers, most properties follow some additive relationship; thus miscible blends are similar to random copolymers in this regard [3]. For blends where the components form separate phases, properties depend on the arrangement of these phases in between and the nature of the interface (i.e. interfacial reactions and strength) between the phases. Immiscible blends behave like composite materials in many respects. Properties like softening temperature, modulus, permeation etc, are dominated by the properties of the component that forms the continuous phase [12].

The nature of the interface is related to the thermodynamic interaction between the components, which then governs morphology generation in the melt via interfacial tension, and adhesion in the solid state via the thickness of the interfacial zone and the degree to which chains from the two phases entangle. When the thermodynamic affinity is very low, the blend can exhibit a degree of toughness well below that of either component and is regarded as incompatible. Improvement of this property response is often called compatibilization and approaches to this important aspect of blend technology are described in the forthcoming part. When the interaction between phases is good enough, additive properties may be obtained without compatibilization [13].

2.3 Polyethylene (PE)

Polyethylene (PE) is the highest-volume polymer in the world. PE which has the simplest basic structure among all over polymers is a member of polyolefins. The monomer of PE is ethylene and polymerization of PE is shown in Figure 2.1.



$$n\ CH_2{=}CH_2 \xrightarrow[\text{small amounts of } O_2 \text{ or organic peroxide present}]{200^\circ C\ \ 20{,}000-35{,}000\ \text{psi}} -(CH_2CH_2)_n-$$

Figure 2.1 Polymerization of PE [1]

Its high toughness, ductility, excellent chemical resistance, low water vapor permeability, and very low water absorption, combined with the ease with which it can be processed, make PE of all different density grades an attractive choice for a variety of goods. PE is limited by its relatively low modulus, yield stress, and melting point. PE is used to make containers, bottles, film, and pipes, among other things. It is an incredibly versatile polymer with almost limitless variety due to copolymerization potential, a wide density range, a MW which ranges from very low (waxes have a MW of a few hundred) to very high ($6x10^6$), and the ability to vary MW distribution [1].

PE homopolymers are made up exclusively of carbon and hydrogen atoms, different grades of PE have markedly different thermal and mechanical properties. While PE is generally a whitish, translucent polymer, it is available in grades of density that range from 0.91 to 0.97 g/cm^3. The density of a particular grade is governed by the morphology of the backbone; long, linear chains with very few side branches can assume a much more three-dimensionally compact, regular, crystalline structure [1]. According to its density and branching, PE is classisified into three major groups:

- Low-density PE (LDPE)
- Linear low-density PE (LLDPE)
- Medium-density PE (MDPE)
- High-density PE (HDPE)

Their density range and degree of branching is given in Table 2.1.

Table 2.1 Types of PE [14]

Name	**Density Range (g/cm^3)**	**Degree of Branching**
Low density PE (LDPE)	0.910 - 0.940	high degree of short and long chain branching
Linear low density PE (LLDPE)	0.915 - 0.925	significant numbers of short branches
Medium density PE (MDPE)	0.926 - 0.940	relatively low branching
High density PE (HDPE)	≥0.941	no branching

Figure 2.2 demonstrates figurative differences in chain configuration which govern the degree of crystallinity, which, along with MW, determines final thermomechanical properties. Generally, yield strength and the melt temperature increase with density, while elongation decreases with increased density [1].

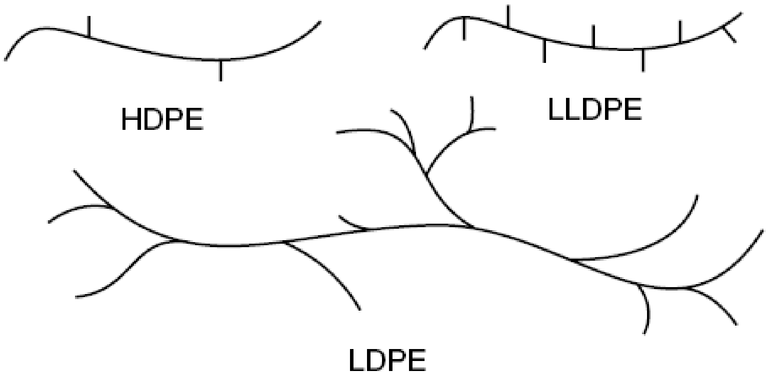


Figure 2.2 Chain configurations of polyethylene [1]

When polyethylene is subjected to high-energy irradiation, gases such as hydrogen and some lower hydrocarbons are evolved, there is an increase in unsaturation and, most important, cross-linking occurs by the formation of C-C bonds between molecules. The formation of cross-link points interferes with crystallisation and progressive radiation will eventually yield an amorphous but cross-linked polymer. Extensive exposure may lead to colour formation and in the presence of air surface oxidation will occur. Oxygen will cause polymer degradation during irradiation and this offsets the effects of cross-linking [3].

2.3.1 Low-Density Polyethylene (LDPE)

LDPE is a highly branched long- chain thermoplastic polymer having density of 0,915- 0,925 g/cm^3 and molecular weight up to 4×10^6 [15]. The thermal properties of LDPE include a melting range 106-112 °C . Its relatively low melting point and broad melting range result in easy process applications. The glass transition temperature of LDPE is well below the room temperature (~ -120 °C), accounting for the polymer’s soft and flexible nature. Also, LDPE does not break when subjected to the Izod impact test [16].

LDPE combines high impact strength, toughness, and ductility to make it the material of choice for packaging films, which is one of its largest applications. Films range from shrink film, thin film for automatic packaging, heavy sacking, and multilayer films (both laminated and co-extruded) where LDPE acts as a seal layer or a water vapor barrier. LDPE is formed via free-radical polymerization, with alkyl branch groups [given by the structure $-(CH_2)_xCH_3$] of two to eight carbon atom lengths. The most common branch length is four carbons long. High reaction pressures encourage crystalline regions [1]. The reactions to form LDPE are shown in Figure 2.3.

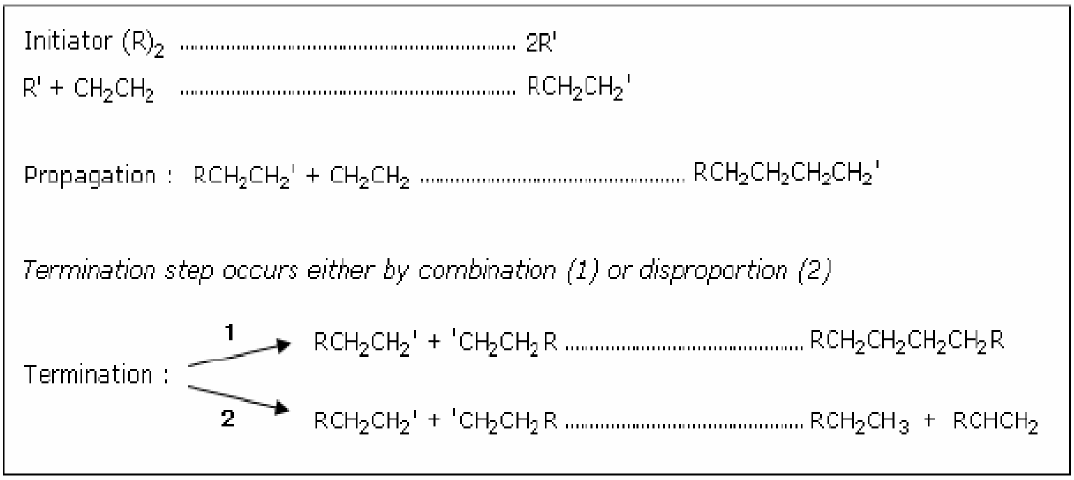


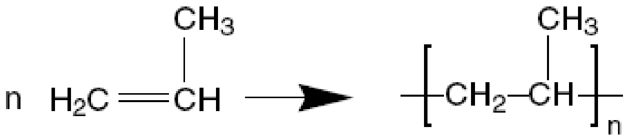
Figure 2.3 Radical polymerization of LDPE [15]

2.4 Polypropylene (PP)

Polypropylene is very important and common polymer used in various applications from films to fibers.

2.4.1 Structure of PP

Polypropylene(PP) is synthesized by the polymerization of propylene, a monomer derived from petroleum products through the reaction shown in Figure 2.4 [1]. It was not until Ziegler-Natta catalysts became available that polypropylene could be polymerized into a commercially viable product. These catalysts allowed the control of stereochemistry during polymerization to form polypropylene in the isotactic and syndiotactic forms, both capable of crystallizing into a more rigid, useful polymeric material. The range of molecular weights for PP is *Mn* _ 38,000 to 60,000 and *Mw* _ 220,000 to 700,000. The molecular weight distribution (*Mn*/*Mw*) can range from 2 to about 11 [3].



$$n\ H_2C{=}\overset{\displaystyle CH_3}{\overset{|}{C}H} \longrightarrow \left[CH_2-\overset{\displaystyle CH_3}{\overset{|}{C}H} \right]_n$$

Figure 2.4 Polymerization of polypropylene [1]

Stereochemical isomerism is possible in PP because propylene monomers can link together such that the methyl groups can be situated in one spatial arrangement or another in the polymer. If the methyl groups are all on side of the chain, they are referred to as being in the ‘‘isotactic’’ arrangement, and if they are on alternate sides of the chain, they are referred to as being in the ‘‘syndiotactic’’ arrangement. Each chain has a regular and repeating symmetrical arrangement of methyl groups that form different unit cell crystal types in the solid state. A random arrangement of methyl groups along the chain provides little or no symmetry, and a polymer with this type of arrangement is known as ‘‘atactic’’ polypropylene [17]. These configurations are shown in Figure 2.5.

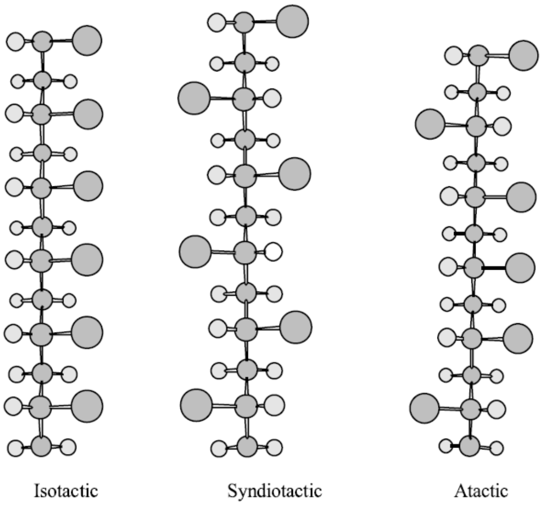


Figure 2.5 Isotactic, syndiotactic and atactic PP chains [1]

Different behavior can be found for each of the three stereoisomers. Isotactic and syndiotactic polypropylene can pack into a regular crystalline array giving a polymer with more rigidity. Both materials are crystalline; however, syndiotactic polypropylene has a lower T_m than the isotactic polymer [18]. The isotactic polymer is the most commercially used form with a melting point of 165°C. Atactic polypropylene has a very small amount of crystallinity (5 to 10%) because its irregular structure prevents crystallization, thus, it behaves as a soft flexible material. It is used in applications such as sealing strips, paper laminating, and adhesives [3].

2.4.2 Properties of PP

Unlike polyethylene, which crystallizes in the planar zigzag form, isotactic polypropylene crystallizes in a helical form because of the presence of the methyl groups on the chain [3]. Commercial polymers are about 90 to 95% isotactic. The amount of isotacticity present in the chain will influence the properties. As the amount of isotactic material (often quantified by an isotactic index) increases, the amount of crystallinity will also increase, resulting in increased modulus, softening point, and hardness [1].

Although, in many respects, polypropylene is similar to polyethylene, since both are saturated hydrocarbon polymers, they differ in some significant properties. Isotactic polypropylene is harder and has a higher softening point than polyethylene, so it is used where higher stiffnes materials are required. Polypropylene is less resistant to degradation, particularly high-temperature oxidation, than polyethylene, but has better environmental stress cracking resistance [19]. The decreased degradation resistance of PP is due to the presence of a tertiary carbon in PP, allowing for easier hydrogen abstraction compared to PE. As a result, antioxidants are added to polypropylene to improve the oxidation resistance. The degradation mechanisms of the two polymers are also different. PE cross-links on oxidation, while PP undergoes chain scission. This is also true of the polymers when exposed to high energy radiation, a method commonly used to cross-link PE [20].

Polypropylene is one of the lightest plastics with a density of 0.905. The nonpolar nature of the polymer gives PP low water absorption. Polypropylene has good chemical resistance, but liquids, such as chlorinated solvents, gasoline and xylene, can affect the material. Polypropylene has a low dielectric constant and is a good insulator. Difficulty in bonding to polypropylene can be overcome by the use of surface treatments to improve the adhesion characteristics [20].

Polypropylene has a higher T_g and melting point than polyethylene with the exception of UHMWPE. Service temperature is increased, but PP needs to be processed at higher temperatures. Because of the higher softening, PP can withstand boiling water and can be used in applications requiring steam sterilization [3]. Polypropylene is also more resistant to cracking in bending than PE and is preferred in applications that require tolerance to bending. This includes applications such as ropes, tapes, carpet fibers, and parts requiring a living hinge. Living hinges are integral parts of a molded piece that are thinner and allow for bending [19]. One weakness of polypropylene is its low-temperature brittleness behavior, with the polymer becoming brittle near 0°C [3]. This can be improved through copolymerization with other polymers such as ethylene.

2.4.3 Processing behavior of PP and comparison with PE

Comparing the processing behavior of PP to PE, it is found that polypropylene is more non-Newtonian than PE and that the specific heat of PP is lower than polyethylene. The melt viscosity of PE is less temperature sensitive than PP. Mold shrinkage is generally less than for PE, but is dependent on the actual processing conditions. Unlike many other polymers, an increase in molecular weight of polypropylene does not always translate into improved properties. The melt viscosity and impact strength will increase with molecular weight, but often with a decrease in hardness and softening point. A decrease in the ability of the polymer to crystallize as molecular weight increases is often offered as an explanation for this behavior [3].

The molecular weight distribution (MWD) has important implications for processing. A PP grade with a broad MWD is more shear sensitive than a grade with a narrow MWD. Broad MWD materials will generally process better in injection-molding applications. In contrast, a narrow MWD may be preferred for fiber formation. Various grades of polypropylene are available tailored to a particular application. These grades can be classified by flow rate, which depends on both average molecular weight and MWD. Lower flow rate materials are used in extrusion applications. In injection-molding applications, low flow rate materials are used for thick parts and high flow rate materials are used for thin-wall molding [1].

Polypropylene can be processed by methods similar to those used for PE. The melt temperatures are generally in the range of 210 to 250°C. Heating times should be minimized to reduce the possibility of oxidation. Blow molding of PP requires the use of higher melt temperatures and shear, but these conditions tend to accelerate the degradation of PP. Because of this, blow molding of PP is more difficult than for PE. The screw metering zone should not be too shallow in order to avoid excessive shear. For a 60 mm screw the flights depths are typically about 2.25 and 3.0 mm for a 90 mm screw [3]. In film applications, film clarity requires careful control of the crystallization process to ensure that small crystallites are formed. This is accomplished in blown film by extruding downwards into two converging boards. In the Shell TQ process the boards are covered with a film of flowing, cooling water. Oriented films of PP are manufactured by passing the PP film into a heated area and stretching the film both transversely and longitudinally. To reduce shrinkage the film may be annealed at 100°C while under tension [3]. Highly oriented films may show low transverse strength and a tendency to fibrillate. Other manufacturing methods for polypropylene include extruded sheet for thermoforming applications and extruded profiles [1].

2.5 Fillers

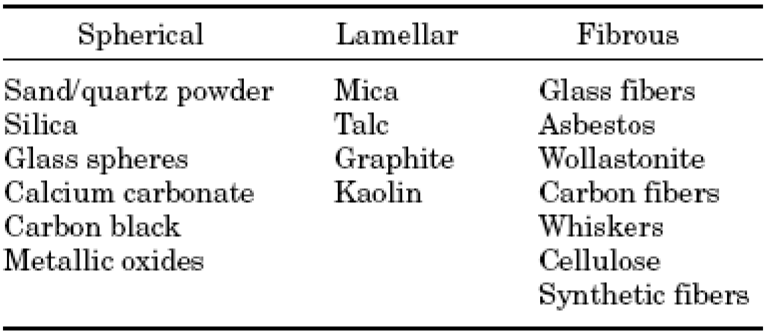
Fillers are solid additives, which are incorporated into the polymer matrix. They are generally inorganic materials, and can be classified according to their effect on the mechanical properties of the resulting mixture. Inert or extender fillers are added mainly to reduce the cost of the compound, while reinforcing fillers are added in order to improve certain mechanical properties such as modulus or tensile strength [1]. Although termed inert, inert fillers can nonetheless affect other properties of the compound besides cost. In particular, they may increase the density of the compound, lower the shrinkage, increase the hardness, and increase the heat-deflection temperature [1].

Reinforcing fillers typically will increase the tensile, compressive, and shear strength; increase the heat deflection temperature; lower shrinkage; increase the modulus; and improve the creep behavior. Reinforcing fillers improve the properties via several mechanisms. In some cases a chemical bond is formed between the filler and the polymer, while in other cases the volume occupied by the filler affects the properties of the thermoplastic. As a result, the surface properties and interaction between the filler and the thermoplastic are of great importance [1].

Certain properties of the fillers are of particular importance. These include the particle shape, the particle size and distribution of sizes, and the surface chemistry of the particle. In general, the smaller the particle, the higher the mechanical property of interest (such as tensile strength) is [3]. Larger particles may give reduced properties compared to the pure thermoplastic. Particle shape can also influence the properties. For example, platelike particles or fibrous particles may be oriented during processing. This may result in properties that are anisotropic. The surface chemistry of the particle is important to promote interaction with the polymer and allow for good interfacial adhesion. It is important that the polymer wet the particle surface and have good interfacial bonding in order to obtain the best property enhancement [1].

Examples of inert or extender fillers include china clay (kaolin), talc, and calcium carbonate. Glass spheres are also used as thermoplastic fillers. They may be either solid or hollow, depending on the particular application. Talc is an important filler with a lamellar particle shape [21]. It is a natural, hydrated magnesium silicate with good slip properties. Kaolin and mica are also natural materials with lamellar structure. Other fillers include wollastonite, silica, barium sulfate, and metal powders. Carbon black is used as a filler primarily in the rubber industry, but it also finds application in thermoplastics for conductivity, UV protection, and as a pigment. Fillers in fiber form are often used in thermoplastics. Types of fibers include wood flour, fiberglass, and carbon [1]. Table 2.2 shows the fillers and their forms.

Table 2.2 Forms of various fillers [1]



Spherical	Lamellar	Fibrous
Sand/quartz powder	Mica	Glass fibers
Silica	Talc	Asbestos
Glass spheres	Graphite	Wollastonite
Calcium carbonate	Kaolin	Carbon fibers
Carbon black		Whiskers
Metallic oxides		Cellulose
		Synthetic fibers

2.5.1 $CaCO_3$

Calcium carbonate is important filler with a particle size of 1-3 µm. It is a natural product from sedimentary rocks and is separated into chalk, limestone, and marble. In some cases the calcium carbonate may be treated to improve the bonding with the thermoplastic [21]. $CaCO_3$ is abundant, largely inert, low cost, white filler. The primary function of calcium carbonate as a filler is to lower costs, while having moderate effects on mechanical properties [2].

The mechanical properties of polymer composites with $CaCO_3$ are dependent on interfaces where the polymer matrix and filler are in contact. As inorganic filler, $CaCO_3$ particles have mostly polar, hydrophilic and high free energy surfaces. Thus, filler particles might be incompatible with polymer matrices having non-polar, more hydrophobic and relatively low free energy surfaces. In order to overcome that possible incompatibility, several methods such as filler surface treatment are conducted and filler's surface becomes appropriate for adhesion with non-polar polymer matrices.

2.6 Titanate Coupling Agents

2.6.1 Description of Coupling Agents

Coupling agents are additives used in reinforced and filled plastic composites to enhance the plastic–filler-reinforcement interface to meet increasingly demanding performance requirements. In general, there is little affinity between inorganic materials used as reinforcements and fillers and the organic matrices in which they are blended. With silicate reinforcements (glass fiber or wollastonite), silane coupling agents act by changing the interface between the dissimilar phases. This results in improved bonding and upgraded mechanical properties. By chemically reacting with the resin and the filler or reinforcement components, coupling agents form strong and durable composites. Coupling agents significantly improve mechanical and electrical properties for a wide variety of resins, fillers, and reinforcements. In addition, they act to lower composite cost by achieving higher mineral loading [22]. Mainly there are two types of coupling agent: silane and titanate (or zirconate) based coupling agents.

2.6.1.2 Silane Coupling Agents

Silane coupling agents comprise more than 90% of the plastic coupling agent market. As shown in Figure 2.6 organosilanes can be represented chemically by the formula Y-Si$(X)_3$ where X- represents a hydrolyzable group such as ethoxy or methoxy and Y- is a functional organic group which provides covalent attachment to the organic matrix.

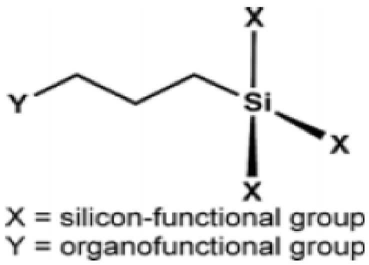


Figure 2.6 General Structure of organosilanes

The silane coupling agent is initially bonded to the surface hydroxy groups of the inorganic component by the Si$(X)_3$ either directly or more commonly via its hydrolysis product, Si$(OH)_3$ which is termed as “silanol”. The Y- functional group (amino, methoxy, epoxy, etc.) attaches to the matrix when the silane-treated filler or reinforcement is compounded into the plastic, resulting in improved bonding and upgraded mechanical and electrical properties [22]. The coupling reaction of silanes to an inorganic filler surface is represented in Figure 2.7.

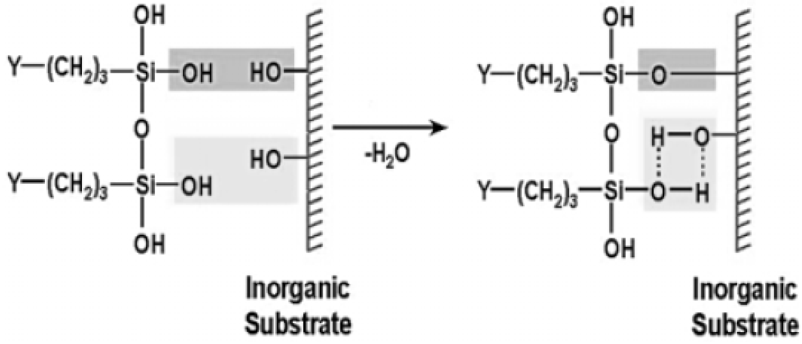
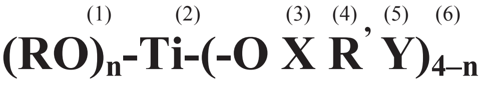


Figure 2.7 Mode of reaction between a silanol and an inorganic surface [22].

2.6.2 Structure and Properties of Titanate Coupling Agents

Titanate coupling agents are organometallic interphase chemicals based on titanium or zirconium. Titanate coupling agents impart increased functionality to fillers in plastics. The different ways that these additives work in filled polymers can be explained by breaking down the various mechanisms of the titanate (or zirconate) molecule into six distinct functions [23]. The titanate structure may be tailored to provide desired properties through the six functionalities on the basic structure shown in Figure 2.8.

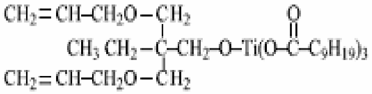
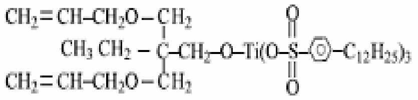
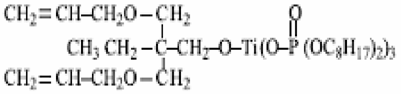
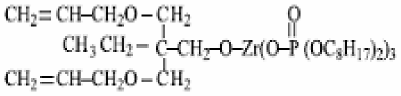


$$\overset{(1)}{(RO)_n}\text{-}\overset{(2)}{Ti}\text{-}(\text{-}\overset{(3)}{O}\ \overset{(4)}{X}\ \overset{(5)}{R'}\ \overset{(6)}{Y})_{4-n}$$

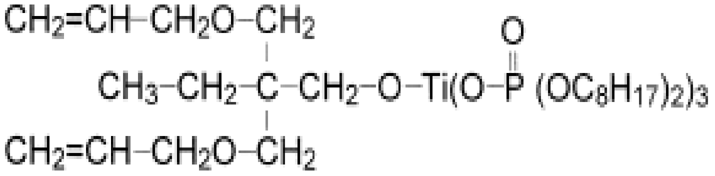
Figure 2.8 Basic chemical structure of a titanate molecule

There are many types of titanate coupling agents with varying chemical structures and contents. These many kinds of titanates are used according to polymer and its several properties. Table 2.3 provides a chemical description and structure of four common coupling agents along with their commercial name. The commercial name is often used alone in this study for the sake of brevity.

Table 2.3 Chemical description and structure of some titanate coupling agents

Comercial name	Chemical description	Chemical structure
Lica 01	Neopentyl(diallyl)oxy, trineodecanonyl titanate	 $\begin{array}{l} CH_2=CH-CH_2O-CH_2 \\ \quad CH_3\,CH_2-C-CH_2-O-Ti(O-\overset{O}{\overset{\|}{C}}-C_9H_{19})_3 \\ CH_2=CH-CH_2O-CH_2 \end{array}$
Lica 09	Neopentyl(dyallyl)oxy, tri(dodecyl)benzene-sulfonil titanate	 $\begin{array}{l} CH_2=CH-CH_2O-CH_2 \\ \quad CH_3\,CH_2-C-CH_2-O-Ti(O-\underset{O}{\underset{\|}{\overset{O}{\overset{\|}{S}}}}-\bigcirc-C_{12}H_{25})_3 \\ CH_2=CH-CH_2O-CH_2 \end{array}$
Lica 12	Neopentyl(diallyl)oxy, tri(dioctyl)phosphato titanate	 $\begin{array}{l} CH_2=CH-CH_2O-CH_2 \\ \quad CH_3\,CH_2-C-CH_2-O-Ti(O-\overset{O}{\overset{\|}{P}}(OC_8H_{17})_2)_3 \\ CH_2=CH-CH_2O-CH_2 \end{array}$
NZ12	Neopentyl(dyallyl)oxy, tri(dioctyl)phosphate zirconate	 $\begin{array}{l} CH_2=CH-CH_2O-CH_2 \\ \quad CH_3\,CH_2-C-CH_2-O-Zr(O-\overset{O}{\overset{\|}{P}}(OC_8H_{17})_2)_3 \\ CH_2=CH-CH_2O-CH_2 \end{array}$

In this study Lica12 is used as titanate coupling agent. Its detailed chemical structure is given in Figure 2.9.



$$\begin{array}{l} CH_2=CH-CH_2O-CH_2 \\ \quad CH_3-CH_2-C-CH_2-O-Ti(O-\overset{O}{\overset{\|}{P}}(OC_8H_{17})_2)_3 \\ CH_2=CH-CH_2O-CH_2 \end{array}$$

Figure 2.9 Chemical Structure of Lica 12 (neopentyl (diallyl) oxy, tri (dioctyl) pyrophospato titanate).

