USE OF FLY ASH
AS AN ALTERNATIVE FILLER MATERIAL
IN PVC-PLASTISOLS

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ABSTRACT

USE OF FLY ASH AS AN ALTERNATIVE FILLER MATERIALIN PVC-PASTISOLS

In this study, an alternative filling material, fly ash was tested in PVC pastisols. Therefore, - 38 μm Soma fly ash sample was used and its results were compared with that of calcite material as a filler. Therefore, this study was conducted to have three sections as: 1) Characterization of powders calcite, fly ash and PVC powder: SEM, XRF, XRD, Size measurement, 2) Preparation and characterization of PVC plastisols with and without fly ash: Rheological measurements 3) Characterization of final PVC product: Surface, hardness and strength tests. The results of fly ash were always compared with the results of calcite and discussed in this thesis.

It was suggested that fly ash could be an alternative filling material for PVC plastisols. It's effect, on the other hand, was found to change depending on the temperature, mixing speed and concentration. In overall, the mechanical properties of PVC-product obtained were affected positively and better PVC materials were obtained. Under some conditions, however, the rheological properties were became shear thickening while it was newtonian and shear thining before. The changes in the rheological properties of PVC plastisols and the mechanical properties (quality) of final PVC-product were all explained by the differences in the composition and shape of the fly ash particles. Because, the composition and shape of the particles are expected to affect the interactions of PVC particles with that of filler material which will definetely affect the quality of material.

ÖZET

UÇUCU KÜLÜN PVC PLASTİSOLLER İÇERİSİNDE ALTERNATİF DOLGU MALZEMESİ OLARAK KULLANILMASI

Bu çalışmada, PVC plastisoller içerisinde alternatif dolgu malzemesi olarak uçucu kül test edilmiştir. Bunun için -38 μm Soma uçucu kül numunesi kullanılmış ve sonuçlar, dolgu malzemesi olarak kalsit kullanılan malzemeler ile karşılaştırılmıştır. Çalışma, aşağıda sıralanan kısımlardan oluşmuşdur. Bunlar: 1) Toz malzemelerin karakterizasyonu: SEM, XRF, XRD, Tane boyutu ölçümleri, 2) Uçucu kül içeren ve içermeyen PVC plastisollerin hazırlanması ve karakterizasyonu: Reoloji ölçümleri ve 3) Son ürünün karakterizasyonu: Yüzey, sertlik ve mukavemet testleri.

Çalışmanın sonuçlarına dayanarak, uçucu külün PVC plastisoller için alternatif dolgu malzemesi olabilecegi önerilmiştir. Bu malzemenin etkisinin sıcaklık, karıştırma hızı ve konsantrasyona göre değiştiği bulunmuştur. Sonuçta, PVC-ürünün mekanik özelliklerinin pozitif olarak etkilendiği ve daha iyi bir malzeme elde edildiği gözlenmiştir. Ancak bazı koşullarda "shear thinning" olan reolojik davranışın "shear thickening" olduğu da gözlenmiştir. PVC plastisollerin reolojik özelliklerinde ve nihai PVC ürünün mekanik özelliklerinde (kalite) gerçekleşen tüm bu değişiklikler uçucu külün yapısındaki ve tane şeklindeki farklılıklarla açıklanmıştır. Çünkü, hem yapıdaki değişikliklerin hemde tane şeklindeki değişiklerin PVC tanecikleri ile dolgu malzemeleri arasındaki ilişkileri etkileyeceğinden sonuçta meydana gelecek olan ürünü kesinlikle etkilemesi beklenmektedir.

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CHAPTER 1

INTRODUCTION

Fillers are one of the most important raw materials of the polymer industry. They are also important in many other sectors. In recent years, there are many scientific and industrial developments done about them. They affect the mechanical properties of the polymer, modify rheology, supply a chemical resistance to the product and reduce the cost of the production. PVC plastisols are one of the fields using fillers in industry to reduce cost and modify rheology. For PVC plastisols, there are many types of commercial fillers in the market to supply properties mentioned above such as calcite, montmorillonite, kaolin, talk, are common fillers. These are inorganic substances with some specific properties, crystalline structure, hardness, etc.

One application of the PVC plastisols is the conveyor belts that are used approximately in all fields of the industry. This is because there will be always a production for human and goods should be transported from production machine. Depending on the goods that are being transported, conveyor belts should have some technical properties. For example, they should not be expensive. Therefore fillers are used in their production to cut the cost and keep the product quality constant.

There are some studies in the pass related to the PVC plastisols. The most of the studies were on the rheological behaviour of plastisols. For example Garcia and Marcilla, 1998 studied the influence of plasticizer type and concentration on the rheological behaviour of plastisols. In their study, commercial resins and plasticizers were used and viscoelastic properties were searched by monitoring gelation and fusion method using Rheometer BOHLIN CS 50 instrument. They found that low plasticizer concentration supplied a higher compatibility with PVC and increasing particle size and MW (molecular weigth) of the PVC caused a decrease in the velocity of gelation (Garcia and Marcilla 1998).

Another study was on the rheological and mechanical properties of PVC/$CaCO_3$ nanocomposites. Nanocomposites were prepared by in situ polymerization of vinyl chloride and $CaCO_3$ nanoparticles. The rheological

properties of these nanocomposites studied using a capillary rheometer (model XLY-1) at 175 ^{0}C. In their study, tensile properties were also determined using an Instron tester (model 4206) at a crosshead rate of 5 mm/min. They concluded that $CaCO_3$ nanoparticles were uniformly distributed in the PVC matrix during in situ polymerization of PVC with 5.0 wt% or less nanoparticles. The nanocomposites all showed shear thinning behaviour and power law behaviors. They concluded that $CaCO_3$ nanoparticles acts as stress concentrators leading to interface debonding/voiding and matrix deformation (Xie, et al. 2004).

