

**MECHANICAL PROPERTIES OF HDPE/CaCO₃/ETHYLENE-OCTENE
COPOLYMER COMPOSITES**

Miss Kannika Surinta

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สมบัติเชิงกลของพอลิเอทิลีนชนิดความหนาแน่นสูง/แคลเซียมคาร์บอเนต/
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By Miss Kannika Surinta
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.....Dean of the Faculty of Science
(Professor Supot Hannongbua, Dr.rer.nat)

THESIS COMMITTEE

.....Chairman
(Professor Pattarapan Prasassarakich, Ph.D.)

.....Advisor
(Professor Suda Kiatkamjornwong, Ph.D.)

.....Examiner
(Assistant Professor Warinthorn Chavasiri, Ph.D.)

..... Examiner
(Assistant Professor Voravee Hoven, Ph.D.)

..... External Examiner
(Wiyong Kangwansupamonkon, Ph.D.)

กรรณิการิ์ สุรินตะ: สมบัติเชิงกลของพอลิเอทิลีนชนิดความหนาแน่นสูง/แคลเซียมคาร์บอเนต/เอทิลีนออกทีนโคพอลิเมอร์คอมพอสิต (MECHANICAL PROPERTIES OF HDPE/CaCO₃/ETHYLENE-OCTENE COPOLYMER COMPOSITES) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ศ. ดร. สุดา เกียรติกำจรวงศ์, 73 หน้า

งานวิจัยนี้ได้ศึกษาผลของแคลเซียมคาร์บอเนตขนาดอนุภาคระดับนาโนเมตรและเอทิลีนออกทีนโคพอลิเมอร์ต่อสมบัติเชิงกลและการเข้ากันได้ของพอลิเมอร์เชิงประกอบพอลิเอทิลีนชนิดความหนาแน่นสูง/แคลเซียมคาร์บอเนต/เอทิลีนออกทีนโคพอลิเมอร์ (HDPE/CaCO₃/EOC) พบว่าแคลเซียมคาร์บอเนตขนาดอนุภาค 60 นาโนเมตรที่ไม่มีการปรับแต่งพื้นผิวร้อยละ 20 โดยน้ำหนักทำให้เกิดการรวมตัวกันเป็นอนุภาคขนาดใหญ่ขึ้น การกระจายตัวที่ไม่ดีของแคลเซียมคาร์บอเนตในพอลิเมอร์เมทริกซ์นี้ ทำให้ความทนแรงกระแทกลดลงร้อยละ 37.7 ความทนแรงดึงยึดที่จุดเปลี่ยนลดลงร้อยละ 2.3 ส่วนความทนแรงดึงยึดที่จุดขาดและค่ามอดุลัสเพิ่มขึ้นเมื่อเทียบกับพอลิเอทิลีนบริสุทธิ์ การปรับแต่งพื้นผิวโดยใช้สารคู่ควบไททานเตต KR TTS หรือ KR 12 บนพื้นผิวของแคลเซียมคาร์บอเนต ช่วยลดการรวมตัวและเพิ่มกระจายตัวของอนุภาคแคลเซียมคาร์บอเนตในพอลิเมอร์เมทริกซ์ ซึ่งตรวจได้ด้วยเทคนิคกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด การปรับแต่งพื้นผิวด้วย KR TTS หรือ KR 12 ที่ร้อยละ 0.8 โดยน้ำหนักแคลเซียมคาร์บอเนต ให้ความทนแรงกระแทกเพิ่มขึ้นร้อยละ 29.6 และ 31.4 ตามลำดับ และความทนแรงดึงยึดที่จุดเปลี่ยนเพิ่มขึ้นขณะที่ค่ามอดุลัสลดลงเมื่อเทียบกับแคลเซียมคาร์บอเนตที่ไม่มีการปรับแต่งพื้นผิว การใช้เอทิลีนออกทีนโคพอลิเมอร์ในพอลิเมอร์เชิงประกอบนี้ ช่วยปรับปรุงความทนแรงกระแทกได้ดี โดยเฉพาะการใช้แคลเซียมคาร์บอเนตที่มีการปรับแต่งพื้นผิวด้วย KR TTS หรือ KR 12 ที่ร้อยละ 0.8 ร่วมกับเอทิลีนออกทีนโคพอลิเมอร์ที่ร้อยละ 2 ทำให้ความทนแรงกระแทกสูงกว่าพอลิเอทิลีนบริสุทธิ์ ขณะที่การใช้แคลเซียมคาร์บอเนตที่ไม่มีการปรับแต่งพื้นผิวนั้น ต้องใช้เอทิลีนออกทีนโคพอลิเมอร์มากถึงร้อยละ 6 จึงทำให้ความทนต่อแรงกระแทกสูงกว่าพอลิเอทิลีนบริสุทธิ์

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Effects of nano-sized CaCO₃ particles and Ethylene-Octene Copolymer (EOC) contents on mechanical properties and compatibility of HDPE/CaCO₃/EOC composites were studied in this research. The results showed that the composites containing 20% loading of 60-nm CaCO₃ particles without a surface treatment caused the particle agglomeration. Its poor dispersion in the polymer matrix lowered the Izod impact strength by 37.7% and yield strength by 2.3% but increased breaking strength and tensile modulus of the composites as compared to the neat HDPE. The surface pre-treatment of CaCO₃ with the titanate coupling agent KR TTS or KR 12 decreased the CaCO₃ particle agglomeration to give better particle dispersion as observed in the SEM micrographs. The KR TTS or KR 12 at 0.8% weight loading of CaCO₃ increased the Izod impact strength by 29.6% and 31.4%, respectively, in comparison with the untreated composites. Tensile modulus was still lower than that of the neat HDPE but the yield strength was increased. The use of EOC markedly improved the Izod impact strength of the HDPE composites especially when the pre-treated CaCO₃ particles with 0.8% weight of KR TTS or KR 12 was used in combination with EOC at 2% loading, a higher Izod impact strength when compared to the neat HDPE was obtained. When the polymer composite contains the untreated CaCO₃, a 6% EOC loading must be incorporated to achieve the higher Izod impact strength as compared to the neat HDPE.

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CHAPTER I

INTRODUCTION

1.1 General Introduction

Thermoplastic polymers, especially polyolefin, are produced and consumed today in vast quantities. High-density polyethylene (HDPE) has been considered as a primary material in the product chain because of its wide availability and recyclables [Selke *et al.* 2004; Tanniru *et al.* 2006]. However, it is seldom used as a neat polymer and is usually compounded with mineral fillers. Initially, fillers were used as extenders for polymer to reduce cost; attention has been more and more focused on functionality enhancement in the filler-filled composites. The use of inorganic filler has been a common practice in the plastic industry to improve mechanical properties of thermoplastics. As an important inorganic filler or pigment, calcium carbonate (CaCO_3) has been used in many fields especially polyolefin [Suwanprateep, 2000; Zuiderduin *et al.*, 2003; Osman *et al.*, 2004; Gai *et al.*, 2005; Yang *et al.*, 2006].

In general, physical and mechanical properties of polymer composites are related closely with the dispersion state of the filler particles in the matrix, especially for nanometer filler because of the larger particle surface contact areas among the particles leading to formation of stronger filler clusters than in micro-composites [Osman *et al.*, 2006]. However, coupling agents, such as, titanate applied on the surface of the mineral filler can promote filler-polymer interaction. As a consequence, it improves filler dispersion in the matrix, ease polymer processing, and increases tensile and impact properties of the composite [Monte, 1995; Wah *et al.*, 2000; Gonzalez *et al.*, 2002; Hsiang *et al.*, 2004; Liang *et al.*, 2007]. Recently, phase polymer composites, containing a soft elastomer and rigid filler, have become the subject of increasing numbers of studies that aim to achieve an optimum balance of impact strength and stiffness [Premphet *et al.*, 2000; Zebarjad *et al.*, 2006; Bao *et al.*, 2007; Ma *et al.*, 2007].

1.2 Objectives

This research aimed to study the influence of nanometer-sized CaCO_3 particle surface treatment, and the synergistic toughening effect of EOC and the CaCO_3 on the properties of HDPE/ CaCO_3 /EOC ternary composites.

1.3 Scope of research

This research will focus on the HDPE/ CaCO_3 /EOC blends on the following topics.

1. Pre-treatment of CaCO_3 with different titanate coupling agents: isopropyl, tri(dioctyl)phosphato titanate (Ken-React[®] KR TTS) and isopropyl, triisostearoyl titanate (Ken-React[®] KR 12) using a high-speed mixer.
2. Blending of HDPE/ CaCO_3 /EOC using a twin screw extruder.
3. To investigate the effects of different titanate coupling agents to pre-treat CaCO_3 for HDPE/ CaCO_3 /EOC blends on CaCO_3 dispersion, melt flow, tensile strength, impact strength and properties.
4. Evaluations of the effects of EOC-to-HDPE/ CaCO_3 /EOC blend ratios on tensile strength, impact strength, thermal and morphological properties.

CHAPTER II

THEORY AND LITERATURE REVIEW

Polyethylene (PE) is a family of addition polymers based on ethylene. Polyethylene can be linear or branched, homopolymer or copolymer. In the case of copolymer, the other comonomer can be an alkene such as propene, butene, hexene or octene. If the molar percent of the comonomer is less than 10, the polymer can be classified as either a copolymer or homopolymer. Figure 2.1 presents a diagram of the family of polymers based on ethylene monomer.

Polyethylene was the first olefinic polymer to find use in food packaging. Introduced in the 1950s, it became a common material by 1960 for uses in film, molded containers, and closures. Since low density polyethylene was first introduced in 1940, strength, toughness, thermal and heat sealing properties, optical transparency, and processing conditions have been much improved. Today there are a number of polyethylene grades of relevance to packaging, as shown in Figure 2.1 [Selke *et al.*, 2004].

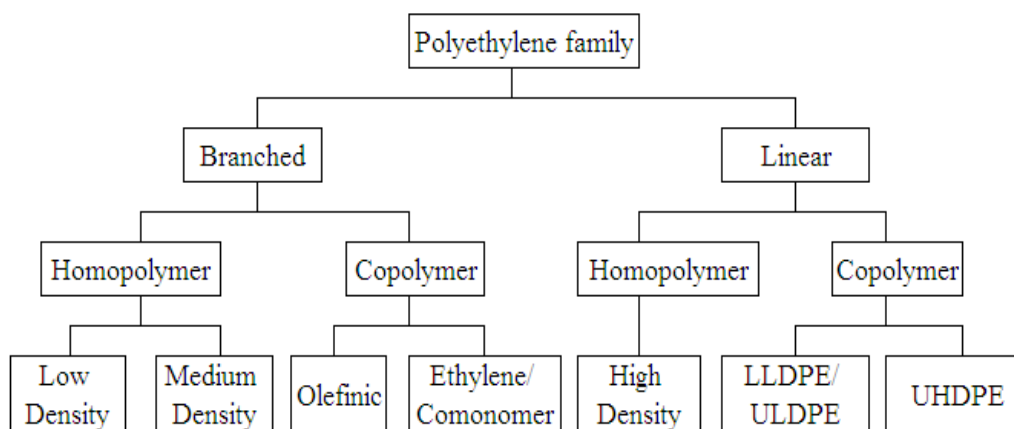


Figure 2.1 The polyethylene family [Selke *et al.*, 2004]

2.1 High density polyethylene (HDPE)

HDPE is a milky-white, nonpolar, linear thermoplastic. Its density ranges from 0.940 to 0.965 g/cm³, and it has a melting temperature ranging from 128-138 °C. It is one of the most versatile polymers, and is the most commonly used plastic in the packaging industry. Typical applications include [Selke *et al.*, 2004]:

- (a) Containers for milk, detergent, bleach, juice, shampoo, water, and industrial chemical drums made by extrusion blow molding.
- (b) Buckets, thin walled dairy containers, and closures made by injection molding.
- (c) Cosmetic containers, pharmaceutical bottles, and deodorant containers made by injection blow molding.
- (d) Blow and cast films utilized in flexible packaging applications such as cereal, cracker and snack food packaging, wrap for delicatessen products, and produce bags.

The molecular chains of HDPE homopolymers are long and strong with little inclusion of branching chains. HDPE forms a large fraction of ordered, crystalline regions as it cools below its melting temperature, T_m . This close packing produces HDPE with a crystallinity of 65-90% and contributes to HDPE's good moisture-barrier properties and non-transparency. HDPE has excellent resistance to a wide range of chemical compounds: water-based products, medium molecular weight aliphatic hydrocarbons, alcohols, acetone, ketones, dilute acids and bases but not being acceptable for aromatic hydrocarbons such as benzene. Tensile strength of HDPE can be as high as 45 MPa. Impact strength is primarily controlled by molecular weight (MW) although it is affected by molecular weight distribution (MWD). HDPE is also characterized by good moisture barrier properties, and poor oxygen and organic compound barrier characteristics. It has good machinability characteristics. Table 2.1 summarizes HDPE properties [Selke *et al.*, 2004].

Table 2.1 Properties of HDPE

Density	0.94 to 0.965 g/cm ³
T _g	-120 °C
T _m	128-138 °C
Tensile strength	17.3-44.8 MPa (2,500-6,500 psi)
Tensile modulus	620-1,089 MPa (89,900-158,000 psi)
Elongation at break	10-1200%
Tear strength	20-60 g/25 μm
WVTR*	126 g μm/m ² d at 37.8 °C, 90% RH (0.32 g mil/100 in ² d at 95 °F, 90% RH)
O ₂ permeability, 25°C	40,000-73,000 cm ³ μm/m ² d atm (100-185 cm ³ mil/100 in ² d atm)
CO ₂ permeability, 25°C	200,000-250,000 cm ³ μm/m ² d atm (500-640 cm ³ mil/100 in ² d atm)
Water absorption	<0.01%

*WVTR (water vapor transmission rate) is the steady state rate at which water vapor permeates through a film at specified conditions of temperature and relative humidity. Values are expressed in g/100 in²/24 hr in US standard units and g/m²/24 hr in metric (or SI) units. Thickness of HDPE film was presented in millimeter (mil) or micrometer (μm) and 1 mil equals to 1000 μm.

2.2 Calcium carbonate

Calcium carbonate (CaCO₃) is the most important filler, in terms of volume, but is relatively low in value. In the plastic industry, it has mainly been used in PVC compounds, but 'engineered' grade (produced by adjusting particle size or geometry, and/or modifying the surface) are opening up a large potential market in polyolefins, where the aim is not to extend the bulk of the compound but to offer positive properties, such as reducing cycle time and improving physical/mechanical properties. For example, very fine particle gives a marked increase in the strength of films. Stearic acid-coated grades give good mechanical properties and improved processing. Suitable calcium carbonates can be used in part replacement of white pigment. A new

area of development is to incorporate the filler permanently into the polymer matrix, by use of a coupling agent. This can increase impact strength [Murphy, 2001]. They can be subdivided into naturally derived and precipitated products.

2.2.1 Natural calcium carbonates

Natural calcium carbonates are produced from one of three types of product, chalk, limestone and marble. All are forms of the mineral calcite. Chalk and limestone are very similar and differ only in degree of compaction (initial hardness of the source mineral). Chalk is less compacted than limestone but in practice there is a gradual transition from one form to other form. The mineral is abundant throughout the world, thus the cost of the product is very low and this forms the basis for much of its use.

Stearic-acid-coated calcium carbonates are also available. The products obtained may be divided into four types according to particle size and coating.

- | | | |
|------------------------|---|---|
| 1. Ultrafine, uncoated | } | Less than 1- μm mean diameter |
| 2. Ultrafine, coated | | |
| 3. Coarse, uncoated | } | Greater than 1- μm mean diameter |
| 4. Coarse, coated | | |

The products with a mean diameter of 1 μm or finer do provide superior properties than those are coarser. This is especially important where hot tear strength is a requirement where the ultrafine products may compete with the precipitated grades in less critical applications [Rothon, 1995].

2.2.2 Precipitated calcium carbonates

Precipitated calcium carbonates are produced by a controlled precipitation from calcium hydroxide solution by carbonation. The products of this process are 0.05-0.1 μm fine particles, which may be coated with fatty acid (stearic) or a reactive resin (carboxylated polybutadiene). Uncoated grades are also available.

Some precipitated calcium carbonate is also available as a byproduct of water-softening plants. These grades are generally coarser with poorer control of properties

and, naturally, less costly. Other precipitated calcium carbonate grades are available but do not find general applicability to plastics.

These materials are all semi-reinforcing in character as a consequence of their fine particle size. The uncoated and fatty acid coated grades exhibit very poor interaction with polymer, so the modulus (a function of polymer-filler interaction) is very low, thus soft compounds with readily ageing performance is superior to naturally derived calcium carbonates. One of the outstanding features of these fillers is their high-temperature tear resistance. The precipitated calcium carbonate with a reactive coating is available and exhibits increased modulus and fatigue properties compared with the stearic-coated ones [Rothon, 1995].

2.3 Agglomeration of particle

A continuing problem with particulate fillers is that they often will not flow smoothly, but tend to agglomerate, leading to irregular distribution of the particles in a compound, with attendant processing problems, poor surface quality, and reduction in mechanical properties. Research has shown that agglomerate is determined by the relative magnitude of attractive and separating forces, the most important factors influencing the homogeneity of polymer composites being the size of the particles, their surface tension, and the shear forces acting on them during homogenization.

The extent of agglomeration is always determined by the relative magnitude of the forces attracting and separating among the particles. In polymer composites, the most important attractive force is adhesion, while hydrodynamic forces (such as shear) lead to separation of particles. The size and surface tension of the particle strongly influence aggregation. The specific surface area tends to give a good indication of the agglomeration tendency of a filler, especially for nanometer filler because of the larger particle surface contact areas among the particles leading to formation of stronger filler clusters than in micro-composites [Osman *et al.*, 2006]. The particle size distribution is even more important since individual particles tend to interact with each other. The results obtained also indicate that the properties of the powder and the suspension may yield valuable indirect information about

agglomeration. The extent of agglomeration may be reduced by non-interactive surface treatment and increasing shear of the composite.

2.4 Surface modification

Surface modification of fillers to give improved properties to a plastic is a topic that has received enormous attention over the last 20 years. Improvements in mechanical properties, dispersion of filler which leads to improved properties, improved rheology and higher filler loading, have all been reported to accrue from rendering the surface more hydrophobic and hence compatible with the polymer; or by enabling the filler to bond covalently, through hydrogen or ionic bonds to the polymer; or by changing the physical nature of the interface so that energy adsorption can occur [Rothon, 1995].