Titanate coupling agents react with free protons at the surface of the inorganic material, resulting in the formation of organic monomolecular layers on the surface as shown schematically in Figure 2.10. Typically, titanate-treated inorganic fillers or reinforcements are hydrophobic, organophilic, and organofunctional and, therefore, exhibit enhanced dispersibility and bonding with the polymer matrix [22].

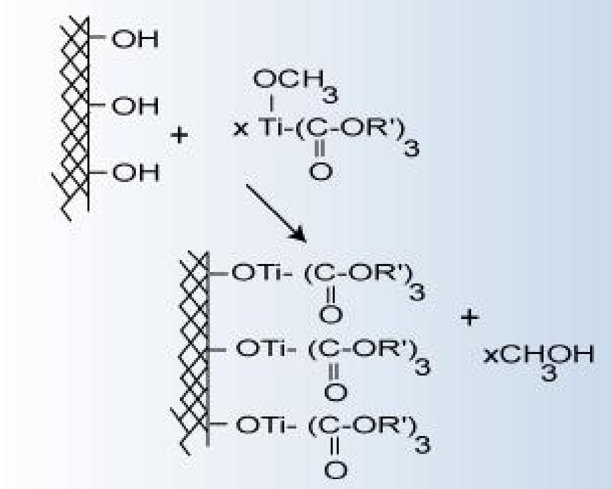


Figure 2.10 Schematic representation of the monomolecular layer formation by titanate [24].

Esters of titanium (or zirconium) couple or chemically bridge two dissimilar species such as an inorganic filler/organic particulate/fiber and an organic polymer through proton coordination. This permits coupling to non-hydroxyl bearing, and therefore non-silane reactive, inorganic substrates such as $CaCO_3$ and boron nitride as well as organic substrates such as carbon black and nitramines without the need of water of condensation as with silanes [23]. Titanate coupling agents are unique in that their reaction with free protons on the substrate surface results in a monomolecular layer on the surface whether it be a filler or substrate. This is likely the cause of one of the problems in using organic titanates - over concentration. Since excess titanate (amount greater than necessary to form a monolayer) does not result in a polymer network at the interface, it is suspected that it can form a weak boundary layer resulting in degraded properties. Thus, the amount of titanate that is used is an important parameter [24].

The thermally stable quaternary carbon structure of the neoalkoxy organometallics permits in situ reactions to take place in the thermoplastic melt. In addition, the coupling of monolayers of a phosphato or a pyrophosphato heteroatom titanate (or zirconate) imparts synergistic intumescence to non-halogenated flame retardants such as $Mg(OH)_2$ and aluminum trihydrate (ATH); flame retardance function to fillers such as $CaCO_3$; control of the burn rate and burn rate exponent of aluminum powder rocket fuels; and extinction of the flame spread of spalls of polymer-bound nitramines used in propellants and explosives [23].

The organometallic monolayer covered filler surface becomes a catalysis support bed for “repolymerization” of the surrounding polymer phase, thus allowing fillers to act as mechanical property improvers. Furthermore, the in situ monomolecular deposition of titanate on the surface of a particulate, such as nanofiller, renders the particulate hydrophobic and organophilic. Under melt compounding shear conditions, the titanate assists in the removal of air voids and moisture from the particle surface, resulting in complete dispersion and formation of a true continuous phase, thus optimizing filler performance.

Minor amounts of thermally stable neoalkoxy titanate and zirconate additives may provide a means for post-reactor, in situ metallocene-like “repolymerization” catalysis of a filled or unfilled polymer during the plasticization phase. This may result in the creation of metallocene-like (titanocene or zirconocene) behavior associated with effects such as increased composite strain to failure, resulting in increased impact toughness, or enhanced polymer foamability. Other effects to be discussed below with specific examples are related to enhanced processability, reduced polymer chain scission, shortened polymer recrystallization time, and the compatibilization of dissimilar polymers [23].

2.6.3 Functions of Titanate Coupling Agents

Organosilanes have long been used to enhance the chemical bonding of a variety of thermoset resins with siliceous surfaces and more recently of thermoplastics. It is observed that organosilanes are essentially non-functional as bonding agents when employing carbon black, $CaCO_3$, boron nitride, graphite, aramid or other organic derived fibers [25]. A comparison of the six functional sites of a titanate (or zirconate) to a silane on basic structures as shown in Figure 2.11 is useful to explain their performance differences.

$$\overset{(1)}{(RO)}_n\text{-}\overset{(2)}{Ti}\text{-(-O }\overset{(3)}{X}\,\overset{(4)}{R'}\,\overset{(5)}{Y}\overset{(6)}{)}_{4-n} \qquad \overset{(1)}{(RO)}_3\text{-Si-(-}\overset{(5)}{R'}Y)$$

Figure 2.11 Number of functions signed on basic structure of titanate coupling agent and silane coupling agent

As shown in the Figure 2.11, titanate coupling agent has 6 functions according to relevant parts on molecular structure where:

Function (1) RO = Hydrolyzable group/substrate-reactive group with surface hydroxyls or protons.

Function (2) Ti (Zr), Si = Tetravalent titanium, zirconium or silicon. The Ti–O (or Zr–O) bond is capable of disassociation allowing transesterification, transalkylation, and other catalyzed reactions such as “repolymerization”, while the Si–C bond is more stable and thus unreactive.

Function (3) X = Binder functional groups such as phosphato, pyrophosphato, sulfonyl, carboxyl, etc., that may impart intumescence, burn rate control, anti-corrosion, quaternization sites, dissociation rate/electron-transfer control, etc.

Function (4) R' = thermoplastic-specific functional groups such as aliphatic and non-polar isopropyl, butyl, octyl, isostearoyl groups; naphthenic and mildly polar dodecylbenzyl groups; or aromatic benzyl, cumyl or phenyl groups. Provide entanglements with long hydrocarbon chains and bonding via van der Waals forces.

Function (5) Y = thermoset (but also thermoplastic)-specific functional groups such as acrylyl, methacrylyl, mercapto, amino, etc. Provide thermoset reactivity chemically bonding the filler to the polymer.

Function (6) 4–n = mono-, di- or triorganofunctionality. Hybrid titanate (or zirconate) coupling agents, such as those containing 1 mole each of a carboxyl [function (3)] and aliphatic isostearoyl [function (4)] ligand and 2 moles of carboxyl [function (3)] and acrylyl [function (5)] ligands, are possible.

Therefore, function (1) relates to filler/fiber substrate reaction mechanisms, while functions (2) to (6) are polymer/curative reactive [23].

2.6.4 Effects of Titanate Coupling Agents

Effects of titanate coupling agents are classified according to functional sites expressed in previous part 2.6.3.

2.6.4.1 Effects of Function (1)

The functional site (1) of the titanate molecule is associated with coupling, dispersion, adhesion, and hydrophobicity effects. These effects are also related to the method of application of the titanate on the filler surface.

2.6.4.1.1 Coupling Effect

In its simplest terms, the titanate function (1) mechanism may be classed as protonreactive through solvolysis (monoalkoxy) or coordination (neoalkoxy) without the need of water of condensation, while the silane function (1) mechanism may be classed as hydroxyl-reactive through a silanol–siloxane mechanism requiring water of condensation. The silane's silanol–siloxane water of condensation mechanism limits its reactions to temperatures below 100^{o}C, thereby reducing the possibility of in situ reaction in the thermoplastic or elastomer melt above 100^{o}C as is possible with titanates. In addition, a variety of particulate fillers such as carbonates, sulfates, nitrides, nitrates, carbon, boron, and metal powders used in thermoplastics, thermosets, and cross-linked elastomers do not have surface silane-reactive hydroxyl groups, while almost all three-dimensional particulates and species have surface protons thereby apparently making titanates more universally reactive [23].

2.6.4.1.2 Dispersion Effect

Dispersion of fillers results from the application of electrochemical and mechanical forces to the interface of the inorganic filler/polymer so as to cause complete deagglomeration to the attrited or original particle size in an organic phase, complete elimination of air voids and water, and the creation of a true continuous inorganic/ organic composition. The coupling of the titanate to the inorganic/organic substrate in monolayers allows for elimination of air voids, enhanced hydrophobicity, and a complete continuous phase for stress/strain transfer. Figure 2.12 shows "before and after" effect of a titanate monolayer on agglomerated fillers [23].

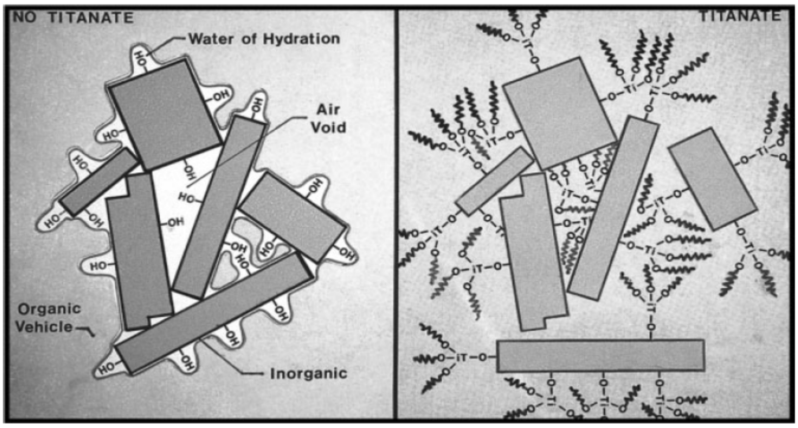


Figure 2.12 Illustration of the dispersion effect of coupling a titanate monolayer on an agglomerated inorganic in an organic phase [23]

C-20 aliphatic mineral oil can be used as a low molecular weight model for polyolefines. Since it is non-polar and, thus, a poor medium for dispersion of most polar fillers, coupling agent effects can be more easily measured. Figure 2.13 shows the effect of 0.5% isopropyl triisostearoyl titanate (KR TTS) on the dispersion of $CaCO_3$ in a non-polar mineral oil. The deagglomeration effect is apparent. Significant viscosity reductions have been observed through the application of the same titanate [23].

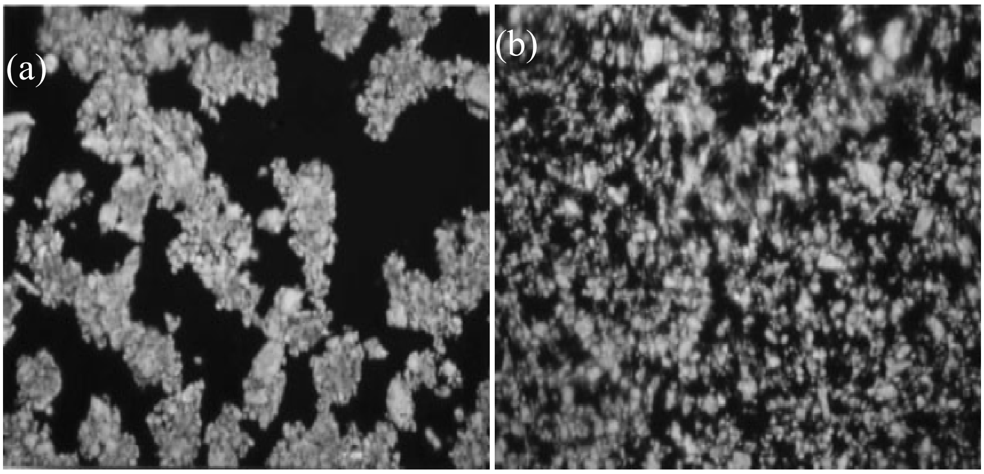


Figure 2.13 a) Micrograph of a suspension of a $CaCO_3$ (untreated)/ liquid paraffin system. b) Micrograph of a suspension of a $CaCO_3$ (treated with KR TTS)/liquid paraffin system demonstrating deagglomeration [23].

The CPVC (critical pigment volume concentration) is defined as that point at which addition of more filler to an organic phase will cause incomplete wetting due to insufficient organic binder being available to wet the additional inorganic filler surface. Figure 2.14 shows the shift in the CPVC point of $CaCO_3$-filled mineral oil using 0.5 wt. % KR TTS which is a kind of titanate coupling agent.The shift in the CPVC as a result of coupling effect may be extended from the mineral oil model to filled thermoplastic and thermoset systems allowing higher loading to equivalent oil demand, and improved relative mechanical properties at any filler loading below the CPVC [23].

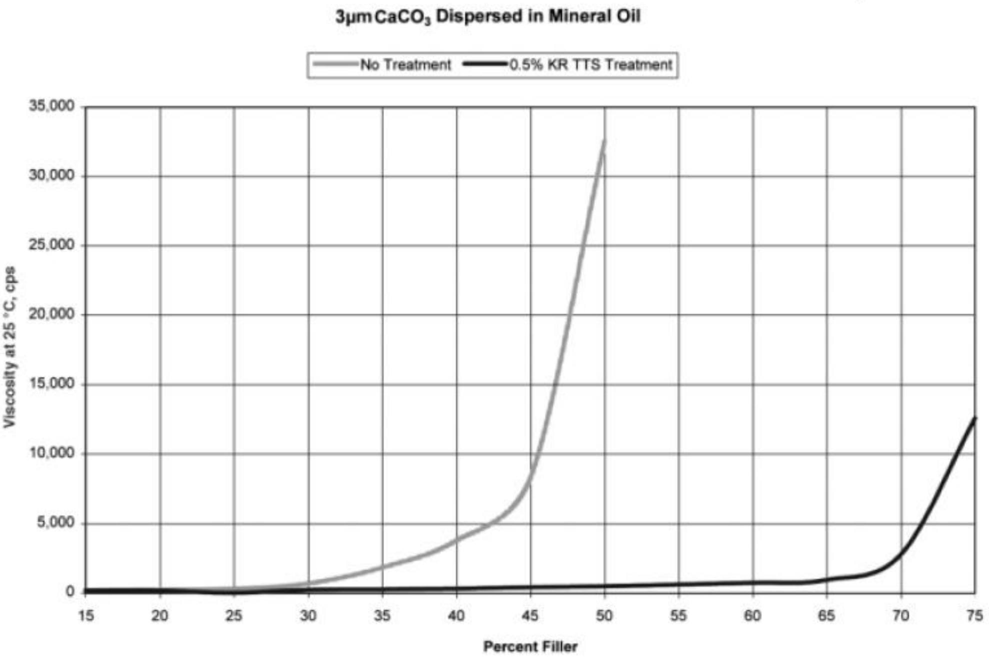


Figure 2.14 Comparision the CPVC point of untreated $CaCO_3$-filled mineral oil (left) with KR TTS treated $CaCO_3$-filled mineral oil (right) [23].

2.6.4.1.3 Adhesion Effect

One of the reasons why the dispersion of inorganics in plastics and the adhesion of a plastic to an inorganic substrate are so difficult is because many thermoplastics and rubbers, such as olefin-based polymers, are non-polar. Titanates and zirconates are well established adhesion promoters. A recent example of bonding polyolefins to metals and another example of the adhesion of polyolefins to foil electrodes using various titanate coupling agents had been observed in some researhes [23].

2.6.4.2 Effects of Function (2)

Repolymerization is a concept that has been patented to explain new and novel rheology and stress/strain effects in thermoplastics and thermosets obtained with titanate and zirconate that are independent of cross-linking and curative effects. The aromatic (e.g., phenyl, naphthyl, styrenic) or aliphatic (e.g., ethyl, propyl, butyl) backbones that typically make up the thermoplastic macromolecule, liquid chemical compounds, or thermoplastic elastomers are reactive with titanate (or zirconate) [functions (2) to (4)], independent of any curative reaction mechanisms [function (5)]. Thus, the monolayered, organometallic-coupled particulate and/or fiber may be considered as a catalyst support bed for single-site, in situ metallocenelike repolymerization of the surrounding polymer [23].

Currently, published efforts in metallocene (titanocene and zirconocene) chemistry by major polymer producers appear to be centered on olefin polymers and copolymers. Metallocene-derived HDPE and engineering plastics seemingly remain a future goal, while titanate and zirconate esters appear to be efficacious to some degree in virtually all polymers synthesized by various routes. Moreover, the titanocene or zirconocene catalysts used in the synthesis of metallocene-derived polymers do not remain in the polymer. With repolymerization, thermoplastics may now be regenerated to virgin or recycled more efficiently since the thermally stable titanate or zirconate ester forms of the relevant organometallics “anneal” or “reconnect” polymer chain lengths that normally undergo scission during processing and remain in the polymer for subsequent repeat thermal cycles [23].

2.6.5 Surface Modification of Fillers with Titanate Coupling Agents

Titanate coupling agents act as a chemical bridge between the adhesive resin and the substrate or filler. Coupling agents were first used to treat fillers before they are incorporated into liquid or melt resin to make composite materials. While the treatment of inorganic fillers, the organic titanates react with surface hydroxyl groups to produce a polymer network at the interface of fillers. This reaction results in formation of monomolecular layer on the surface of the filler [24]. In Figure 2.15 coating of filler by titanates is represented schematically.

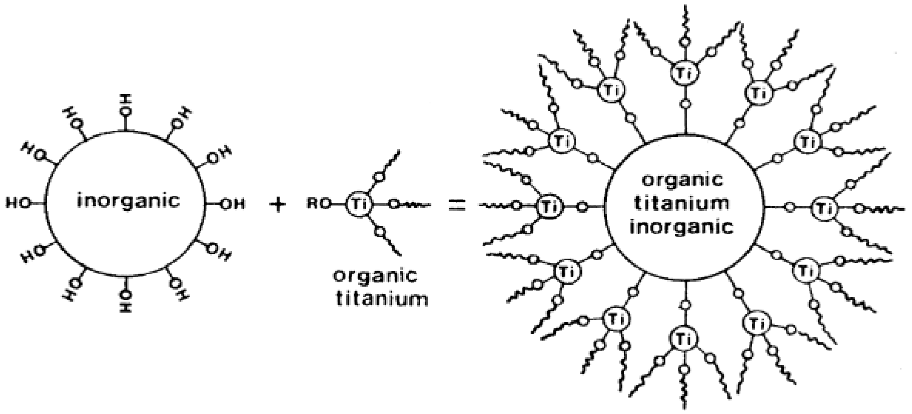


Figure 2.15 Schematic representation of coating of filler by titanates

Typically, titanate treated inorganic fillers or reinforcements are hydrophobic, organophilic and organofunctional thus they exhibit enhanced dispersability and bonding with the polymer matrix. The use of organic titanates and zirconates for surface modification is based on their ability to hydrolyze to a coating that is very thin, amorphous, and primarily inorganic. The properties of this film depend on the type and amount of organometallic coupling agent used, the chemistry of the organometallic, and the processing properties used to apply the coating. These coatings modify the surface of the filler or substrate to provide the following unique properties [24]:

- They promote adhesion of adhesives and coatings to glass, metal and plastics.
- The organometallic interface improves dispersability of pigments and fillers in aqueous and non-aqueous systems and reduces viscosity.
- It can provide scratch-resistant and reflective properties to glass.
- It can modify frictional characteristics of the substrate.
- Modify surface characteristics (water repellency or hydrophobicity)
- Improves wet-out between resin and filler
- Decreases water-vapor transmission

2.7 Polymer Processing

Polymer processing is the operation by which solid or liquid polymers are converted to finished products. It consists of several steps, such as, pre-shaping, shaping (molding, casting, die-forming, calendering etc.), post-shaping (decorating, fastening, sealing, welding, dyeing, printing, etc.). Pre-shaping involves melting and softening, pressurization and pumping of the polymer melt, homogeneous mixing and devolatilization and stripping of residual monomers, solvents, contaminants [2].

In this study extrusion and internal mixing are used for polymer melting and homogeneous mixing of polymers with each other and fillers. For shaping the resultant products, injection molding is used.

2.7.1 Extrusion

Extrusion is a polymer conversion operation in which a solid thermoplastic material is melted or softened, forced through an orifice (die) of the desired cross section, and cooled. The process is used for compounding plastics and for the production of tubes, pipes, sheet, film, wire coating, and profiles. All extrusion lines include a melt pump called an extruder, but other equipment is specific to the particular process [26]. This process is also used to produce the plastic pellets that are later used by all the other plastics manufacturing processes. In addition to the shaping of parts by the extrusion process, extrusion is the most efficient and widely used process for melting plastic resin as part of the process of adding or mixing fillers, colorants, and other additives into the molten plastics. Extrusion can be used to shape the part directly after this mixing or an extruder can be used as the melting device that is coupled with other shaping processes [27].

In normal plastics extrusion, plastics granules or pellets and any other materials to be mixed with them are fed into a hopper attached to the extrusion machine. From the hopper the materials falls through a hole in the top of the extruder onto the extrusion screw. This screw, that turns inside the extruder barrel, conveys the plastic forward into a heated region of the barrel where the combination of external heating and heating from viscous dissipation melts the plastic. The screw moves the molten plastic until it exists through a hole in the end of the extruder barrel to which a die has been attached. The die imparts a shape to the molten plastic stream which is immediately cooled by a water bath [27]. A kind of single-screw extruder is shown in Figure 2.16.

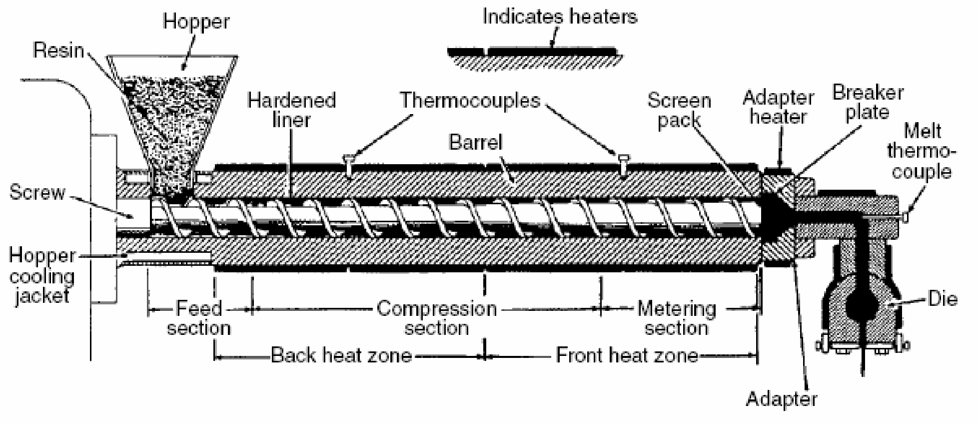


Figure 2.16 Schematic Representation of Single-screw extruder [26]

The screw is the main part of the extruder which directly affects the performance of the machine. It performs a number functions as followings:

- conveying the plastic pellets
- melting the material
- conveying the molten material
- mixing the plastic melt to obtain homogeneity.

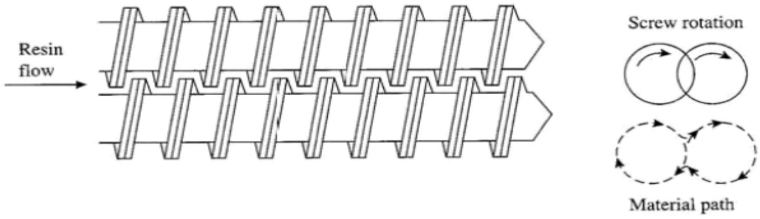
The screw is placed inside the cylinder extruder barrel. It provides the bearing surface where shear is imparted to the plastic granules. The barrel consists of cast or fabricated steel sections and a smooth inner liner, often made of a wear-resistant material. Heating and cooling media surrounds the barrel to keep it at the desired temperatures.

The polymer is shaped in the die zone. The objective of an extrusion die is to distribute the polymer melt in the flow channel in such a way that the material exits from the die with a uniform velocity. The polymer melt is forced through the die by means of the die-head pressure [27]. According to screw numbers, extruders are classified into single screw and multi screw extruders. In this study twin-screw extruder is used for compounding applications.

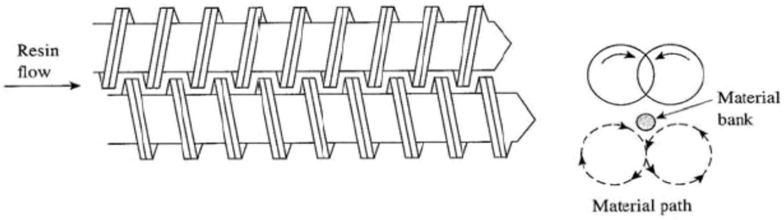
2.7.1.1 Twin-Screw Extruders

Although twin-screw extruders are used less than single-screw extruders they are widely employed for difficult compounding applications, devolatilization, chemical reaction, and profile extrusion of thermally sensitive materials in the polymer processing industry [27].

The complex flow patterns in twin-screw extruders have several advantages, such as good mixing, good heat transfer, large melting capacity, good devolatilization capacity, and good control over stock temperatures [27]. Type of transport in extruder is different in single-screw and twin-screw extruders. Material transport in single-screw extruder is by frictional drag in solid conveying zone and viscous drag in the melt conveying zone. On the other hand, the transport in an intermeshing twin-screw extruder is a positive displacement type of transport [27]. There is a tremendous variety of twin-screw extruders, with vast differences in design, principle of operation and field of applications. The twin-screw construction substantially increases the number of design variables, such as direction of rotation, intermeshing, non-intermeshing, etc. [27]. There are two different patterns for intermeshing twin-screw extruders according to the direction of rotation of the screws: co-rotating and counter-rotating twin- screw extruders. Figure 2.17 shows intermeshing co-rotating and counter-rotating twin-screws.



(a) Corotating



(b) Counterrotating

Figure 2.17 Intermeshing twin screw extruder (a) Co-rotating and (b) Counter-rotating

Co-rotating twin screw extruders in which both screw rotate in the same direction, are typically used in applications where mixing and compounding need to be accomplished in addition to the molding of the plastic melt. They are highly capable of dispersing small agglomerates such as carbon black or clay [27]. In the other intermeshing type, the screws rotate counter to each other, one rotates clockwise and the other counterclockwise thus it is called counter-rotating extruder. In this type, material is brought to the junction of the two screws and a material bank occurs on the top of the junction. Only a small amount of material passes between the screws so the total shear applied to material is lower than the single-screw extruders and co-rotating twin-screw extruders. Most of the material in the bank along the junction of the screws is simply carried toward the end of the extruder. Hence, pumping is more efficient in counter-rotating screw systems than in co-rotating systems [27].

2.7.2 Internal Mixing

Internal mixer equipped with a ram is introduced by Banbury around 1920 after single-rotor mixers and primitive twin-rotor mixers are developed. Ram is used to force the material into the mixing chamber and to provide sealing. The rotors in the Banbury mixer are nonintermeshing and counterrotating. Most internal mixers use counter-rotating rotors. Figure 2.18 illustrates a commercially available torque rheometer [28].