There are many studies done to investigate the effect of fillers on some properties of the materials. One of this study was related with the characterization of PVC and agalmatolite composites and effect of mineral filler through thermal analysis and mechanical properties. The glass transition temperature and mechanical properties were evaluated with respect to PVC and calcium carbonate composites. The results showed that when the agalmatolite content was increased from 10 to 40 phr(part per resin), the glass transition temperature decreased, but the same result was not observed for materials filled calcium carbonate. As a mechanical properties, agalmatolite filled materials had higher Young's modulus and elongation at break of the composites than calcium carbonate filled composites (Pedro, et al. 2000).

Fly ash is a pozzolanic material generated from coal-burning thermal power plants. Though a significant fraction of coal fly ash is used as a cement and concrete additive in the world, only a very small portion of the 15 million tons of fly ash generated is re-utilized in Turkey (Baba 2004). Fly ash contains a range of heavy metals of different mobilities in its structure (Polat, at al. 2002). Since it is usually disposed of in the form of a slurry in the vicinity of the power plant, fly ash possesses significant environmental risk due to the possibility of leaching of these metals into environment (Baba 2004, Polat, et al. 2002, Pandian 2004). This risk has led to extensive studies on the physical-chemical properties and leaching behavior of fly ash (Vassilev, et al. 2005, Singh, et al., 2003, Mohapatra and Rao 2001, Landman 2002, Nathan, et al. 1999, Puertas, et al., 2003, Murugendrappa, et al. 2005). There is a large body of work on the use of fly ash in cement and brick production (Majko and Pistilli 1984, Demirbas 1996, Djuric 1996, Palamo, et al. 1999, Kula, et al. 2001, Canpolat, et al. 2004). In one study, the Derjaguin–Landau–Verway–Overbeek (DLVO) theory for dispersion–flocculation of heterogeneous particles with different

surface potentials was applied to explain the effect of fly ash on the rheology of cement paste containing naphthalene sulfonate superplasticizer. The fly ash and ordinary porland cement were compared. The fly ash–cement paste without superplasticizer resulted the sign of zeta potential of fly ash was different from ordinary porland cement. So, the extent of the potential energy barrier between particles was small or showed negative value, and the change in the rheology of the fly ash–cement paste was mainly dependent on the bulk solid volume of fly ash. The fly ash–cement paste with naphthalene sulfonate superplasticizer, fly ash and cement had the same sign and dispersed well due to higher potential barrier. The extent of potential energy barrier depended on the absolute value of surface potential, which was represented by a function of the amount of adsorbed superplasticizer. The bulk solid volume of fly ash also affected the change in flow ability (Termkhajornkit and Nawa 2003).

The purpose of this study was to investigate the usage of fly ash as an alternative filler material in PVC pastisols. Therefore the study was design to have three parts as:

1) Characterization of powders: SEM, XRF, XRD, size measurement

2) Characterization of PVC plastisols prepared with and without flyash: Rheological measurements.

3) Characterization of final product: Hardness and strenght tests.

CHAPTER 2

PVC PLASTISOLS AND CONVEYOR BELT

2. 1. PVC Plastisols

PVC (Polyvinyl Chloride) plastisols are mixtures that are formed as a result of dispersion of PVC dust in plasticizer. In addition, in order to give different properties to the product, additive materials as fireproof provider, thermal stability provider, etc. are used as.

Raw materials and their amounts which are used in the preparation of plastisol can be listed as follows:

- PVC-powder → 50-60 %
- Plasticizer → 25-35 %
- Additives (Epoxized soybean oil, viscosity regulators, defoamer, flame retardants, stabilizers (heat and light), antistatic agents → change in 0.5-5 %
- Pigments, TiO2 pigments → 0.5 -1.5 %
- Calcite and talk as a filler → 15-20 %

PREPARATION OF PVC PLASTISOLS

All the liquids that is used for the preparation of PVC plastisols

are mixed by using a mixer device

PVC powder is added

It is mixed at 700-800 rpm for 10-15 min.

Some part of the first prepared plastisol is get into the vacuum tube

Color pigment is added inside

It is mixed for 10-15 min under vacuum

(until a homogeneous mixture is provided)
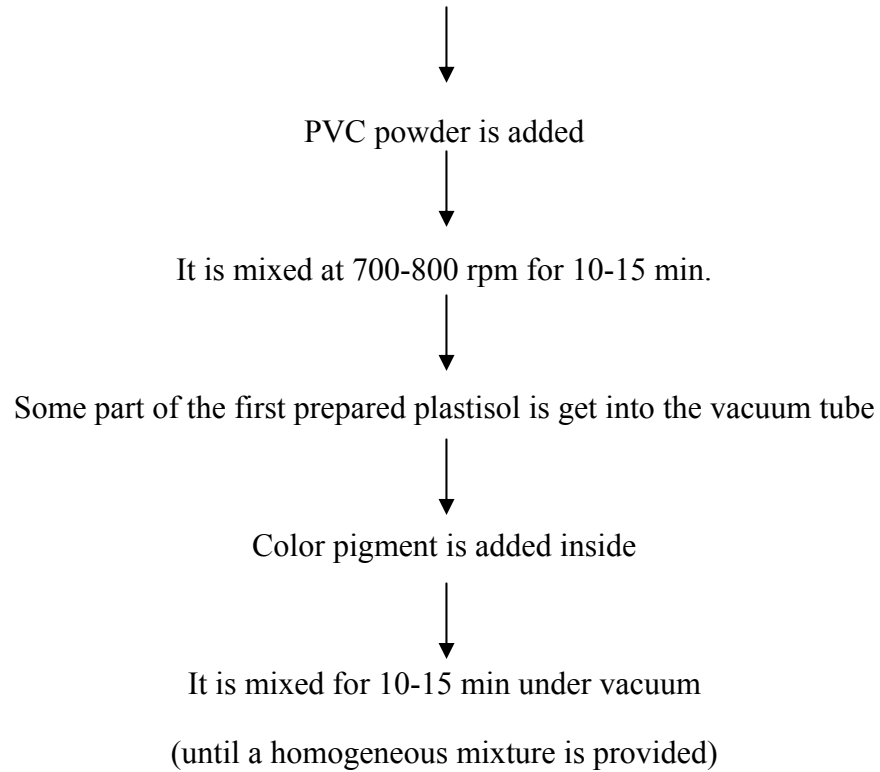
Figure 2.1. A schematic presentation of the production of the PVC plastisol

2.1.1. Raw Materials of PVC Plastisols

PVC plastisols are formed by PVC resin, and some additives, that is plasticizer, stabilizers, filler, etc. Usage of additives in the formulation, improves some properties of the PVC, such as flexibility and workability (Jimenez, et al. 2000).