2.4.1 Stearic acid

The most widely used surface modification is treatment with stearic acid; metal stearates are also used. Stearic acid will react with basic minerals to give a surface that is covered with strongly bonded long organic ions. Stearic acid modified silicates are commercially available but in these cases the stearic acid is certainly weakly adsorbed and probably desorbed during melt compounding. Metal stearate similarly will form weak bonds with mineral surfaces and desorbs from them. These relatively labile coating will in the initial stages of a compounding operation, before they desorbed, help improve dispersion. They also give a protective coating to the filler minimizing any polymer degradation that may occur before stabilizers, antioxidant, etc are fully dispersed [Rothon, 1995].

2.4.2 Coupling agent

Surface treatments with bifunctional additives, which form very strong covalent bonds to the filler and then bond to a polymer by a variety of mechanisms,

are widely available. They are based on organometallic compounds with the general formula:



where M is a metal ion with the valencies of $a + b$. R^I is an organic group, the choice of which depends on the polymer to be used. R^{II} is a group designed to react with a mineral surface.

The R^{II} in most of the coupling agents is an alkoxy group (methoxy, ethoxy or 2-methoxyethoxy are common), which is reactive to hydroxyl groups and to water. The preferred reaction mechanism is for hydrolysis to occur, initially by reaction with environmental or adsorbed water, with the kinetics being affected by the nature of both alkoxy and other reactive groups on the molecule. The organometallic hydroxide then condenses with hydroxyls on the mineral surface or it can form oligomers followed by polymers through self-condensation reactions.

The most commonly employed compounds are organosilanes and organotitanates.

2.4.3 Organotitanate

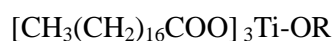
Organotitanates are a very interesting class of surface modifier, which have aroused great interest in recent years. They can all be regarded as derivatives of orthotitanic acid, $Ti(OH)_4$, and hence are commonly known as organotitanates rather than by their systematic name. In concept, the organotitanate are similar to silanes. That is they are designed to have groups (generally alkoxy) that readily hydrolyse to titanium hydroxyl groups that can condense with surface hydroxyls and also to carry other organic groups, which are more hydrolytically stable and may also provide some reactive functionality. Depending on their chemical nature, organotitanates can be precoated from organic or aqueous solution, dry blended or use in situ.

Monte's basic approach [1995] is to use alkoxy groups as the hydrolysable group of the titanium and acid groups (carboxylate, phosphate, sulphonate) to give

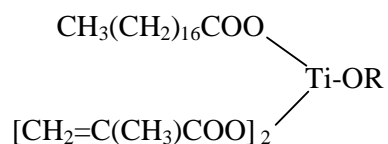
stable attachment of other organic groups. Initially, single isopropoxy groups were used as the hydrolysable group and the products known as monoalkoxytitanate.

While no comprehensive study has been made, it is generally claimed that organotitanates are effective on a wide variety of particulate mineral surfaces. This claim is, however, often based on a dispersant action in simple tests where adsorption rather than strong surface bonding is often sufficient to produce an effect. Based on the proposed mode of action, one would expect the best performance to be produced on heavily hydroxylated surfaces such as silica, silicates and hydroxides. Organotitanates seem especially effective on calcium carbonate, however, even though surface has few hydroxyls and orthotitanic acid is too weak to displace carbonate. Some other bonding mechanism must thus be involved. It must be borne in mind that considerable free carboxylic acid is potentially present and may play a significant role on this particular surface.

The simplest organotitanates in general use as filler modifiers are nominally triacyloxy isopropoxy derivatives. As mentioned earlier, the supposed mode of action is hydrolysis and surface condensation through the isopropoxy group and stable bonding of the acyloxy groups to the titanium atom. Where these acyloxy groups are long chain fatty acids, then simple hydrophobing and dispersion effects are observed. If, however, they contain some reactive functionality, then chemical coupling to the matrix polymer is possible. Typical compounds of these types are non reactive such as



and reactive like the following



The sort of structure claimed to be formed on filler surfaces is shown in Figure 2.2(a). Several points need to be made about this structure. Firstly, the molecule is very bulky and in this scheme only has one attachment point to the surface. Thus it is unlikely to be able to react with more than a small fraction of the surface hydroxyls

present on many types of filler. Secondly, these idealized structures differ from the silane coupling agents in having no bonding between adjacent coating molecules. One would expect that such a coating may exhibit poor hydrolytic stability. Finally, the acylate groups themselves are also of doubtful hydrolytic stability. It could well be then that some of these hydrolyze leading to further surface reaction and condensation similar to that observed with the silanes.

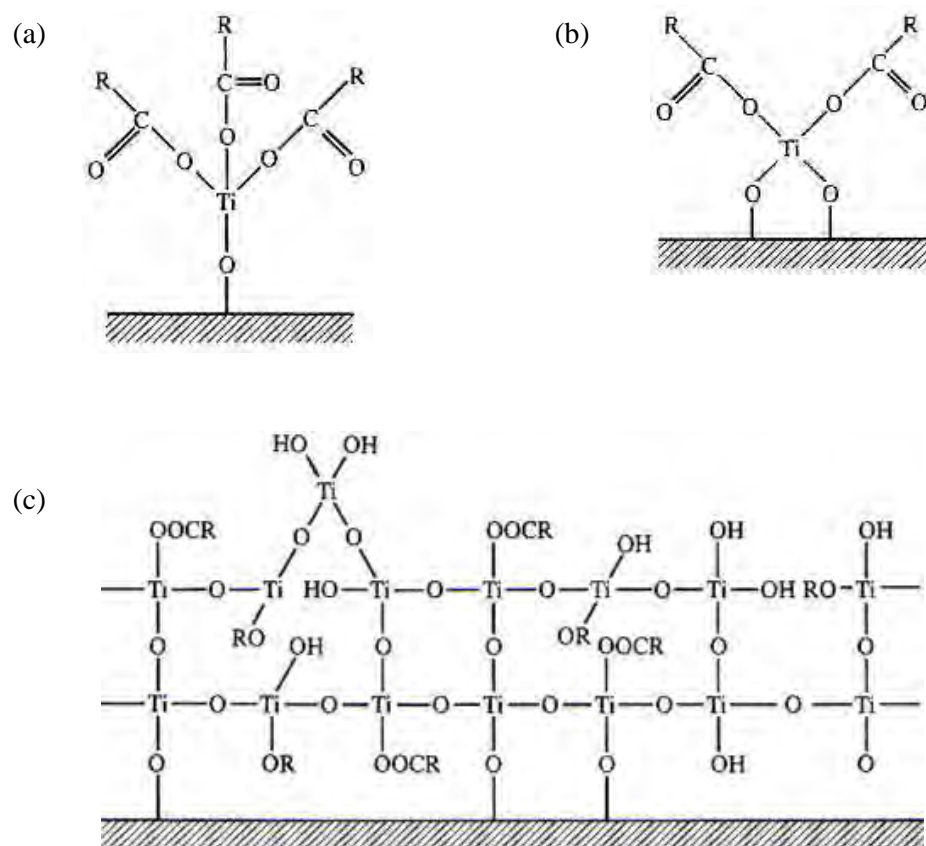


Figure 2.2 Structures proposed for the reaction of monoalkoxy titanates on filler surfaces: (a) Mono-functional reaction, (b) bi-functional reaction, (c) the complex, partly hydrolyzed, and condensed layer.

Irrespective of the controversy over the structure of the organotitanates and their mode of action, they do appear to give useful effects. Their main utility appears to give excellent dispersion of particles and hence low-viscosity, easily processable

formulations with good end properties, In this respect they must then be judged against other materials used to achieve the same effects, notably surfactants and fatty acids. The latter are especially relevant as the organotitanates in use are largely based on these and, as we have seen, may indeed contain or form considerable quantities of the free acids. Unfortunately, very little data exist on which can properly judge the relative merits of the organotitanates and other treatments.

As mentioned earlier, Kenrich KR TTS is probably the most widely studied organotitanate in the present respect and serves as a good example of the utility of organotitanates. Several examples of its use to produce low viscosity dispersions of fillers such as calcium carbonate and aluminium hydroxide in organic liquid can be found in the manufacturer's literature and the papers by Monte [1995].

It is claimed that a significant part of their effectiveness is due to chemical removal of the surface water layer on the particles, which promotes agglomeration. Such an effect is not present with other common types of dispersants.

2.4.4 Method of surface modification

Modification of surface of filler may be brought about in variety of ways. The filler may be pre-coated or the coating agent may be added during compounding and make its way to the filler surface (*in-situ* coating). The main advantages and disadvantages of the two procedures are summarized in Table 2.2. The relative importance of the various factors will vary depending on the nature of the coating and filler, and the composite processing conditions.

When the filler is pre-coated, various methods may be used depending on the nature of the filler, the coating and the filler preparation procedure. When the filler is produced from aqueous solution, it is often advantageous to add a water-dispersible form of the coating prior to filtration and drying. If the coating is carefully chosen, it can actually aid filtration and reduce cracking during drying. In most instant, however, the cost of solvent removal makes solution coating uneconomic and dry coating is favored wherever possible. Dry coating is often achieved during a milling process or by use of a high speed mixer [Rothon, 1995].

Table 2.2 Relative merits of precoating and *in-situ* addition of surface modifiers

Precoating	<i>In situ</i>
Expensive, additional step often required.	Usually, a less expensive procedure.
Volatile byproducts are easily dealt with.	Volatile byproduct can be a problem.
Often improved filler handling and reduced moisture pick-up, may also aid wet-out of Polymer.	No assistance with filler handling or water pick-up, may give some improvement in polymer wet-out
Assured surface reaction with coating level readily controlled but will not treat any fresh surface generated during compounding. No competition from other surface-active species in the formulation.	Less control over surface reaction and coating level but has the opportunity to coat freshly formed surfaces. Competition formed surface-active species must be guarded.
Interpenetration of coating and matrix may be limited.	Greater opportunities for the coating matrix to interpenetrate.
Less formulation freedom.	Greater formulation freedom

2.5 Elastomer modification

Elastomer has always been used as a component or additive to plastic. Essentially the elastomer provides a network of ‘buffers’ in the plastic matrix, forming an energy-absorbing or dissipating phase, that will physically absorb or dissipate the energy of an impact, over the broad range of temperature (especially at the lower rather than the higher end of scale). It is important, through, to choose an elastomer with the right volume fraction, morphology and interaction with the plastic matrix are commonly obtained by *in-situ* reactor polymerization, grafting or melt blending.

The classic technology is the modification of general purpose polystyrene with styrene butadiene to produce high impact polystyrene (PS). Butadiene has also long been used, especially in acrylonitrile butadiene styrene (ABS), polyisoprene is a more recent modifier. Initially modification could be achieved simply by compounding but, with improvement in technology, copolymers were developed and the function was taken upstream to the reactor.

With the advent of polyolefins, a different system was needed, especially when, with the development of polypropylene (PP), it was clear that its useful mechanical properties fell off rapidly at temperatures below 0°C. A compatible elastomer such as ethylene propylene rubber (EPR) [Zebarjad *et al.*, 2006], maleated styrene-ethylene/butylene-styrene block copolymer (SEBS-g-MA) [Bao and Tsong, 2007], ethylene-octene copolymer (EOC) [Premphet and Horanont, 2000; McNally *et al.*, 2002; Zhang *et al.*, 2002; Ma *et al.*, 2007] was used as a mechanical blend.

2.5.1 Polyolefin Elastomers

Polyolefin elastomers (POEs) are a relatively new class of polymers that emerged with recent advance in metallocene polymerization catalyst. Representing one of the fastest growing synthetic polymers, POEs which are compatible with most olefinic materials, are an excellent impact modifier for plastics, and offer unique performance capabilities for compounded products. In less than a decade, POEs have emerged as a leading material for automotive exterior and interior applications, primarily in thermoplastic olefins (TPOs) via impact modification of polypropylene, wire and cable, extruded and molded goods, film applications, medical goods, adhesives, footwear, and foams [Scheirs and Kaminsky, 1999].

Most commercially available POEs are copolymers of either ethylene-butene or ethylene-octene. Today, wide arrays of products are available with properties ranging from amorphous to crystalline, and from low to very high molecular weight.

POEs are often chosen over alternatives because they are:

1. Suited for thermoplastic or thermoset (peroxide or moisture-cure) applications, either as the main polymer or as a value-enhancing ingredient in compound formulations,

2. In a pellet-form for use in both batch and continuous compounding operations,
3. Providing superior elasticity, toughness, and low temperature ductility,
4. Designed to optimize processing and end-use performance
5. Saturated polymers providing excellent thermal stability and UV resistance, and
6. Recyclable.

POEs are being adopted in a variety of applications and markets resulting in global demand approaching 200 metric tons since their inception in the early 1990s. This volume should double by the mid-2000s with increasing demand and projected production expansion.

Polyolefin elastomers are copolymers of ethylene and another alpha-olefin such as butene or octane as shown in Figure 2.3 in which elastomeric character increases with increasing of alpha-olefin content [Scheirs and Kaminsky, 1999].

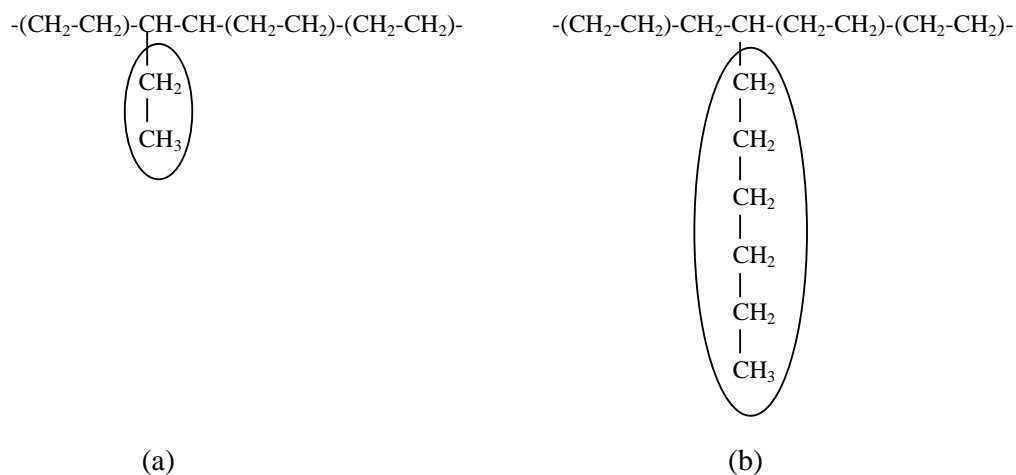


Figure 2.3 Chemical structures of (a) Ethylene-1-butene copolymer and (b) Ethylene-1-octene copolymer.

The metallocene catalyst selectively polymerizes the ethylene and comonomer sequences and increasing the comonomer content will produce polymers with higher elasticity as the comonomer incorporation disrupts the polyethylene crystallinity.

Furthermore, the molecular weight of the copolymer will help determine its processing characteristics and end-use performance properties with higher molecular weights providing enhanced polymer toughness.

POEs are produced using a refined metallocene catalyst often referred to as single-site or constrained geometry catalysts (Figure 2.4). These catalysts have a constrained transition metal (generally a Group 4B metal such as Ti, Zr, or Hf) sandwiched between one or more cyclopentadienyl ring structures to form a sterically hindered polymerization site. This unique catalyst provides a single polymerization site instead of the multiple sites of conventional catalysts and provides the capability to tailor the molecular architecture of ethylene copolymers. (Note: Metallocene catalysts and process technologies can also be used to produce ethylene propylene rubbers).

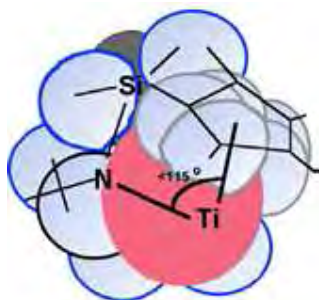


Figure 2.4 Constrained geometry catalyst of polyolefin elastomers [Scheirs and Kaminsky, 1999]

The metallocene catalyst can be used in a number of polymerization processes including slurry, solution, and gas phase operations. The polyolefin elastomer solution polymerization process was shown in Figure 2.5. The catalyst is usually first mixed with an activator or a co-catalyst, which can significantly enhance the polymerization efficiencies to beyond a million units of polymer per unit of catalyst. Very low levels of the catalyst mixture are continuously metered into a reactor along with a predetermined ratio of ethylene and comonomer of choice. The molecular weight of the polymer continues to build with the polymerization of ethylene and comonomer at the catalyst site until the polymerization was stopped by catalyst deactivation or chain

termination with hydrogen introduction to the reactor. Polymerization is very exothermic and requires efficient heat removal from the transport media of gas or solvent. Furthermore, reactor conditions must be carefully maintained to avoid loss of process control.

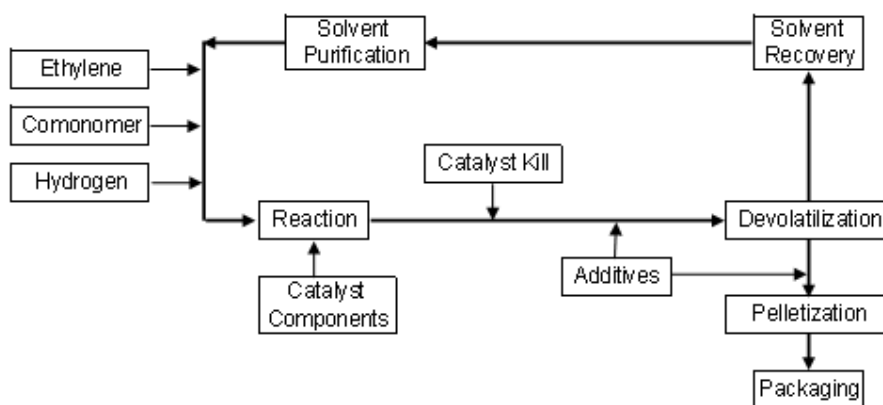


Figure 2.5 Polyolefin elastomer solution process [Scheirs and Kaminsky, 1999]

2.6 Literature Review

Lazzeri *et al.* [2004] studied the effect of surface interactions of stearic acid (SA) on physico-mechanical properties and rheological behavior of CaCO₃/HDPE nanocomposites. The results showed that the addition of 10 vol% CaCO₃ to HDPE caused a rise in Young's Modulus and yield stress of its composites. The addition of SA caused decreases in both Young's Modulus and yield stress of the composites compared to the uncoated PCC composites. The microscopic evaluation showed the particle aggregation of the uncoated CaCO₃ system leading a sharp drop in impact strength. The addition of SA could not completely prevent the particle from aggregate but it could reduce the size of agglomerates and progressively increased the impact strength of the composites compared to the uncoated PCC composites.