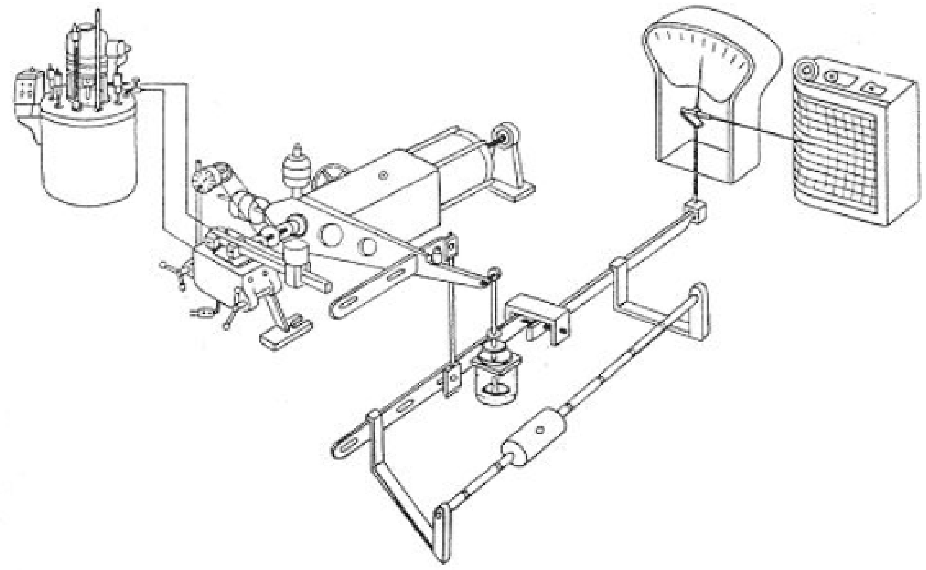


Figure 2.18 Schematic representation of Brabender (Courtesy C. W. Brabender Instruments, Inc.) [29]

The main components of a batch internal mixer are the rotors, the mixer housing, the ram, the ram air cylinder, the feed hopper, and the door for discharge (Figure 2.18).

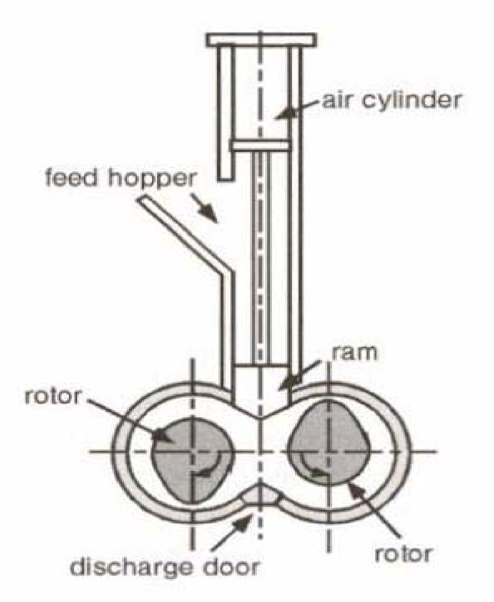


Figure 2.19 Schematic representation of a batch internal mixer [28]

The advantages of the batch internal mixer are:

1. It accepts feed stock in various forms,
2. It has intensive mixing action,
3. It has a well-defined residence time,
4. Quick material changes can be made, and
5. A wide range of mixing procedures can be used [28].

The mixing action of the internal mixer is concentrated in the narrow gaps between the rotor and the housing. In these regions, high rates of shear and elongation occur, resulting in intensive mixing action. Because the mixer is usually equipped with high horse power drives, the mixer can handle high-viscosity materials quite well. Some disadvantages of the batch internal mixer are:

1. It is not a self-wiping mixing device,
2. Batch-to-batch variations can affect product quality,
3. It is difficult to achieve fine process control,
4. It cannot handle high-temperature engineering plastics [23].

The sequence of the addition of the ingredients is key to good mixing in internal mixers. Generally, the objective is to arrange the sequence to maintain adequate stiffness in the mixture until the most difficult step in the dispersion is achieved. Normal sequence of mixing of a filled polymer is as follows:

- Step 1. Load polymer and one-half of the filler and mix until the material softens.
- Step 2. Add remaining filler and mix until fully incorporated.
- Step 3. Add plasticizers and/or softeners and complete mixing [28].

In some cases, a batch may soften too quickly before a good dispersion is obtained. In this case, an alternate technique may be used, referred to as "upside down mixing". In this technique, all ingredients are added at once, maximum ram pressure is applied, and maximum rotor speed is used. The main process variables in the batch mixing process are batch weight (fill factor), material feed temperature, mixer temperature, rotor speed, ram pressure, and sequence and timing of the feeding of the ingredients [28].

2.7.3 Injection Molding

Injection molding is a widely used process to produce parts with variable dimensions. It is a major processing technique for converting thermoplastic and thermosetting materials into all types of products.

The injection molding process cycle includes melting of plastic resin, injection of melt into the mold under high pressure, cooling of the mold, and removing the part. Cycle time depends on the cooling time of the thermoplastic or the curing time of the thermosetting plastic [26].

The injection unit may be ram fed or screw fed. Their schematic representation is shown in Figure 2.19. The ram fed injection molding machine uses a hydraulically operated plunger to push the material through a heated region. The reciprocation single screw injection molding machine is the most common injection unit used. In this system, the screw rotates and axially reciprocates. A hydraulic motor produces the rotation and acts to melt, mix, and pump the polymer. In addition to the material properties, the injection molding process itself has a large influence on the final properties of the material, since the polymer chains undergo orientation in the flow direction during the melt-filling phase of the injection cycle [26].

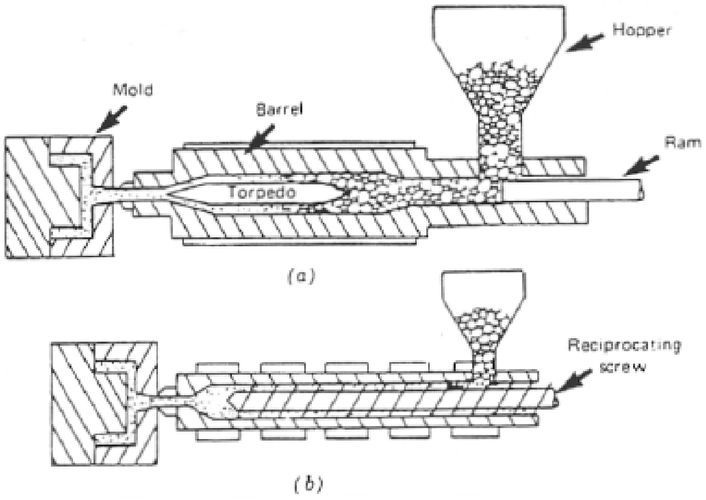


Figure 2.20 a) a ram-fed b) a screw fed injection molding machine [17].

2.8 Polymer Characterization

Polymer characterization is applied to polymer blends and composites in order to analyze and determine their mechanical, thermal, morphological and rheological properties. In this study characterization techniques are used for this purpose as following:

- Mechanical properties → Tensile test and impact test
- Morphological properties → SEM (Scanning Electron Microscopy)

2.8.1 Mechanical Properties

In many industrial applications mechanical properties is very important for polymer blends and composites as multi-functional materials. According to different purposes of usage, different types of polymers are desired in industry with varying mechanical properties. Enhancement of mechanical properties of polymer blends and composites is very large area for researchers. There are various mechanical tests to observe properties such as tensile strength, elongation, modulus, impact strength, compression, abression etc. In this study tensile and impact tests are applied to detect the enhancement of mechanical properties of studied polymer blends and composites.

2.8.1.1 Tensile Test

Tensile properties are measured according to a standard test method of ASTM D 638M-91a. In this test specimen should have a specified shape, typically a dog-bone as seen in Figure 2.19. The ends of the specimen are clamped into the jaws of the testing machine and the jaws are separated by the application of a known force. Since the specimen is pulled up, it elongates or breaks when the load applied is higher than the load which the specimen can resist. The tensile test mechanism is given in Figure 2.14. Tensile test provides a stress-strain diagram, which is used to determine the tensile modulus. Stress-strain tests not only give the modulus and an indication of the strength of the material but also toughness which is an indication of the energy that a material can absorb before breaking [19].

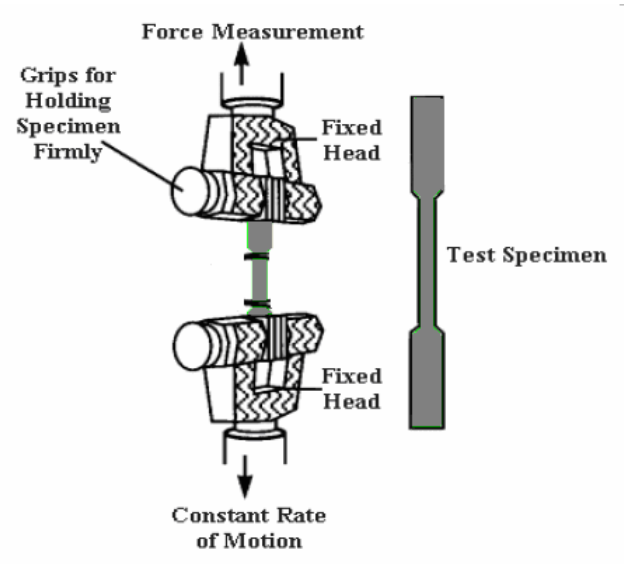


Figure 2.21 Tensile specimen and test mechanism [19].

The initial length of a central section contained within the narrow region of the tensile specimen is called the initial gauge length, L_0. During deformation, force F, is measured as a function of elongation at the fixed end by means of a transducer. Usually, the tensile response is plotted as nominal stress σ, versus nominal strain ε.

$$\sigma = F / A_o \qquad (2.1)$$

$$\varepsilon = (L-L_0) / L_0 \times 100 = (\Delta L/L_0) \times 100 \qquad (2.2)$$

Where A_0 is the original (undeformed) cross-sectional area of the gauge region and ΔL is the change in sample gauge length ($L-L_0$) due to the deformation [30].

Tensile stress (nominal), σ is the tensile load per unit area of minimum original cross-section, within the gauge boundaries (eq. 2.1). Tensile strain, ε is the ratio of the elongation to the gauge length of the test specimen, that is, the change in length per unit of original length. It is expressed as a dimensionless ratio (eq. 2.2) [30].

$E = \sigma / \varepsilon$ (2.3)

Modulus of elasticity, E is the ratio of stres (nominal) to corresponding strain below the proportional limit of a material. It is also known as elastic modulus or Young's modulus (eq. 2.3) [25]. Figure 2.20 represents the stress-strain behavior for a typical polymeric material .

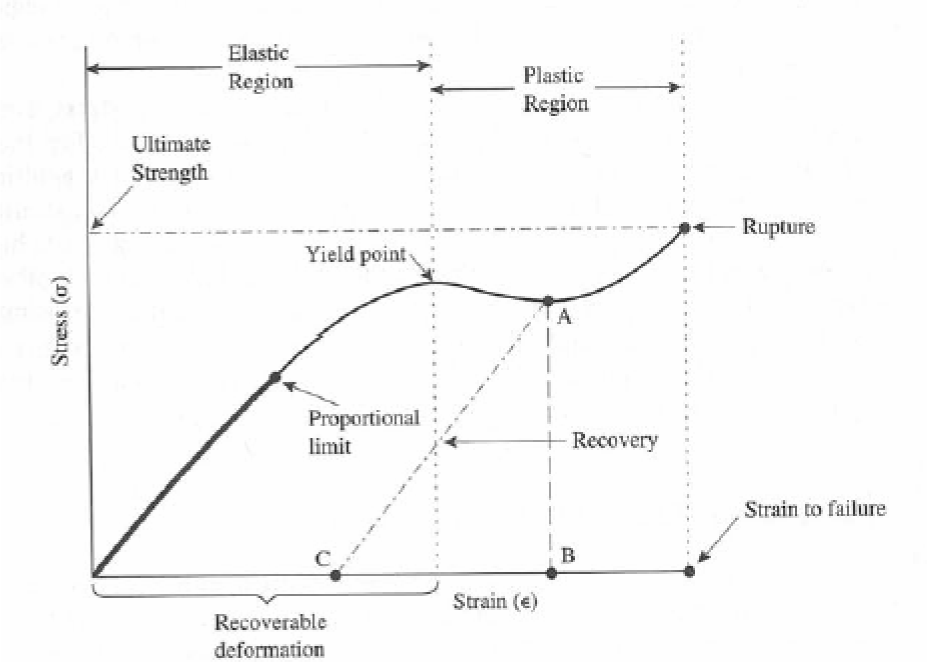


Figure 2.22 Stress-strain behavior over the entire strain range for a typical polymeric material [31].

Tensile strength (nominal), σ_m is the maximum tensile stress sustained by the specimen during a tension test. When the maximum stress occurs at the yield point, it is designated tensile strength at yield. When the maximum stress occurs at break, it is designated tensile strength at break [30].

2.8.1.2 Impact Test

Impact tests measure the energy required for failure when a standard specimen receives a rapid stress loading. The impact strength of a polymer can be measured employing a number of techniques including the Izod and the Charpy tests. For both the Izod and Charpy tests a hammer like weight strikes a specimen and the energy-to-break is determined from the loss in the kinetic energy of the hammer [20]. The specimen can be a notched or unnotched bar.

The standart test method of these two tests are found in ASTM D256-92. In this study, Charpy impact test was applied to polymer blends and composites to find out their degree of toughness. In Charpy test, the specimen is supported on both ends and struck in the middle. If the notch is present, it is on the side away from the striker. The hammer is released and allowed to strike through the specimen as represented in Figure 2.21.

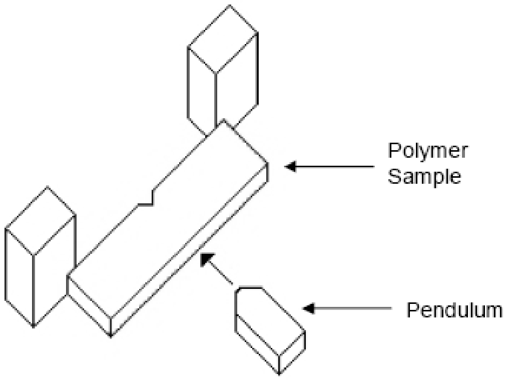


Figure 2.23 Schematic representation of Charpy impact test with notced bar

In high speed tensile tests and similar tests on unnotched specimens, the impact strength is defined in terms of the area under the stress-strain curve or as energy to break. For notched Charpy tests, impact strength is defined as:

Impact Strength = absorbed energy / initial cross-sectional area behind notch (2.4)

2.8.2 Scanning Electron Microscopy (SEM)

Scanning electron microscopy is very important and useful technique to examine the surface of the material with higher magnifications. SEM has become one of the most used instruments in research areas today because of the large depth of focus, greater resolution, and ease of sample preparation. SEM shows very detailed 3-dimensional images at much higher magnifications than is possible with a light microscope [7].

In SEM analysis, the surface of a specimen to be examined is scanned with an electron beam, and the reflected (or back-scattered) beam of electrons is collected, and then displayed at the same scanning rate on a cathode ray tube. The image on the screen, which may be photographed, represents the surface features of the specimen. The surface must be electrically conductive; therefore a very thin metallic surface coating must be applied to nonconductive materials. Magnifications ranging from 10 to in excess of 50000 diameters are possible [32]. Schematic representation of SEM mechanism is given in Figure 2.22.

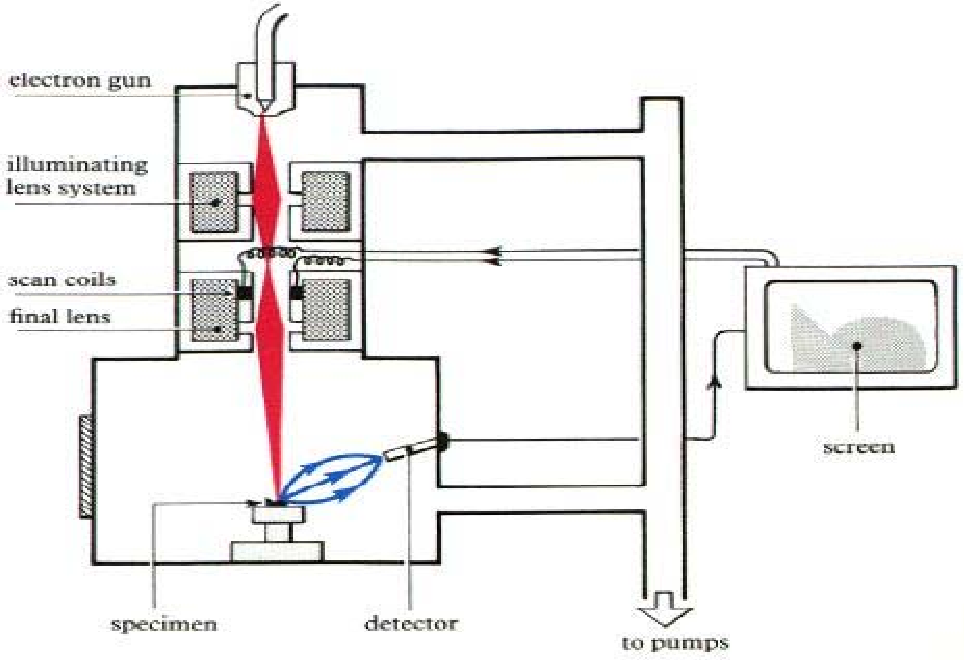


Figure 2.24 Schematic representation of scanning electron microscope [33].

CHAPTER 3

EXPERIMENTAL

3.1 Materials

In this study low-density polyethylene and polypropylene is used as polymer matrices, $CaCO_3$ is used as inorganic filler and Lica 12 is used as titanate coupling agent. This section involves origins and properties of these materials briefly.

3.1.1 Low-Density Polyethylene (LDPE)

Low density polyethylene was purchased from Petkim Petrokimya Holding A.Ş, İzmir, Turkey. The commercial name of the LDPE used is "*Petilen G 03-5* " and it is packaged as pellet form in 25 kg white colored PE bags. This type of LDPE is used in production of industrial films, bottles, containers and pipes, cable coating, etc. Physical properties of LDPE obtained from the company are given in Table 3.1.

Table 3.1 Physical Properties of LDPE

Property	Unit	Value	Test Method
MFI (Melt Flow Index) (2.16 kg, 190°C)	g /10min	0.2 – 0.4	ASTM D-1238
Density (23°C)	g /cm^3	0.919 – 0.923	ASTM D-1505

3.1.2 Polypropylene (PP)

Polypropylene was supplied from İŞBİR Holding A.Ş., Bursa, Turkey and has a trade name of "*100-GA02*". This homopolymer PP resin is a versatile general purpose grade which can be used in many different applications such as thermoforming, flexible packaging, etc. Some physical, mechanical and thermal properties are illustrated in Table 3.2.

Table 3.2 Properties of PP

Property	Unit	Value	Test Method
MFI (Melt Flow Index) (2.16 kg, 230°C)	g /10min	2.0	ISO 1133
Density (at 23°C)	g /cm^3	0.905	ASTM D-1505
Tensile Strength (at 23°C)	MPa	35	ISO 527-1,-2
Izod Impact Strength (notched, at 23°C)	kJ/m^2	4	ISO 180/1A
Melting Point	°C	163	ASTM D-3417

3.1.3 $CaCO_3$

$CaCO_3$ used in this study was supplied from Omya Mining A.Ş., İstanbul, Turkey. Its trade name is "*OMYACARB 2-KA*". The chemical composition and physical properties of this filler are illustrated in Table 3.3 and 3.4, respectively.

Table 3.3 Chemical Composition of $CaCO_3$

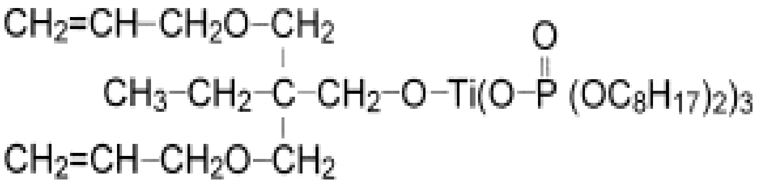
Materials	Composition (wt%)
$CaCO_3$	98.5
$MgCO_3$	1.5
Fe_2O_3	0.05
Amount insoluble in HCl	0.2

Table 3.4 Physical properties of $CaCO_3$

Property	Value
Average Particle Size	3.0 µm
Density	2.7 g/cm^3
pH	9.5
Humidity (plant outlet)	0.3 %

3.1.4 Titanate Coupling Agents

In this study titanate coupling agents were used to investigate their effects on mechanical and morphological properties of LDPE and PP blends and composites. For this purpose a kind of neoalkoxy organo-titanate which is appropriate for these polymers and filler was selected and purchased from Kenrich Petrochemical Inc., USA. The trade name of this titanate coupling agent is "**Lica 12**" and its chemical name is "*Titanium IV 2,2 (bis 2-propenolatomethyl) butanolato, tris (dioctyl) pyrophospato -O* ". Chemical structure of Lica12 is illustrated in Figure 3.1.



$$\begin{array}{l} CH_2{=}CH{-}CH_2O{-}CH_2 \\ \qquad\qquad\quad | \\ \qquad CH_3{-}CH_2{-}C{-}CH_2{-}O{-}Ti(O{-}\overset{\overset{\displaystyle O}{\|}}{P}(OC_8H_{17})_2)_3 \\ \qquad\qquad\quad | \\ CH_2{=}CH{-}CH_2O{-}CH_2 \end{array}$$

Figure 3.1 Chemical structure of Lica 12

Lica 12 has three physical forms that can be used for different purposes in many areas: liquid, powder and pellet forms. In this study two forms of Lica 12 were used:

1- Capow L12/H: It is the powder form of Lica 12 and its name comes from the abbreviation of "**C**oupling **A**gent **Pow**der form of **L**ica **12**". Its chemical composition involves 65% Lica 12 and 35% hydrated amorphous silica. This type of Lica 12 was used to coat the surface of $CaCO_3$ by a treatment before incorporation to polymer melt compounding. When Capow L12/H is added directly into polymer melt at about 190°C, decomposition of titanate molecules occurs and their activity between filler and polymer is restricted.

2- Caps L12/L: This is the pellet form of Lica 12 and its name comes from the abbreviation of "**C**oupling **A**gent **P**ellet **S**ystem form of **L**ica **12**". It has a chemical composition of 20% Lica 12, 69% LLDPE as binder and 11% hydrated amorphous silica. This type of Lica 12 was used in PP/LDPE blends by direct addition into melt blending.

3.1.4.1 Treatment of $CaCO_3$ with Capow L12/H

$CaCO_3$ particles surface were coated with Capow L12/H which is powder form of titanate coupling agent Lica 12. This treatment is done by using toluene as solvent. Titanate amount was set as 0.7 wt % of $CaCO_3$ employed. Since 65% of Capow L12/H contains active titanate, calculation of amounts was done in accordance. For instance, 400 g $CaCO_3$ requires 2.8 g titanate for treatment which corresponds to 4.31 g Capow L12/H. The calculated amount of Capow L12/H was dissolved in 400 ml toluene at 30°C on a heater then, 400 g $CaCO_3$ was added to this solution and they were stirred intensively to achieve good dispersion of titanate molecules among filler particles. After mixing and waiting for 10 minute interval, the slurry was taken on a wide tray and put into an oven at 30°C in order to remove toluene. The mixture is kept in the oven for 24 hours and then fine particles of titanate-treated filler were powderized. The temperature was kept rather low for dissolution and drying since titanate may be lost by evaporation.

3.2 Experimental Procedure

Materials were processed in two ways to prepare two different types of material:

1- Internal mixing was applied by using Brabender to obtain PP and LDPE homopolymer composites.
2- Extrusion process was done for obtaining PP/PE blends and their composites.

After these melt processes, products obtained are injection molded to form in a dog-bone shaped specimen. Specimens were used for tensile and impact tests. After tensile tests, fractured surfaces were examined with scanning electron microscopy (SEM) for morphological analysis.

3.2.1 Internal Mixing

A counter-rotating internal mixer was used in order to obtain PP and PE composites. The model of the internal mixer is Brabender Plasti-Corder Torque Rheometer, PLV-151. Figure 3.2 shows the equipment used in this study.

Figure 3.2 a) Photograph of Brabender with its heating tank and indicators

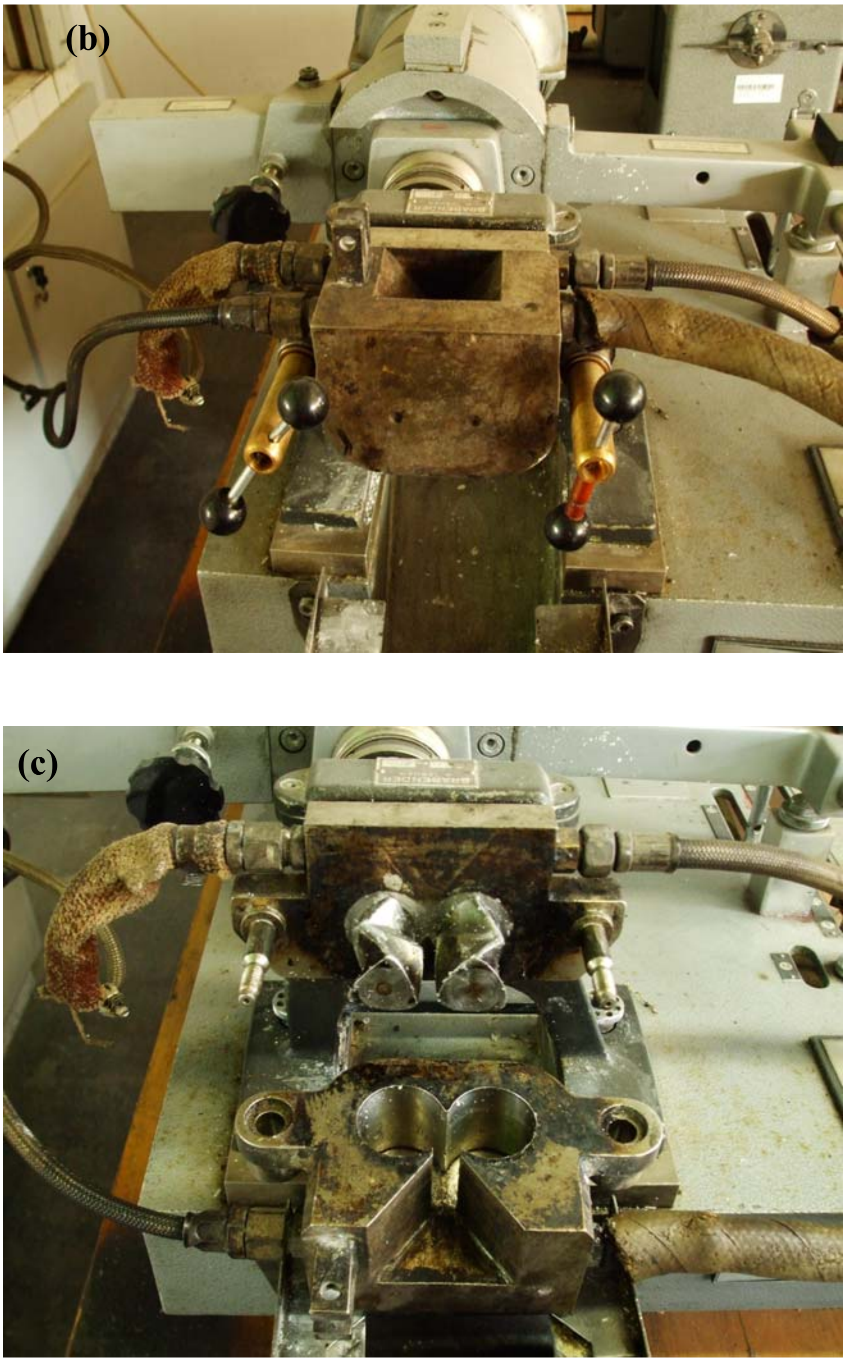


Figure 3.2 (cont'd) b) Mixing chamber of Brabender (closed as in operation)
c) Screw configuration and open chamber of Brabender

3.2.1.1 Sample Preparation and Mixing Parameters in Brabender

Composites of PP and LDPE with $CaCO_3$ were produced by internal mixing in Brabender. In the first set of experiments PP/$CaCO_3$ composites were prepared with the filler contents of 20, 40, 60 % as control experiments. Then in the second set of experiments Capow L12/H treated $CaCO_3$ was used with the same ratios for producing PP/$CaCO_3$ composites with titanate coupling agent. Same experiments were done for LDPE/ $CaCO_3$ composites with the same filler contents. In all mixing processes polymers were molten in Brabender's chamber which has $50cm^3$ volume and then filler was added onto melt polymer. Brabender was operated with constant screw speed of 60 rpm and mixing time was 10 min for PP/$CaCO_3$ composites and 20 min for LDPE/$CaCO_3$ composites. Process temperature was adjusted to 190^oC for LDPE composites and 200^oC for PP composites. The temperatures were decreased by 10^oC for PP and LDPE composites with titanate coupling agents in order to compensate the viscosity reduction effect of the titanate. At a lower temperature the shear rate will be approximately the same for both cases. Total of 12 polymer composites were produced; 6 for LDPE composites, 6 for PP composites. These samples are listed in Table 3.5 with their compositions and sample codes. In sample codes the numbers of 100, 80, 60 and 40 coming after polymers' abbreviations indicates the percentage of defined polymer in the composite. The letters of "Cpw" used after that number represents the presence Capow L12/H as titanate coupling agent.