2.1.2. Plasticizers for plastic

For producing flexible plastics, engineering and medical applications plasticizers have been used with polymers (Rahman 2006).

Plasticizers are low molecular weight (MW) resins or liquids indeed, which form secondary bonds to polymer chains and spread them apart.

Therefore, plasticizers decrease polymer-polymer chain secondary bonding and more mobility for the macromolecules, consequential in a softer and more easily deformable mass is provided (Rahman and Brazel 2004). Common types of plasticizers are shown in Figure 2.2 and Figure 2.3.
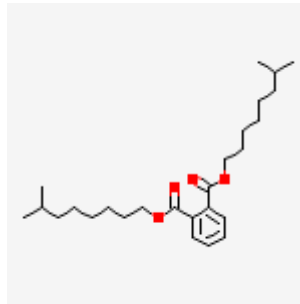
Figure 2.2. Diisononyl Pthalate (DINP), $C_{26}H_{42}O_4$
(Source: Chemicalregister 2010)
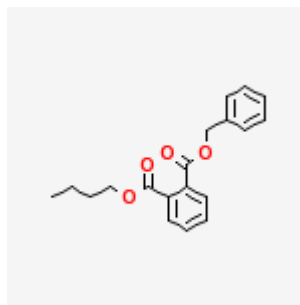
Figure 2.3. Butylbenzyl Phthalate (BBP), $C_{19}H_{20}O_4$
(Source: Chemicalregister 2010)

Plasticizers are generally chosen on the basis of the following criteria

- Compatibility of a plasticizer with a given polymer,

- Processing characteristics,

- Desired thermal, electrical and mechanical properties of the end product,

- Resistance to water, chemicals, solar radiation,

- Weathering, dirt, microorganisms, (Rahman and Brazel 2004).

Table 2.1. Plasticizer-related technical challenges

1. Migration out of plastic a. Solid–solid migration b. Evaporation c. Liquid leaching
2. High temperature flexibility
3. Low temperature lubricity
4. Health and environmental effects (cytotoxicity)
5. Flammability concern regarding plasticizers
6. Compatibility with new polymers
7. Stability to ultraviolet rays
8. Biodegradability
9. Improved material lifetime

2.1.3. Fillers

Filler can be chosen as any low cost solid, liquid, or gas which resides in volume in order to reduce its volume-cost. Functional fillers are added to improve specific properties. For instances, calcined clays are added to wire insulation formulas to raise electrical volume resistivity, fumed silica or bentonite clay added to plastisols to increase their yield value. Moreover, hollow microspheres used to lower specific gravity while achieving other desired filler effects. The most common used fillers in flexible and semi-rigid PVC are graduated as dry-ground, wetground, or precipitated calcium carbonate which are derived from limestone or marble (Wilkes, et al. 2005).

This is the stable crystal structure of $CaCO_3$ at normal temperatures and pressures. Pure calcium carbonate fillers are low in abrasivity to processing equipment because of its low hardness (Mohs of 3) (Wilkes, et al. 2005).

Considerations in chosen a particular grade of calcium carbonate filler contain the purity of the original ore, if it has been dry-ground or wet-ground or precipitated,

the average particle size and size distribution, and if the particles have had a surface treatment. The "packing fraction" (PF) is a efficiency measure of finer particles for filling the voids between coarser particles (Wilkes, et al. 2005).

Equivalent spherical diameter (esd) is the definition term of average size of filler particles and "aspect ratio" is the ratio of the average lengths of the major to minor axes of filler particles. Aspect ratios of the most used fillers have less than 4 : 1. Strengthening materials such as glass or metal fibers have aspect ratios in excess of 10 : 1 generally. Vinyl floor tile made by calendering tolerates filler particle sizes up to 99% through a U.S. Typical 50 mesh screen having 297 micron openings (11.7 mils). Typical electrical insulations and extruded cable jackets need fillers with an average esd of 3 microns. Or, diameter of coarsest particles must be less than 12 microns (0.47 mils). In general, precipitated calcium carbonates having 0.6 micron esd is used by cable jackets that release low HCl emission on burning. Determination of the best filler particle sizes for most flexible PVC applications are made by experience, in optimizing end-use properties and minimizing cost. Talc is the softest non-carbonate filler that used in flexible PVC (Wilkes, et al. 2005).

It is represented by the formula; $3\ MgO \cdot 4\ SiO_2 \cdot H_2O$.

Zero or very low amount of asbestos-related minerals comprise is defined for talcs used with PVC. In order to improve flow in bulk handling systems and hopper cars, talc can also be dusted at rate of 0.1 to 0.25% over PVC compound cubes or pellets (Wilkes, et al. 2005).

In order to impart a non-blocking surface and to supply stiffening, mica is added to PVC compound. Typical grades used in non-blocking calendered films are fine-ground so that > 99% passes a 325 mesh screen (with openings of 1.7 mils or 44 microns). In order to increase viscosity and yield value and to reduce surface gloss after fusion diatomite (amorphous silica) is added to PVC plastisols. As a scrubbing agent, fumed silica can be added to hot-processed compounds. In order to increase viscosity and yield value it can be added to plastisols (Wilkes, et al. 2005).

2.2.   Conveyor Belt

Conveyor is a device that is used for transportation by moving on drive pulleys by the help of actuation drum. Plate or drum on this system which carries the

transporting material is the product that is called conveyor belt. Conveyor systems in food sector are shown in Figure 2.4.