Osman and Attlah [2006] reported about CaCO₃ filled polyethylene nanocomposites that more and strong clusters were formed in microcomposites due to

the large contact area between the particles. The clusters had different shapes and maximum packing than the nearly spherical primary particles, thus enhanced the moduli and viscosity of the composites. The obtained results indicated that the higher moduli and viscosity of the nanocomposites were not a direct consequence of the particle size but was due to the presence of agglomerates and aggregates.

Wah *et al.* [2000] studied the effect of titanate coupling agent (LICA 12) on rheological behaviour, dispersion characteristics and mechanical properties of talc-filled polypropylene. It was found that the melt viscosity of the filled PP decreased and dispersion quality was improved in the presence of titanate coupling agent. Further investigation on molecular weight distribution (MWD) showed that PP molecules had undergone some chain scission and coupling reactions to give the broader MWD. Glass transition temperature (T_g) measurement revealed the plasticizing effect caused by the coupling agent, which had imparted changes in morphological character and mechanical properties. Tensile and Flexural properties were observed to decrease whilst impact and elongation properties were improved with the incorporation of coupling agent in the filled system.

Gonzalez *et al.* [2001] studied the effects of coupling agents on mechanical and morphological behavior of the PP/HDPE blend with two different CaCO_3 . The structural difference between CaCO_3 and PP/HDPE gave rise to the formation of large filler agglomerates in the polymer matrix, which influenced the mechanical response of the material. Therefore, the coupling agents of the Lica 12 type at various concentrations was used to facilitate the linkage between filler and matrix (the latter consisting of PP/HDPE 80/20 wt ratio). Filler was added to the PP/HDPE blend at a 30 wt.% concentration. Two types of calcium carbonate (CaCO_3) were used. These had different average sizes (3.0 and 1.8 μm) which were determined by means of laser diffraction techniques. In addition, other coupling agents of the titanate type, such as Lica 09, Lica 01, zirconates ZN 12, and a 1:1 mixture of Lica 12 and Lica 01, were used. This study clearly demonstrated that the addition of the coupling agent to CaCO_3 modified the mechanical properties of the PP/HDPE/ CaCO_3 composites. The mechanical properties indicated that due to its characteristics, each coupling agent

gave rise to increases in a particular mechanical property. In the case of Lica 01, an increase was verified in Young's modulus at 0.7 wt.% and in elongation at break at both concentrations (0.3 and 0.7 wt.%), whereas ZN 12 brought about an increase in elongation at break. The 1:1 mixture of Lica 12 and Lica 01 caused impact resistance of the blend of PP/HDPE with CaCO₃ to increase considerably.

Liang [2007] studied the effect of surface treatment method on the dispersion of nano-CaCO₃ particles in polypropylene matrix. The dispersion of the nano-CaCO₃ particles in the PP matrix was observed by means of a scanning electron microscope (SEM), and the dispersion effect or formation was preliminarily evaluated by applying a fractal model based on statistic means from the SEM images. The results showed that the dispersion of the nano-CaCO₃ particles in PP matrix was more homogeneous when the fractal dimensionality was less than about 1.5. In addition, the smaller the fractal dimensionality, the better the dispersion of the particles in the matrix was, within a certain limit. Under the same conditions, the dispersion of titanate coupling agent pretreated system was better than that of surface activation with fatty acid system.

Premphet and Horanont [2000] studied the phase structure of ternary polypropylene/elastomer/calcium carbonate composites using scanning electron microscopy, dynamic mechanical analysis and differential scanning calorimetry. Two kinds of phase structure were observed either a separate dispersion of the phases or encapsulation of the filler by elastomer. The composite phase structure was determined mainly by the chemical characteristics of the components and, to a lesser degree, by the sequential mixing of each component. In this study, the use of non-polar ethylene–octene copolymer (EOR) resulted in a composite having separate dispersion of elastomer and filler particles. When the polar ethylene–vinyl acetate (EVA) elastomer was used, an encapsulation structure was formed.

Guimaraes *et al.* [2003] studied the effect of molecular weight and long chain branching of metallocene elastomer on the properties of high density polyethylene blends. The rheological properties and morphological characteristics of the blends

based on high density polyethylene (HDPE) and two different grades of poly(ethylene-*co*-octene) metallocene elastomer (EOC) were studied. These elastomers were commercial samples differing in molecular weight, and rheology index (DRI). The blends were processed in a single screw extruder having an L/D = 32, at 230 °C and 50 rpm, using a mass fraction weight percent of EOC in the range from 5-80%. The rheological properties were evaluated in dynamic experiments at 190°C and frequency range from 10^{-1} s^{-1} to 10^{-2} s^{-1} . The blends exhibited pseudoplasticity and complex rheological behavior. The complex behavior was intensified by increasing molecular weight and long chain branching proportion (DRI) of EOC elastomer. The morphological characterization was carried out using scanning microscopy (SEM). The blends exhibited dispersed morphologies with EOC domains distributed homogeneously in PE and with particle size inferior to 2 μm .

Ma *et al.* [2007] reported on properties improvement of polypropylene (PP) by incorporating ethylene–octene copolymer (POE) and nanosized calcium carbonate. Two types of CaCO_3 nanoparticles (stearic acid treated and untreated) and two processing sequences (one-step and two-step mixing) were used to adjust the phase structure of the ternary composites. The experimental results indicated that the one step mixing generated segregated dispersion of POE and CaCO_3 nanoparticles in PP. The two-step process resulted in core-shell structures having 100–200 nm in size throughout the matrix, in which POE acts as the shell part encapsulating one or two nano- CaCO_3 . These specific phase structures were independent on the surface features of CaCO_3 nanoparticles. In comparison with PP/POE blend or neat PP, notched impact toughness of the ternary composites of PP/POE/nano- CaCO_3 was significantly increased. Meanwhile, stiffness and tensile strength of the latter were almost unchanged or slightly enhanced. It is believed that the synergistic effect of both the POE elastomer and CaCO_3 nanoparticles should account for the balanced performance of the ternary composites.

CHEPTER III

EXPERIMENTAL

3.1 Materials

3.1.1 High density polyethylene (HDPE)

High density polyethylene used is Polene[®] V1160, an injection grade, a product from IRPC Public Company Limited (Rayong, Thailand) having a melt flow index of 15 g/10 min (2.16 kg/190 °C), density of 0.957 g/cm³ and melting temperature of 130 °C.

3.1.2 Precipitated calcium carbonate (CaCO₃)

Precipitated calcium carbonate used is Socal[®] 31, a product from Solvay Advanced Functional Minerals (Salin-de-Girand, France), having an average diameter of 60 nm.

3.1.3 Ethylene-octene copolymer (EOC)

Ethylene-octene copolymer resin used is Engauge[®] 8150, a product from DuPont Dow Elastomer PTE Ltd. (Singapore), having a co-monomer content 39% and melt flow index of 0.5 g/10 min (2.16 kg/190 °C).

3.1.4 White mineral oil

White mineral oil used called Carnation[®], a product from Witco Refined Product Group (Tarrytown, NY, U.S.A.) was used as an internal lubricant.

3.1.5 Titanate coupling agent

There are two types of titanate coupling agent used:

- 1) Ken-React[®] KR TTS (see chemical structure in Figure 3.1)
- 2) Ken-React[®] KR 12 (see chemical structure in Figure 3.2)

Both titanate coupling agents are the products from Kenrich Petrochemicals, Inc. (Bayonne, NJ, U.S.A.).

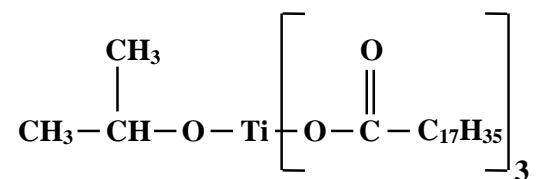


Figure 3.1 Chemical structure of isopropyl, triisostearoyl titanate (Ken-React[®] KR TTS)

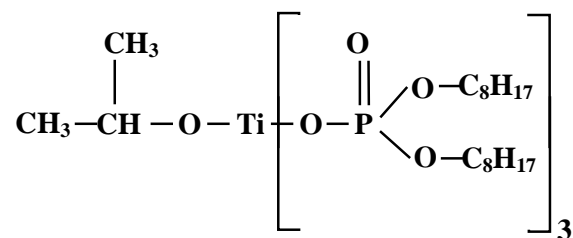


Figure 3.2 Chemical structure of isopropyl, tri(dioctyl) phosphato titanate (Ken-React[®] KR 12)

3.2 Instrument and Apparatus

Instruments used are listed below:

1. High speed mixer (LMX1,5-VS, Labtech Engineering, Bangkok, Thailand)
2. Co-rotation twin screw extruder (Prism TSE 24 MC, Thermo Fisher Scientific Inc., Waltham, MA, U.S.A.)

3. Filter test machine (LFT4-GP, Labtech Engineering, Bangkok, Thailand)
4. Melt flow meter (6542, Ceast, Pianezza, TO, Italy)
5. Injection moulder (Allrounder 221-55-250 & 221-75-350, Arburg GmbH & Co., Lossburg, Germany)
6. Fourier-Transform infrared spectrometer (Spectrum 100, PerkinElmer, Waltham, MA, U.S.A.)
7. X-Ray Fluorescence spectrometer (Minipal 2, PANalytical, Almelo, Netherlands)
8. Universal tensile tester (Instron 4466, Instron Worldwide Headquarters, Norwood, MA, U.S.A.)
9. Universal impact tester (KT-7045B, Kao-Tieh Machinery Inc., Taichung, Taiwan)
10. Differential scanning calorimetry (DSC 100, TA instrument, Newcastle, U.K.)
11. Thermogravimetric analyzer (TGA 50, TA instrument, Newcastle, U.K.)
12. Color spectrophotometer (SF650, Datacolor, Lawrenceville, NJ, U.S.A.)
13. Scanning electron microscope (Quanta 200 FEG, FEI Worldwide Corporate Headquarters, Hillsboro, OR, U.S.A.)

3.3 Procedure

3.3.1 Pretreatment of CaCO₃ particles

The nanometer-sized CaCO₃ particles were treated with the two different titanate coupling agents: Ken-React[®] KR TTS and Ken-React[®] KR 12, each was weighed at 0.2, 0.5 and 0.8% weight of CaCO₃ loading. The weighed coupling agent was diluted with mineral oil at 5% weight of CaCO₃ loading and stirred for 2 min. The diluted solution was slowly added (drop wise) for over 5 min for a batch size of 400 g CaCO₃ and it was then post mixed for 15 min at 3500 rpm by a high speed mixer.

3.3.2 Preparation of polymer composites

The composites were mixed in a co-rotation twin screw extruder with an L/D ratio of 20/1. The HDPE/CaCO₃/EOC samples with different weight ratios as shown in Table 3.1 were each mechanically mixed, and then were introduced into the extruder feeding port. The temperature profile was set at 70, 100, 170, 185, 185, 180 °C and the screw speed was 300 rpm. The feeding port was adjusted to get the screw torque at 30 Nm. The composites were run through the twin screw extruder for two times to accomplish good homogeneity.

Table 3.1 Recipe of the polymer composites

Run	Composites code*	Material loadings (%wt. composites)			
		HDPE	CaCO ₃	Coupling agent (%wt. CaCO ₃)	EOC
1	Neat HDPE	100	0	0	0
2	PE80-0-0	80	20	0	0
3	PE78-0-2	78	20	0	2
4	PE76-0-4	76	20	0	4
5	PE74-0-6	74	20	0	6
6	PE72-0-8	72	20	0	8
7	PE70-0-10	70	20	0	10
8	PE80-2A-0	80	20	0.2 (KRTTS)	0
9	PE80-5A-0	80	20	0.5 (KR TTS)	0
10	PE80-8A-0	80	20	0.8 (KR TTS)	0
11	PE80-2B-0	80	20	0.2 (KR 12)	0
12	PE80-5B-0	80	20	0.5 (KR 12)	0
13	PE80-8B-0	80	20	0.8 (KR 12)	0
14	PE78-8A-2	78	20	0.8 (KR TTS)	2
15	PE76-8A-4	76	20	0.8 (KR TTS)	4
16	PE74-8A-6	74	20	0.8 (KR TTS)	6
17	PE72-8A-8	72	20	0.8 (KR TTS)	8
18	PE70-8A-10	70	20	0.8 (KR TTS)	10
19	PE78-8B-2	78	20	0.8 (KR 12)	2
20	PE76-8B-4	76	20	0.8 (KR 12)	4
21	PE74-8B-6	74	20	0.8 (KR 12)	6
22	PE72-8B-8	72	20	0.8 (KR 12)	8
23	PE70-8B-10	70	20	0.8 (KR 12)	10

*The code, such as PE70-8B-10, as an example can be interpreted as follows: PE70 stands for 70 parts of polyethylene; B for KR 12, A for KR TTS, the number before it for the decimal amount added; the last number for the added EOC concentration.

3.3.3 The titanate coupling agent characterization by X-Ray Fluorescence spectroscopy (XRF)

The titanate coupling agent solution as prepared in Section 3.3.1 was poured in a sample cell with a 6-micron Mylar film window and subjected to an XRF spectrometer with an Rh anode, a Th cathode and a Si PIN detector. The analysis condition was 30 kV, 4 mA using a Kapton filter; total analysis time was 200 s per sample. The XRF feature is shown in Figure 3.3.

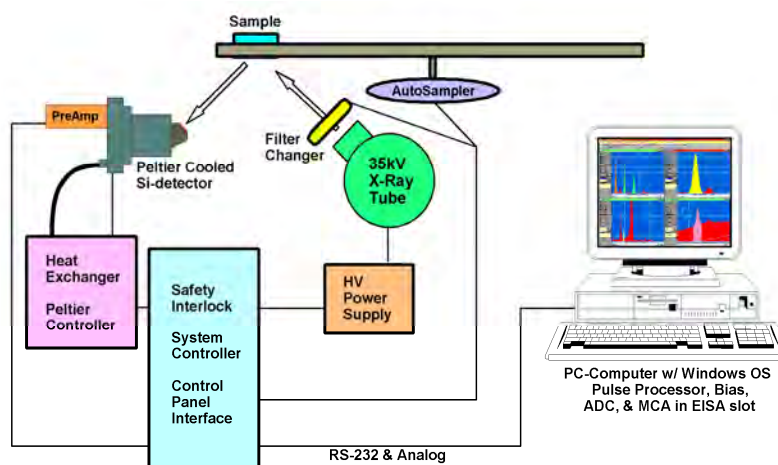


Figure 3.3 A typical PIN detector in an XRF instrument [PANalytical, 2004]

The XRF spectroscopy works via the 2 steps as follows:

- (1) An X-ray ray emitting from a source strikes an inner shell electron. If at high enough energy (above the absorption edge of an element), it is ejected it from the atom.
- (2) Higher energy electrons cascade to fill vacancy, giving off the characteristic fluorescent X-rays.

The electron cascade diagram is shown in Figure 3.4.

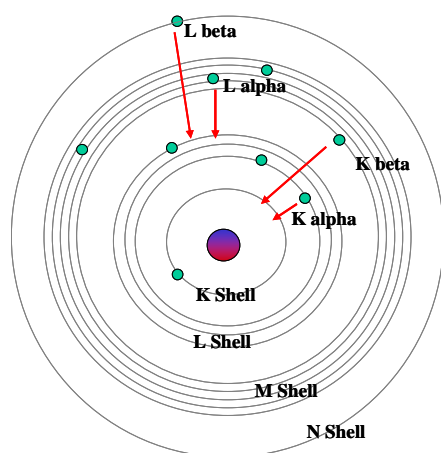


Figure 3.4 Diagram for electron cascaded from X-rays attacking [PANalytical 2004]

The samples were analyzed by the dispersive energy of cascaded electrons as follows [PANalytical 2004]:

- (1) Ti element K_{α} at 4.508 keV and K_{β} 4.931 keV
- (2) P element K_{α} at 2.013 keV and K_{β} 2.139 keV
- (3) Rh element (from anode) L_{α} at 2.696 keV and L_{β} 2.834 keV

3.3.4 Identification of functional groups by Fourier-Transform Infrared Spectroscopy (FT-IR)

The functional groups of KR TTS, KR 12, and the pretreated and untreated CaCO_3 were analyzed by a Fourier-Transform Infrared Spectroscopy (FT-IR). The analyses were made in a transmittance mode on a PerkinElmer spectrophotometer (Spectrum 100), using 32 scans per resolution. The KR TTS/mineral white and KR 12/mineral white oil solutions were each dropped on a KBr cell while the pretreated and untreated CaCO_3 powder sample were dispersed in a KBr disc. The samples were then scanned by the FT-IR spectrometric technique.

3.3.5 Measurement of melt flow index

The melt flow index of the polymer was measured according to ASTM D1238 using a melt flow meter (Ceast model 6542). The molten resin pressed through an orifice for 10 min under a loading of 2.16 kg at temperature 190 °C for the preheating time of 300 min and the specified length of the molten polymer was recorded in g.

3.3.6 The filler dispersion analysis

The composites of HDPE/CaCO₃ with different percentages, type of the treating coupling agents were tested by a built up pressure through the wire mesh filter media at 15 µm diameter in a filter test machine (LFT44-GP from LabTech Engineering, Bangkok, Thailand). The HDPE composites were mixed with CaCO₃ at 5%. The 100 g of the mixed polymer composite was fed to the hopper; the extruder temperature was set at 230 °C. The extruder ran to get a constant pressure of 50 bar (P1), the gear pumped the feed of the molten polymer composites through the filter media. The maximum pressure in the front of the filter media (P2) was measured as described in Figure 3.5.

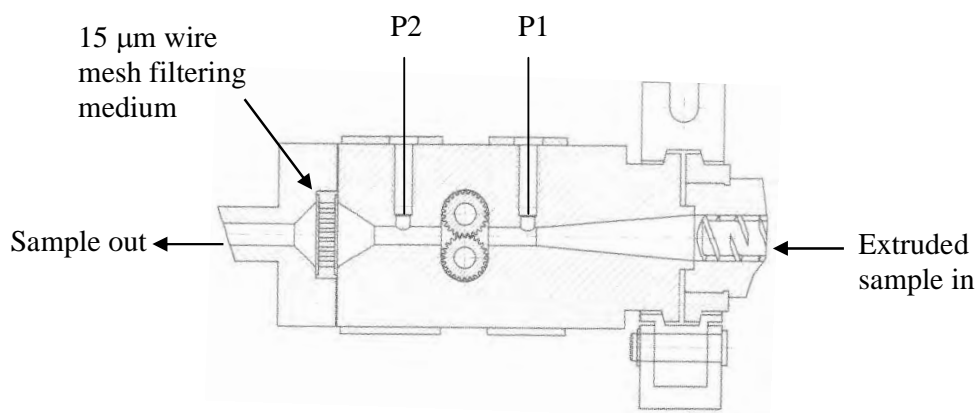


Figure 3.5 The LFT44-GP filter test machine

3.3.7 Thermal properties by differential scanning calorimetry (DSC)

A TA instrument DSC Q100 was used to analyze the pelletized samples from the twin screw extruder. The samples were first heated at a rate 10 °C/min from 30 °C to above 300 °C and held at this temperature for about 5 min. The samples were then cooled to room temperature at the 10 °C/min rate. To erase a thermal history, the second heating was performed at the same rate through the full melting range. All measurements were performed under nitrogen gas.