Table 3.5 Sample Codes and compositions produced with Brabender

			Concentration (wt%)		
Polymer	**Sample No**	**Sample Code**	**Polymer matrix** (wt%)	**$CaCO_3$** (wt%)	**Capow L12/H treated $CaCO_3$** (wt%)
PP	**1**	**PP100**	100	-	-
	2	**PP80**	80	20	-
	3	**PP80-Cpw**	80	-	20
	4	**PP60**	60	40	-
	5	**PP60-Cpw**	60	-	40
	6	**PP40**	40	60	-
	7	**PP40-Cpw**	40	-	60
LDPE	**8**	**LDPE100**	100	-	-
	9	**LDPE80**	80	20	-
	10	**LDPE80-Cpw**	80	-	20
	11	**LDPE60**	60	40	-
	12	**LDPE60-Cpw**	60	-	40
	13	**LDPE40**	40	60	-
	14	**LDPE40-Cpw**	40	-	60

3.2.2 Melt Blending with Extrusion

In this study a co-rotating twin screw extruder was used for melt blending in order to obtain PP/PE blends and their composites. The model of extruder is "*Thermo Prism TSE 16 TC*" with L/D ratio of 24. The specifications of this extruder are illustrated in Table 3.6. In this extruder there are two feeders that can be operated simultaneously: first is main feeder that polymer pellets can be fed through and the second is side feeder that fillers can be fed through into the extruder. Their feeding rates can be adjusted according to desired composition of polymers and fillers. Also barrel zone temperatures including die temperature can be set at five points and screw speed is set by using the same control panel. Figure 3.3 shows the extruder with its control panel (a) and its screw configuration (b).

Table 3.6 Specifications of Thermo Prism TSE 16 TC Extruder

Thermo Prism TSE 16 TC	Unit	Value
Barrel Length	mm	384
Barrel bore diameter	mm	16
Screw diameter	mm	15.6
Screw speed (max.)	rpm	500
Torque (max.)	Nm	12
Internal free volume	cm^3	68
Peripheral surface area	cm^2	316
Surface area/unit free volume	m^2/ lt	0.47

Figure 3.3 a) Picture of Thermo Prism TSE 16 TC Extruder and its control panel

Figure 3.3 (cont'd) b) Screw configuration of Thermo Prism TSE 16 TC Extruder.

3.2.2.1 Sample Preparation and Extrusion Parameters

Polypropylene/low-density polyethylene (PP/LDPE) blends and their composites were produced in twin-screw extruder. Prior to extrusion, materials were dried to remove moisture at different conditions that are shown in Table 3.7.

Table 3.7 Drying conditions of materials before extrusion

Material	Drying Temperature (^{o}C)	Drying Time (h)
PP	80	24
LDPE	60	12
$CaCO_3$	60	24
Capow L12 treated $CaCO_3$	30	24
Caps L12	30	12

In the first set of experiments PP/LDPE blends were prepared with ratios of 75/25, 50/50 and 25/75 as control experiments. PP and LDPE pellets were fed into extruder from main feeder together according to blend ratios with flowrate of 20 g/min. The other experiments in extruder were done by the basis of these three blends and the other blends and composites were compared with them. In the second set of experiments ternary blends of PP/LDPE/Caps L12 was prepared by feeding all pellets through the main feeder into the extruder. The flowrate is adjusted to 20 g/min. In the third set of experiments Capow L12 treated and untreated CaCO3 was mixed with PP/LDPE blends of three different ratios as mentioned. Polymer pellets with desired ratio are put into main feeder and fed to extruder with flowrate of 20g/min while the filler is fed through side feeder with flowrate of 5g/min. Thus, composites include 80% of polymer matrix (PP+LDPE) and 20% of filler. All samples produced in the extruder are illustrated in Table 3.8 with their sample codes and concentrations.

Table 3.8 Sample Codes and compositions produced with extruder

			Concentration (wt%)			
PP/LDPE (wt/wt)	**Sample No**	**Sample Code**	**Polymer matrix** (wt%)	**$CaCO_3$** (wt%)	**Capow L12 treated $CaCO_3$** (wt%)	**Caps L12** (wt%)
75/25	**1**	**PP75/0**	100	-	-	-
	2	**PP75/0-Caps L12**	100	-	-	0.5
	3	**PP75/20**	80	20	-	-
	4	**PP75/20-Capow L12**	80	-	20	-
50/50	**5**	**PP50**	100	-	-	-
	6	**PP50/0-Caps L12**	100	-	-	0.5
	7	**PP50/20**	80	20	-	-
	8	**PP50/20-Capow L12**	80	-	20	-
25/75	**9**	**PP25**	100	-	-	-
	10	**PP25/0-Caps L12**	100	-	-	0.5
	11	**PP25/20**	80	20	-	-
	12	**PP25/20-Capow L12**	80	-	20	-

The temperatures and screw speed were adjusted from the control panel as extrusion parameters. Screw speed was set to 200 rpm in all experiments. The temperature profile of the barrel was 200-200-200-200-200°C from hopper to the die for PP/PE blends and composites without titanates. The temperatures were decreased to 190°C at all barrel zones for PP/PE blends and composites with titanates because titanates have viscosity reduction effect and so make the melt less viscous leading to low shear rate. Since mixing is more effective at high shear rates, temperatures were decreased in order to decrease the effect of viscosity reduction on shear rate. Temperature profiles are given in Table 3.9.

Table 3.9 Temperature profle of extruder for all experiments

	Temperatures (°C)				
	Inlet	Mixing Zones			Die
PP/PE systems without titanates	200	200	200	200	200
PP/PE systems with titanates	190	190	190	190	190

3.2.3 Injection Molding

Samples were dried at 80°C for 24 hours before injection molding process. The specimens for mechanical tests were obtained by using injection molding machine (*Daca Instruments*). Its schematic representation is illustrated in Figure 3.4. In this molding machine the parameters that can be controlled are: barrel temperature, mold temperature, injection time, speed and pressure. Barrel temperature was adjusted to 220°C for PP/$CaCO_3$ composites and all PP/LDPE blends and composites. This temperature was taken as 200°C for LDPE/$CaCO_3$ composites. All materials were kept in this barrel for 1.5 minute and they were injected to mold.

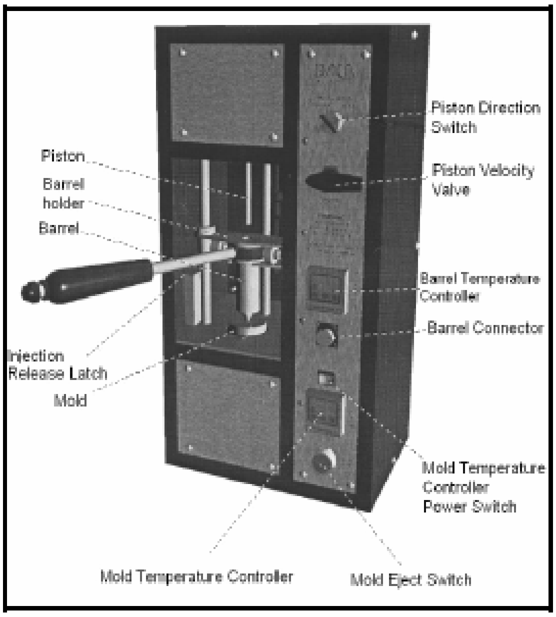


Figure 3.4 Injection molding machine

3.3 Characterization

Morphological and mechanical properties of polymer blends and composites were examined by SEM analysis, tensile test and impact test. Aim of this characterization is to investigate the effects of titanate coupling agents, filler ratio and composition of polymers on the properties of final products.

3.3.1 Mechanical Tests

3.3.1.1 Tensile Tests

Tensile tests are performed with "*Lloyd LS 5000*", computer controlled mechanical testing machine, which is shown in Figure 3.5.

Figure 3.5 Picture of Lloyd LS 5000 tensile test machine

The test was carried out under constant strain rate of 5cm/min. The specimen was pulled at this constant rate of extension until the center of the specimen fails. The shape and dimensions of the specimens are given in Figure 3.6 and Table 3.10, respectively. After stress vs. strain diagrams of the measurements were examined; tensile strength, percentage strain at break and Young’s modulus values were obtained from the computer program of Lloyd tensile machine. For each sample, average results of at least five measurements were recorded.

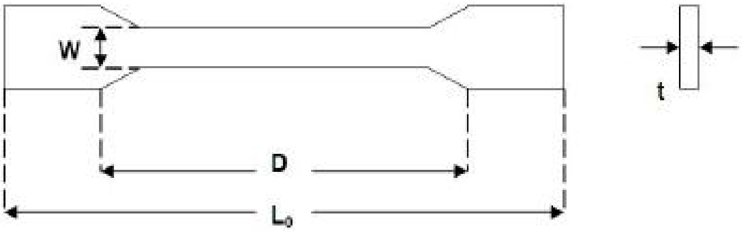


Figure 3.6 Dog-bone shaped specimen for tensile test

Table 3.10 Dimensions of tensile test specimen

Symbol, Term	Dimension (mm)
D - distance between grips	80
L_0- overall length	110
T- Thickness	2
W-width of narrow section	7.6
Gauge length	50

3.3.1.2 Impact Test

Bar shaped specimen, obtained by cutting out of grips of dog-bone shaped specimen, were used for impact test. The dimensions of the bar shaped samples were 60mm x 7.5mm x 2mm. The notches were formed by a notcher (Notchvis, Ceast) with using a V-shaped knife in it. The depth of notch was determined as 2 mm in the middle of the specimen by electronic displacement measurement. V-shape notched specimens were tested with pendulum impact tester of Ceast Resil Impactor at room temperature of 22°C.

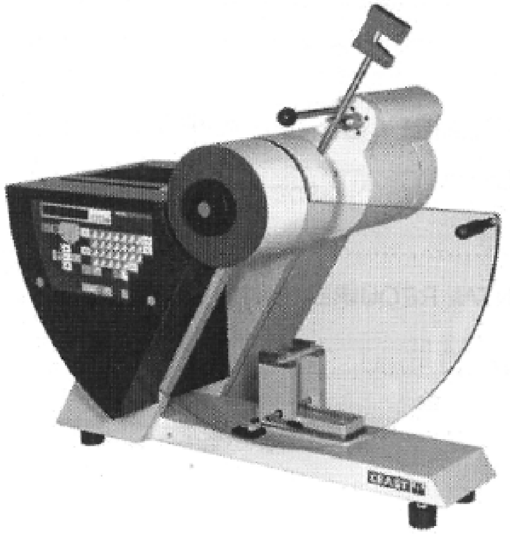


Figure 3.7 Ceast Resil Impactor Machine

3.3.2 Morphological Analysis (SEM)

In morphology observation, samples that were fractured in tensile test were investigated. In tensile test dog-bone shaped samples were elongated up to rupture and obtained fracture surface was prepared for SEM observation. The fracture surfaces of the samples were investigated by using "*QUANTA 400F Field Emission SEM*" with high resolution of 1.2 nm**.** The instrument is demonstrated in Figure 3.8. The surfaces were coated with a thin layer of gold to provide a conductive surface. Several micrographs of fracture surfaces were taken for each sample at various magnifications. This analysis was made to investigate the effect of titanate coupling agent on dispersion and behaviour of fillers in the polymer matrix for LDPE and PP composites and compatibility of PP/LDPE blends.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Mechanical Analysis

Effects of titanate coupling agents on the mechanical properties of polypropylene and low density polyethylene composites and their blends were investigated by mechanical tests. Tensile and impact tests were performed on injection molded specimens of produced polymeric materials. Mechanical properties were measured on at least five specimens and the test results discussed in this part are the average values of appropriate specimens for each material. Test results are given and discussed in this section by classifying them into 3 parts according to material and their process types. These are PP/$CaCO_3$ composites, LDPE/$CaCO_3$ composites and PP/LDPE blends and composites. Polymer composites were processed in Brabender and polymer blends were processed in extruder so, test results of different types of composites were not compared. The test results were compared with each other for 3 types of polymer compounds separately. Effects of titanate coupling agents were investigated according to polymer type, filler content, titanate type and composition of polymer blends.

4.1.1 Tensile Properties

Tensile tests were performed for all samples to obtain stress-strain curves. Stress – strain curves provide information about tensile strength, percentage strain at break and Young's (elastic) modulus values of materials. In this part these three properties are discussed for three different types of material.

4.1.1.1 Tensile Properties for PP/$CaCO_3$ Composites

The tensile tests performed on PP/$CaCO_3$ composites where untreated and titanate treated filler was incorporated with ratios of 20, 40, 60%. Their tensile properties are compared with each other to investigate effects of titanate coupling agent and filler content. Titanate coupling agent was used to coat $CaCO_3$ surface with the dosage of 0.7% of filler and added to polymer matrix via treated $CaCO_3$. Neat PP was processed under the same conditions in Brabender in order to obtain its tensile properties as reference to the other PP containing compositions. Stress-strain curves are illustrated in Figures 4.1 to 4.3.

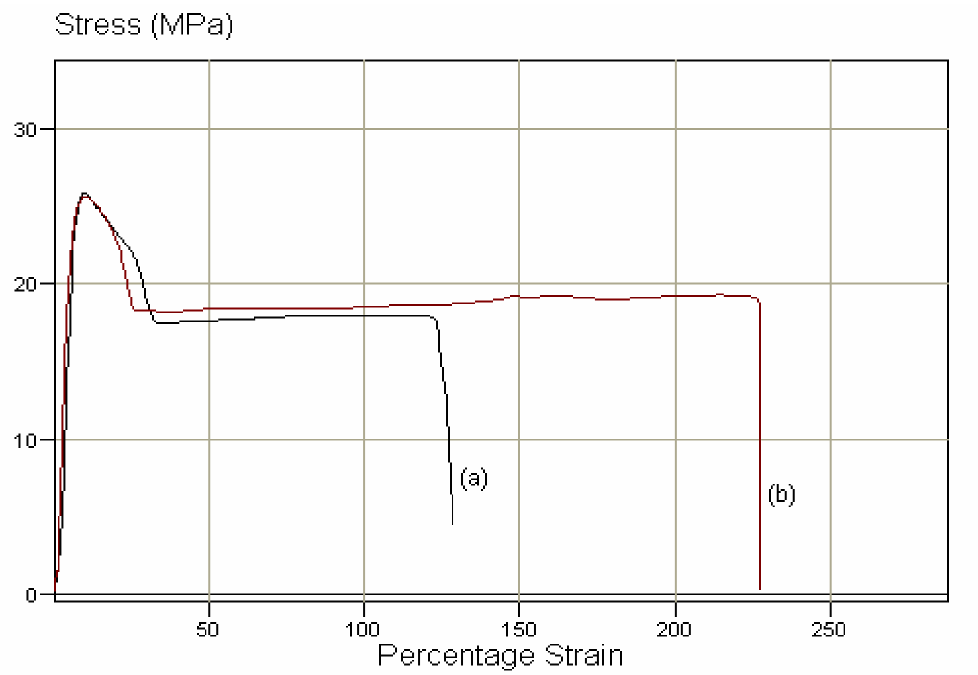


Figure 4.1 Stress-strain curves for PP composites 20% filled with a) untreated $CaCO_3$ b) titanate-treated $CaCO_3$.

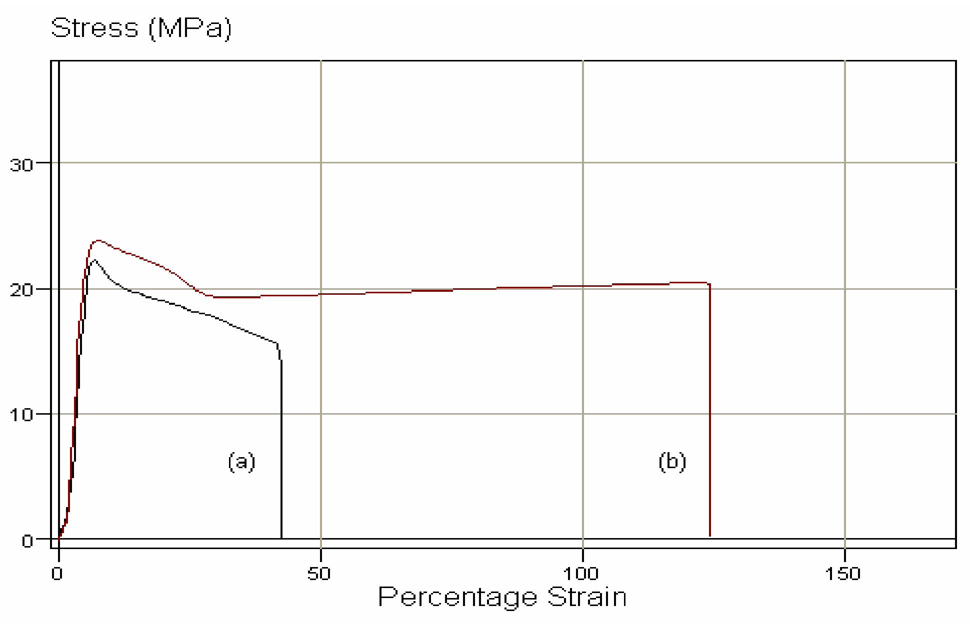


Figure 4.2 Stress-strain curves for PP composites 40% filled with a) untreated $CaCO_3$ b) titanate-treated $CaCO_3$.

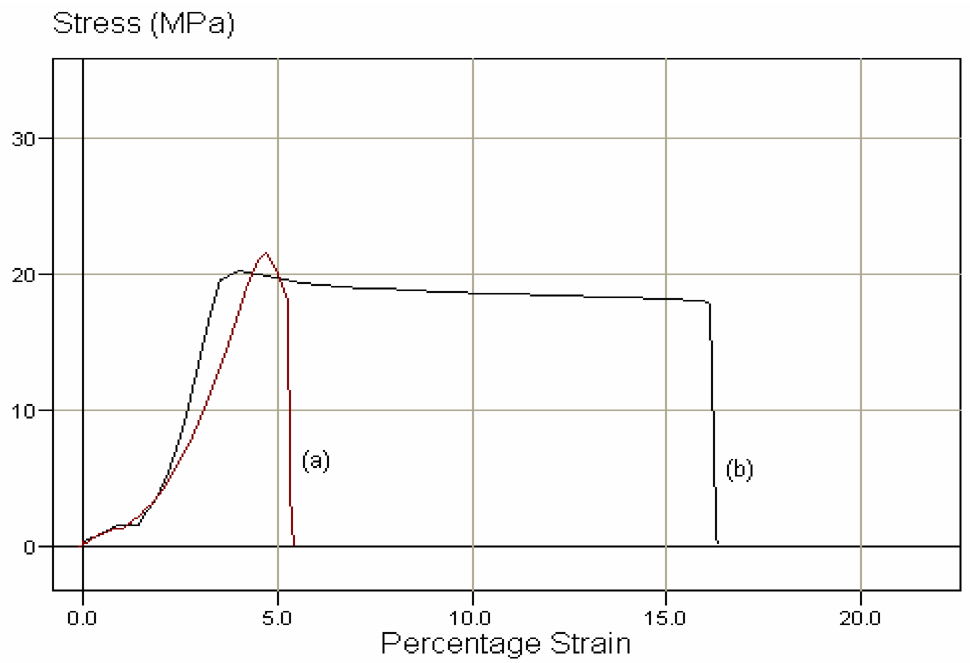


Figure 4.3 Stress-strain curves for PP composites 60% filled with (a) untreated $CaCO_3$ b) titanate-treated $CaCO_3$.

From these curves tensile property values of PP/$CaCO_3$ composites were obtained and their averages were calculated. These results are shown in Figures 4.4 to 4.6.

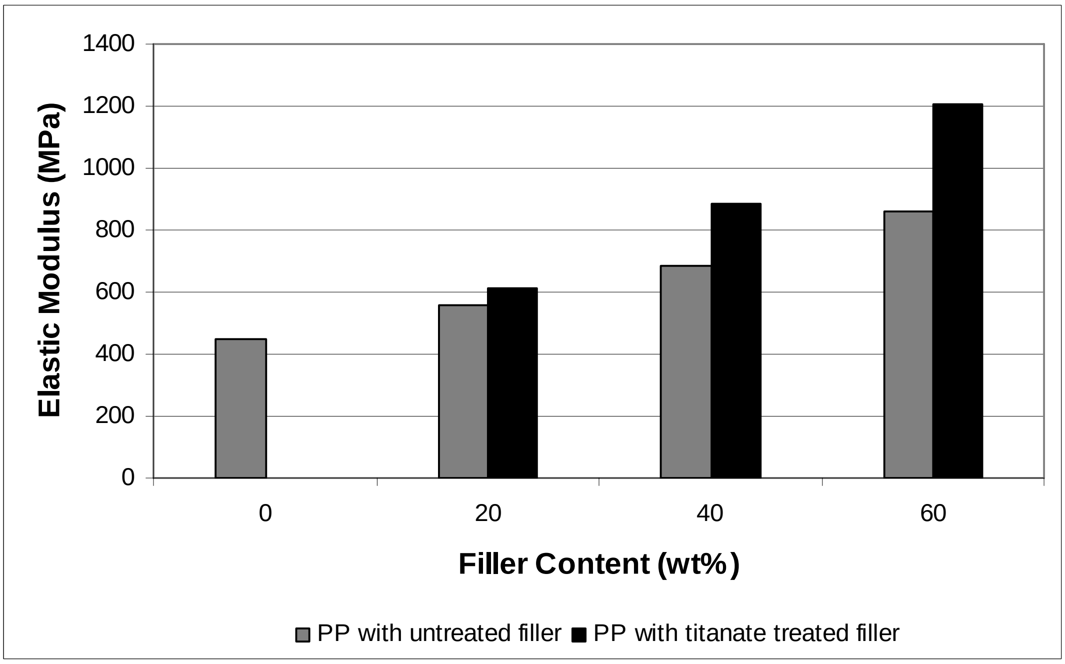


Figure 4.4 Elastic modulus values of PP/$CaCO_3$ composites

As shown in Figure 4.4 elastic (Young's) modulus values of PP/ $CaCO_3$ composites increase as filler content increases. It is seen that titanate coupling agents have positive effect on elastic modulus in all compositions. As filler content increase, titanate makes the composite's modulus much higher. This can be explained by the improvement of the interaction between polymer matrix and filler due to effective interfacial adhesion of titanate molecules. Thus, PP/$CaCO_3$ composites can resist to high stresses with the aid of coupling agent.

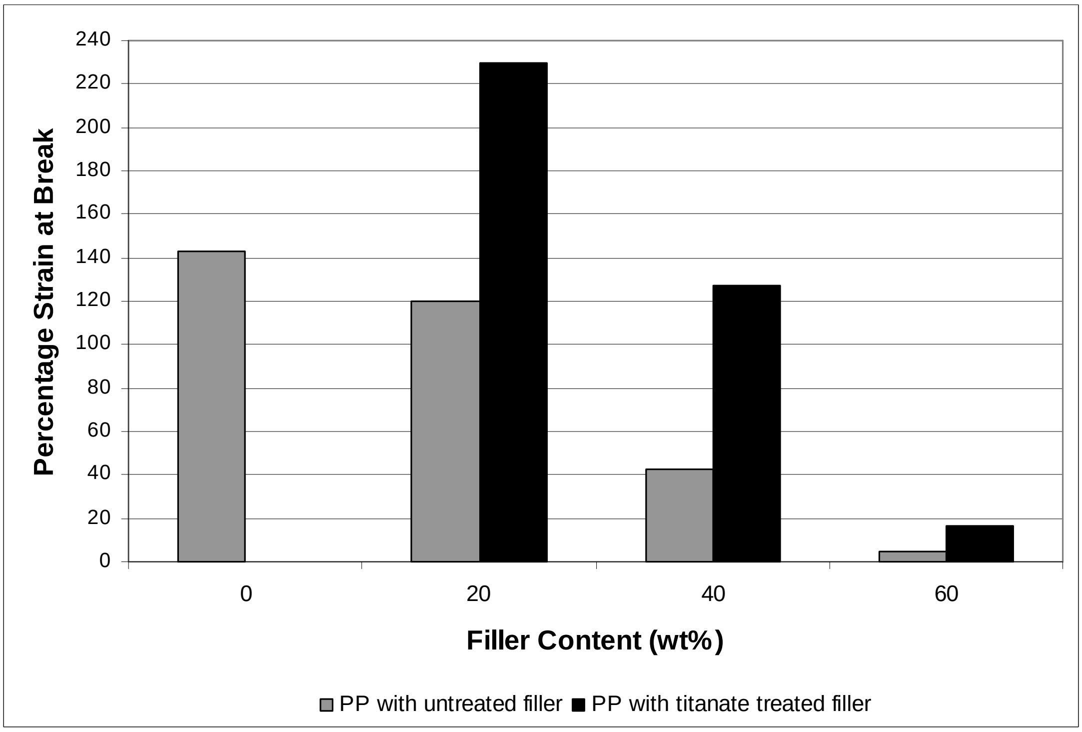


Figure 4.5 Percentage strain at break values of PP/$CaCO_3$ composites

In Figure 4.5 results of percentage strain at break values are given. Neat PP has the highest strain among untreated filled PP composites. As the ratio of untreated $CaCO_3$ goes up from 0 to 60%, percentage strain of composites decreases from about 142% to 4.7%. It is known that inorganic filler restricts the segmental mobility of polymer since continuity of segments is impeded by inorganic particles. Therefore, elongation of PP/$CaCO_3$ composites decreases with respect to increasing filler content. However, PP composites with titanate-treated filler have significantly higher strains than the ones with untreated filler. At 20% filler level, titanate coupling agents raised the percentage strain from 120% to 224%, approximately 2 times higher which is even higher than that of neat PP. At 40 % filler level percentage strain increased from 40% to 120% and at 60 % filler level it improved from 4.7% to 16.8%. Capow L12 treated samples have about 3 times higher strain values. With a different view, neat PP and 40% titanate-treated $CaCO_3$ filled PP have similar strain values. These results indicate that at 20% treated filler addition, a considerable improvement is obtained which should have a very positive effect on impact strength. Addition of treated filler also has an economic advantage as it makes possible to lower the cost per kg of PP.