<table>
<tr><td>(a)</td><td>(b)</td></tr>
</table>
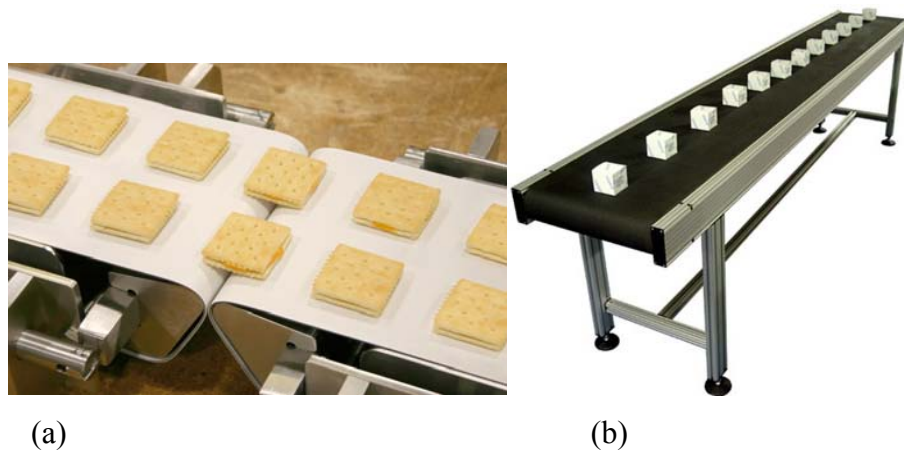
Figure 2.4 (a) and (b) represent conveyor belt and systems.

Conveyor belts are prepared by using different chemicals and additives with different processes in our country and also in the world.

Conveyor belts are generally grouped as PVC (Polyviniyl Chloride); PO (Polyolefine) PU (Polyurethane) and etc.

PVC conveyor belts are manufactured within Rultrans Incorporated.

Actually installer on conveyor system is conveyor belt. Material property of fabric may be, polyester, nylon, cotton, nylon / nylon, nylon / polyester, nylon / cotton, etc. There are wefts and warps in the structure of the fabric as shown in Figure 2.5. Transition direction of conveyor belt through machine is the same with direction of warp which have higer strength.
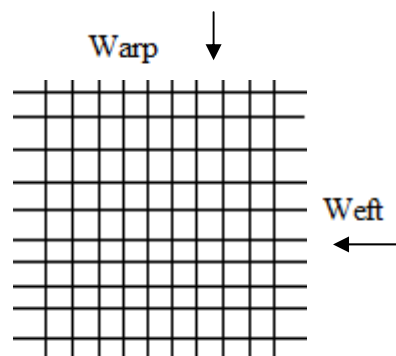
Figure 2.5. Warp and weft of the fabric

Fabric and PVC plastisol process is a system which consists such coating units, ovens, thrust and cooling cylinder. In later stages, the scheme of fabrication will be shown. At this stage the purpose of units are stated.

In production, PVC mixtures are dumped on polyester fabric which have different features in the desired thickness with the help of a knife and polymerization is done by passing it through a furnace at 220 ºC.

Then it is twined around a different cylinder after it is crushed with the help of cooling cylinders and embossing rollers.

Production is performed in the 2000-3000 mm wideness and in approximately 600000 mm in length.

Conveyor belts are manufactured as they have 1-2-3 floored fabric. Product thickness varies between 1 mm and 10 mm.
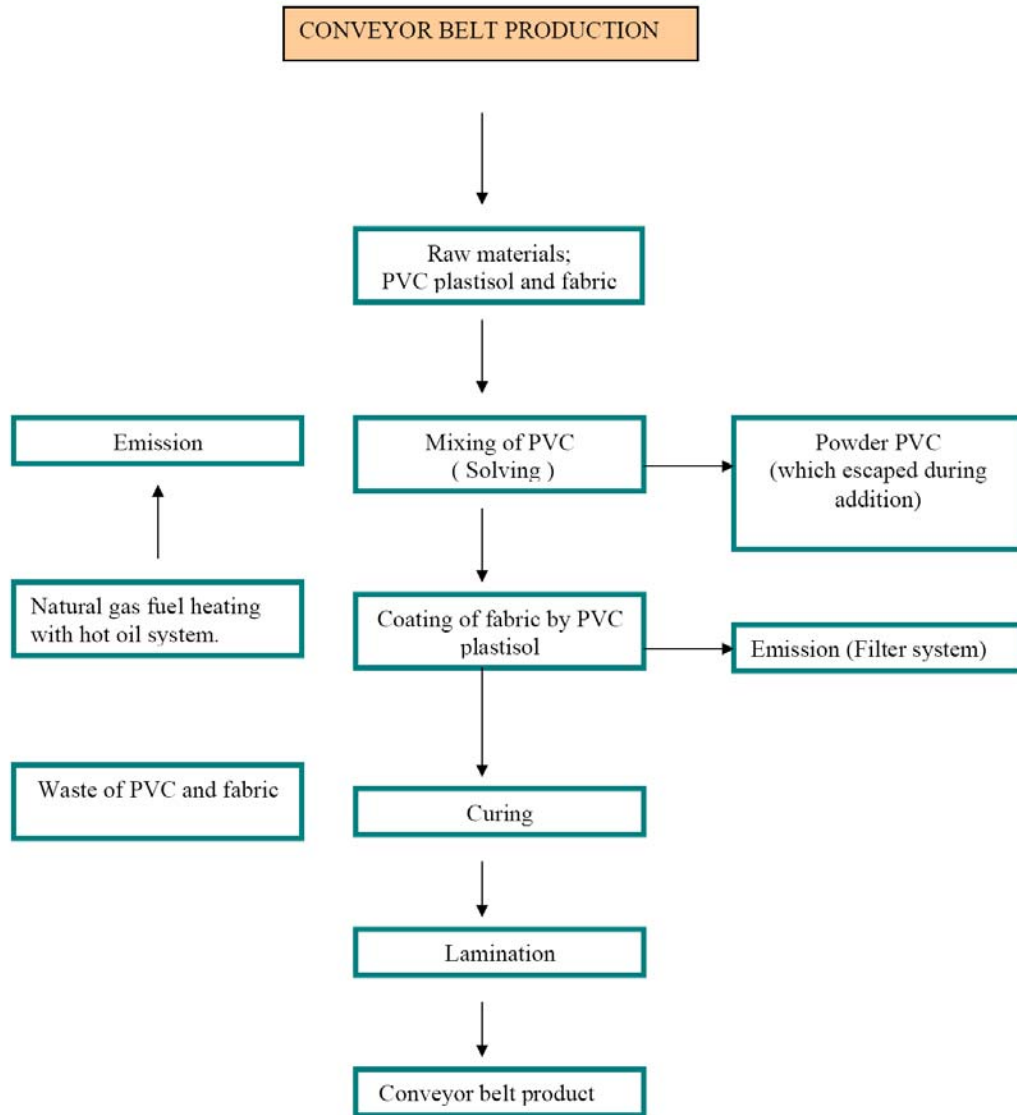
Figure 2.6. A schematic representation of conveyor belt production