3.3.8 Thermal degradation by thermal gravimetric analyzer (TGA)

Thermal degradation of the polymer composites was performed by a TGA Q50 from TA Instrument, New Castle, U.K. The samples were heated from 30 °C to 550 °C with a heating rate at 10 °C/min under the dried nitrogen gas.

3.3.9 Characterization

3.3.9.1 Tensile properties

Tensile specimens of HDPE and its composites having a dumbbell shape were molded, based on ASTM D638 type I, using Arburg 221-75-350 injection molding with the conditions described below:

Extruder temperature	210	°C
Injection pressure	65	bars
Holding pressure	65	bars
Back pressure	15	bars
Screw dosage	20.1	cm ³
Cooling time	200	min

Tensile specimens were tested with Instron tensile tester at a crosshead speed 50 mm/min. The average of five measurements was reported for the tensile strength at break, tensile strength at yield, and tensile elongation.

3.3.9.2 Impact properties

The Izod impact test bars of HDPE and its composites were molded based on ASTM D256 using Arburg 221-75-350 injection molding with the condition described below:

Extruder temperature	210	°C
Injection pressure	60	bars
Holding pressure	60	bars
Back pressure	15	bars
Screw dosage	21.4	cm ³
Cooling time	450	min

The impact tests were carried out with Kao-tieh impact tester hit by a hammer force of 20 kg-cm. The average of five measurements was reported for the impact strength.

3.3.10 Morphological analysis

The fractured surface of the Izod impact tested specimens was analyzed for particle dispersion using a high voltage scanning electron microscope, FEI Quanta 200 FEG operated at 15 kV.

3.3.11 Color measurements and analysis

The 2-mm thick specimen of HDPE and its composites were molded using the Arburg 221-55-250 injection molding with the condition described below:

Extruder temperature	210	°C
Injection pressure	55	bars
Holding pressure	55	bars
Back pressure	15	bars
Screw dosage	8.4	cm ³
Cooling time	200	min

The specimens were measured for their color values by the CIELAB system according to ASTM E308-90 by the Datacolor SF650 spectrophotometer having a spherical geometry (diffuse/8°). The samples were measured at a reflectance port with 3-mm aperture with specula and UV light included in the range between 400-700 nm with an interval wavelength of 10 nm. The results were reported as an average in L*, a* and b* on an illuminant D65/10° observer.

The white mineral oil and titanate coupling agent KR TTS and KR 12 were measured for its color value at a transmittance mode as a reference data for comparison.

The total color difference (ΔE^*) between the test specimen and the reference is reported based on ASTM D2244. The calculated equation was as follows [Huff, 1994]:

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \quad 3.1$$

The yellowness indexes (YI) of the specimens were also measured and reported according to ASTM E313-73 (1993).

CHEPTER IV

RESULTS AND DISCUSSION

In this research, the effects of nano-particle CaCO_3 and ethylene-octene copolymer (EOC) content on the physical properties and morphology of HDPE/ CaCO_3 /EOC composites were studied. Two grades of titanate coupling agent with different organically compatible groups were used to pre-treat CaCO_3 nano-particles.

4.1 The titanate coupling agent pretreated CaCO_3 particles

4.1.1 The actual weight of the KR coupling agent pretreated CaCO_3 by gravimetric method

All materials for pre-treating CaCO_3 were weighed and recorded. The loadings of the titanate coupling agent for pre-treating CaCO_3 particles are shown in Table 4.1.

Table 4.1 The pre-treatment of CaCO₃ particles in the polymer composites

Run	Composite code	Recipe			Treated content (% wt. CaCO ₃) %(b/a)
		CaCO ₃ (g) <i>a</i>	Coupling agent (g) <i>b</i>	White mineral oil (g) <i>c</i>	
1	Neat HDPE	0	0	0	0
2	PE80-0-0	400.1	0	20.0024	0
3	PE78-0-2	400.1	0	20.0068	0
4	PE76-0-4	400.2	0	20.0049	0
5	PE74-0-6	400.1	0	20.0082	0
6	PE72-0-8	400.2	0	20.0039	0
7	PE70-0-10	400.2	0	20.0067	0
8	PE80-2A-0	400.1	0.8281	20.0228	0.207
9	PE80-5A-0	400.1	2.0302	20.0084	0.507
10	PE80-8A-0	400.1	3.2086	20.0024	0.802
11	PE80-2B-0	400.1	0.8139	20.0251	0.203
12	PE80-5B-0	400.1	2.0223	20.0038	0.505
13	PE80-8B-0	400.0	3.2122	20.0093	0.803
14	PE78-8A-2	400.2	3.2089	20.0031	0.802
15	PE76-8A-4	400.1	3.2039	20.0079	0.801
16	PE74-8A-6	400.2	3.2034	20.0075	0.800
17	PE72-8A-8	400.1	3.2045	20.1595	0.801
18	PE70-8A-10	400.0	3.2015	20.0047	0.800
19	PE78-8B-2	400.2	3.2077	20.0048	0.802
20	PE76-8B-4	400.0	3.2027	20.0082	0.801
21	PE74-8B-6	400.1	3.2069	20.0054	0.802
22	PE72-8B-8	400.0	3.2086	20.0068	0.802
23	PE70-8B-10	400.0	3.2025	20.0097	0.801

4.1.2 The coupling solution characterization by XRF

The coupling agent was diluted with white mineral oil following the weights as shown in Table 4.1. The solutions were characterized using X-ray fluorescence spectroscopy techniques (XRF). The signal intensities for Rh (L_{α} and L_{β} electron), P (K_{α} electron), and Ti (K_{α} and K_{β} electrons) are shown in Table 4.2 and Figure 4.1.

Table 4.2 The XRF intensity of the coupling agent solution

Coupling agent type	Coupling solution (% wt. CaCO_3)	Intensity (count)		
		Rh (L_{α} and L_{β})	P (K_{α})	Ti (K_{α} and K_{β})
KR TTS	0.2	549.7	-	905.3
KR TTS	0.5	470.2	-	1576.4
KR TTS	0.8	472.3	-	2291.3
KR 12	0.2	480.4	71.9	892.2
KR 12	0.5	479.0	109.5	1455.2
KR 12	0.8	489.6	174.1	2054.7

Figures 4.1(a), 4.1(c) and 4.1(e) show the X-ray energy intensity for the KR TTS solutions of 0.2%, 0.5% and 0.8% weight for pre-treating the CaCO_3 particles, respectively, in which increasing concentrations of KR TTS increased the intensity of Ti element. Similarly, Figures 4.1(b), 4.1(d) and 4.1(f) show the X-ray energy intensity for the KR 12 solutions of 0.2%, 0.5% and 0.8% weight for pre-treating CaCO_3 particles, respectively. The signal intensities of Ti and P elements from the KR 12 molecules were increased with increasing its concentrations. The higher Ti signal of the same concentration of KR TTS solution was observed when compared with that of the KR 12 because the weight fraction of Ti atoms in KR TTS was higher. One must mention that the signal of Rh element as shown in every XRF spectrum came from the Rh anode of the instrument.

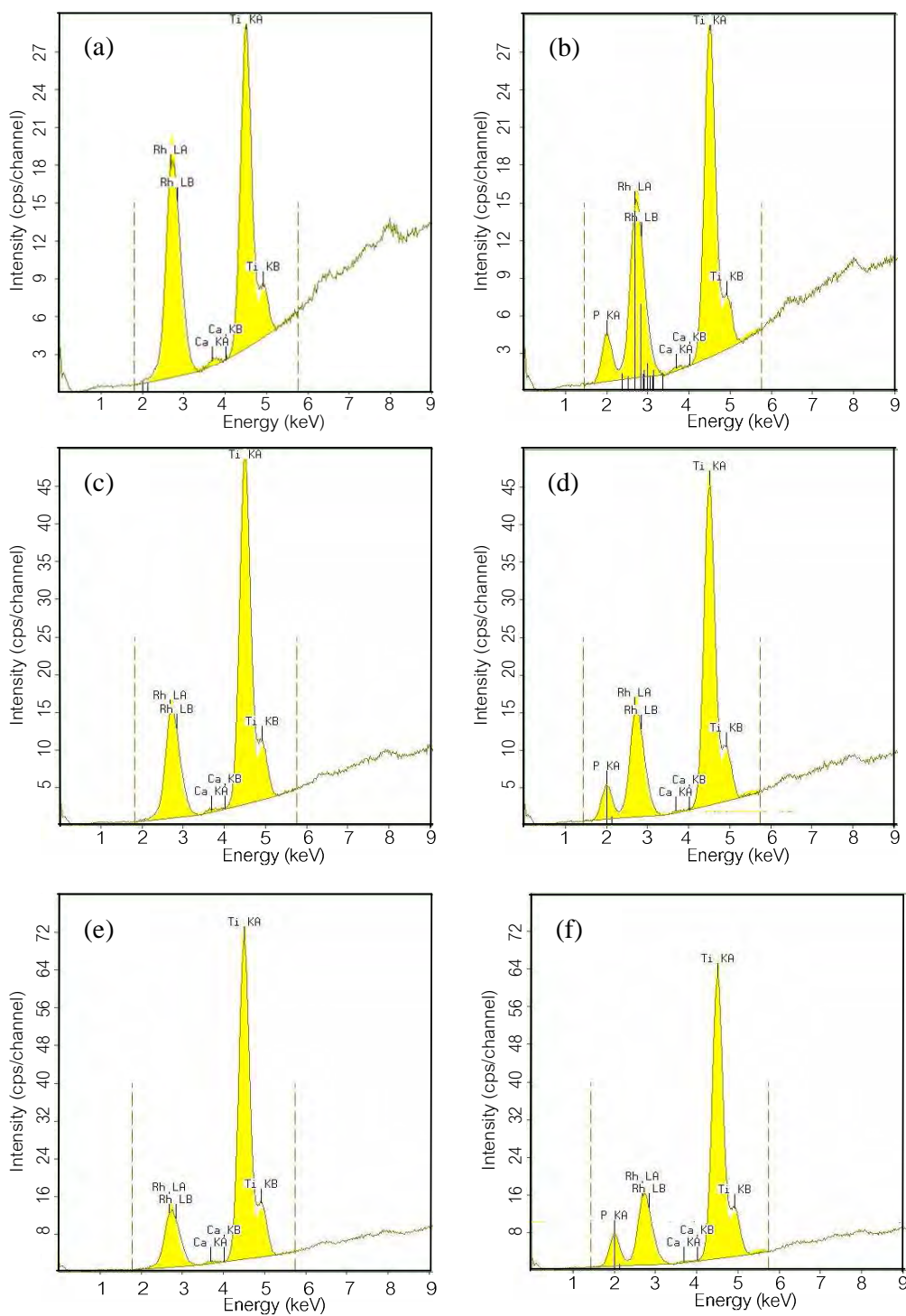


Figure 4.1 The XRF spectra of the coupling solution for pre-treating CaCO_3 particles: (a) 0.2% weight of KR TTS, (b) 0.2% weight of KR 12, (c) 0.5% weight of KR TTS, (d) 0.5% weight of KR 12, (e) 0.8% weight of KR TTS, (f) 0.8% weight of KR 12

4.1.3 Functional group characterization of the pretreated CaCO₃ by FTIR spectroscopy

Figure 4.2(a) and 4.2(b) show infrared spectra of the CaCO₃ and white mineral oil, respectively. General characteristic absorption peaks of white mineral oil at 2923 and 2854 cm⁻¹, are attributed to CH₃ symmetrical and non-symmetrical vibrational of C-H stretching, respectively. The peaks at 1462 and 1375 cm⁻¹ are attributed to the CH₂ bending of straight chains [Charkrit, 2007]. The CaCO₃ spectrum in Figure 4.2(b) shows the absorption band in the 1500-1400 cm⁻¹, the peak at 875 and 713 cm⁻¹ are for the calcite structures which are in good agreement with that reported in the literature [Campos *et al.*, 2006].

The FT-IR spectra of the KR TTS and KR12 are shown in Figure 4.29(c) and 4.2(e), respectively, and the FT-IR spectra of CaCO₃ treated with KR TTS or KR12 are shown in Figure 4.2(d) and 4.2(f), respectively. The absorption peaks at 1030 and 1235 cm⁻¹ are for the P-O-C, P=O in the KR 12 molecule. The peak at 1737 cm⁻¹ is for the C=O stretching, and the peak at 1173 cm⁻¹ due to Ti-O is observed in all spectra of all the treated CaCO₃ and the pure coupling agent [Hsiang *et al.*, 2005]. The spectra in Figure 4.2 can be used as an indicator for the KR TTS or KR 12 pre-treatment on the surface of the CaCO₃ particles.

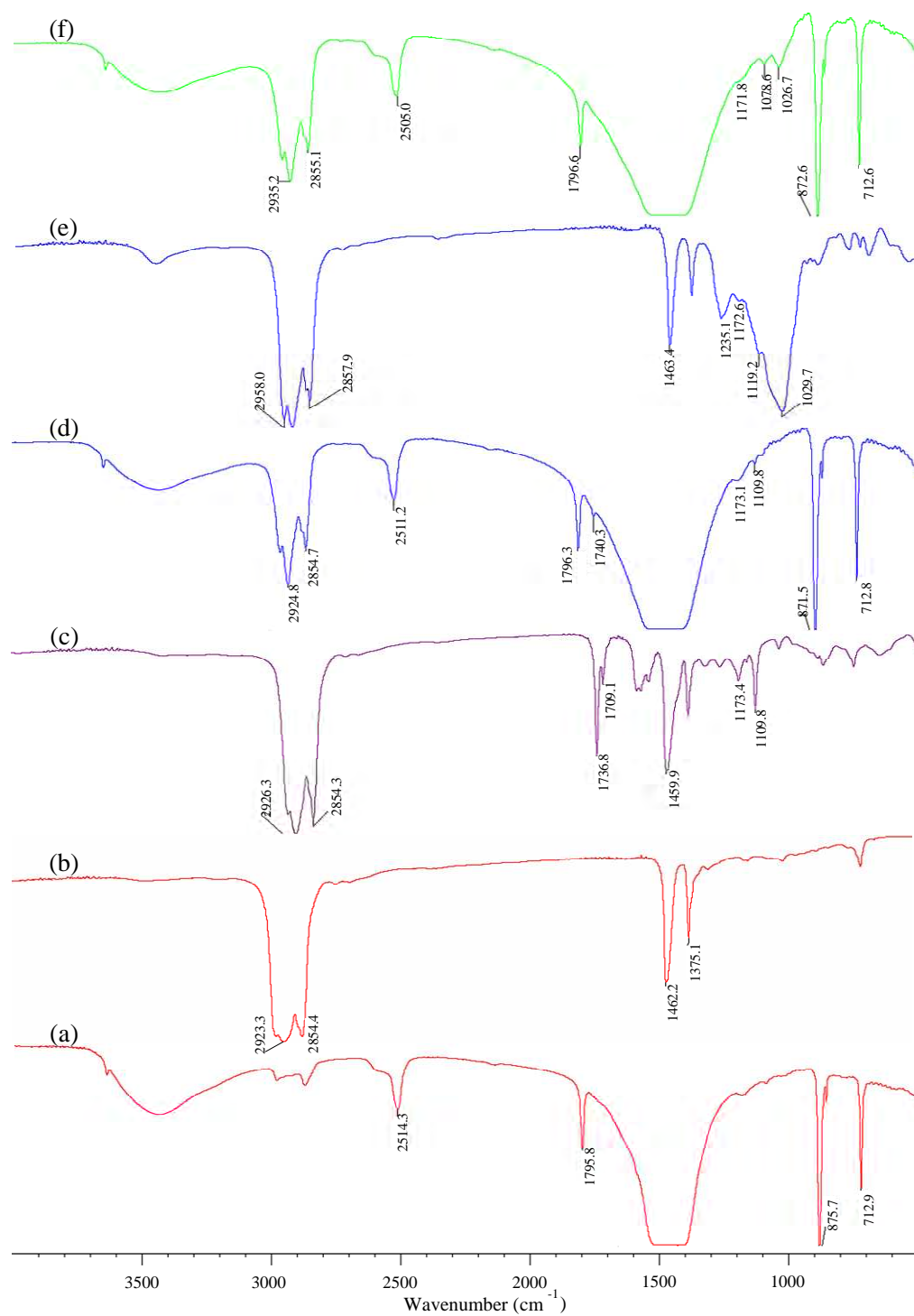


Figure 4.2 The FTIR spectra of (a) the untreated CaCO₃, (b) white mineral oil, (c) KR TTS, (d) the treated CaCO₃ with 0.8% KR TTS, (e) KR 12, (f) the treated CaCO₃ with 0.8% KR 12

4.2 Effect on titanate coupling agent on flow property

The effect of titanate coupling agent on flow behavior was studied using a melt flow indexer (MFI). As a result shown in Table 4.3, it gives a lower MFI value when a 20% CaCO₃ loading was added in HDPE matrix. It is known that the addition of filler to polymer matrix restricts molecular motion in the matrix, thus imposed resistance to flow and caused the lowering MFI value. Tang *et al.* [2003] observed the similar result in the ABS/CaCO₃ composites with a lowering MFI value when 10% CaCO₃ was added.

Recently, Wah *et al.* [2000] reported that a titanate coupling agent, LICA 12, with 0.2-1.6% loadings could improve flow ability by increasing MFI values of the 30% and 40% talcum-filled polypropylene. Figure 4.3 shows the data which indicate that our result is in good agreement with Wah *et al.* [2000]. The addition of KR TTS or KR 12 titanate coupling agent to the CaCO₃-filled HDPE polymer composites increased the MFI values. The MFI values are increased with the increasing coupling agent concentrations; the KR 12 treated CaCO₃ polymer composites provide better flow ability compared to that of the KR TTS treated CaCO₃ polymer composites. Figure 4.4 shows that the MFI values decreased with increasing EOC contents in the matrix but still gave better flow ability in the presence of 0.8% KR TTS or KR 12 compared with the untreated CaCO₃ polymer composite.