These results can be explained with the plasticizing effect of titanate coupling agents. In the presence of titanate coupling agent, the dispersion of filler particles in polymer phase is enhanced by the lack of hydration water at surface of inorganic filler, with organofunctional titanate causing inorganic/polymer interface compatible, thereby eliminating air voids in the system [34]. A representation of this event has been mentioned in Figure 2.12 at "Dispersion Effect" part in Chapter 2. In addition to these results as seen in Figure 4.5, higher filler content would tend to reduce the plasticizing effect of the coupling agent, so percentage strain values of composites with titanate decrease as treated-filler content increase.

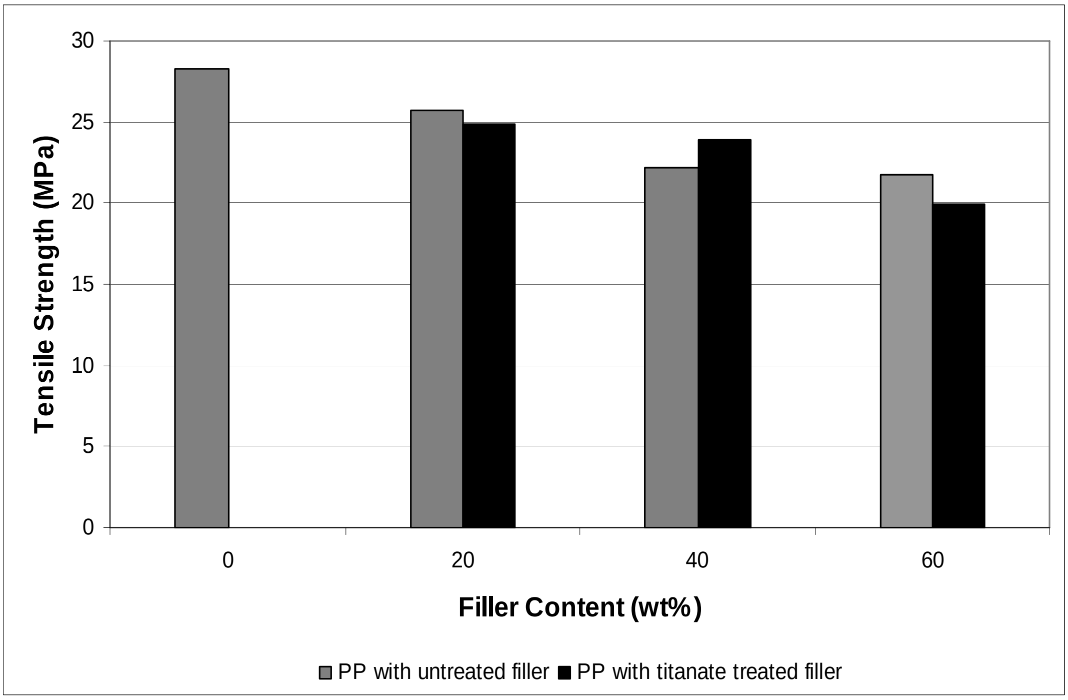


Figure 4.6 Tensile strength values of PP/$CaCO_3$ composites

There is no significant variation in tensile strength values as represented in Figure 4.6. The highest tensile strength value of 28.3 Mpa has been reached by neat PP. The other tensile strength values decrease very slightly as untreated-filler content increases as expected since inorganic fillers impede the mechanical resistance of polymers. Titanate treated-filler has little negative effect at 20% and 60% filler contents; however titanate molecules have a small positive effect at 40% filler level. According to these results it can be claimed that titanate coupling agents have not improved the tensile strength of PP/$CaCO_3$ composites.

4.1.1.2 Tensile Properties for LDPE/$CaCO_3$ Composites

LDPE/$CaCO_3$ composites were prepared with untreated and titanate treated filler with ratios of 20, 40 and 60%. Their tensile properties were measured to investigate effects of the titanate coupling agent and the filler content on LDPE/$CaCO_3$ composites. Neat LDPE processed with the same condition was used as reference sample. Stress-strain curves obtained from tensile testing machine are illustrated in Figures 4.7 to 4.9 at different filler contents.

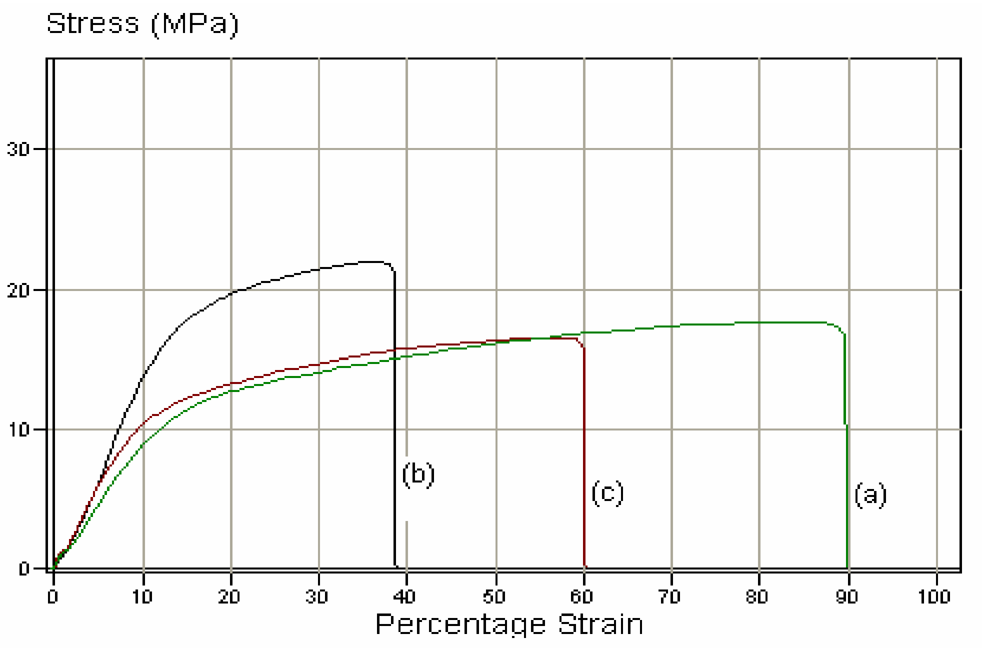


Figure 4.7 Stress-strain curves for a) 100% (Neat) LDPE b) LDPE filled with 20% untreated $CaCO_3$ c) LDPE filled with 20% titanate-treated $CaCO_3$

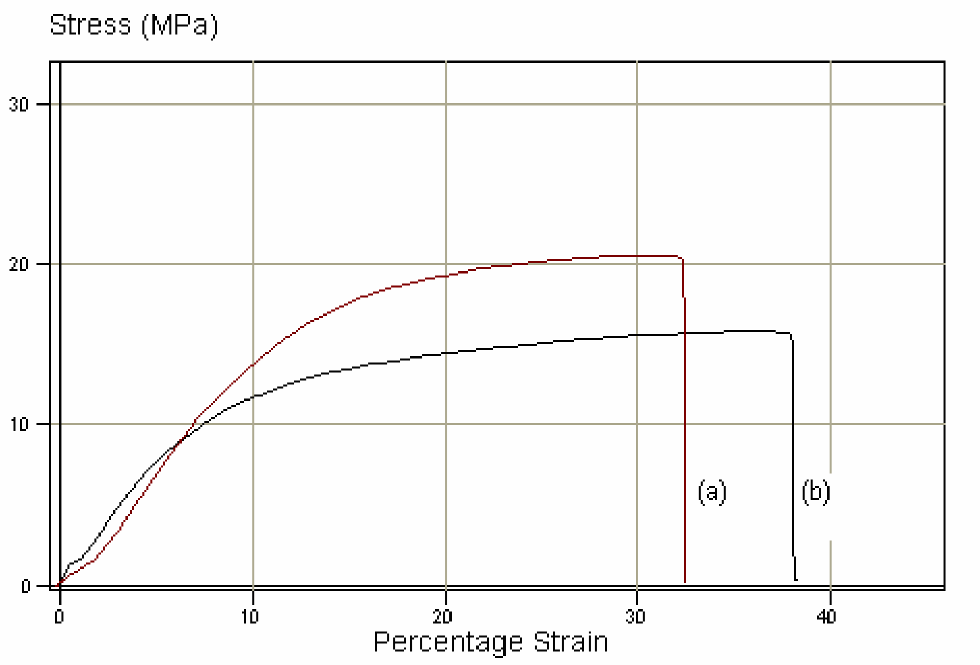


Figure 4.8 Stress-strain curves for LDPE composites 40% filled with a) untreated $CaCO_3$ b) titanate-treated $CaCO_3$

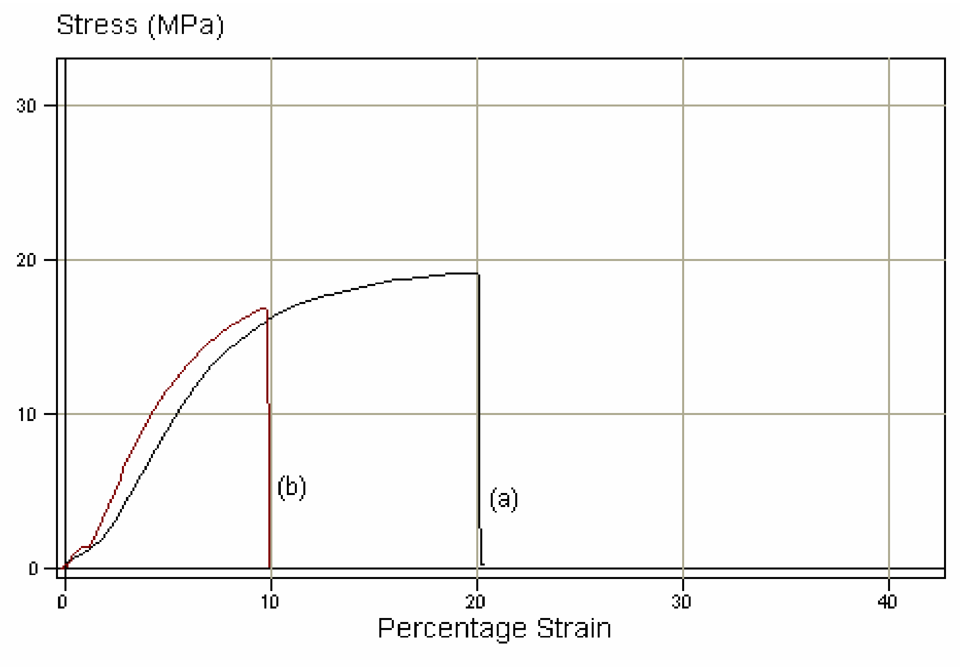


Figure 4.9 Stress-strain curves for LDPE composites 60% filled with a) untreated $CaCO_3$ b) titanate-treated $CaCO_3$

As it is seen from stress-strain curves, no necking is observed during tensile tests for all LDPE/$CaCO_3$ composites. Firstly a specimen was passing elastic region with a certain tensile modulus is observed, then it reached to a maximum stress and fracture of specimen occurred. Contrary to PP/$CaCO_3$ composites, decreasing of stress after maximum point was not seen and so, any drawing stress leading to elongation of specimen was not accomplished. The maximum elongation was achieved in neat LDPE and it can be considered as the most ductile material among all LDPE/$CaCO_3$ composites. Addition of untreated $CaCO_3$ to the virgin LDPE makes it less ductile. Also, the decrease in strain at break due to increasing of filler content is clearly observed in all Figures from 4.7 to 4.9. When titanate-treated $CaCO_3$ is added to LDPE, enhancement in strain at break and ductility can be observed at two filler ratios of 20% and 40%. On the other hand LDPE composites with titanate reached to lower maximum stress compared to the ones without titanate. This effect is observed at all filler levels.

Average values of tensile properties obtained from stress-strain curves for each composition were evaluated and the tensile results are shown in Figures 4.10 to 4.12.

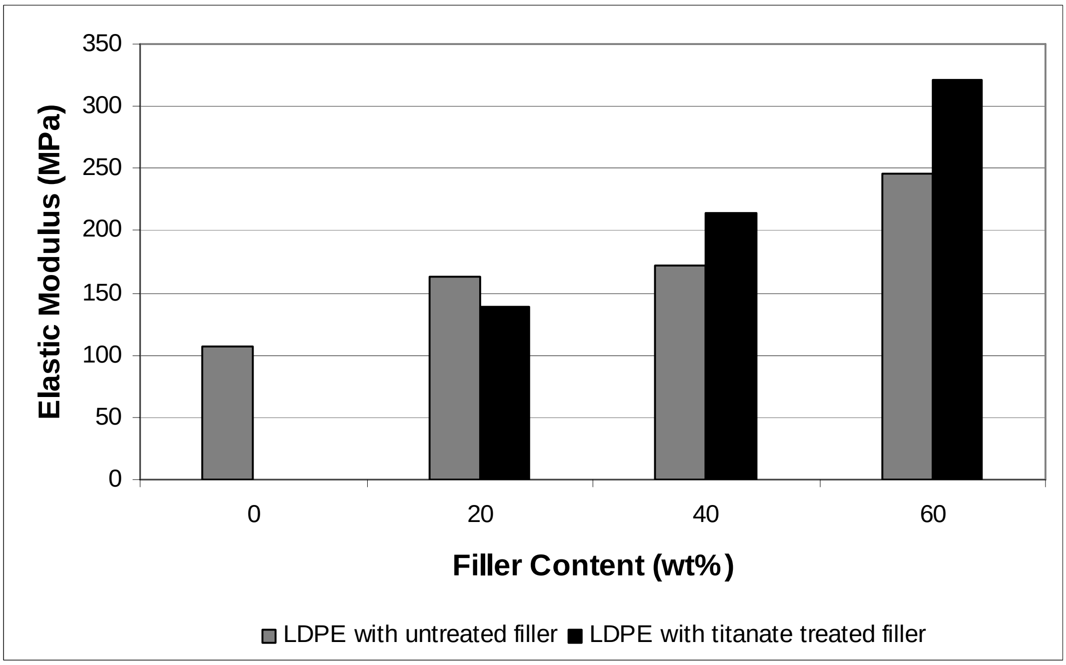


Figure 4.10 Elastic modulus values of LDPE/$CaCO_3$ composites

The Figure 4.10 shows that the elastic modulus increase gradually with increasing untreated filler content as observed in most particulate filled polymers. Titanate molecules have varying effects on Young’s modulus values according to different filler content. At 20% filler content, it is seen that elastic modulus of material decreased from 162 MPa to 140 MPa approximately with the presence of titanate coupling agents. At the other filler ratio of 40% and 60%, titanate molecules raised the elastic modulus of composites considerably. The results of young modulus values can be related to strain results, because high modulus causes the composite to be more brittle and it can restrict the elongation of the material.

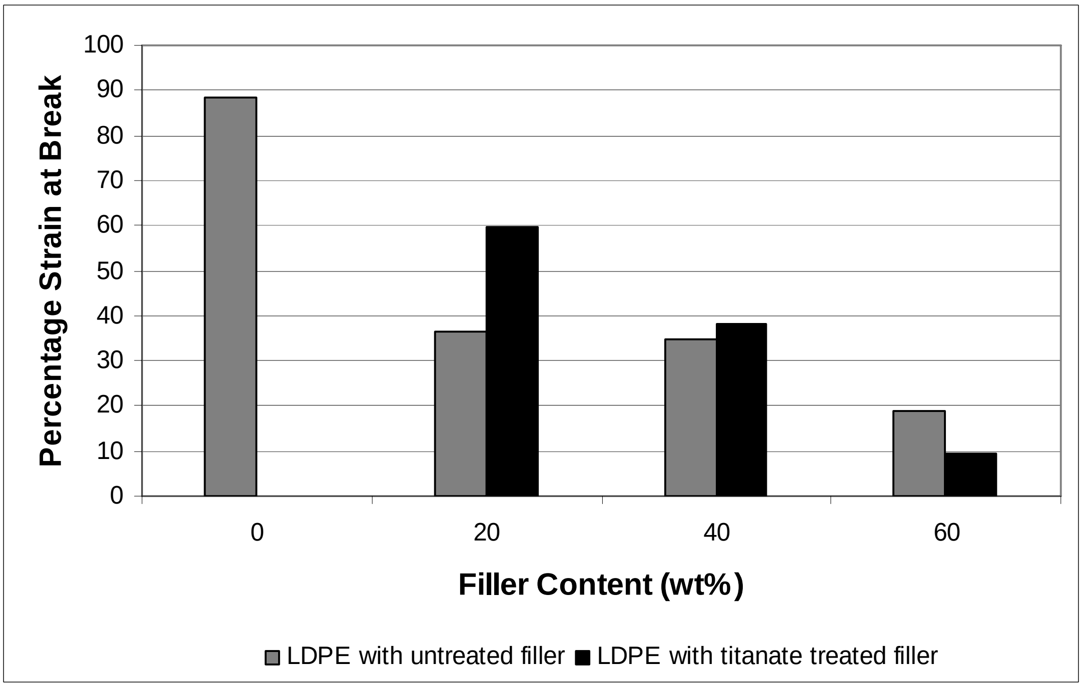


Figure 4.11 Percentage strain at break values of LDPE/$CaCO_3$ composites

According to Figure 4.11 showing percentage strain results, pure LDPE has the highest strain with the value of 89%. Composites 20% and 40% filled with untreated $CaCO_3$ have values of about36% and 34%, respectively. This means that percentage strain decreased by about 60% with addition of 20% untreated filler. As filler content goes to 60%, percentage strain decreased quitely to 19%. Titanate treated samples show almost 66% increase in 20% filled LDPE; they raised the percentage strain of this composite from 36% to 60%. However, this plasticizing effect of titanate coupling agent is not observed in 40% and 60% filled LDPE composites. At 40% filler lever, very slight increase from 34% to 38% can be achieved and at 60% level, a remarkable decrease from 19% to 9% can be seen.

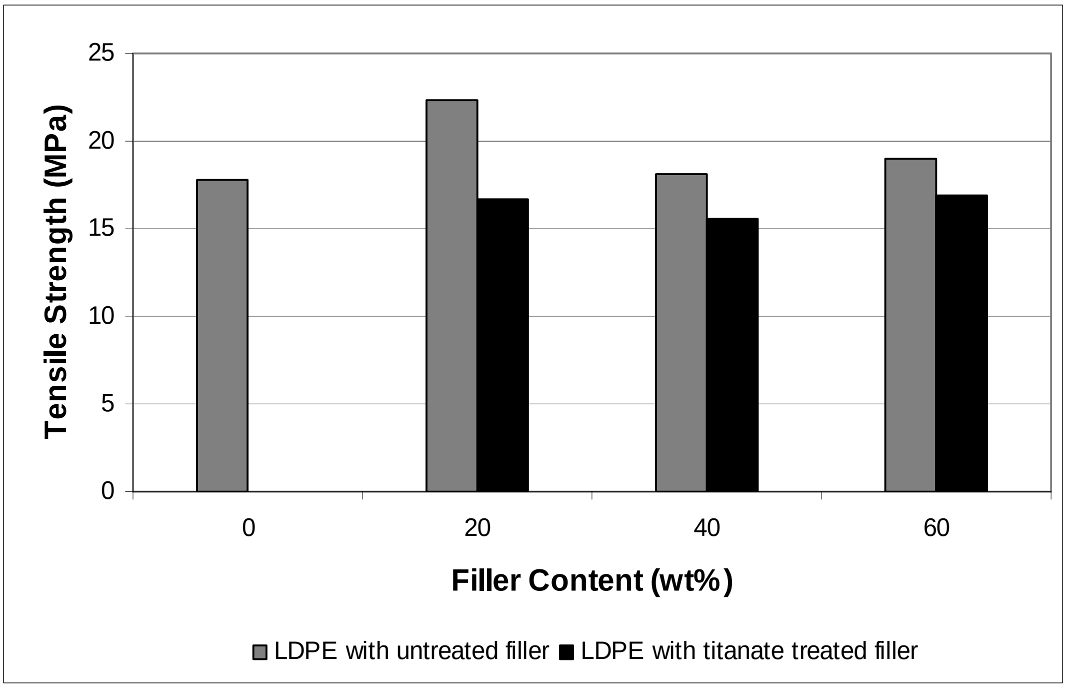


Figure 4.12 Tensile strength values of LDPE/$CaCO_3$ composites

In Figure 4.12 results of tensile strength show an oscillation between the values of 15.8 MPa to 22.3 MPa among all LDPE/$CaCO_3$ composites. Neat LDPE has a tensile strength of 17.8 MPa and with the addition of untreated $CaCO_3$ these values became 22.3 MPa, 18.1 MPa and 19.0 MPa with respect to filler contents of 20, 40 and 60%. It is seen that incorporation of titanate coupling agent to all compositions resulted in slight decrease in tensile strengths.

Influences of titanate coupling agent on tensile strength is relatively negative as seen in Figure 4.12. LDPE was moderately affected by untreated filler since fillers provide the polymer to gain mechanical resistance against applied load. Especially with 20% filler, composite reached maximum tensile strength value of 22.3 MPa. When titanate-treated filler was employed, the resistive compact chain became less compact and weaker compared to composites with untreated filler. The reason is that titanate molecules improves the dispersion of fillers so, agglomerations causing compactness can be eliminated. Therefore, tensile strengths of composites with titanate are lower than those of the untreated ones. A gradual decrease in tensile strength with incorporation of titanate coupling agents is observed as filler content goes higher. This gradually decrease result also supports dispersion effect of titanates on LDPE including composites. As filler content increases, dispersion effect of titanates becomes less efficient due to too high compactness that titanate molecules do not exhibit their function. Consequently, higher filler content tend to reduce activity of titanate coupling agents.

It is possible to say that the mechanical improvement was achieved considerably with appropriate filler content of up to 40% for LDPE/$CaCO_3$ composites. It is seen that titanate molecules did not work effectively for higher level filler composition.

4.1.1.3 Tensile Properties for PP/LDPE Blends and Composites

PP/LDPE blends were prepared in twin-screw extruder with ratios of 75/25, 50/50 and 25/75 from virgin polymers. The blends were produced with addition of Caps L12 which is in pellet form. The composites were formed by addition of titanate (Capow L12) treated and untreated $CaCO_3$ separately at a constant filler ratio of 20%. The PP/LDPE blends and composites were injection molded and dog-bone shaped samples were tested in tensile machine. Their test results were examined to investigate effects of titanate coupling agent on PP/LDPE blends and composites. Stress-strain curves were obtained and illustrated in Figures 4.13, 4.17 and 4.21 according to blend compositions of 75/25, 50/50 and 25/75, respectively.

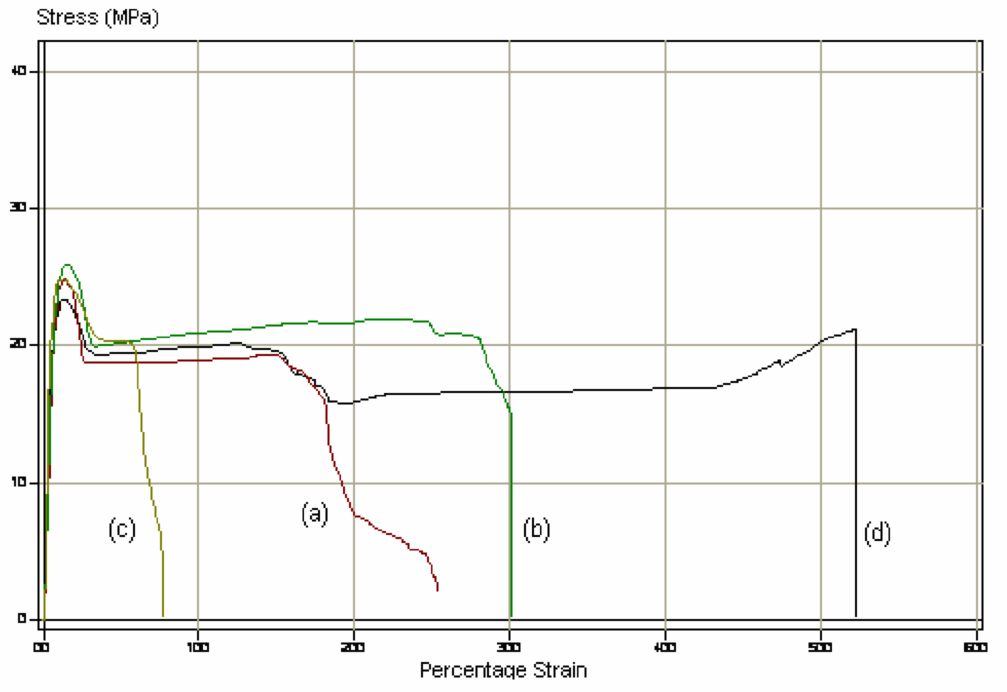


Figure 4.13 Stress-strain curves of PP/LDPE (75/25) blends and composites:

a) PP75/0 - Neat
b) PP75/0-Caps L12 - with 0.5% Caps L12
c) PP75/20 - with 20% untreated $CaCO_3$
d) PP75/20-Capow L12 - with 20% Capow L12-treated $CaCO_3$

Elastic (Young's) modulus, percentage strain at break and tensile strength values of PP/LDPE(75/25) blends and composites are shown as a function of filler content in Figures 4.14, 4.15 and 4.16 respectively.