2.3. Rheology

Rheology is the science of the change in form and flow of matter, encloses elasticity, viscosity and plasticity. Rheology is important in many industries such as food, paint, rubber, textiles. Rheological behaviour is also of major importance in biology and medicine (Shaw 1992).

Viscosity is a measure of the resistance of a slip to flow, the internal friction of a fluid. This friction becomes apparent when a layer of fluid is made to move in relation to another layer. The greater the friction, the grater the amount of force

required to cause this movement, which is called shear. Shearing occurs whenever the fluid is physically moved or distributed, as in pouring, spreading, spraying, mixing, etc. Highly viscous fluids, therefore, require more force to move than less viscous materials (Vlachopoulos 2005).
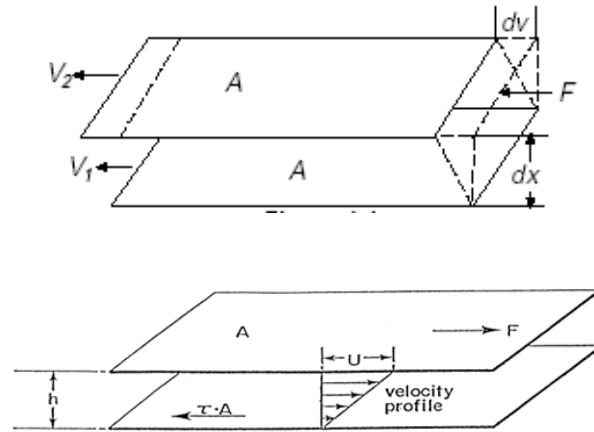
Figure 2.7. Viscosity Model
(Source: Vlachopoulos 2005)

Two paralel flat areas of fluid of the same size A are separated by a distance dx and are moving in the same direction at different velocities V_1 and V_2. Newton assumed that the force required to maintain this difference in speed was proportional to the difference in speed through the liquid, or the velocity gradient.

$$\frac{F}{A} = \eta \frac{dv}{dx}$$
(2.1)

Where η is a constant for a given material and is called its viscosity. The velocity gradient, dv/dx, is a measure of change in speed at which the intermediate layers move with respect to each other. It describes the shearing the liquid experiences and is thus called shear rate. This is symbolized as γ and its unit of measure is called the reciprocal second (sec^{-1}). Plotting shear rate against viscosity determines the rheology of the slip.

The term F/A indicates the force per unit area required to produce shearing action. It is referred to as shear stress and is symbolized as τ. Its unit of measurement is "dynes per square centimeter" (dynes/cm^2) or "Newtons per square meter" (N/m^2).

Viscosity may be defined mathematically by Equation 2.2:

$$\eta = \text{viscosity} = \frac{\tau}{\gamma} = \frac{\text{shear stress}}{\text{shear rate}} \qquad (2.2)$$
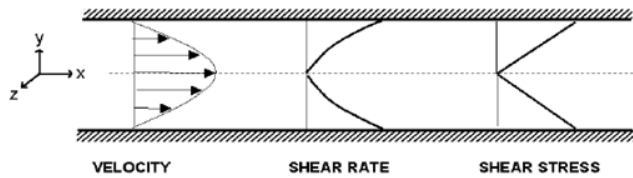
Figure 2.8. Velocity, shear rate and shear stress for flow between two plates

The fundamental unit of viscosity measurement is "poise". Sometimes "Pascal-seconds" (Pa.s) or "milliPascal-seconds" (mPa.s) are used.

Fluids have different rheological characteristics. Generally fluids are divided into two classes as Newtonian and Non-Newtonian (Brookfield Engineering 2005).

2.3.1. Newtonian Fluids

Newton assumed that all materials have, at a constant temperature and pressure, a viscosity that is independent of the shear rate. In other words, the shear viscosity does not vary with shear rate and viscosity remains same at different shear rates (different rpm's). Newtonian behavior is more typical of nonpolar liquids such as hydrocarbons, thin motor oils or water. Newtonian fluids have proportional relationship between shear stress (τ) and shear rate (γ) as shown in Figure 2.9.
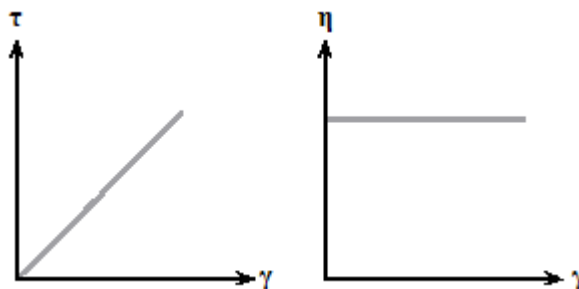
Figure 2.9. Diagram for Newtonian Behaviour

2.3.2. Non-Newtonian Fluids

These fluids have different viscosities at different shear rates (different rpm's). When the shear rate is varied, the shear stress does not vary in the same proportion. The viscosity of such fluids will therefore change as the shear rate is varied. This measured viscosity is called the apparent viscosity of the fluid.