Table 4.3 The MFI values of the polymer composites

Run	Material	MFI, 190 °C/2.16 kg (g/10 min)
1	Neat HDPE	17.64 ± 0.04
2	PE80-0-0	8.31 ± 0.06
3	PE78-0-2	7.26 ± 0.11
4	PE76-0-4	6.84 ± 0.06
5	PE74-0-6	6.18 ± 0.17
6	PE72-0-8	5.28 ± 0.09
7	PE70-0-10	4.21 ± 0.05
8	PE80-2A-0	8.47 ± 0.08
9	PE80-5A-0	8.58 ± 0.10
10	PE80-8A-0	9.81 ± 0.03
11	PE80-2B-0	9.69 ± 0.12
12	PE80-5B-0	9.80 ± 0.04
13	PE80-8B-0	10.4 ± 0.08
14	PE78-8A-2	8.89 ± 0.05
15	PE76-8A-4	7.73 ± 0.08
16	PE74-8A-6	7.33 ± 0.16
17	PE72-8A-8	7.31 ± 0.21
18	PE70-8A-10	5.69 ± 0.15
19	PE78-8B-2	9.74 ± 0.12
20	PE76-8B-4	9.60 ± 0.08
21	PE74-8B-6	8.52 ± 0.11
22	PE72-8B-8	7.42 ± 0.21
23	PE70-8B-10	7.42 ± 0.09

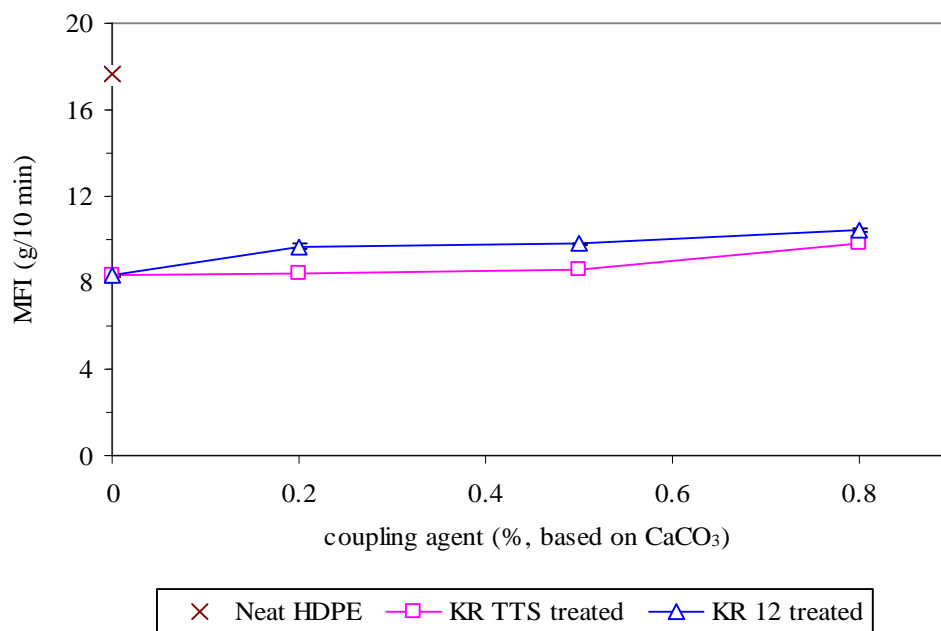


Figure 4.3 Effect of titanate coupling agent contents on the MFI of the CaCO₃-filled HDPE composites

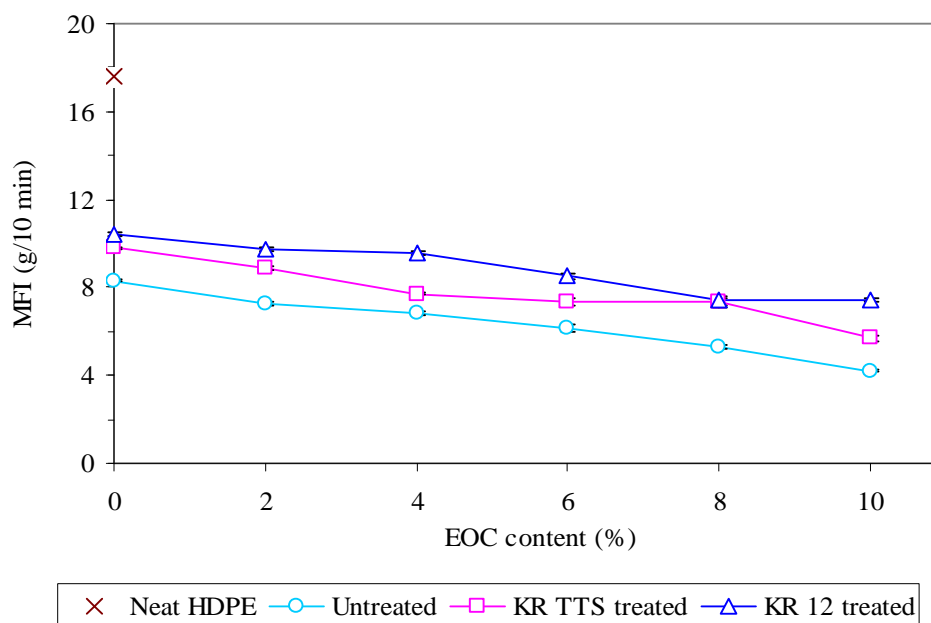


Figure 4.4 Effect of EOC contents on the MFI value of the untreated and treated CaCO₃-HDPE composites

4.3 Effect of titanate coupling agent on particulate filler dispersion

4.3.1 Filter test

Table 4.4 shows the degree of particulate CaCO_3 dispersion investigated by the filter test using a 15- μm sieve mesh filtering medium.

Table 4.4 The built-up pressure of the polymer composites through a 15- μm wire mesh filter to give the filter value

Run	Material	max P2 (bar)	Filter value (bar/g CaCO_3)
1	Neat HDPE	0	0
2	PE80-0-0	80	16.0
8	PE20-2A-0	52	10.4
9	PE20-5A-0	49	9.8
10	PE20-8A-0	49	9.8
11	PE20-2B-0	49	9.8
12	PE20-5B-0	41	8.2
13	PE20-8B-0	29	5.8

Figure 4.5 shows the loading effect of KR TTS or KR 12 treated on the CaCO_3 filled HDPE composites in terms of filter values at the 15 μm wire mesh filtering medium. Both the coupling agents reduced the treated CaCO_3 /HDPE composite built-up pressures through 15 μm wire mesh filtering medium. This is because the pretreatment improved dispersion of CaCO_3 particles as shown in Figures 4.6 and 4.7. The KR 12 gave a better CaCO_3 particle dispersion when comparing with the KR TTS treatment. The filter value at 0.8% KR 12 treatment was reduced by 63.8% (from 16 to 5.8 bar/g CaCO_3) while that of the 0.8% KR TTS treatment was reduced by 38.8% (from 16 to 9.8 bar/g CaCO_3).

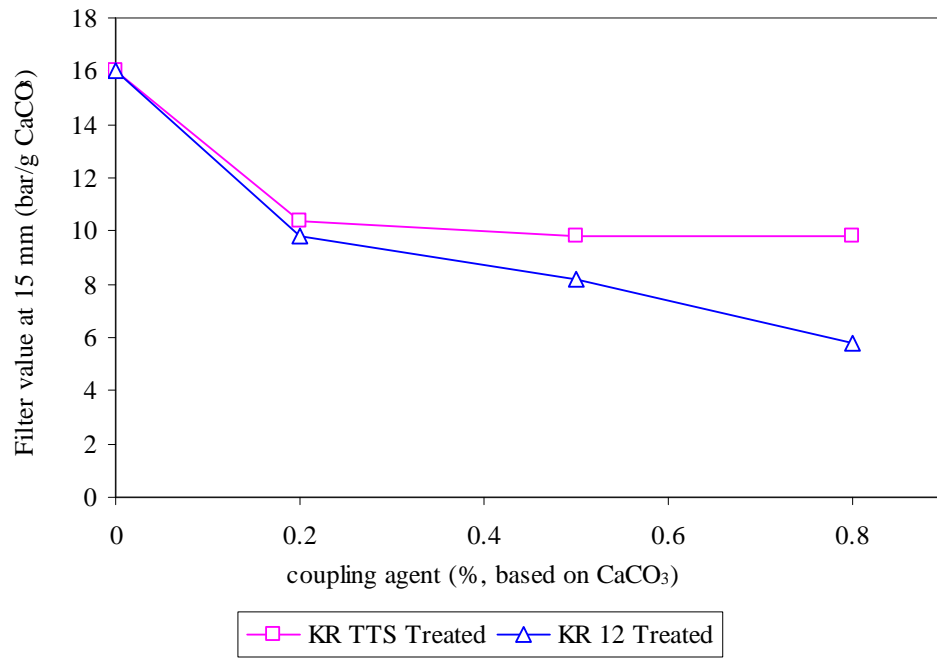


Figure 4.5 Effect of titanate coupling agent contents on the 15- μm filter value of the CaCO_3 -HDPE composites

4.3.2 Scanning Electron Microscopy (SEM) of the composites

The dispersion of CaCO_3 nano-particles in the composites is presented in Figures 4.6 and 4.7. The untreated CaCO_3 nano-sized particles gave huge aggregate structures (Figure 4.6(b)) due to their high specific areas as described in the recent report [Osman *et al.*, 2006]. In nano-composites, more and larger filler clusters are formed than those in the microcomposites due to the large contact area between the nanoparticles. After the particles had been treated with the titanate coupling agent, the large aggregate clusters were markedly reduced to become much small agglomerates or minute aggregates, and some fine particles which were better dispersed in polymer composites as illustrated in Figure 4.6(c) and 4.6(d).

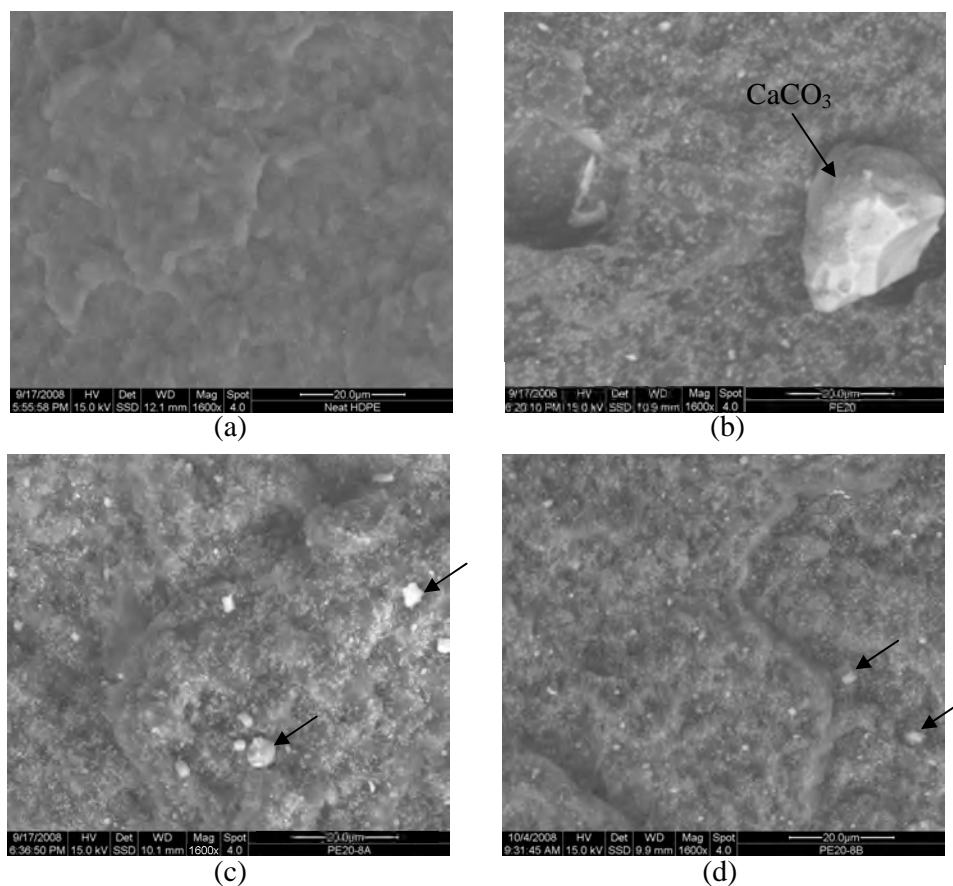


Figure 4.6 Scanning electron micrographs of HDPE/ CaCO_3 composites (a) the neat HDPE, (b) the untreated CaCO_3 , (c) 0.8% KR TTS treated CaCO_3 , (d) 0.8% KR 12 treated CaCO_3

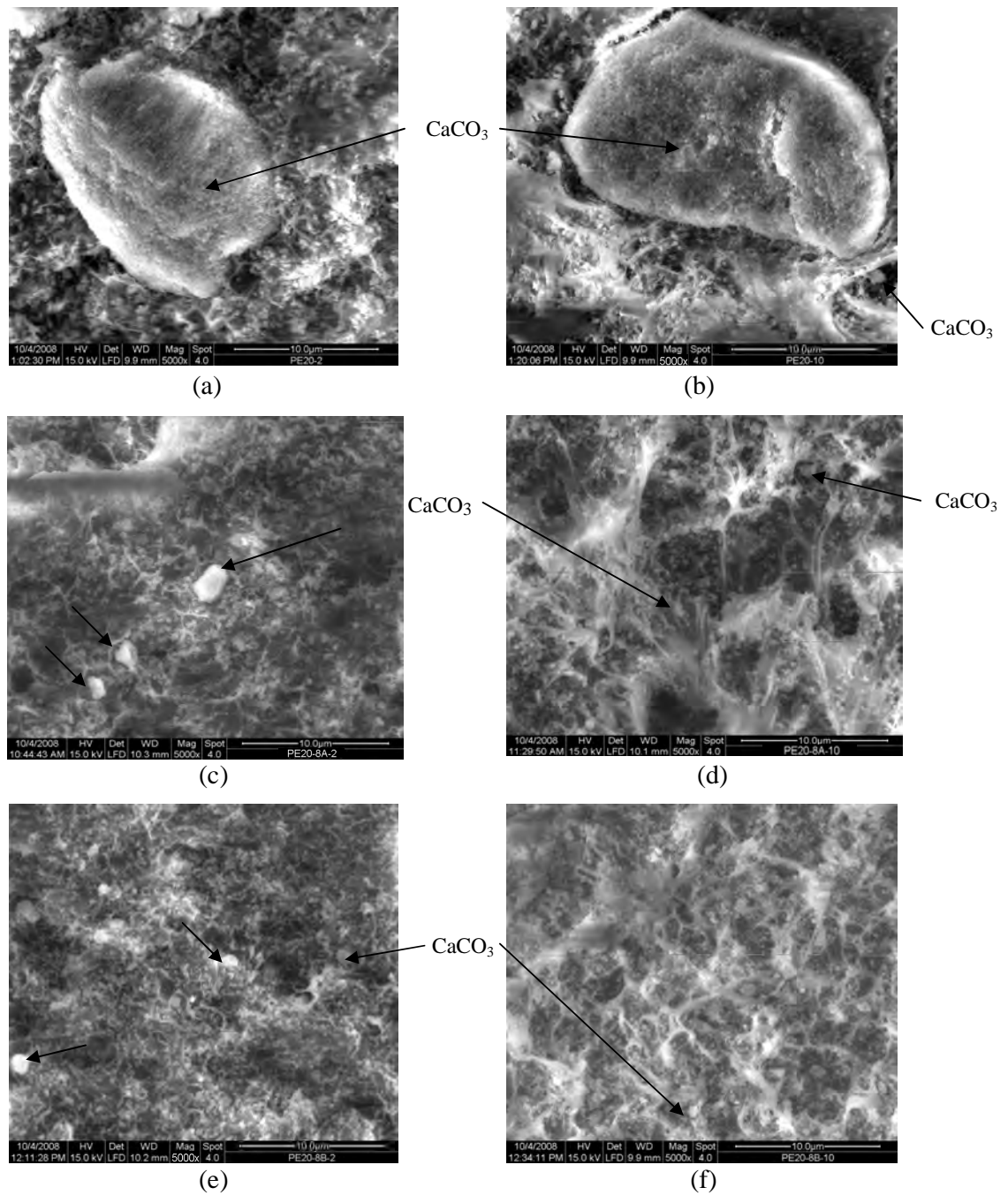


Figure 4.7 Effect of coupling agent and EOC on CaCO_3 dispersion. Scanning electron micrographs of HDPE/ CaCO_3 /EOC composites (a) the untreated CaCO_3 with 2% EOC, (b) the untreated CaCO_3 with 10% EOC, (c) KR TTS treated CaCO_3 with 2% EOC, (d) KR TTS treated CaCO_3 with 10% EOC, (e) KR 12 treated CaCO_3 with 2% EOC, (f) KR 12 treated CaCO_3 with 10% EOC

Considering the chemical structure of KR TTS and KR 12 as shown on Figures 3.1 and 3.2 described in Chapter III, it is shown that the polymer compatibilization group, tri(dioctyl) phosphato group of KR 12 was more steric hindrance as compared to the triisostearoyl group of KR TTS. The former helps decrease the particle-particle agglomeration or aggregation and thus gives a better particle dispersion in the polymer matrix. This is confirmed by Figure 4.7(e) that the particle dispersion by the aid of KR 12 is better than that of KR TTS as shown in Figure 4.7(c). The state of CaCO_3 dispersion in the polymer matrix corresponds nicely with the extent of Izod impact strength. Uniform dispersion is indeed an important factor for filler dispersion especially in nano-size filler dispersion. This phenomenon is demonstrated in the mechanical properties where the stress field will be concentrated around the aggregate/agglomerate structures as such the cracks will propagate easily and rapidly and cause premature material failure.

The dispersion of filler particles in the polymer phase was enhanced by the replacement of water or hydration at the surface of the inorganic filler by the organofunctional titanate to produce an inorganic/polymer interface that is compatible and enhances their interfacial adhesion whose mechanism is shown in Figure 4.8 in which the monomolecular titanate layer is formed by an alcoholysis reaction mechanism of a monoalkoxy (KR), triorganofunctional titanate coupling agent with the idealized surface of a proton bearing inorganic. Figure 4.9(a) shows agglomerated inorganic particles having deleterious water of hydration and air voids mixed into an organic vehicle (polymer) without the role of titanate. Figure 4.9(b) shows the particle de-agglomeration and elimination of air and water achieved with the use of titanate coupling agent [Monte, 1995]. The titanate coupling agent has been used for an inorganic particle – polymer dispersion, such as, the talc-filled PP [Wah *et al.* 2000], CaCO_3 -filled PP/HDPE [Gonzalez *et al.*, 2002], Co_2Z ferrite in poly(vinyl butyral) [Hsiang *et al.*, 2004].