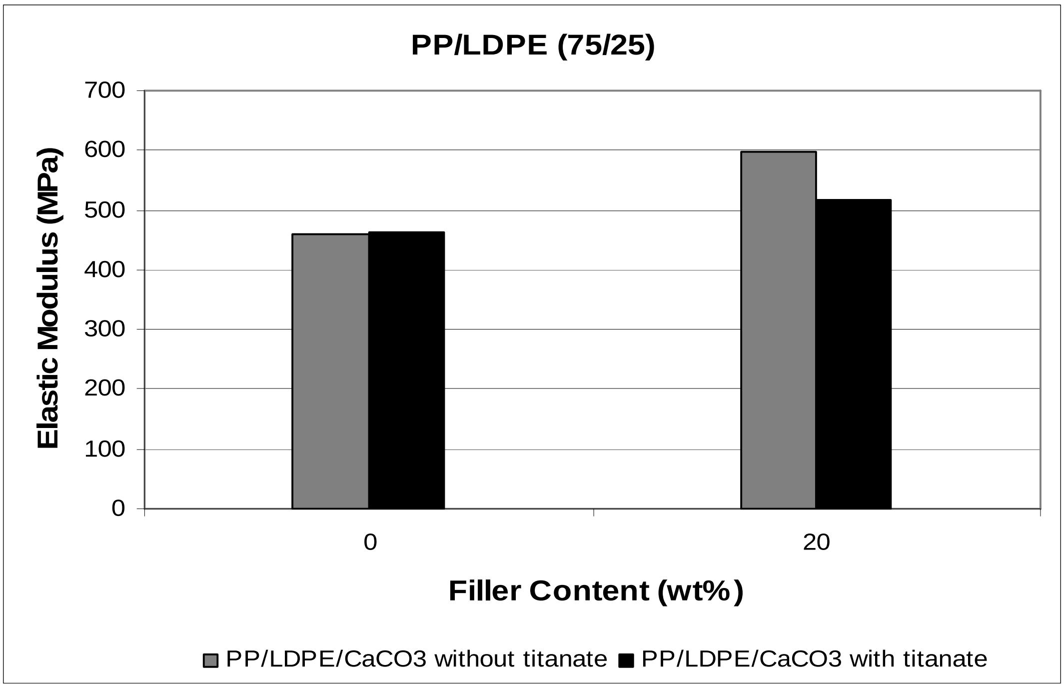


Figure 4.14 Elastic Modulus values of PP/LDPE (75/25) blends and composites

Due to the polymer blend ratio, the continuous polymer phase should be polypropylene and the dispersed phase is low-density polyethylene. There is no significant change between the Young's modulus value of neat PP75/0 and that of titanate added PP75/0-Caps L12 at levels of 460 MPa. With addition of 20% untreated $CaCO_3$ as filler, this value increased to 596 MPa since inorganic filler made the polymer more brittle as seen in Figure 4.4. Capow L12 treated filler at the same filler level of 20% lowered this elastic modulus value to 515 MPa due to plasticizer effect of titanate coupling agent by better dispersing the inorganic filler. However, this effect can not be seen in unfilled polymer blend since there are no inorganic particles causing brittleness and naturally titanate molecules did not affect any dispersion. The other reason of the difference might be that compatibility of these immiscible polymers was accomplished by Capow L12 type but was not done effectively by Caps L12 type due to difference in their physical forms. As Caps L12 is present in pellet form with LDPE, its activity can be hindered. On the other hand, Capow L12 is in powder form and was added to polymer as coated on $CaCO_3$ with a treatment operation. Thus, activity of Capow L12 should be higher than Caps L12 leading to a modification the interfaces in polymer blend more effectively than Caps L12 does. This result of activity difference is observed very remarkably in percentage strain at break values between samples with and without titanate coupling agents.

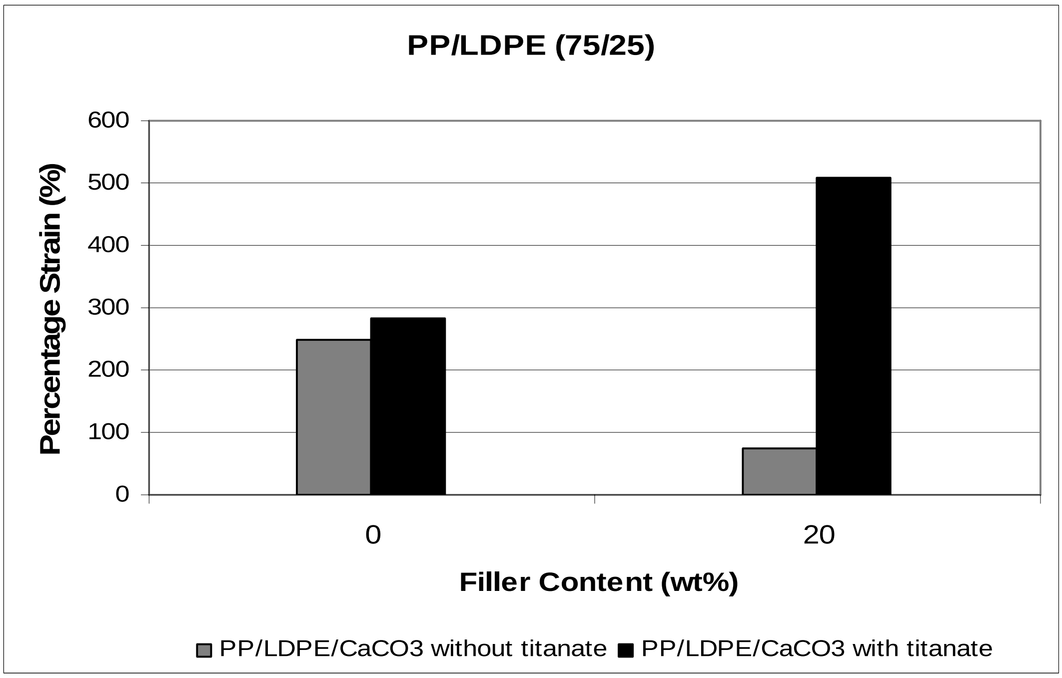


Figure 4.15 Percentage strain at break values of PP/LDPE (75/25) blends and composites

According to Figure 4.15 it is seen that percentage strain value of Caps L12 added polymer blend is slightly higher than neat blend. Caps L12 raised this value from 247% to 283 %. It can be deduced that pelletized titanate molecules modify the compatibility of intermolecular chains of polymers up to a certain degree but not very much due insufficient activity of Caps L12. Percentage strain value of PP75/20 composite considerably decreased to about 75% compared to neat one. When the polymer components in a blend are partially miscible and untreated inorganic filler was added into them, phase separation can form large areas with weak interfacial bonding among ternary system. This formation make the polymer system less ductile and cause that dramatic decrease in percentage strain at break Titanate coupling agents are used in order to prevent this formation of phase separation and strengthen interfacial adhesion. As a result Capow L12 treated $CaCO_3$ gave rise to very high strain about 509% degrees. This result shows that compatibility of two distinct polymers was achieved with incorporation of Capow L12 treated $CaCO_3$. Such increase leads to consider that these polymers behave like nearly single-phase polymer system against tension load. The coupling of the titanate to the organic polymer matrix and inorganic filler provided a continuous phase for stress transfer leading to compatibility of molecular chains of two different polymer types. Also better dispersion of fillers attained by Capow L12 has influence on this result causing elimination of air voids and agglomerations substantially. Otherwise, with presence of them, sample could no longer sustain its elongational deformation under tensile stress and fracture occurs easily. The strain values indicate that titanate coupling agents may act as compatabilizers promoting phase miscibility of polymers in the presence of acceptable filler amounts.

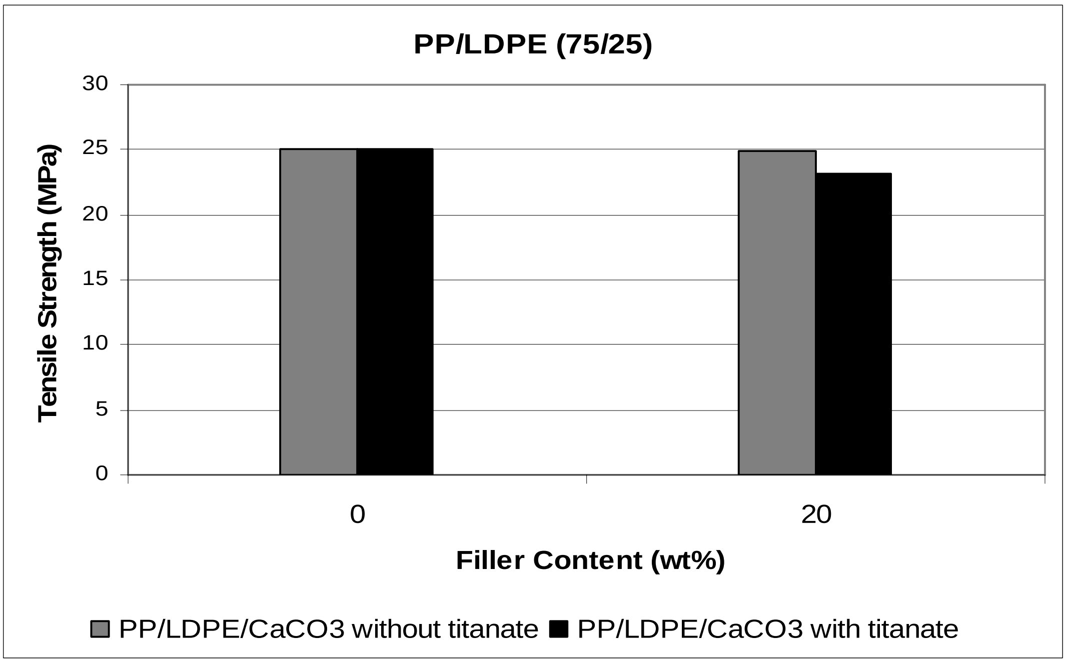


Figure 4.16 Tensile strength values of PP/LDPE (75/25) blends and composites

As seen in Figure 4.16 tensile strength values exhibit the same trends as elastic modulus values. There are no important changes among all tensile strength values. Neat PP75/0 has a value of 25 MPa and incorporation of Caps L12 to that polymer blend nearly has no effect on tensile strength since its value is the same with neat one's averagely. When polymer blend was filled with 20% untreated and Capow L12 treated $CaCO_3$, approximately values of 25 MPa and 23 MPa can be observed from the figure respectively. A slight decrease is observed with incorporation of Capow L12. According to plasticizer effect of coupling agent, titanate molecules might have caused reduction of intermolecular forces between PP and LDPE molecular chains. This reduction may lead the specimen to withstand lower tensile strength under tensile stress. It is observed that titanate coupling agent could not reinforce the tensile strength of this polymer blend.

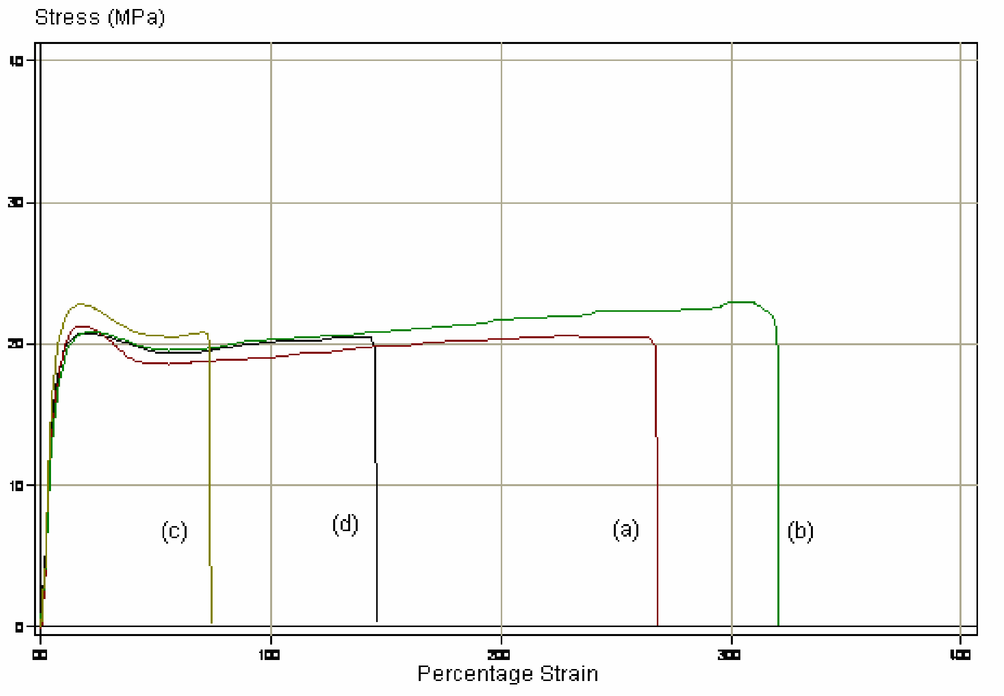


Figure 4.17 Stress-strain curves of PP/LDPE (50/50) blends and composites:

a) PP50/0 - Neat
b) PP50/0-Caps L12 - with 0.5% Caps L12
c) PP50/20 - with 20% untreated $CaCO_3$
d) PP50/20-Capow L12 - with 20% Capow L12-treated $CaCO_3$

The second type of polymer blend that was prepared in this study contains PP and LDPE with equal amounts as polymer matrix and has a sample code of PP50. Its blend and composites contains the same additives with the same ratios as PP/LDPE (75/25). Tensile tests were applied on this material and stress-strain curves of PP/LDPE (50/50) blends and composites are illustrated in Figure 4.17

According to this figure the highest ductility can be seen in sample of PP50/0- Caps L12 and the least one is seen in PP50/20. Necking is also seen in all samples as seen in PP75 ones. After necking, stress hardening is observed just below the lower-yield point among all samples. As both polymer types are present with the same amount, no one polymer forms a continuous phase. This situation can be called as bicontinuous morphology for PP and LDPE blend.

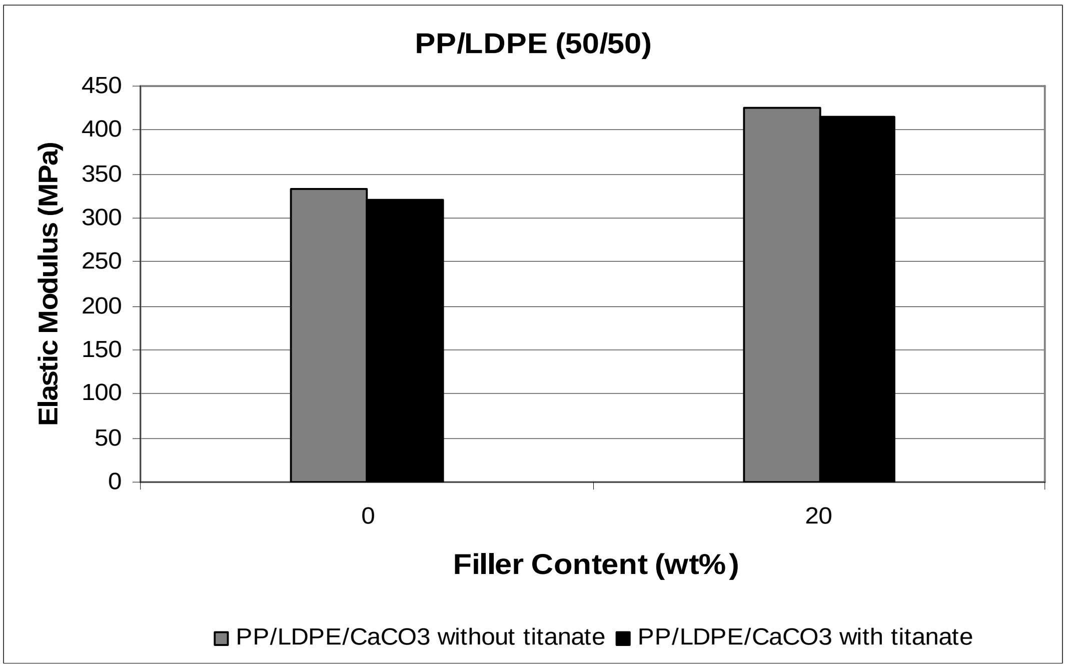


Figure 4.18 Elastic Modulus values of PP/LDPE (50/50) blends and composites

As shown in Figure 4.18 there are slight reductions in the elastic modulus values of samples with titanate compared to ones without titanate, independent of the presence of filler. Without inorganic filler, neat PP50/0 has a value of 332 MPa while PP50/0-Caps L12 has 320 MPa approximately. Influence of Caps L12 on neat blend is seen slightly comparing to the previous blend of PP75. In this blend type; titanate lowered the Young's modulus value because Caps L12 might have incorporated to interface of two polymers more effectively providing more compatibility. Thus, intermolecular forces in the PP50 blend reduced and stiffness of blend decreased. Also, activity of Caps L12 with this blend can be higher than the previous one's since binder of titanate molecules is LLDPE and amount of LDPE is higher in this blend type. With addition of 20% untreated $CaCO_3$ as filler, Young's modulus value increased to 425 MPa due to reinforcement effect of the inorganic filler. With the same filling ratio, Capow L12 treated filler lowered this value slightly to 414 MPa due to plasticizer effect of titanate coupling agent. However, this effect of Capow L12 was not so significant as the effect in the previous PP75 blend. In summary, elastic modulus values of PP50 are lower than corresponding values of PP75 since LDPE ratio is higher in PP50 blend and mechanical properties of LDPE are lower than that of PP.

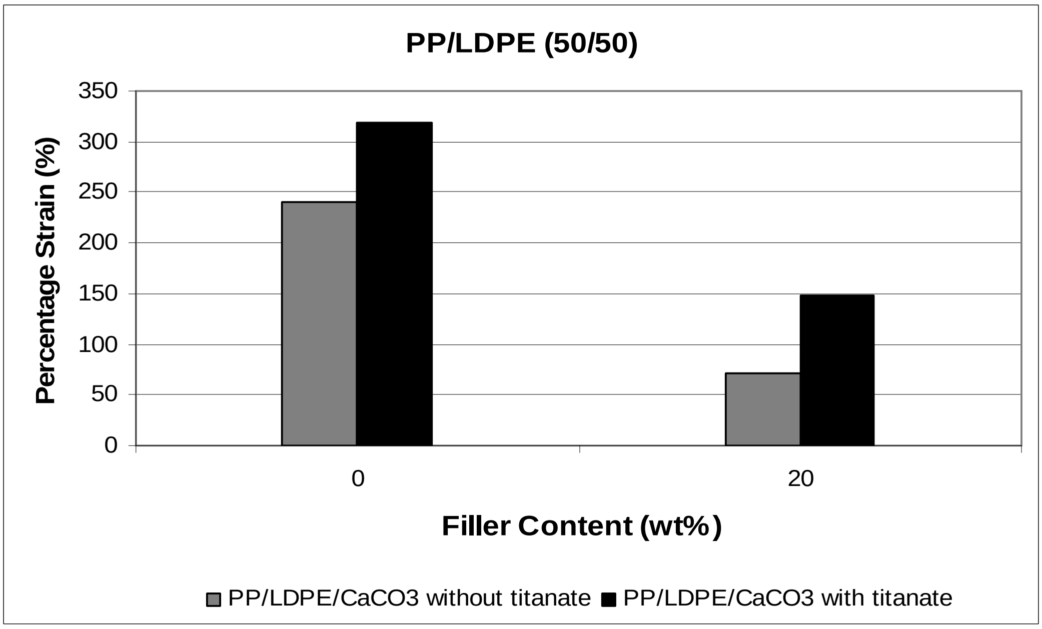


Figure 4.19 Percentage strain at break values of PP/LDPE (50/50) blends and composites

In percentage strain at break values shown in Figure 4.19, for PP50 blends and composites positive influences of titanate coupling agents can be observed similar to PP75. Neat PP50/0 has a percentage strain value of 240% which is very close to the value of neat PP75/0. When Caps L12 was added to neat blend, that value rose up to about 320% . Here the rate of increase is nearly 33% whereas it is about 14% in PP75 samples. It can be claimed that Caps L12 is more effective when used in bicontinuous PP/LDPE blend rather than PP/LDPE (75/25) blend where the continuous phase is PP. In both types of blends titanate molecules raised elongation of materials because of plasticizer effect. However, elongation of PP50/0- Caps L12 blend is more than the PP75/0-Caps L12. As a result compatibility of two polymers improved by Caps L12 in PP50 blend better since Caps L12 with LLDPE binder formed a better interaction with LDPE phase which is present in this blend with higher ratio than PP75 blend.

As expected, addition of 20% untreated $CaCO_3$ decreased the percentage strain at break value from 240% to 71% in PP50 blend which is also close to PP75 result. With incorporation of 20% Capow L12-treated $CaCO_3$ increased this value to 148%. This result can be explained by compatibility and filler dispersion effects of titanate coupling agents mentioned in previous blend part. However, these effects are not observed in PP50 blend as significant as seen in PP75 blend where the increasing rate in percentage strain is 580%. The reason might be that compatibility of PP/LDPE/$CaCO_3$ in PP50 ternary system can not be associated by Capow L12 effectively due to presence of higher ratio of LDPE comparing to amount in PP75. Since Capow L12-treated $CaCO_3$ is more effective on PP matrix than LDPE matrix, high ratio of LDPE in PP50 inhibited the compatibility effect of Capow L12 on this blend. In spite of this inhibition, a remarkable increase in percentage strain at break value can be seen in Figure 4.19.

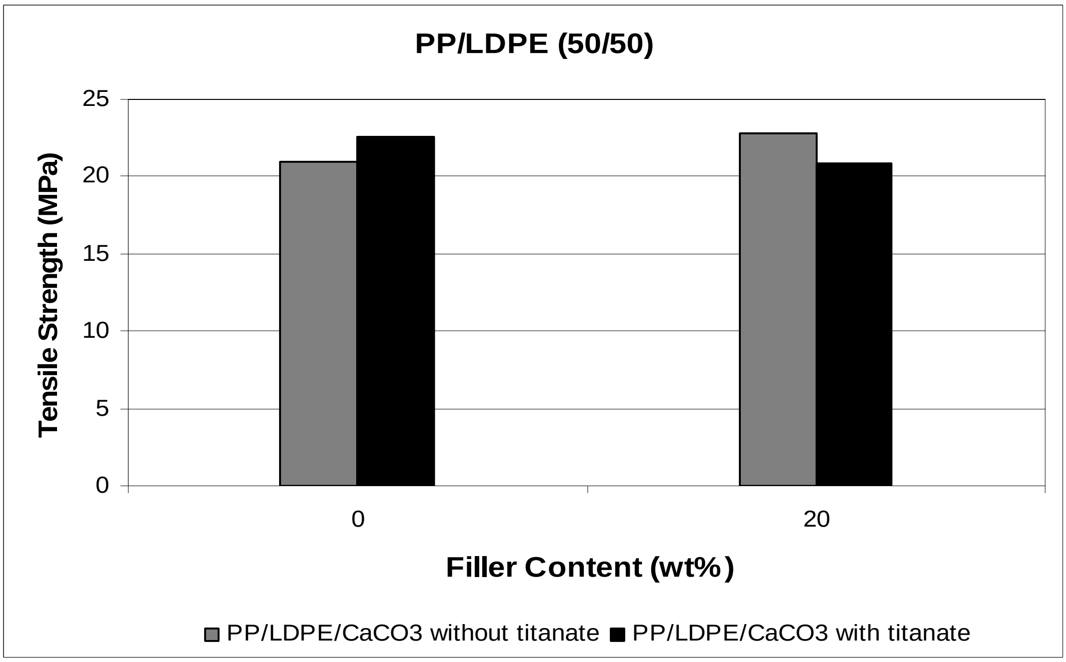


Figure 4.20 Tensile strength values of PP/LDPE (50/50) blends and composites

As shown in Figure 4.20 tensile strength values of PP50 do not exhibit significant variations like values of PP75 but they are lower than previous blend's results since ratio of LDPE increased. Neat PP50/0 has a value of 21.0 MPa and incorporation of Caps L12 to that polymer blend has slightly positive effect on tensile strength as its value is 22.5 MPa. This little increase can be explained with good interaction between titanate molecules and LDPE which is not observed in PP75 blend. Caps L12 with LLDPE binder cause little entanglements among branches of LDPE molecules. These entanglements act as load-bearing elements and provide material to strengthen and withstand to maximum stress at higher levels of load.

When the polymer blend is prepared with 20% untreated and Capow L12 treated $CaCO_3$, approximately values of 22.8 MPa and 20.8 MPa in tensile strength is observed, respectively. At this filler level, moderately positive effect of untreated $CaCO_3$ is seen since it is a reinforcing inorganic additive. A decrease occurred with incorporation of Capow L12, the same trend is observed in PP75 blend. The reason of the decrease should be the same with that of previous blend. Capow L12 could not form strong interfacial adhesion among ternary polymer system and weak adhesion caused lower tensile strength compared to the untreated filler. It is observed that titanate coupling agent exhibits different effects according to physical form of titanate and polymer matrix type. Caps L12 has positive effect on tensile strength of PP50 polymer blend while Capow L12 does not have such effect on PP50/$CaCO_3$ composite.

The third type of polymer blend that was examined in this study contains 25% PP and 75% LDPE with weight fraction and has a sample code PP25. The other filler and titanate types and amount that were added to PP25 are the same with those of previous blends. After tensile tests, stress-strain curves of PP/LDPE (25/75) blends and composites were obtained and illustrated in Figure 4.21.

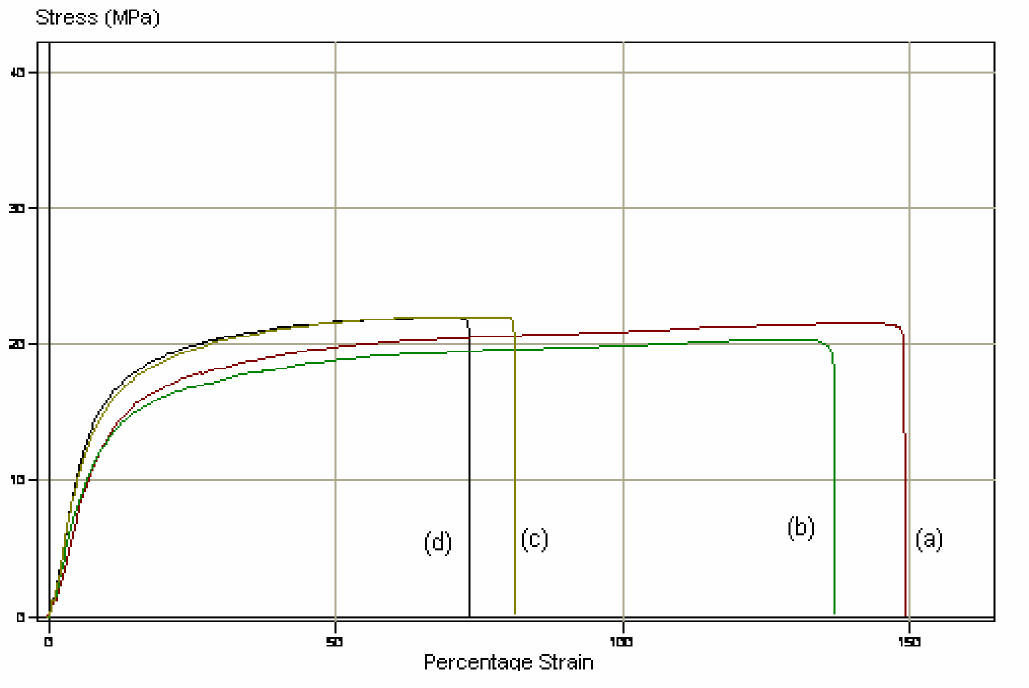


Figure 4.21 Stress-strain curves of PP/LDPE (25/75) blends and composites:

a) PP25/0 - Neat
b) PP25/0-Caps L12 - with 0.5% Caps L12
c) PP25/20 - with 20% untreated $CaCO_3$
d) PP25/20-Capow L12 - with 20%Capow L12-treated $CaCO_3$

PP25 blend consisting of two phases: continuous phase is LDPE and dispersed phase is PP. As shown in Figure 4.21, PP25 blends and composites have lower mechanical properties comparing to PP75 and PP50 blends since LDPE is the dominant phase and its mechanical properties are lower than PP. Necking formation is not seen in any sample and at maximum stress fracture occurred. Consequently, PP25 blends and composites do not exhibit an elongation trend after maximum stress is achieved. Besides, the ductility of these samples are at the lowest level comparing to other PP/LDPE blends and composites.