Non-Newtonian flow can be envisioned by thinking of any fluid as a mixtures of molecules with different shapes and sizes. As they pass by each other, as happens during flow, their size, shape, and cohesiveness will determine how much force is required to move them. At each specific rate of shear, the alignment may be different and more or less force may be required to maintain motion (Brookfield Engineering 2005).

There are several types of non-Newtonian flow behavior, characterized by a fluid's viscosity changes in response to variations in shear rate. Flow behaviour may depend only on shear rate and not on the duration of shear that is time-independent, or may depend also on the duration of shear, time-dependent.

2.3.2.1. Time Independent Non-Newtonian Fluids

Time independency is also called as steady-state phenomena. There are three types of time-independent fluids.

2.3.2.1.1. Shear-Thinning

Shear-thinning fluids are popularly called pseudoplastic, include paints, emulsions, and dispersions of many types. This type of fluid will display a decreasing viscosity with an increasing shear rate. The faster the rotation, the more the structure is destroyed and the less structure of molecules slide in together therefore viscosity will be lower.
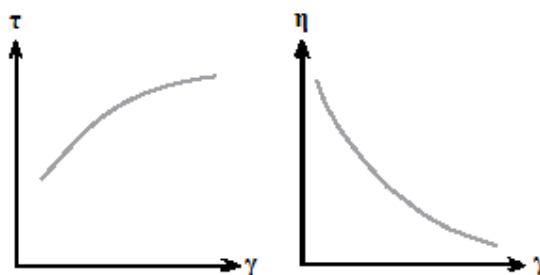
Figure 2.10. Diagram for Shear-Thinning Behaviour

If particle aggregation occurs in a colloidal system, then an increase in the shear rate will tend to break down the aggregates, which will result in a reduction of the amount of solvent immobilised by the particles, thus lowering the apparent viscosity of the system.

Shear-thinning is particularly common to systems containing asymmetric particles. Asymmetric particles disturb the flow lines to a greater extent when they are randomly orientated at low-velocity gradients than when they have been aligned at high-velocity gradients. In addition, particle interaction and solvent immobilisation are favoured when conditions of random orientation prevail. The apparent viscosity of a system which thins on shearing is most susceptible to changes in the shear rate in the intermediate range where there is a balance between randomness and alignment, and between aggregation and dispersion (Shaw 1992).

2.3.2.1.2. Shear-Thickening

Shear-thickening, dilatancy, is characterized by increasing viscosity with an increase in shear rate. Dilatancy is frequently observed in fluids containing high levels of deflocculated solids, such as clay slurries, candy compounds, and sand/water mixtures.
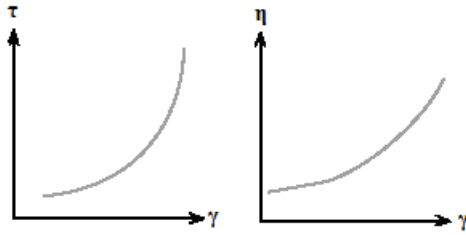
Figure 2.11. Diagrams for Shear-Thickening Behaviour

2.3.2.1.3. Plasticity

This type of fluid will behave as a solid under static conditions. A certain amount of stress must be applied to the fluid before any flow is induced; this stress is called yield stress or yield value (f´). Plasticity is due to a continuous structural network which imparts rigidity to the sample and which must be broken before flow can occur. Tomato catsup is a good example for this type of fluid. Once the yield value is exceeded and flow begins, plastic fluids may display Newtonian, or dilatant flow characteristics (Shaw 1992, Brookfield Engineering 2005).
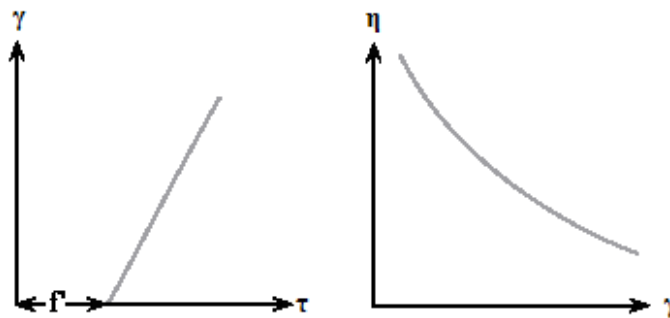
Figure 2.12. Diagrams for Plastic Behaviour
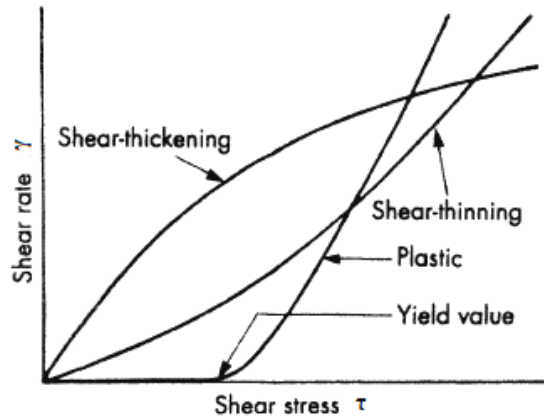
Figure 2.13. Types of Time Independent Non-Newtonian Flow

2.3.2.2. Time Dependent Non-Newtonian Fluids

Some fluids will display a change in viscosity with time under conditions of constant shear rate. There are two categories to consider: Thixotropy and Rheopexy.