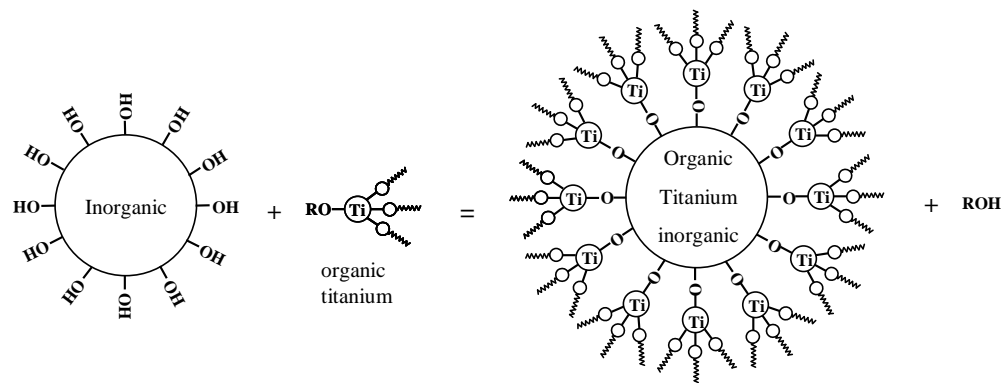


Figure 4.8 Mechanism of titanate reaction in inorganic filler surface [Monte, 1995]

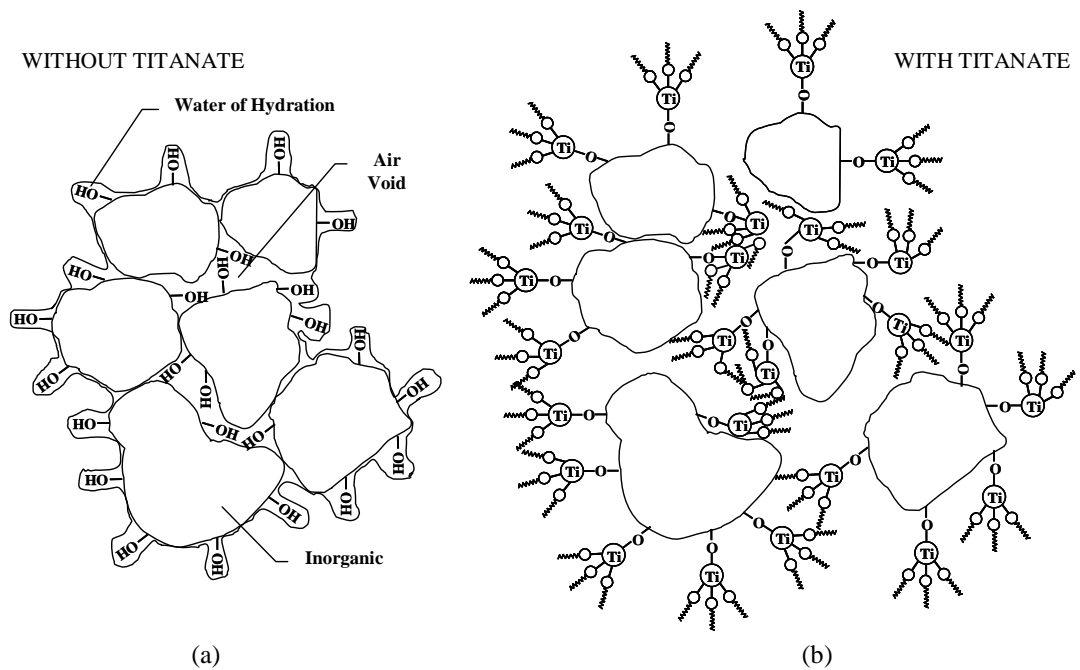


Figure 4.9 Mechanism of the filler dispersion in HDPE matrix (a) without the presence of a coupling agent before dispersion, (b) after dispersion with a titanate coupling agent [Monte, 1995]

To give a good indication of the role of coupling agent aided in CaCO_3 dispersion in polymer composite, more details can be extracted from Figure 4.7. Figure 4.7 shows the improved dispersion of CaCO_3 nano-particles in the composites containing 2% EOC (Figures 4.7(c)) for KR TTS treated CaCO_3 particles and in Figure 4.7(e) for KR 12 treated CaCO_3 particles, which strongly supports the dispersion phenomena as illustrated in Figure 4.9 from which the titanate coupling agent improved the CaCO_3 particle wetting, good mixing and well dispersion. The micrographs in Figure 4.7(d) and (f) also show the synergistic effect beside the compatibility effect of the EOC content which helped the particles to perfectly disperse in the polymer composites. Because the EOC is a hydrophobic, the non-polar compound which has good compatibility with the non-polar HDPE molecules due to the similar solubility parameters. Figure 4.7(d) and (f) show that the CaCO_3 -HDPE composites containing 10% EOC has a finer texture of the particles well distributed in the HDPE matrix.

4.4 Effect on mechanical properties

4.4.1 Tensile properties

The tensile properties of the HDPE composites are shown in Table 4.5. The modulus was increased from 959 to 1061 MPa by adding 20% of the untreated CaCO_3 and lowered when CaCO_3 particles were treated with titanate coupling agent and incorporating EOC as shown in Figures 4.10 and 4.11, respectively. The elongation of composites was sharply dropped with 20% CaCO_3 loading (Figure 4.12) but increased with increasing EOC content (Figure 4.13). The break strength was constant with increasing coupling agent loadings (Figure 4.14) but decreased with increasing EOC content in Figure 4.15. It is clearly demonstrated that the yield strength decreased upon the addition of CaCO_3 particles and increased with increasing the pre-treating coupling agent loadings as shown in Figure 4.16. It has been reported previously that tensile yield strength decreased with increasing CaCO_3 loading in polyethylene composites. The loading of CaCO_3 particles, which surface is either treated with surface coupling agent or without, into a polymer matrix results in a heterogeneous morphology. Under the external load such as tensile forces, these heterogeneities induce stress concentration. If the interfacial adhesion between the filler and matrix is not strong, de-bonding of the particles from the polymer matrix by breaking the HDPE- CaCO_3 interface takes place when applying a high strain, this results in the decrease in tensile yield strength. While the modulus increased with increasing particle loading because the particles did not debond at the low strains. [Suwanprateep, 2000; Zuiderduin *et al.*, 2003]. The pre-treating of coupling agent on CaCO_3 particles increase the HDPE- CaCO_3 adhesion which leads to increase the tensile yield strength in comparison with the untreated particles which remain unaffected in tensile break strength (Figure 4.14) because HDPE has already been debonded completely from CaCO_3 particles. The pre-treating also decreased the particle-particle agglomeration/aggregation leading to better particle dispersion as shown in Figures 4.6 and 4.7. Figure 4.17 shows that increases in EOC contents can lower the yield strength of the polymer composites.

Table 4.5 The tensile properties of the polymer composites

Run	Material	Properties			
		Young's Modulus (MPa)	Elongation (%)	Yield strength (MPa)	Break strength (MPa)
1	Neat HDPE	959 ± 6	159.3 ± 18.8	21.3 ± 0.4	6.1 ± 1.1
2	PE80-0-0	1061 ± 29	9.2 ± 2.9	20.9 ± 0.5	20.8 ± 0.6
3	PE78-0-2	972 ± 9	13.7 ± 2.4	19.8 ± 0.1	19.7 ± 0.2
4	PE76-0-4	959 ± 12	17.3 ± 1.7	20.9 ± 0.2	20.1 ± 0.3
5	PE74-0-6	842 ± 20	41.4 ± 15.3	18.6 ± 0.4	9.7 ± 3.5
6	PE72-0-8	844 ± 31	45.7 ± 15.6	18.6 ± 0.1	5.8 ± 2.7
7	PE70-0-10	818 ± 12	39.4 ± 24.0	18.4 ± 0.1	12.0 ± 3.8
8	PE80-2A-0	999 ± 18	12.6 ± 0.4	20.7 ± 0.4	20.6 ± 0.4
9	PE80-5A-0	1003 ± 17	13.9 ± 0.4	21.1 ± 0.3	21.1 ± 0.3
10	PE80-8A-0	1006 ± 26	13.4 ± 1.0	21.7 ± 0.2	21.4 ± 0.2
11	PE80-2B-0	994 ± 23	11.7 ± 1.9	21.0 ± 0.3	20.9 ± 0.2
12	PE80-5B-0	1013 ± 16	12.0 ± 0.4	21.4 ± 0.2	21.4 ± 0.2
13	PE80-8B-0	991 ± 30	12.1 ± 0.7	21.7 ± 0.4	21.3 ± 0.8
14	PE78-8A-2	966 ± 26	12.8 ± 1.0	20.8 ± 0.3	20.7 ± 0.4
15	PE76-8A-4	920 ± 20	16.3 ± 2.6	19.7 ± 0.1	19.4 ± 0.4
16	PE74-8A-6	826 ± 7	27.3 ± 4.6	18.4 ± 0.1	15.1 ± 1.5
17	PE72-8A-8	812 ± 21	79.6 ± 34.2	17.9 ± 0.5	4.8 ± 2.2
18	PE70-8A-10	737 ± 20	144.4 ± 17.1	16.7 ± 0.2	4.8 ± 0.9
19	PE78-8B-2	953 ± 29	14.0 ± 1.6	20.4 ± 0.3	20.3 ± 0.3
20	PE76-8B-4	876 ± 4	20.7 ± 3.2	19.0 ± 0.2	18.1 ± 0.6
21	PE74-8B-6	836 ± 15	45.6 ± 24.1	18.1 ± 0.1	10.2 ± 4.7
22	PE72-8B-8	777 ± 9	85.7 ± 9.5	17.2 ± 0.1	5.3 ± 2.2
23	PE70-8B-10	732 ± 11	228.4 ± 34	16.5 ± 0.2	4.6 ± 0.2

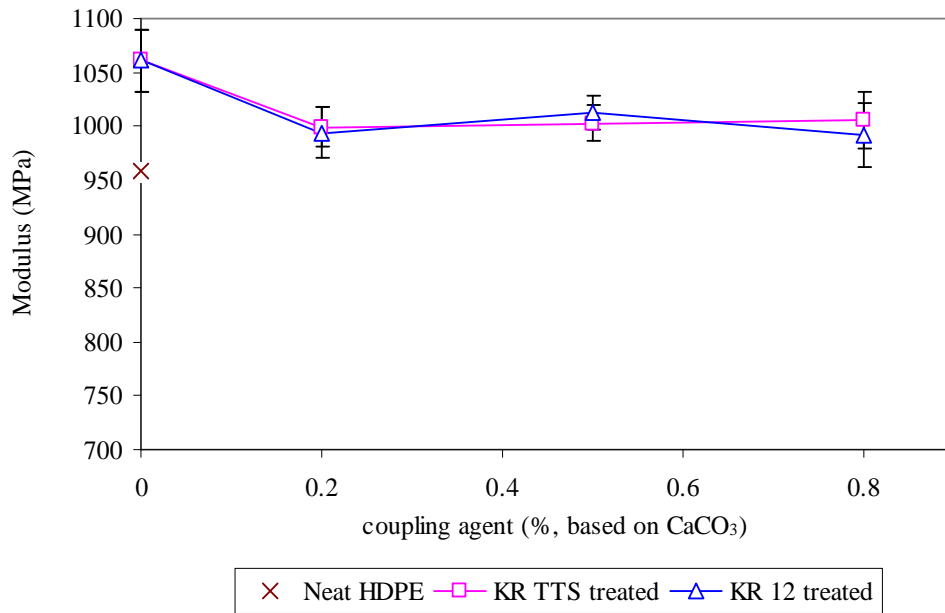


Figure 4.10 Effect of coupling agent content on the Young's Modulus of the polymer composites

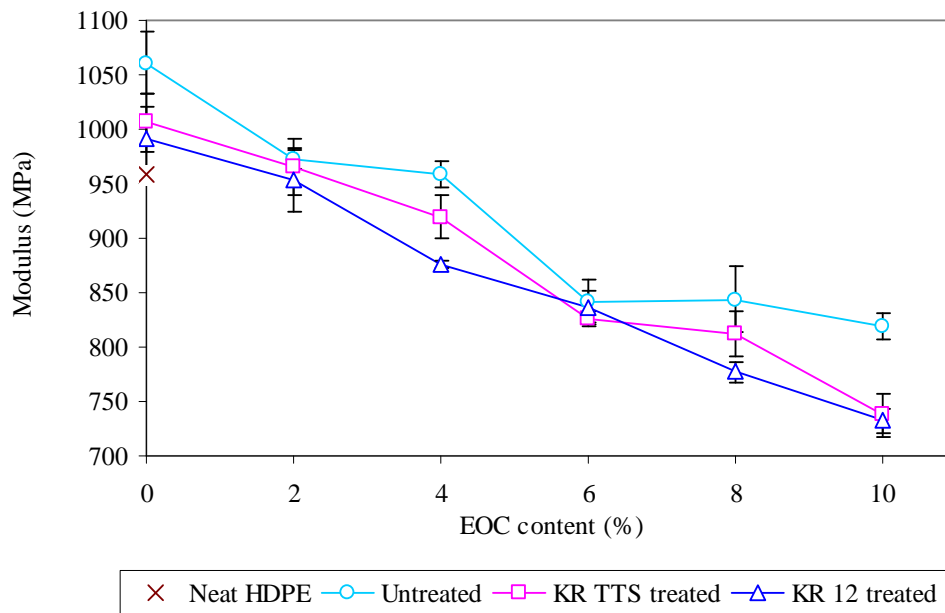


Figure 4.11 Effect of EOC content on the Young's Modulus of the polymer composites

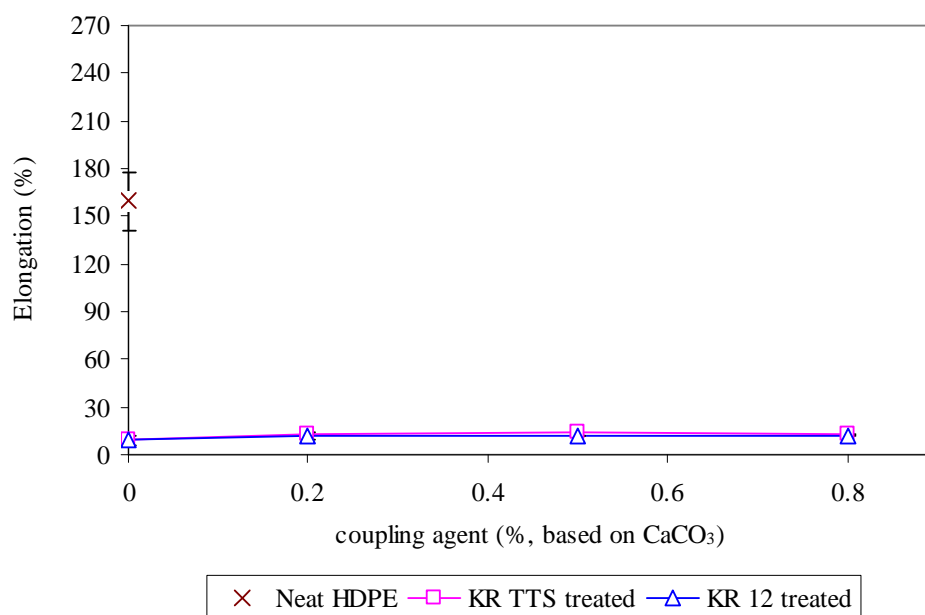


Figure 4.12 Effect of the coupling agent content on the tensile elongation of the polymer composites

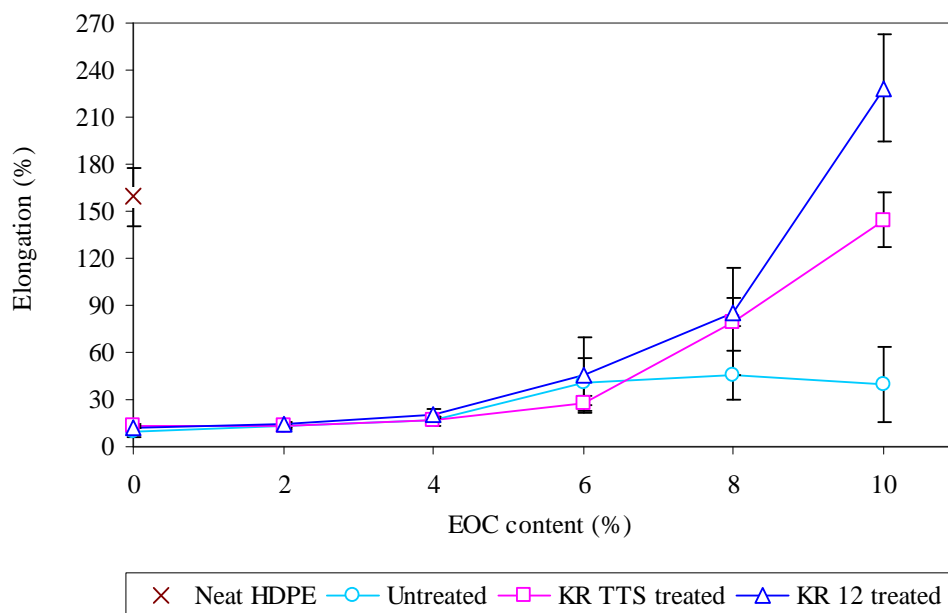


Figure 4.13 Effect of EOC content on the tensile elongation of the polymer composites

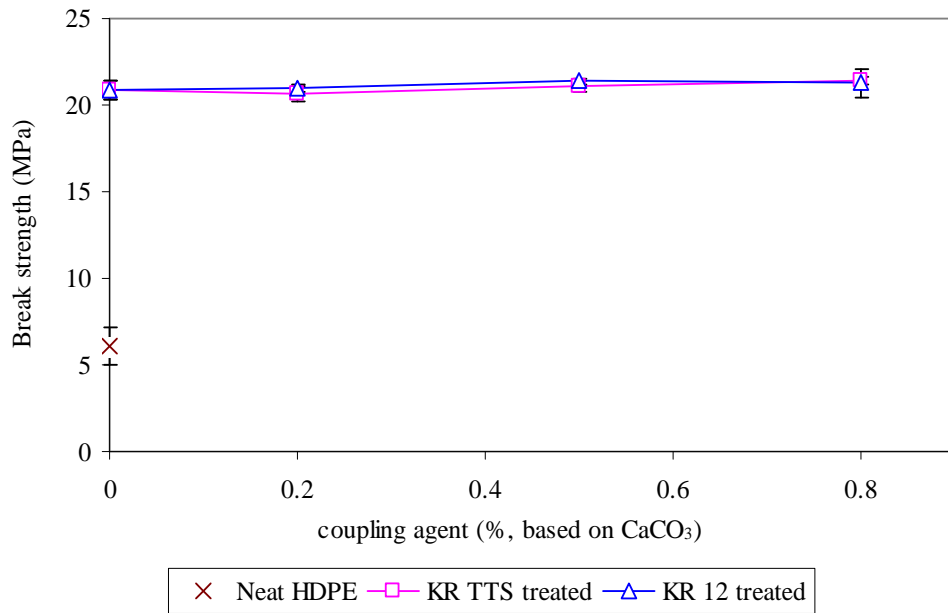


Figure 4.14 Effect of coupling agent content on the tensile break strength of the polymer composites