Tensile properties of PP25 blends and composites are given in Figures 4.22, 4.23 and 4.24 according to elastic modulus, percentage strain at break and tensile strength values, respectively.

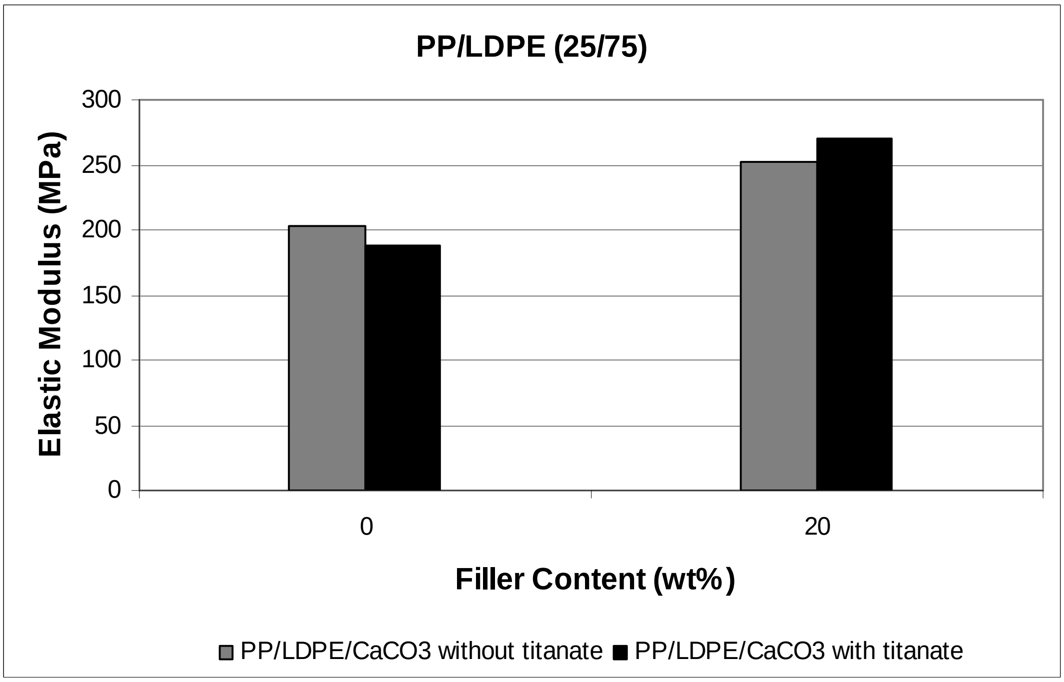


Figure 4.22 Elastic Modulus values of PP/LDPE (25/75) blends and composites

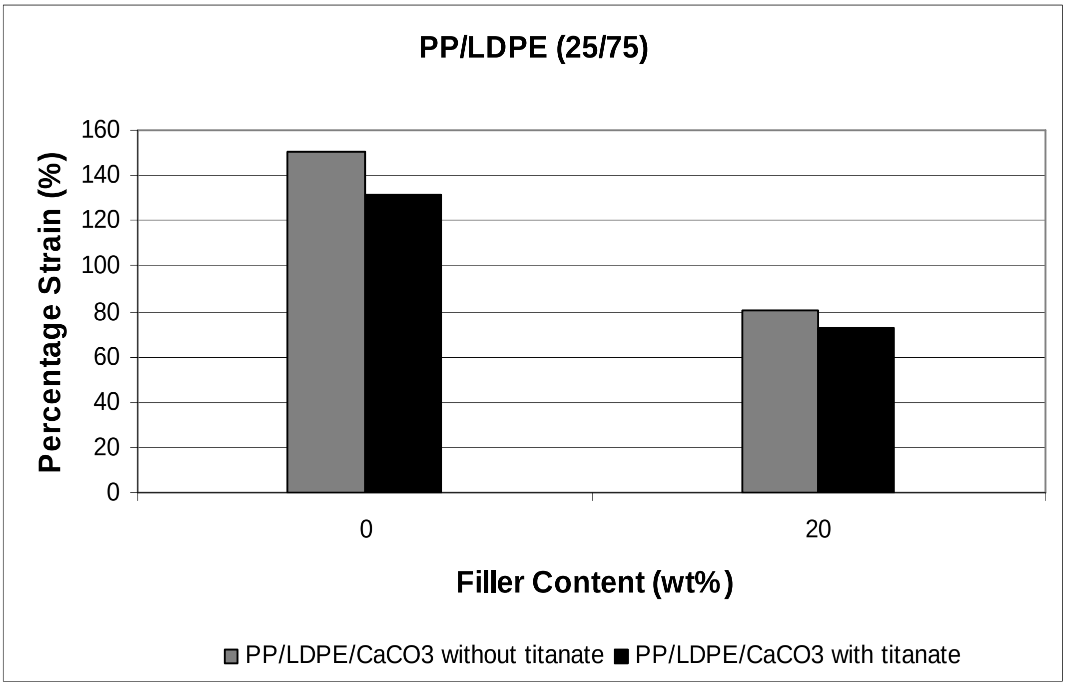


Figure 4.23 Percentage strain at break values of PP/LDPE (25/75) blends and Composites

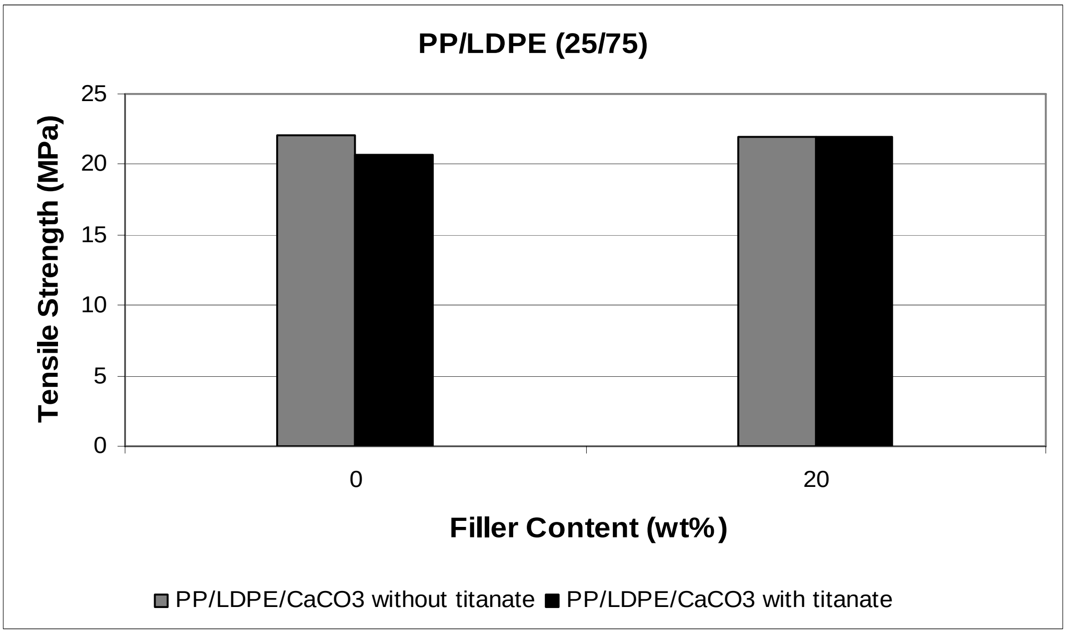


Figure 4.24 Tensile strength values of PP/LDPE (25/75) blends and composites

As shown in Figure 4.22 elastic modulus values of PP25 are the lowest values comparing to previous PP/LDPE blends since content of LDPE in blend reached the highest amount among all blend types. For instance neat PP25 has a Young's modulus value of 202 MPa showing that increasing LDPE amount reduced the stiffness of PP/LDPE blend. When Caps L12 was added to this blend making ternary polymer system, Young's modulus value slightly decreased to 188 MPa due to reduction of intermolecular forces by titanate coupling agent as seen before in other blends. However, as shown in Figure 4.23 Caps L12 also caused a decrease in percentage strain at break value from 150% to 131% which was not observed in other blends. Its reason might be that Caps L12 was not able to affect the interface of two polymers sufficiently for improvement of compatibility of them because continuous phase is LDPE. Much amount of slightly cross-linked LDPE which does not let necking formation during elongation should be the main reason for inhibition of Caps L12 functionality. As a result of insufficiency of Caps L12, good interfacial adhesion could not be achieved and tensile strength was negatively affected too. According to Figure 4.24, tensile strength values decreased from 22.1 MPa to 20.7 MPa with incorporation of Caps L12 to neat blend PP25.

There is no remarkable change in tensile properties of PP25 composites containing 20% untreated and Capow L12-treated $CaCO_3$. No influence of Capow L12 was observed in PP25 blend where the continuous phase is LDPE. Only slight increase in Young's modulus value is observed, percentage strain at break values decreased and tensile strength value remained the same with titanate coupling agent. According to the results effective interfacial adhesion can not be achieved by Capow L12 with PP/LDPE/$CaCO_3$ composites.

It can be concluded that Caps L12 does not have a positive effect on providing a good adhesion between the continuous LDPE phase and dispersed phase PP in neat blends. Since Capow L12 also did not give an improvement in mechanical values, one can say that both coupling agent types do not work effectively with LDPE. When PP is the continuous phase in PP75/0 and PP75/20 blends and composite, an improvement in percentage strain values were observed.

4.1.2 Impact Properties

Impact tests with charpy method were applied to polypropylene and low-density polyethylene blends and composites prepared for this study. To investigate effect of titanate coupling agent on impact properties, impact strength values were obtained. Five bar shaped V-notched specimens were used for each composition and averages of impact strength values were evaluated.

4.1.2.1 Impact Properties for PP/$CaCO_3$ Composites

Impact strength values of PP/$CaCO_3$ composites are given in Figure 4.25.

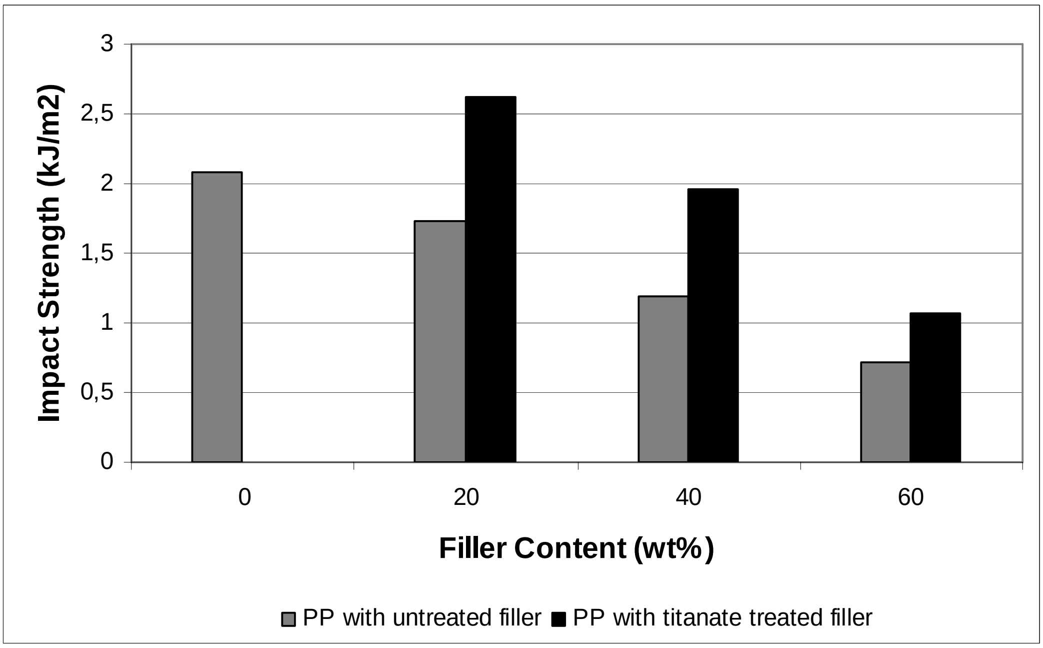


Figure 4.25 Impact strength values of PP/$CaCO_3$ composites

Processed neat PP has an impact strength value of about 2 kj/m^2 and with addition of inorganic filler this value decreases gradually up to 0.7 kj/m^2 level at 60% filler level.

With incorporation of titanate coupling agent of Capow L12 treated $CaCO_3$, significant improvement in impact properties are observed compared to samples with untreated filler. This improvement is strongly related with modification of interfacial adhesion and interaction between polymer and filler by titanate molecules. Better adhesion and interaction give polypropylene composites a degree of toughness against impact load. One should notice that PP has inherently a low impact strength value compared to LDPE as expected.

4.1.2.2 Impact Properties for LDPE/$CaCO_3$ Composites

Figure 4.26 shows impact strength values with respect to filler content for LDPE/$CaCO_3$ composites. Impact strength values of LDPE composites are higher than ones of PP composites since LDPE is more ductile polymer than PP. Especially processed neat LDPE has an impact strength of 207 kj/m^2 and they were not broken during the test.

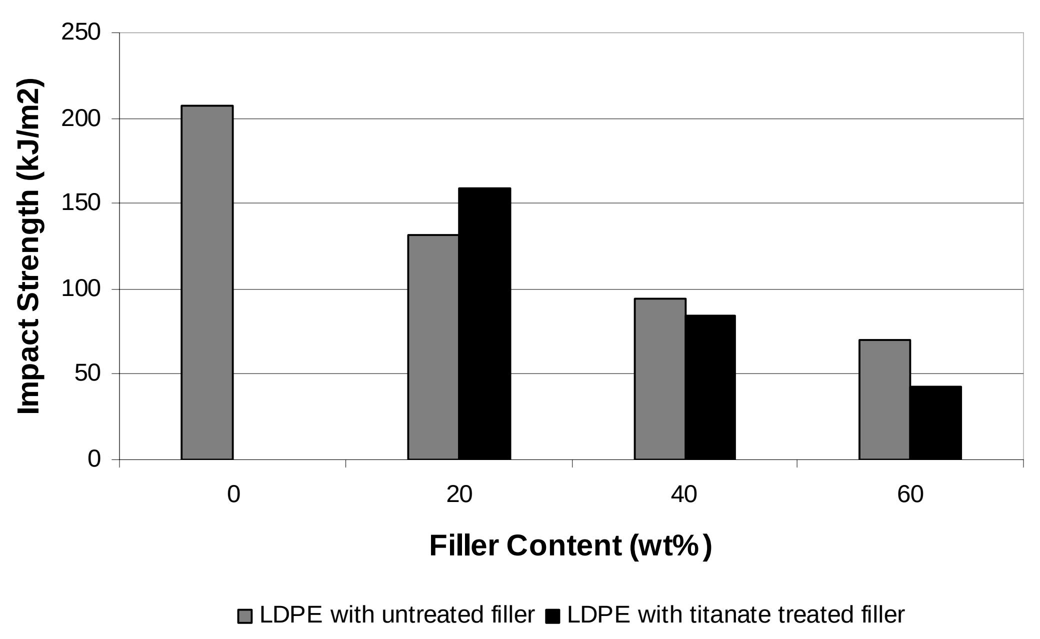


Figure 4.26 Impact strength values of LDPE/$CaCO_3$ composites

The impact strength was lowered quitely to 131.5 kj/m^2 by addition of 20% untreated filler and specimens were broken under impact load. Inorganic particles give rise to brittle interfaces due to incompatibility of filler and polymer matrix. When 20% titanate-treated $CaCO_3$ was employed, interfacial adhesion was accomplished more than in untreated filled ones and impact strength was raised slightly to 158.5 kj/m^2. Increasing amount of inorganic filler leads to decrease of impact strength of LDPE/$CaCO_3$ due to agglomerations among filler particles. At 40% and 60% filler content levels, the values were observed 94.2 kj/m^2 and 70.5 kj/m^2, respectively. Contrary to samples with 20% titanate-treated filler, titanate coupling agents did not give an improvement in impact strength with high filler contents. The impact results are consistent with tensile results of LDPE/$CaCO_3$ composites and probably due to the same reasons, influence of titanate coupling agent on impact property becomes insufficient for highly filled compositions.

4.1.2.3 Impact Properties for PP/LDPE Blends and Composites

Impact strength values of PP/LDPE blends are presented with respect to 3 blend types in Figure 4.27. Each blend type includes 4 different samples according to inorganic filler content and presence of titanate coupling agent. The definitions of sample codes written in label of figure can be listed in order of columns like this:

1- Neat PP75* - no additive
2- PP75/0-Caps L12 - with 0.5% Caps L12
3- PP75/20 - with 20% untreated $CaCO_3$
4- PP75/20-Capow L12 - with 20%Capow L12-treated $CaCO_3$
* PP75 is the sample code of PP/LDPE (75/25) blend type for the sake of brevity.

As expected, impact strength values of these blends are in the range between values of neat polymers of PP (2 kj/m^2) and LDPE (207 kj/m^2). Also it is seen that impact strength values exhibit an increasing trend with increasing ratio of LDPE.

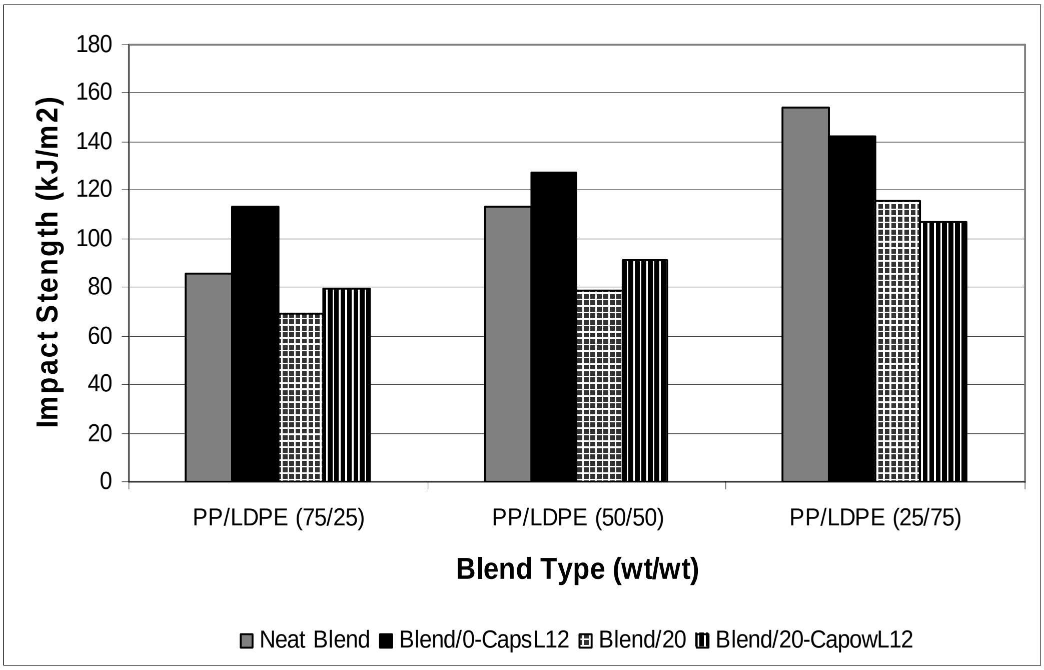


Figure 4.27 Impact strength values of PP/LDPE blends and composites

The results of impact strength values for PP75 and PP50 blend types exhibit similar variations as seen in Figure 4.27. In both blends, the pellet form of titanate coupling agent Caps L12 has positive influence on ductility of materials compared to neat blends since it raised the impact strength of both blends. This effect of Caps L12 can be explained by improvement of compatibility between PP and LDPE which are known as immiscible polymers. This compatibility provides these blends to have more ductile fracture in response to impact load. With addition of 20% untreated $CaCO_3$, a significant decrease is observed for both blend types due to effect of inorganic fillers on brittle fracture. Capow L12 improved this brittle fracture by enhancing interfacial adhesion between filler and polymer matrix leading to higher ductility for these composites.

The highest impact strength of 154 kj/m^2 was obtained with neat PP25 blend among all blend compositions. The reason of this high toughness is probably related to the relative amount of LDPE which is highest. Contrary to PP75 and PP50 blend types, incorporation of Caps L12 on unfilled PP25 blend did not improve the impact strength. When PP25 blend was filled with 20% untreated CaCO3, impact resistance decreased even more and composite became more brittle as expected. Addition of 20% Capow L12 treated filler reduced the impact strength more than untreated one. Thus, Capow L12 caused the same negative effect as Caps L12 in PP25 blend and composites. When considered together with tensile results of PP25 blend, it can be claimed that functionality of both titanate coupling agents on impact properties probably inhibited by physical cross-links of LDPE due to its branched structure.

4.2 Morphological Analysis with Scanning Electron Microscopy (SEM)

Morphological analysis was performed on surfaces of tensile fractured samples by using SEM technique. The aim of this analysis is to examine the effect of titanate coupling agents on morphology of PP and LDPE blends and composites which were prepared in Brabender and twin-screw extruder. In SEM micrographs of these materials, calcium carbonate particles in micron dimension and their dispersion can clearly be seen. Also in most of samples including titanate coupling agent, effect of titanate molecules on filler dispersion and filler-polymer interaction can be observed.

Morphology analysis will be discussed in two sections according to material type; the first is LDPE/$CaCO_3$ composites produced in Brabender and the second is PP/LDPE blends and composites prepared in twin-screw extruder.

4.2.1 Morphological Analysis of LDPE/$CaCO_3$ Composite

SEM micrographs of LDPE/$CaCO_3$ composites were illustrated in Figures 4.28, 4.29 and 4.30 with respect to filler contents of 20%, 40% and 60%, respectively. Each composition was prepared by addition of untreated $CaCO_3$ and Capow L12 treated $CaCO_3$, separately and their micrographs are given in the same figure with two different magnifications at x1000 and x10 000.

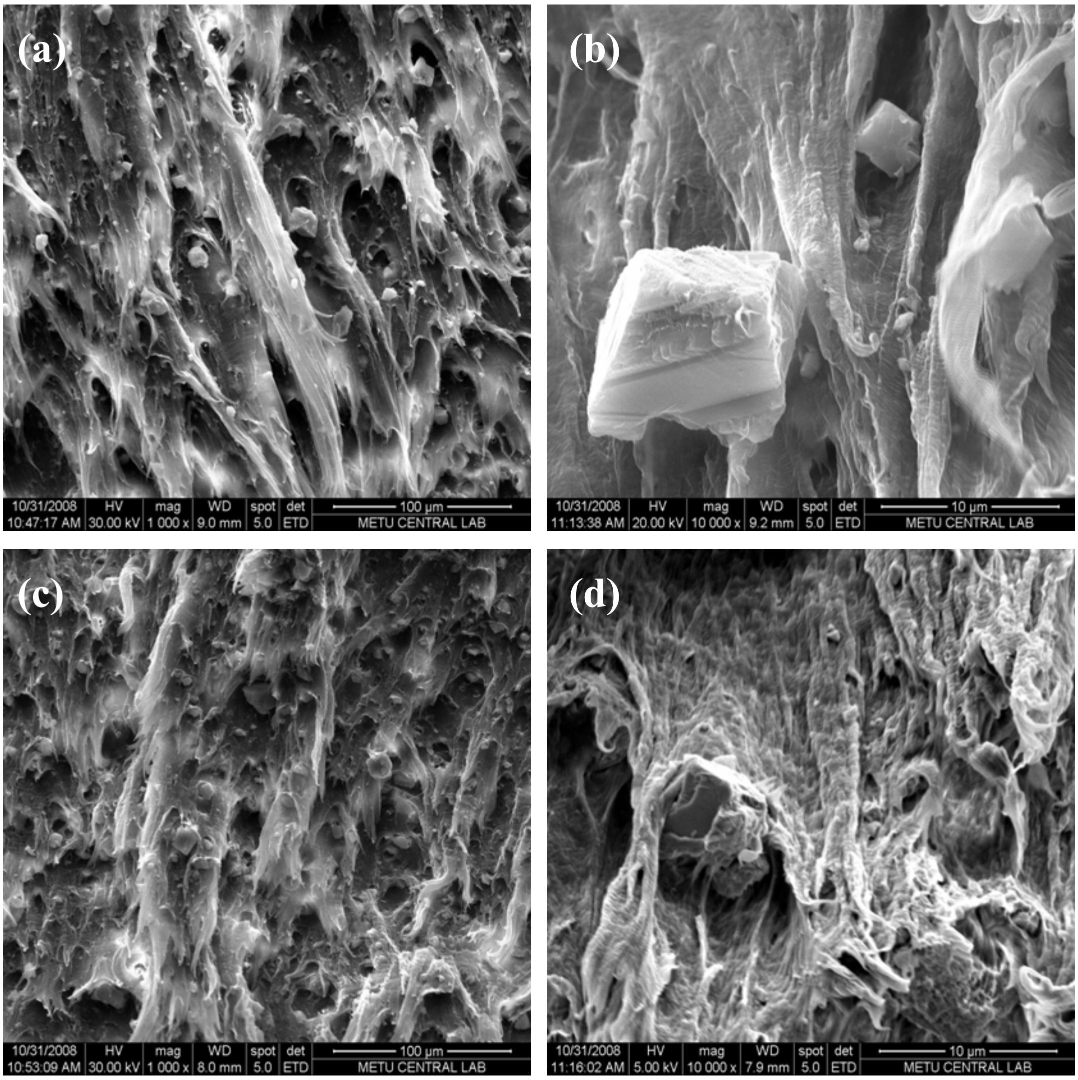


Figure 4.28 SEM micrographs of LDPE/$CaCO_3$ composites with 20% $CaCO_3$
a) untreated filler x1000 b) untreated filler x10 000
c) treated filler x1000 d) treated filler x10 000

In Figure 4.28 it can be seen that the titanates did not cause much improvement on filler particle dispersion, especially seen in pictures (a) and (c) with magnification of x1000. However, titanate molecules leads better polymer–filler interaction as seen in images (b) and (d) with high magnification of x10000. As seen in 4.28-d, some filler particles are clinging to polymer by the help of titanates and they are embedded in the matrix. On the other hand, such a clinging is not seen in 4.28-b which shows lack of interaction between untreated filler and polymer.