2.3.2.2.1. Thixotropy

Thixotropy is the time-dependent analogue of shear-thinning and plastic behaviour. A thixotropic fluid undergoes a decrease in viscosity with time, while it is subjected to a constant shear rate. The classical examples of thixotropic behaviour are the weak gel systems, such as flocculated sols of iron(III) oxide, alumina and many clays, which can be liquefied on shaking and solidify on standing (Shaw 1992).
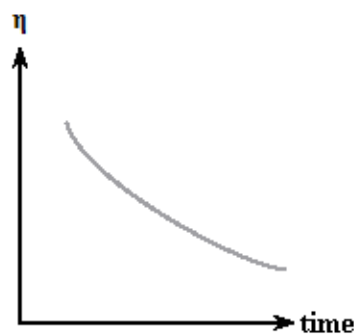
Figure 2.14. Diagram of Thixotropic Flow

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2.3.2.2.2. Rheopexy

This is time-dependent shear-thickening, the opposite of thixotropic behavior, in that the fluid's viscosity increases with time as it is sheared at a constant rate.
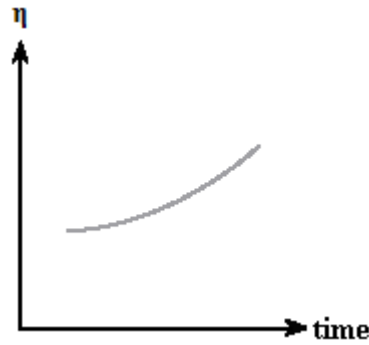
Figure 2.15. Diagram of Rheopectic Flow

2.3.3. Rheology of Ceramics

Rheology is important in ceramic processing and the rheological behaviour of colloidal suspensions depends mainly on the following factors (Shaw 1992, Funk and Dinger 1994):

- viscosity of the dispersion medium
- particle concentration (volume percentage of solids)
- particle size distribution and shape
- deflocculant concentration
- pH
- ionic strength
- particle – particle and particle – dispersion medium interactions.

Measured viscosities and rheologies directly correlate to the behaviours of bodies and suspensions during processing. All particle/fluid suspensions, abroad category which includes all ceramic suspensions and forming bodies, are non-Newtonian fluids. For this reason it is important to characterize each suspension and forming body by measuring its viscosities at each shear rate and its rheology.

Viscosity behaviour over a range of imposed shear rates defines a body's rheological properties (Funk and Dinger 1994).

2.4. Fly Ash as an Alternative Filler Material

By-product material of a coal combustion process for energy generation is recognized as an environmental pollutant. Therefore a good deal of work on the utilization of fly ash has been undertaken world over.

Different applications (cements, roads and backfill) of them already allow a recycling of an important part of fly ash production which, for instance, reached 450,000 tons in 1997 in France. Their use as an adsorbent material, however, is being investigated recently. Some studies have shown that these materials might be beneficial for removal of heavy metal ions from waste waters (Rio and Delebarre 2003)

2.4.1. Production of Fly Ash

The fly ash produced from the burning of pulverized coal in a coal-fired boiler is a fine-grained, powdery particulate material that is carried off in the flue gas and usually collected from the flue gas by means of electrostatic precipitators, baghouses, or mechanical collection devices such as cyclones. The term fly ash is not applied to the residue extracted from the bottom of boilers. A general flow diagram of fly ash production in a dry-bottom coal-fired utility boiler operation is presented in Figure 2.16.
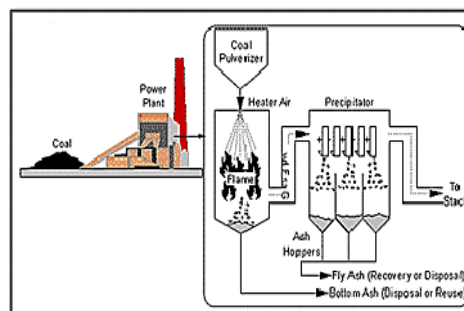
Figure 2.16. Production of fly ash in a dry-bottom utility boiler with electrostatic precipitator

Fly ash is defined as "the finely divided residue resulting from the combustion of ground or powdered coal which is transported from the firebox through the boiler by flue gases; known in UK as pulverized fuelash (pfa)" (ACI Committee 226, 1987) (Dermatas and Meng 2003).

Fly ashes may be sub-divided into two categories, according to their origin (ASTM):

Class F : Fly ash normally produced by burning anthracite or bituminous coal which meets the requirements applicable to this class.

Class C : Fly ash normally produced by burning lignite or sub-bituminous coal which meets the requirements applicable to this class. Class C fly ash possesses some cementitious properties. Some Class C fly ashes may have lime contents in excess of 10 % (Weshe 1991).

Bottom ash is the ash which is removed from a fixed grate by hand or which falls by gravity from the combustion zone. It is coarser and heavier than fly ash particles. Bottom ash forms when ash particles agglomerate to form aggregates similar to volcanic rock.

Slag is the material retained in the furnace. It is a kind of a solidified molten ash. Hence, the material is glassy and the larger pieces resemble obsidian. Compared to bottom ash, slag may have slightly higher bulk density and lower absorption capacity (Çanci 1998).

2.4.2. Composition of Fly Ash

Mineralogical Composition: The chemical and mineralogical composition of fly ashes depends upon the characteristics and composition of the coal burned in the power plant. Owing to the rapid cooling of the material, fly ashes are composed chiefly (50 – 90 %) of mineral matter in the form of glassy particles. A small amount of ash occurs in the form of crystals. Unburned coal is collected with the fly ash as particles of carbon, which may constitute up to 16 % of the total, depending on the rate and temperature of combustion, the degree of pulverization of the original coal, the fuel/air ratio, the nature of the coal being burned, etc.

The most important minerals found in fly ashes from bituminous coal are:

Magnetite	0.8 – 6.5%
Hematite	1.1 – 2.7%
Quartz	2.2 – 8.5%
Mullite	6.5 – 9.0%
Free calcium oxide	up to 3.5%

Other minerals like goethite, pyrite, calcite, anhydrite and periclase range from trace amounts to 2.5 % (Weshe 1991).

Geochemistry of Fly Ash: The elements in the fly ash are mainly litophiles and chalcophiles. Lithophiles are the elements that are concentrated in aluminosilicates as oxide forms rather than in the metallic and sulfide phases. They are mainly, Al, Ca, K, Mg, Na, Si and the rare earth elements. Chalcophiles are the elements that are concentrated in the sulfide phases rather than in the metallic and silicate phases. They are mainly, As, Cd, Ga, Ge, Pb, Sb, Sn, Tl and Zn. Being nonvolatile, lithophiles form the matrix of fly ashes. Chalcophiles, on the other hand, are volatile elements and are associated with the non-matrix structure. They are concentrated at the surface of the fly ashes. Br, Cl and F are halogens which remain mainly in the gas phase. Others, such as Ba, Be, Bi, Co, Cr, Cu, Mn, Ni, U, V and W are intermediate, showing an equal distribution between the matrix and non-matrix structure.