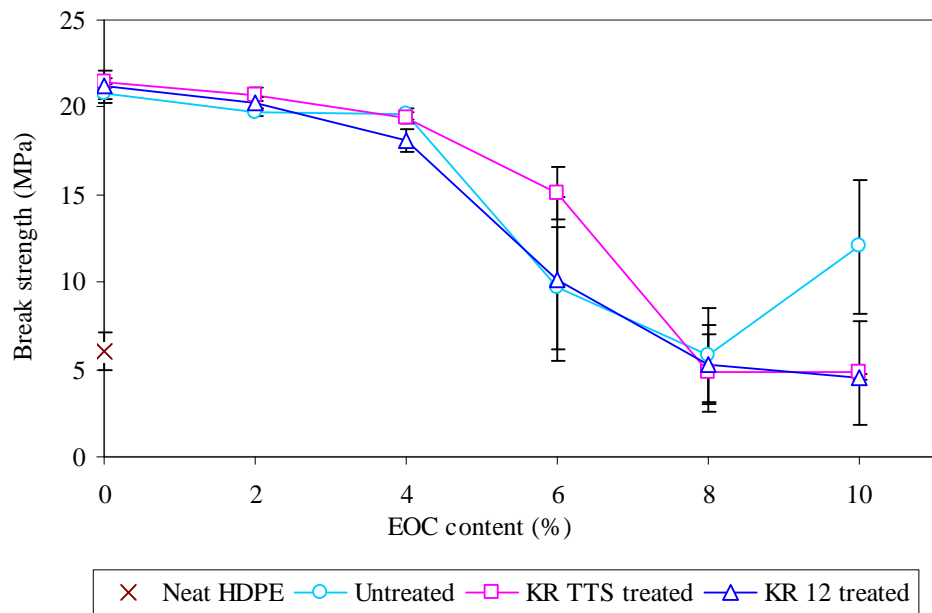


Figure 4.15 Effect of EOC content on the tensile break strength of the polymer composites

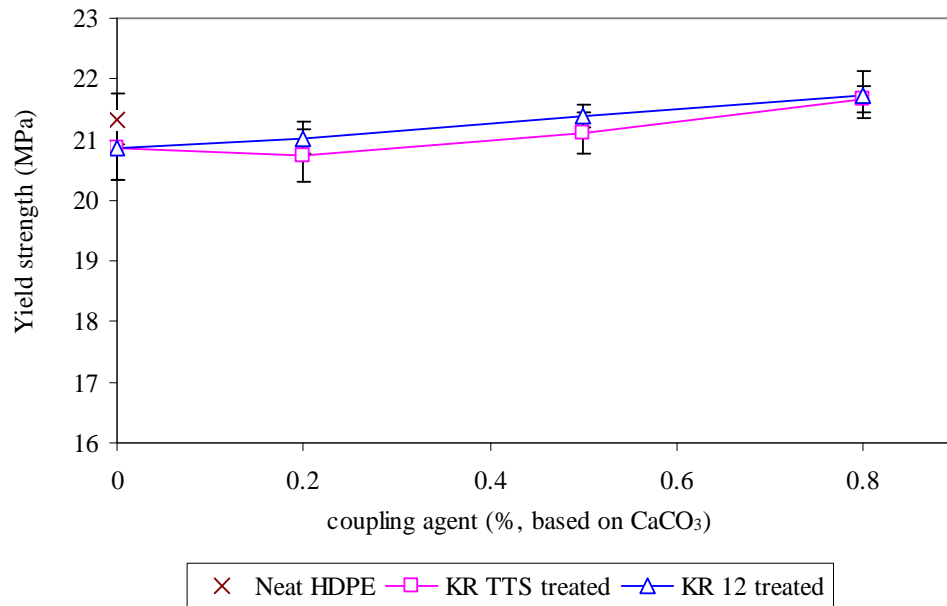


Figure 4.16 Effect of coupling agent content on the tensile yield strength of the polymer composites

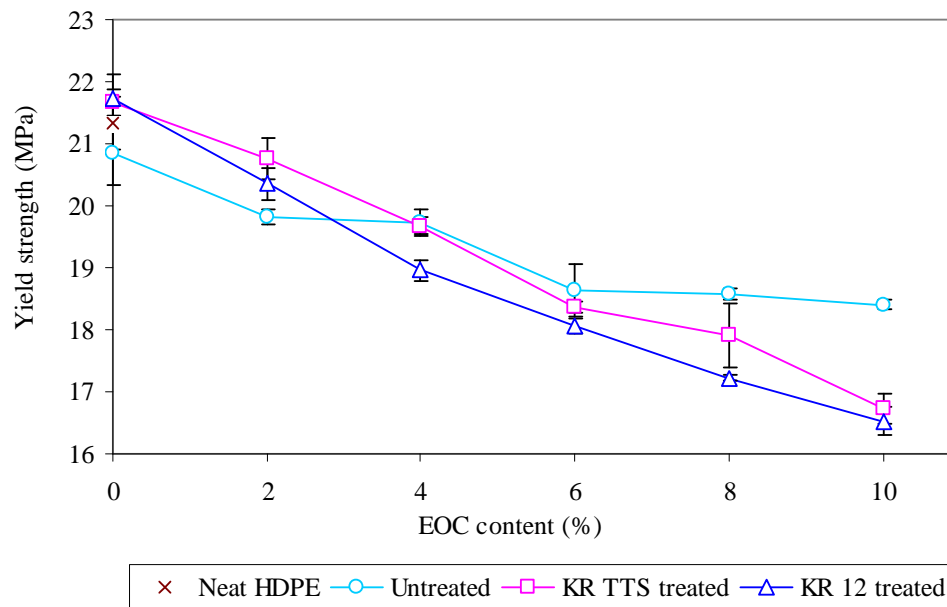


Figure 4.17 Effect of EOC content on the tensile yield strength of the polymer composites

4.4.1 Impact properties

The Izod impact properties of the composites are shown in Table 4.6 and Figures 4.18-4.19.

Table 4.6 The Izod impact strength of the polymer composites

Run	Material	Izod impact strength (J/m)
1	Neat HDPE	13.7 ± 2.2
2	PE80-0-0	8.5 ± 0.6
3	PE78-0-2	10.8 ± 1.1
4	PE76-0-4	13.1 ± 2.2
5	PE74-0-6	26.5 ± 1.0
6	PE72-0-8	36.8 ± 2.6
7	PE70-0-10	41.6 ± 3.2
8	PE80-2A-0	8.9 ± 0.6
9	PE80-5A-0	9.9 ± 1.0
10	PE80-8A-0	11.1 ± 1.1
11	PE80-2B-0	9.6 ± 0.7
12	PE80-5B-0	10.1 ± 0.7
13	PE80-8B-0	11.2 ± 1.3
14	PE78-8A-2	15.6 ± 2.0
15	PE76-8A-4	16.7 ± 1.0
16	PE74-8A-6	29.7 ± 1.3
17	PE72-8A-8	40.4 ± 0.5
18	PE70-8A-10	59.0 ± 2.5
19	PE78-8B-2	17.7 ± 0.7
20	PE76-8B-4	25.0 ± 0.6
21	PE74-8B-6	34.2 ± 1.0
22	PE72-8B-8	47.4 ± 1.3
23	PE70-8B-10	62.2 ± 2.4

Figure 4.18 shows that the composites containing 0.8% wt of KR TTS or KR 12 and 20% wt CaCO_3 increase the Izod impact strength by 29.6% and 31.4%, respectively, compared with the untreated one but the strength was still lower than those of the neat HDPE by 19% and 18%, respectively. The increases of Izod impact strength were mainly caused by the improved dispersion of the treated CaCO_3 particles in the composites [Wah *et al.*, 2000; Gonzalez *et al.*, 2002]. Figure 4.19 reveals that increases in EOC content clearly improve the Izod impact strength. When 0.8% loading of KR TTS or KR 12 coupling agent was used to pre-treat CaCO_3 , only 2% EOC was needed in the composite to produce the higher Izod impact strength compared to the neat HDPE. The untreated CaCO_3 polymer composite needs at least 6% EOC to achieve the same Izod impact strength. The effect of EOC content on the impact properties of the composites of the present work shows good agreement with the previous work of Yang *et al.*, [2003], McNally *et al.*, [2003], Zhang *et al.*, [2002].

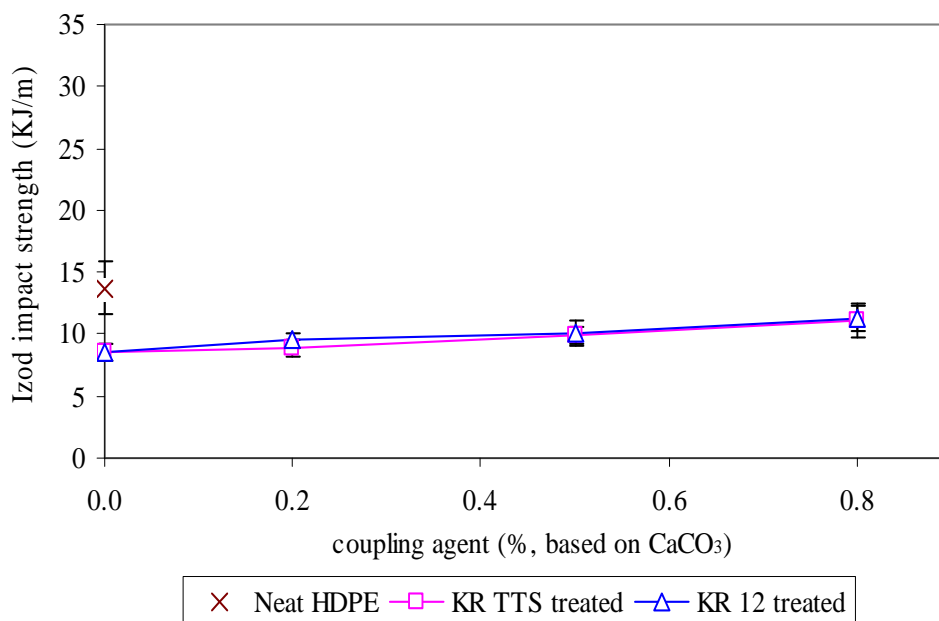


Figure 4.18 Effect of coupling agent content on the Izod impact strength of the polymer composites

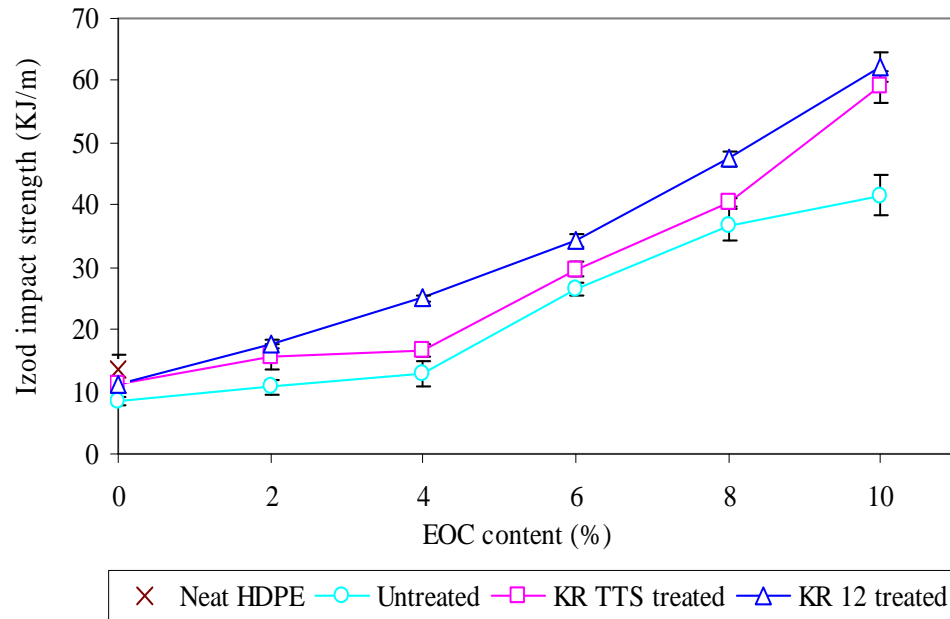


Figure 4.19 Effect of EOC content on the Izod impact strength of the polymer composites

4.5 Thermal properties

4.5.1 Differential scanning calorimetry characterization of the composites

Table 4.7 summarizes the differential scanning calorimetry (DSC) results of HDPE and its composites with CaCO₃ and EOC.

Table 4.7 Thermal properties and calculated crystallinity of the polymer composites

Run	Material	Heating I		Heating II		Cooling		X _c , %
		T _{mI} (°C)	ΔH _{mI} (J/g)	T _{mII} (°C)	ΔH _{mII} (J/g)	T _C (°C)	ΔH _C (J/g)	
1	Neat	134.2	193.0	132.3	242.1	111.9	229.5	83
2	PE80-0-0	132.1	190.0	133.1	210.7	113.2	196.4	90
3	PE78-0-2	132.0	186.3	132.1	202.7	113.5	194.7	89
7	PE70-0-10	133.1	155.8	132.2	172.1	114.1	167.2	84
10	PE80-8A-0	132.0	180.6	131.5	201.3	114.0	191.7	86
13	PE80-8B-0	132.6	176.9	131.9	207.2	113.9	187.9	88
14	PE78-8A-2	133.1	180.4	131.8	198.2	113.5	190.3	87
18	PE70-8A-10	132.9	152.4	133.5	171.7	112.2	162.4	84
19	PE78-8B-2	132.1	173.5	132.1	196.0	113.4	185.4	86
23	PE70-8B-10	131.6	150.5	132.5	164.4	110.3	150.0	80

The crystallinity (%X_c) of the HDPE was calculated from the ratio of the melting enthalpy of the composites by Equation 4.1. The melting enthalpy of a theoretically 100% crystalline HDPE was taken as 293 J/g, and was used to adjust the nominal mass fraction of HDPE in the composites [Tanniru *et al.*, 2006].

$$X_c = \frac{\Delta H_m / \phi_{\text{HDPE}}}{\Delta H_m^o} 100 \quad 4.1$$

where ΔH_m = enthalpy of mixing of the blend (J g^{-1}), ΔH_m^o = enthalpy of mixing of the neat polymer (J g^{-1}), ϕ_{HDPE} = weight fraction or content of HDPE in blends and X_c = degree of crystallinity in blends.

To erase the past thermal history, ΔH_{mII} of the second heating was run and used for the crystallinity calculation. It was found that the crystallinity increased with the addition of nano-sized CaCO_3 from 83% in the neat HDPE to 90% in 20% wt. $\text{CaCO}_3/\text{HDPE}$ nano-composite, but the crystallization and melting temperatures (T_c and T_m) remained unaffected which is consistent with the previous work [Tanniru *et al.*, 2005, 2006; Zuiderduin *et al.*, 2003; Deshmane *et al.*, 2006]. It is well known that a nucleating agent added to the polymer system is to increase the rate of crystallization [Charkrit, 2007], so the increase in crystallinity can be ascribed to the nucleating effect of CaCO_3 which gave the similar result with the recent work of Lazzeri *et al.* [2005].

The previous work of Gonzalez *et al.* [2002] stated that incorporation of Ken-React[®] LICA 12 titanate coupling agent induced a decrease in crystallinity of the PP/HDPE/ CaCO_3 composites. Likewise our experiment found that the X_c was decreased from 90% to 86%, and from 90% to 88% for 0.8% incorporation of KR TTS, or KR 12 coupling agent for CaCO_3 polymer composite, respectively. When adding EOC, our X_c data were also further decreased as a function of EOC content which is similar with the literature data from McNally *et al.* [2002].

4.5.2 Thermal gravimetric analysis (TGA) of the composites

Table 4.8 and Figures 4.20 to 4.21 show the results from the TGA thermograms of the polymer composites. The higher degradation temperature (T_d) of the composites containing the 20% CaCO_3 was found at 454 - 469 °C, while the coupling agent treated CaCO_3 polymer composite did not impose any significant

effect on the T_d because the T_d range was 459-467 °C. However, Figure 4.21 shows that the 10% EOC content in the composites caused T_d of the composites to reduce from 469 °C to 454 °C for the untreated polymer composites, and from 466 °C to 459 °C for the KR TTS treated polymer composites. In the KR 12 treated polymer composites, the T_d remained unchanged when the 10% EOC was added because the KR 12 molecule contains phosphorus (P) atom which can act as a flame retardant additive [Murphy, 2001]. The actual CaCO_3 content on the polymer composites was determined from the retain weight after the heating temperature was over 500 °C, the weight retain is in the range of 18.1 to 19.5% which is the inorganic residue of the polymer composite or CaCO_3 particles. Generally, CaCO_3 releases carbon dioxide on heating above 840 °C to form calcium oxide, commonly called quicklime, with a reaction enthalpy of 178 kJ/ mole.