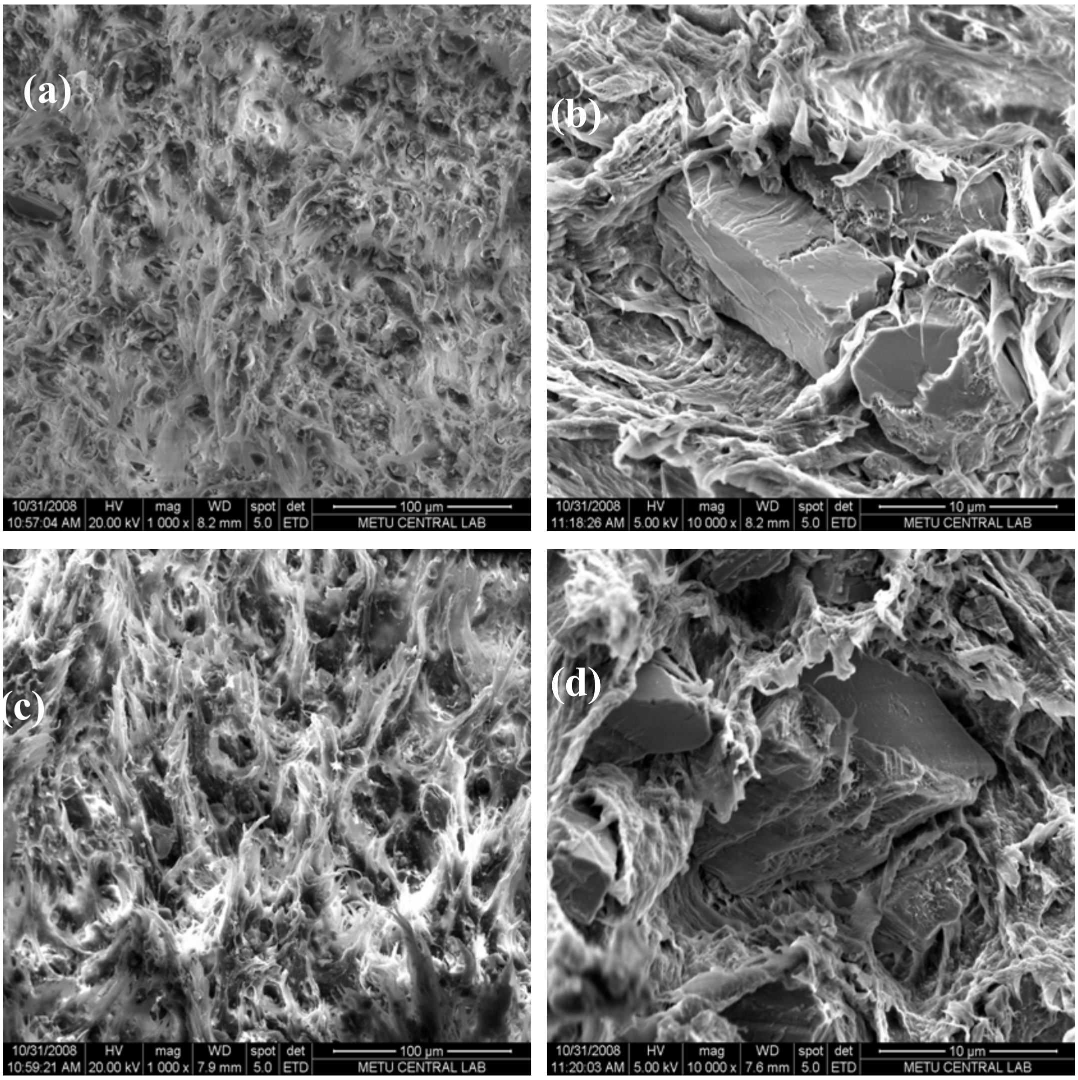


Figure 4.29 SEM micrographs of LDPE/$CaCO_3$ composites with 40% $CaCO_3$
a) untreated filler x1000 b) untreated filler x10 000
c) treated filler x1000 d) treated filler x10 000

According to SEM images of (a) and (c) in Figure 4.29, there is no significant difference in dispersion of filler particles between samples with untreated and titanate-treated filler at 40% filler level. The pictures at x10000 magnifications show that presence of titanate molecules cause adhesion of fillers to polymer matrix better than untreated ones.

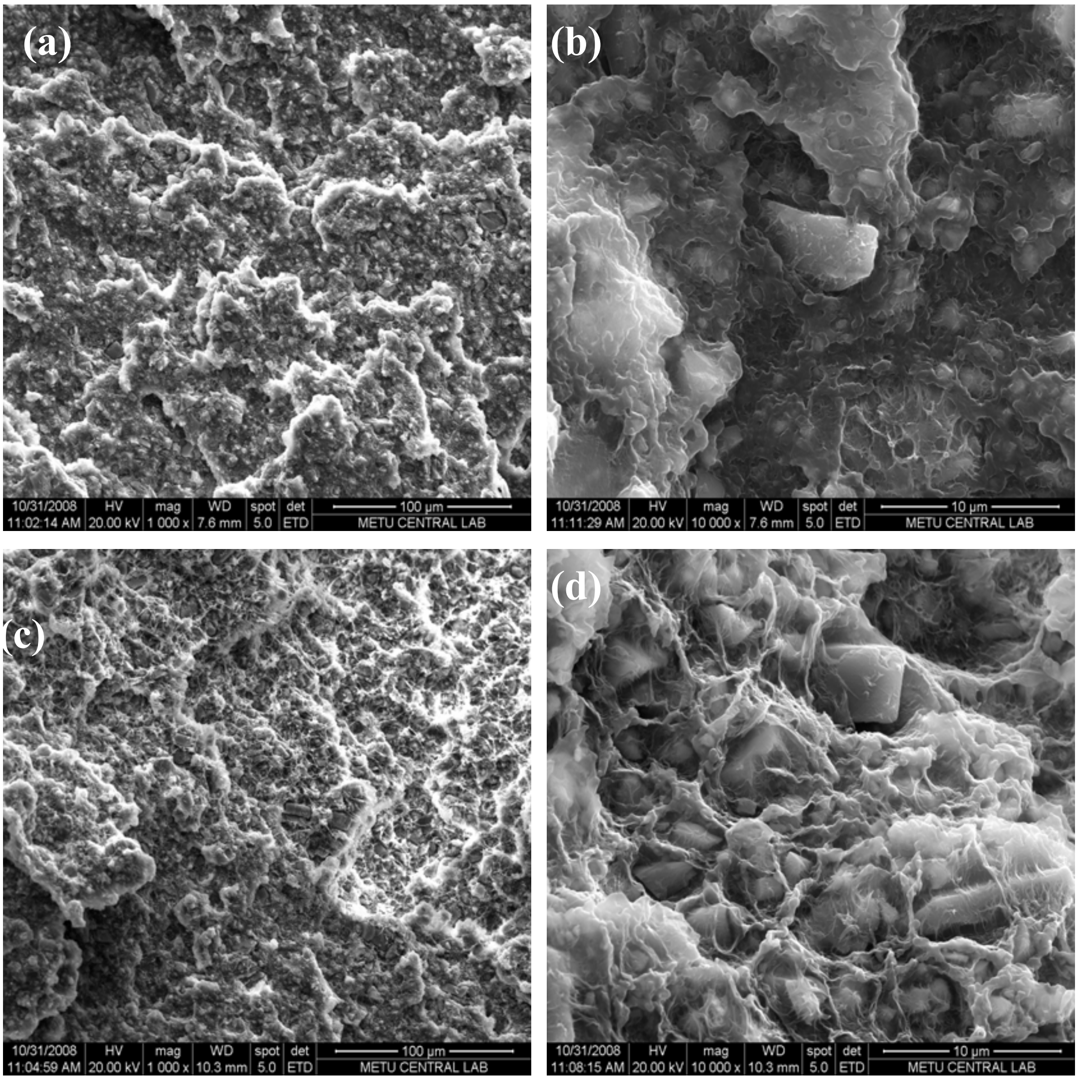


Figure 4.30 SEM micrographs of LDPE/CaCO3 composites with 60% $CaCO_3$
a) untreated filler x1000 b) untreated filler x10 000
c) treated filler x1000 d) treated filler x10 000

In Figures 4.30-a and 4.30-c crack propagation lines appear discretely on the fracture surfaces due to high inorganic filler content of 60%. There is no important distinction in filler particle dispersion between two figures of (a) and (c). Besides that, it is clearly observed in SEM images 4.30-b and 4.30-d that titanate coupling agents do not enhance the filler-polymer interaction. The continuity of the polymer matrix is broken by the presence of high filler amount and cracks can easily form.

4.2.2 Morphological Analysis of PP/LDPE Blends and Composites

SEM micrographs of PP/LDPE blends and composites were illustrated in Figures 4.31, 4.32 and 4.33. Three blend types were prepared in twin-screw extruder with ratios of PP/LDPE: 75/25, 50/50 and 25/75. Their composites were filled with untreated and Capow L12-treated CaCO3 at 20%.

In Figure 4.31 fractured surfaces of neat PP75 blend is seen in pictures (a) and (b), blend containing 20% untreated $CaCO_3$ is seen in pictures (c) and (d), blend with 20% titanate-treated $CaCO_3$ is seen in pictures (e) and (f). In general view of neat PP75 at x300 magnification (image a), distinction of PP and LDPE is seen at tensile fractured surface where PP forms fibrillation during tensile deformation and LDPE does not. So, some PP fibrils leave the initially continuous blend phase and phase separation is seen in some areas where fracture occurs. Addition of 20% untreated filler give rise to this phase separation in more areas since incompatibility of PP/LDPE/$CaCO_3$ composite is higher than neat PP/LDPE blend as seen in SEM images (b) and (d) of Figure 4.31. When titanate-treated filler is used instead of untreated one, dispersion of filler particles improved according to (c) and (e) pictures. Also titanate coupling agent increase the compatibility between filler and polymer matrix since treated filler particles hold on to polymer much more than untreated ones as seen in (d) and (f) images. As a result, this improved compatibility provides much better stress transfer for polymer matrix and it can be elongated to higher strain levels compared to untreated filled PP75 blend.

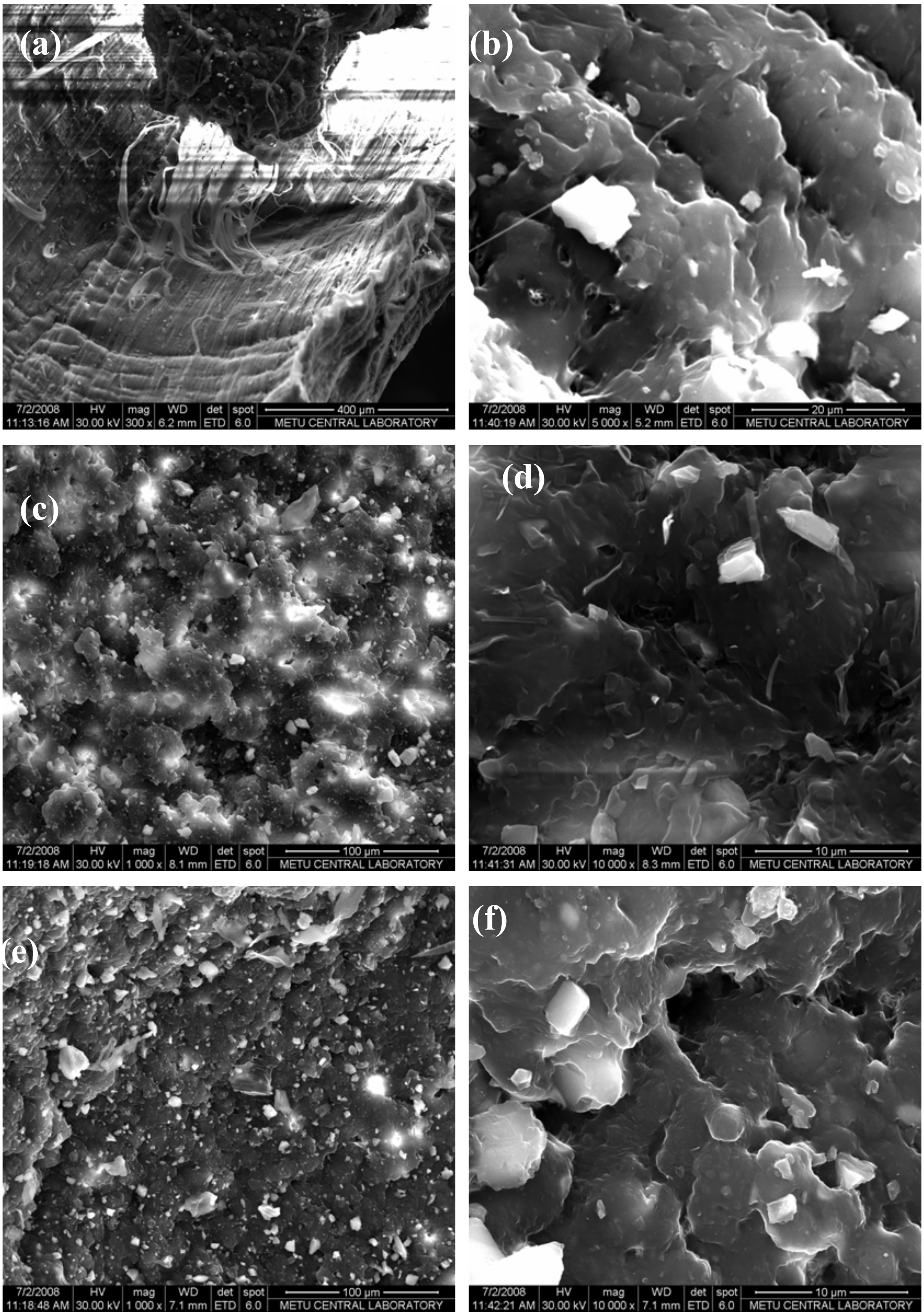


Figure 4.31 SEM micrographs of PP/LDPE (75/25) blends and composites with

a) no filler x300 b) no filler x5000

c) 20% untreated $CaCO_3$ x1000 d) 20% untreated $CaCO_3$ x10 000

e) 20% treated $CaCO_3$ x1000 f) 20% treated $CaCO_3$ x10 000

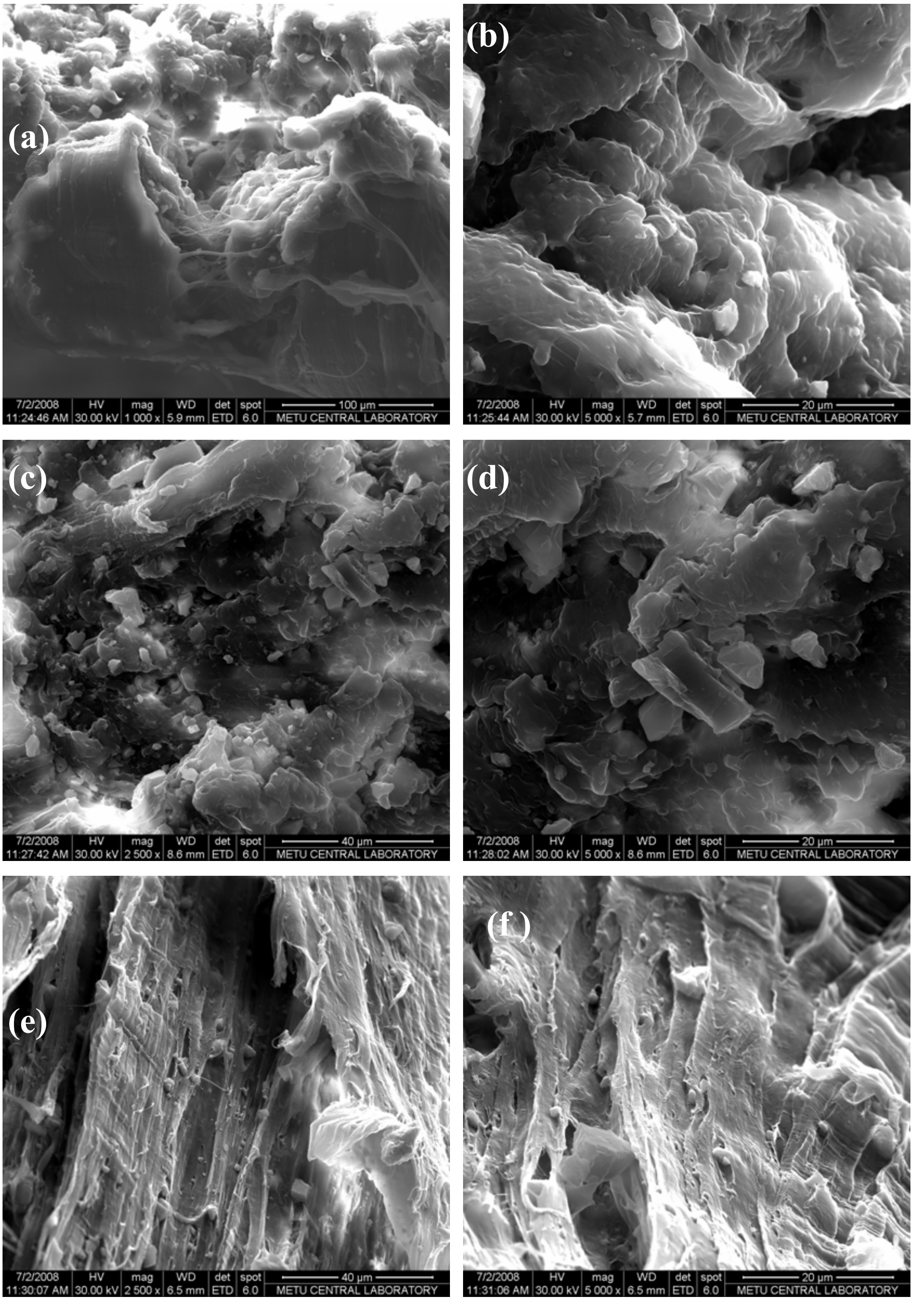


Figure 4.32 SEM micrographs of PP/LDPE (50/50) blends and composites with

a) no filler x1000 b) no filler x5000

c) 20% untreated $CaCO_3$ x2500 d) 20% untreated $CaCO_3$ x5000

e) 20% treated $CaCO_3$ x2500 f) 20% treated $CaCO_3$ x5000

In Figure 4.32 SEM micrographs of neat PP50 blend and its composites containing 20% untreated and titanate-treated $CaCO_3$ are demonstrated. In neat PP50's SEM images of (a) and (b) a fine continuous polymer phase can not be seen and PP fibrils can be observed distinctly among PP/LDPE polymer matrix at tensile fractured surface. In Figures 4.32-c and 4.32-d showing fracture surfaces of blend containing 20% untreated filler, polymer phase seems discontinuous and there are remarkable spaces among polymer matrix. Incorporation of titanate coupling agents makes the polymer more continuous although some detachments between PP and LDPE exist on the surface as seen in Figure 4.32-e and 4.32-f. Comparison of SEM images of (d) and (f) show that improved adhesion of filler particles with polymer blend is provided by titanate molecules. Figure 4.32-f shows that filler particles are drawn with the stretching polymer molecules indicating strong interaction between filler and polymer.

Figure 4.33 illustrates SEM micrographs of PP25 blend and composites at two different magnifications of x1000 and x5000. In images (a) and (b) it can be seen easily continuous phase LDPE is dominant with its semi-crystalline surface. These surfaces become much rougher with addition of 20% $CaCO_3$ indicating that poor interaction between filler and polymer matrix exists as seen in figures (c) and (d). Same trend is observed in Figures 4.33-e and 4.33-f which shows surfaces with titanate-treated filler do not enhance the interaction. In addition, there are no remarkable difference between figures (c) and (e) in terms of filler dispersion.

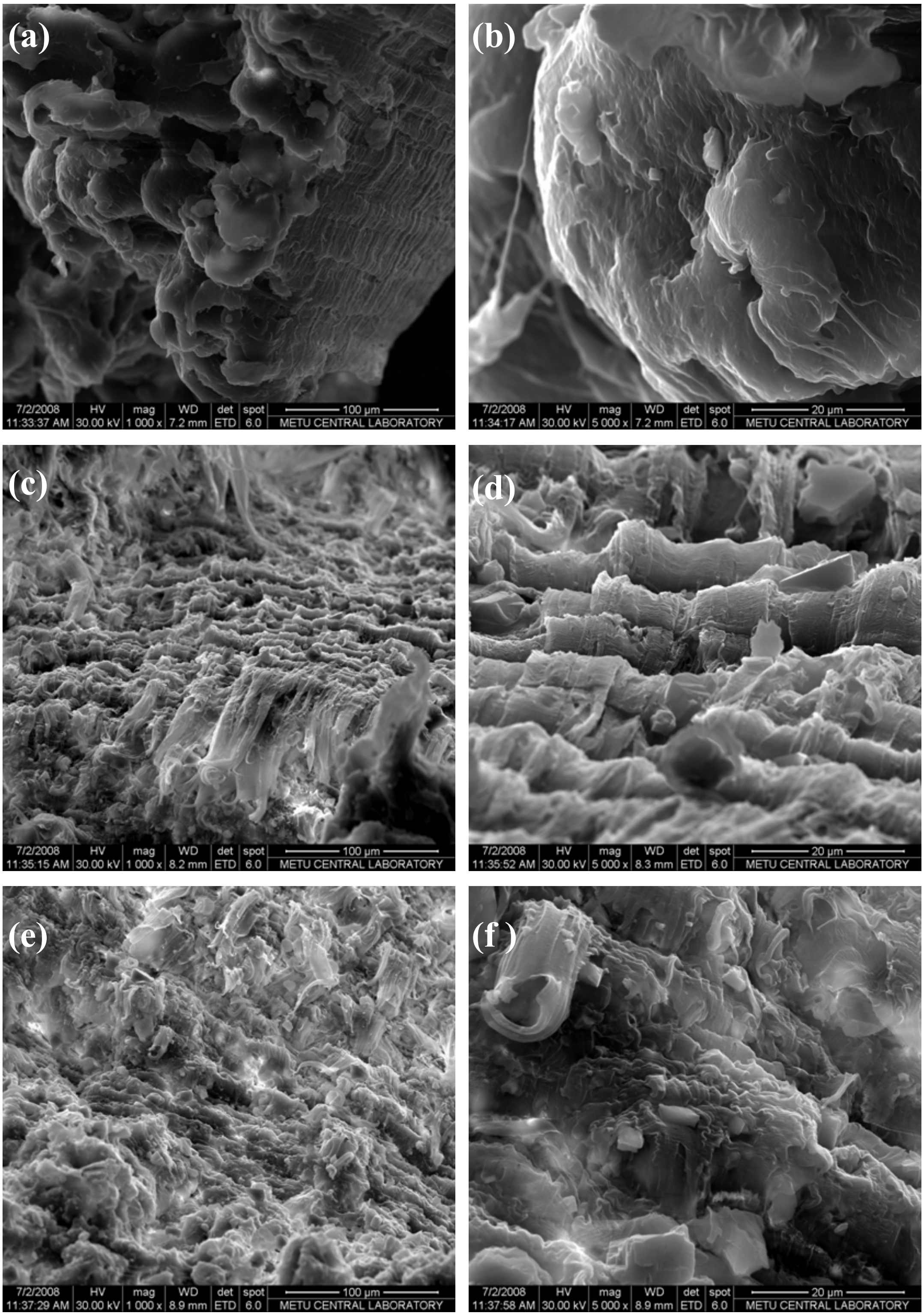


Figure 4.33 SEM micrographs of PP/LDPE (25/75) blends and composites with

a) no filler x1000 b) no filler x5000

c) 20% untreated $CaCO_3$ x1000 d) 20% untreated $CaCO_3$ x5000

e) 20% treated $CaCO_3$ x1000 f) 20% treated $CaCO_3$ x5000

CHAPTER 5

CONCLUSIONS

PP/$CaCO_3$ and LDPE/$CaCO_3$ composites were prepared in Brabender by addition of untreated and Capow L12 treated filler with filler content of 20, 40 and 60%. In twin-screw extruder, PP/LDPE blends were produced at ratios of 75/25, 50/50 and 25/75 with and without 0.5% Caps L12 as titanate coupling agent. PP/LDPE/$CaCO_3$ composites were produced with addition of 20% untreated and Capow L12 treated filler. Effects of titanate coupling agents on mechanical and morphological properties were investigated.

Tensile test results for PP/$CaCO_3$ composites show that titanate coupling agents have positive effects on percentage strain at break and Young's modulus values. Percentage strain values decreased with increasing untreated $CaCO_3$ but titanate molecules improved those percentage strain values up to 2 and 3 times higher comparing to untreated ones at 20% and 40% filler level, respectively. Also titanate coupling agents improved impact strength of PP composites which showed that polymer-filler interaction was enhanced. However, tensile strength values of PP/$CaCO_3$ composites were not affected by titanate molecules. It is concluded that Capow L12 has remarkable plasticizing effect on PP/$CaCO_3$ composites.

Mechanical tests on LDPE/$CaCO_3$ composites demonstrated that Capow L12 has enhanced strain at break and impact strength values up to 20% filler content. However the tensile strength values were adversely affected by the inclusion of titanates. Modification of polymer-filler adhesion was observed in SEM micrographs for the composite containing 20% filler. Thus it is concluded that titanates can not bring substantial improvements to LDPE composites. This may well be attributed to the branched nature of the polymer which does not allow high rates of shear to be attained in polymer titanate interface. It is claimed by the manufacturer that interfacial shear is an important parameter to bring about the titanate functionality.

In PP/LDPE (75/25) blend; there has been no important change in tensile properties between unfilled blends with and without Caps L12. However, Caps L12 elevated impact strength of neat blend. Addition of 20% $CaCO_3$ resulted in very sharp decrease in percentage strain at break as expected. Capow L12 increased the compatibility of PP/LDPE/$CaCO_3$ composite by improving polymer-filler interaction which is observed in SEM micrographs. The percentage strain increased significantly up to 500% which is the highest value among all blends and composites in this study. Impact strength also improved but slight decreases occurred in elastic modulus and tensile strength values. Results of PP75 blend show that compatibility of these immiscible polymers was accomplished by Capow L12 but, Caps L12 employed for unfilled blends exhibited no improvement.

Effects of titanate coupling agents on tensile properties of PP/LDPE (50/50) blend and composites are similar to ones in PP75 blend. The main difference occurred in extent of changes in percentage strain between samples with and without titanate. Both titanate coupling agents increased the strain values but activity of them varied according to continuous phase. Caps L12 has higher influence on unfilled PP50 than PP75 due to higher LDPE content in PP50. Capow L12 exhibited more activity on PP75 than PP50 due to continuous phase of PP. SEM micrographs show that Capow L12 increased the adhesion of fillers to PP50 polymer blend phase. As result impact strength values increased with incorporation of both Caps L12 and Capow L12.

Increased LDPE amount in PP25 blend causes titanate coupling agent to be less effective compared to other blends. No improvement is observed in tensile and impact properties of PP25 blend for both Caps L12 and Capow L12. Consistent with these mechanical results, SEM results show that improved filler dispersion and enhanced interfacial adhesion with titanates were not observed.

In conclusion, titanate coupling agents of Capow L12 exhibited its functions in polypropylene matrix much more effectively than in low-density polyethylene matrix. Caps L12 has limited effects on unfilled PP/LDPE blends since it is already incorporated in LLDPE.

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