Table 4.8 The degradation temperature of the polymer composites

Run	Material	T_d (°C)	Weight retain (%)
1	Neat HDPE	456	0.2
2	PE80-0-0	469	18.1
7	PE70-0-10	454	18.3
10	PE80-8A-0	466	18.7
18	PE70-8A-10	459	19.0
13	PE80-8B-0	464	19.5
23	PE70-8B-10	467	18.3

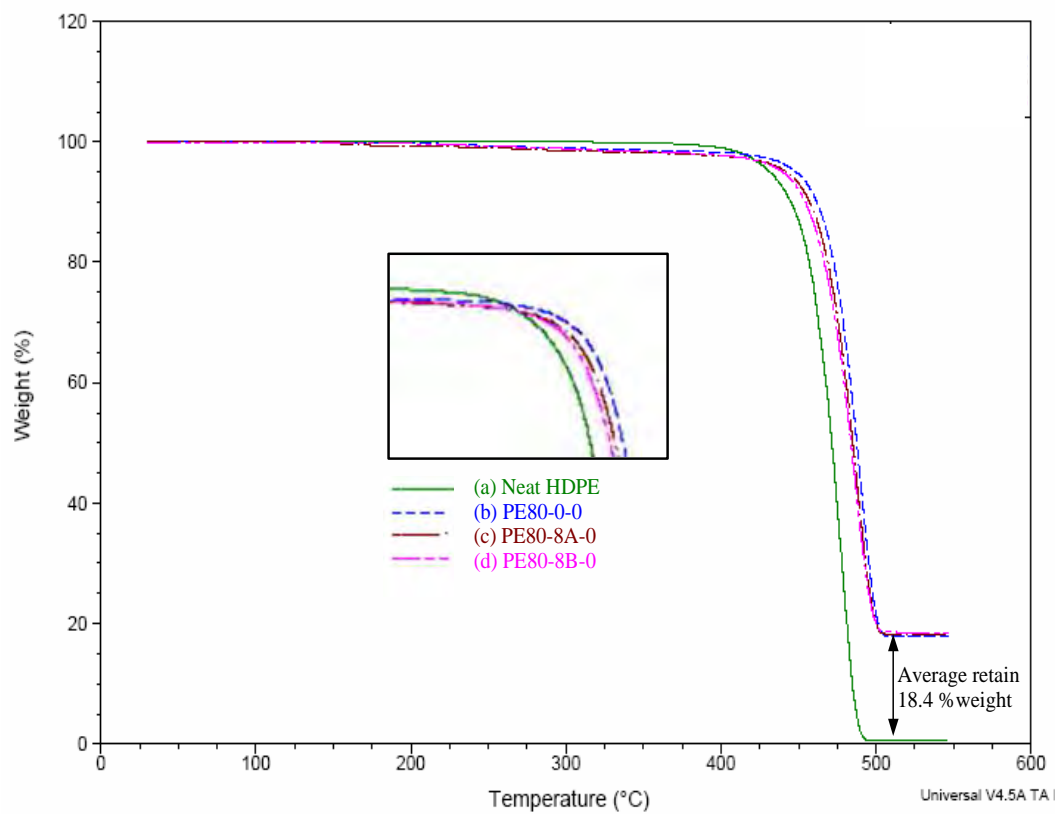


Figure 4.20 TGA thermograms of (a) the neat HDPE, (b) the untreated CaCO_3 polymer composite, (c) 0.8% KR TTS treated CaCO_3 polymer composite, (d) 0.8% KR 12 treated CaCO_3 polymer composite

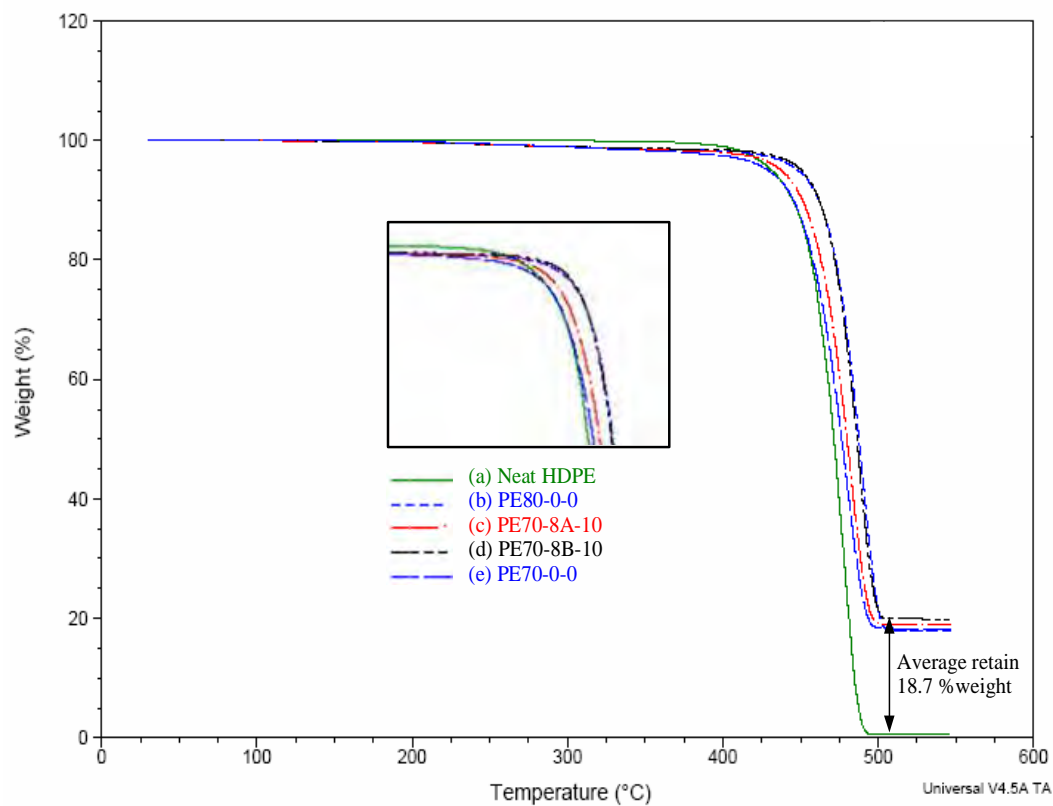


Figure 4.21 TGA thermograms of (a) the neat HDPE, (b) the untreated CaCO_3 /HDPE composite, (c) 0.8% KR TTS treated CaCO_3 -10% EOC polymer composite, (d) 0.8% KR 12 treated CaCO_3 -10% EOC polymer composite, (e) the untreated CaCO_3 -10% EOC polymer composite,

4.6 Color measurement

Table 4.9 shows the CIE $L^*a^*b^*$ values of the composites measured under the condition of the illuminant D65 at 10° observer by a spherical geometry (diffuse/8°) spectrophotometer. The L^* value shows the light/dark axis, the a^* shows the red/green axis and the b^* shows the yellow/blue axis. The total color difference between the reference (PE80) and the sample (s) in the color space is referred to as ΔE^* as calculated by Equation 3.1 as described in Chapter III [Huff, 1994].

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \quad 3.1$$

The directions of the color of the composites were identified as below. When $\Delta a^* = a^*_s - a^*_r$, “a +” sign means the composite sample is redder than the reference and the “a –” sign means the composite sample is greener than the reference. For $\Delta b^* = b^*_s - b^*_r$, “b+” sign means the composite sample is yellower than the reference, and the – sign means the composite sample is bluer than the reference. In the lightness scale, $\Delta L^* = L^*_s - L^*_r$, the “L+” sign means the composite sample is lighter than the reference and “L –” sign means the composite sample is darker than the reference. ΔE^* is a single number that represents the 'distance' between two colors. The idea is that a ΔE^* of 1.0 is the smallest color difference that human eye can see. So any ΔE^* less than 1.0 is imperceptible and it stands to reason that any ΔE^* greater than 1.0 is noticeable.

A measure of the yellowing of a plastic is to measure the deviation in chroma from whiteness in the dominant wavelength range from 400 to 700 nm as compared to a magnesium oxide standard. Yellowness is calculated using the three tristimulus values of a specimen as follows:

$$\text{Yellowness} = [100(1.28X_{\text{CIE}} - 1.06Z_{\text{CIE}})]/Y_{\text{CIE}} \quad 4.2$$

where X_{CIE} is the tristimulus value for Red, Y_{CIE} is the tristimulus value for Green, and Z_{CIE} is the tristimulus value for Blue. Positive yellowness values indicate the

presence and magnitude of yellowness, while a negative yellowness value indicates that a material appears bluish. Yellowness is a function of thickness, so comparison between data should be between specimens of comparable thickness.

Table 4.9 shows that increasing the coupling agent and EOC concentrations increases the ΔE^* values of the polymer composite from its neat polymer composite. The ΔE^* values are greater than +1 (1.63 to 3.50), i.e., there are significant difference in the color and those can be detected by the naked eye. For the yellowness of the polymer composites measured at the 400-700 nm wavelength based on Y313 standard, the neat polymer composite itself has a relatively higher yellowness value. Incorporating of increasing EOC content in the composites (tests 2 -7) decreased the yellowness of the composites while incorporating the KR TTS coupling agent (tests 8-10) decreased less yellowness of those containing KR 12 (tests 11-13). When both the coupling agent and EOC were incorporated in the polymer composites, the yellowness increased slightly in the trend that yellowness was found to be higher in the KR TTS incorporated polymer composites.

Table 4.9 The spectrophotometric color value expressed as the CIEL*a*b* and yellowness

Run	Material	Measurement			Calculation				YI
		L*	a*	b*	ΔL^*	Δa^*	Δb^*	ΔE^*	313
C	CaCO ₃	98.96	-0.03	1.14	-	-	-	-	2.10
E	EOC	93.47	0.29	2.46	-	-	-	-	4.51
A**	KR TTS	65.79	32.12	108.77	-	-	-	-	159.21
B**	KR 12	84.95	-3.43	33.22	-	-	-	-	55.11
W**	White oil	88.71	-0.13	4.72	-	-	-	-	9.32
1	Neat HDPE	90.49	-0.77	2.99	-	-	-	-	5.31
2	PE80-0-0	88.16	1.42	9.94	-	-	-	-	20.55
3	PE78-0-2	89.72	1.10	9.60	1.56	-0.32	-0.34	1.63	19.38
4	PE76-0-4	89.91	0.83	9.17	1.75	-0.59	-0.77	2.00	18.34
5	PE74-0-6	88.98	0.96	7.21	0.82	-0.46	-2.73	2.89	14.95
6	PE72-0-8	90.05	0.50	7.40	1.89	-0.92	-2.54	3.30	14.79
7	PE70-0-10	90.41	0.48	7.40	2.25	-0.94	-2.54	3.52	14.72
8	PE80-2A-0	87.39	1.79	11.69	-0.77	0.37	1.75	1.95	24.21
9	PE80-5A-0	87.16	2.21	12.54	-1.00	0.79	2.60	2.90	26.15
10	PE80-8A-0	87.51	2.26	12.87	-0.65	0.84	2.93	3.12	26.70
11	PE80-2B-0	88.79	-0.30	8.32	0.63	-1.72	-1.62	2.45	16.03
12	PE80-5B-0	89.96	-0.15	9.72	1.80	-1.57	-0.22	2.40	18.54
13	PE80-8B-0	90.04	-0.09	10.55	1.88	-1.51	0.61	2.49	20.08
14	PE78-8A-2	87.98	0.80	11.83	-0.18	-0.62	1.89	2.00	23.51
15	PE76-8A-4	89.30	0.23	11.33	1.14	-1.19	1.39	2.16	21.87
16	PE74-8A-6	90.32	0.54	10.29	2.16	-0.88	0.35	2.36	20.07
17	PE72-8A-8	89.55	0.45	11.78	1.39	-0.97	1.84	2.50	22.81
18	PE70-8A-10	90.39	0.20	10.83	2.23	-1.22	0.89	2.69	20.75
19	PE78-8B-2	90.36	0.33	11.13	2.20	-1.09	1.19	2.73	21.39
20	PE76-8B-4	90.40	0.23	10.82	2.24	-1.19	0.88	2.68	20.75
21	PE74-8B-6	90.55	0.01	10.36	2.39	-1.41	0.42	2.81	19.73
22	PE72-8B-8	90.65	-0.04	10.22	2.49	-1.46	0.28	2.90	19.42
23	PE70-8B-10	90.64	-0.03	10.04	2.48	-1.45	0.10	2.87	19.10

** measured by the transmittance mode in Datacolor SF650 spectrophotometer.

Figure 4.22(a) and 4.22(b) show the effect of KR TTS and KR 12 on the color appearance of CaCO₃-filled polymer composites, respectively. The KR TTS pre-treated CaCO₃-filled polymer composites are yellower to reddish color while the KR 12 pre-treated CaCO₃-filled polymer composites are greener or yellower (lemon color) and compared to the untreated CaCO₃-filled polymer composites. Referring to the product data sheet of KR TTS and our measurement as shown in Table 4.9, the color is transparent reddish brown while KR 12 color is translucent slightly yellowish green. Therefore the color changes of the polymer composites are mainly related to the color of titanate coupling agent.

Figures 4.22(c), 4.22(d) and 4.22(f) show the effects of EOC content on color of the composites when the composites were treated with KR TTS or KR 12 and the un-treatment, respectively. The EOC gave the color towards the slightly lemon green region of the polymer composites compared to the slightly yellow color of the untreated polymer composites.

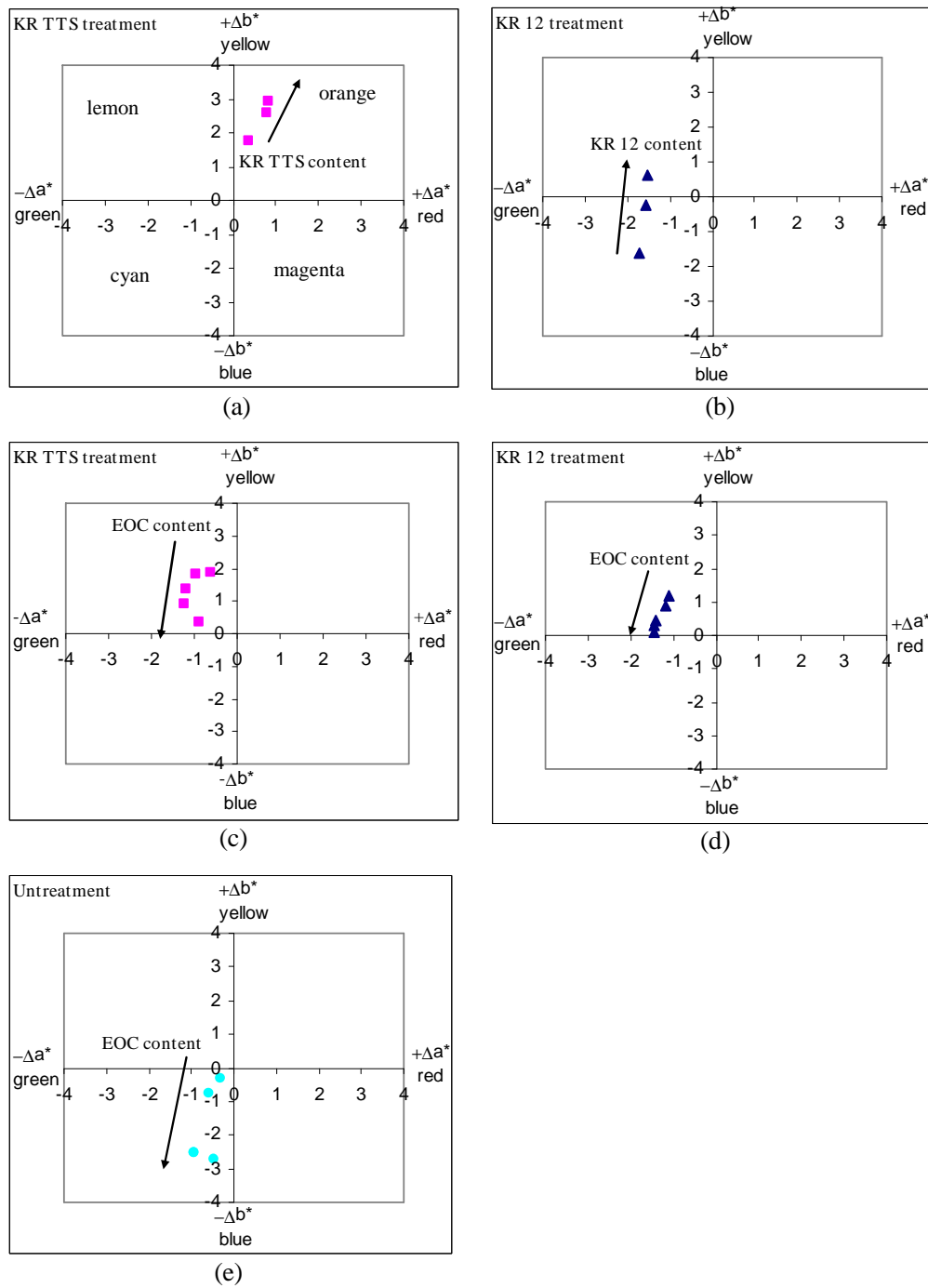


Figure 4.22 The effects of EOC content and KRTTS or KR12 treatment on CaCO_3 on the color appearance of the polymer composites

CHAPTER V

CONCLUSIONS AND SUGGESTIONS

5.1 Conclusions

The CaCO₃ particle pre-treated with titanate coupling agent improved particle dispersion in HDPE/EOC matrix by enhancing the interfacial wetting, mixing and adhesion between CaCO₃ particles and polymer matrix. The SEM micrographs exhibited large particle agglomerates of the un-treated CaCO₃ while the treated CaCO₃ particle revealed much better particle dispersion in the polymer matrix. These better particle dispersions are also proven by the reduction of built up melt pressure through wire mesh filter media at 15 µm in the presence of titanate coupling agent treated particle. The KR 12 treated CaCO₃ reveals better particle dispersion in comparison with the KR TTS treated CaCO₃.

The better particle dispersion of the treated CaCO₃ led to increased tensile yield strength and Izod impact strength. The EOC content significantly improved Izod impact strength but lowered tensile yield strength. The coupling agent pretreatment is a pre-requisite for enhancing Young's modulus while the synergistic effect of the coupling agent and EOC enhanced most of the physical properties.

The thermal properties of the composites were studied using the differential scanning calorimetry (DSC). It was found that the crystallinity increased with the addition of 20% nano-CaCO₃ due to their nucleating effect while the crystallinity decreased with the presence of KR TTS and KR 12 treated particles and EOC content.

Addition of the titanate coupling agent induced some yellowness in the polymer composites while EOC helped somewhat reduce the yellowness. Both the coupling agent and EOC incorporation in the CaCO₃-filled PE produced an appreciable amount of color difference (ΔE^*) to the naked eye from the neat CaCO₃-filled PE due to the ΔE^* values in the range of 1.63 to 3.50.

5.2 Suggestion for further studies

1. It is interesting to apply this concept to other polyethylene grades, such as, extrusion blow molding, blow and cast film and other polyolefin family, such as, polypropylene.

2. Colorant and loading, such as organic pigment and carbon black should be added to the CaCO_3 -filled PE with incorporations of the titanate coupling agent and EOC.

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VITAE

Miss Kannika Surinta was born on December 10, 1978 in Chiangmai. She graduated with a Bachelor's degree of Science in Industrial Chemistry from Chiangmai University in 2000. She is working in Laboratory section, Bayer Thai Co., Ltd. She graduated with a Master's Degree in Petrochemistry and Polymer Science, Graduate School, Chulalongkorn University, in 2009.