The matrix of fly ash particles is principally composed of aluminum-silicon-oxygen compounds (non-volatile oxides of the major elements), with smaller amounts of Fe, Mg, Na, K, Ca, Th, Ti and the rare earth elements. This structure is commonly called the aluminosilicate matrix (Çanci 1998).

2.4.3. Material Properties

2.4.3.1. Physical Properties

Fly ash consists of fine, powdery particles that are predominantly spherical in shape, either solid or hollow, and mostly glassy (amorphous) in nature. The carbonaceous material in fly ash is composed of angular particles. The particle size distribution of most bituminous coal fly ashes is generally similar to that of a silt

(less than a 0.075 mm or No. 200 sieve). Although subbituminous coal fly ashes are also silt-sized, they are generally slightly coarser than bituminous coal fly ashes (DiGioia and Nuzzo 1972).

The specific gravity of fly ash usually ranges from 2.1 to 3.0, while its specific surface area (measured by the Blaine air permeability method) (Annual Book of ASTM Standards) may range from 170 to 1000 m^2/kg.

The color of fly ash can vary from tan to gray to black, depending on the amount of unburned carbon in the ash. The lighter the color, the lower the carbon content. Lignite or subbituminous fly ashes are usually light tan to buff in color, indicating relatively low amounts of carbon as well as the presence of some lime or calcium. Bituminous fly ashes are usually some shade of gray, with the lighter shades of gray generally indicating a higher quality of ash.

2.4.3.2. Chemical Properties

The chemical properties of fly ash are influenced to a great extent by those of the coal burned and the techniques used for handling and storage. There are basically four types, or ranks, of coal, each of which varies in terms of its heating value, its chemical composition, ash content, and geological origin. The four types, or ranks, of coal are anthracite, bituminous, subbituminous, and lignite. In addition to being handled in a dry, conditioned, or wet form, fly ash is also sometimes classified according to the type of coal from which the ash was derived.

The principal components of bituminous coal fly ash are silica, alumina, iron oxide, and calcium, with varying amounts of carbon, as measured by the loss on ignition (LOI). Lignite and subbituminous coal fly ashes are characterized by higher concentrations of calcium and magnesium oxide and reduced percentages of silica and iron oxide, as well as a lower carbon content, compared with bituminous coal fly ash (Meyers, et al. 1976). Very little anthracite coal is burned in utility boilers, so there are only small amounts of anthracite coal fly ash.

Table 2.9 compares the normal range of the chemical constituents of bituminous coal fly ash with those of lignite coal fly ash and subbituminous coal fly ash. From the table, it is evident that lignite and subbituminous coal fly ashes have a higher calcium oxide content and lower loss on ignition than fly ashes from

bituminous coals. Lignite and subbituminous coal fly ashes may have a higher concentration of sulfate compounds than bituminous coal fly ashes.

The chief difference between Class F and Class C fly ash is in the amount of calcium and the silica, alumina, and iron content in the ash (Annual Book of ASTM Standards). In Class F fly ash, total calcium typically ranges from 1 to 12 percent, mostly in the form of calcium hydroxide, calcium sulfate, and glassy components in combination with silica and alumina. In contrast, Class C fly ash may have reported calcium oxide contents as high as 30 to 40 percent (McKerall, et al. 1982). Another difference between Class F and Class C is that the amount of alkalis (combined sodium and potassium) and sulfates (SO_4) are generally higher in the Class C fly ashes than in the Class F fly ashes.

Table 2.2. Normal range of chemical composition for fly ash produced from different coal types(expressed as percent by weight).

Component	Bituminous	Subbituminous	Lignite
SiO2	20-60	40-60	15-45
Al2O3	5-35	20-30	10-25
Fe2O3	10-40	4-10	4-15
CaO	1-12	5-30	15-40
MgO	0-5	1-6	3-10
SO3	0-4	0-2	0-10
Na2O	0-4	0-2	0-6
K2O	0-3	0-4	0-4
LOI	0-15	0-3	0-5

Although the Class F and Class C designations strictly apply only to fly ash meeting the ASTM C618 specification, these terms are often used more generally to apply to fly ash on the basis of its original coal type or CaO content. It is important to recognize that not all fly ashes are able to meet ASTM C618 requirements and that, for applications other than concrete, it may not be necessary for them to do so.

The loss on ignition (LOI), which is a measurement of the amount of unburned carbon remaining in the fly ash, is one of the most significant chemical properties of fly ash, especially as an indicator of suitability for use as a cement replacement in concrete.

CHAPTER 3

MATERIALS AND METHODS

3.1. Materials

One type of commercial PVC resin, emulsion type of PVC (E-PVC), was employed for preparation of PVC plastisols. The K value of this resin is 75. The other properties of PVC resin is given in Table 3.1. DINP (Diisononyl pthalate) was used as a plastcizer. The properties of this plasticizer is given in Table 3.2. Liquid butyl tin carboxylate was used as a commercial heat stabilizer to cure PVC films at 150°C. The properties of heat stabilizer is given in Table 3.3.

Table 3.1. Properties of PVC resin
(Source: Arkema 2008)

Property	Unit	Reference Standart	Value
K Value		ISO 1628-2	75
Physical Form	White Powder		
Humidity	%	ISO 1269	< 0.25
Rheological Behaviour	Pseudo plastic		
Plasticizer Range	pcr	5-100	

Table 3.2. Properties of plasticizer
(Source: Plastay 2010)

Property	Unit	Reference standart	Value
Appearance	Clear, colorless liquid		
Molecular weigth	148		
Viscosity	cp , 20 ^{0}C	ASTM D 1045	70-80
Density	g/cm3	ASTM D 1045	0.970-0.974

Table 3.3. Properties of stabilizer
(Source: Baerlocher 2006)

Property	Unit	Value
Physical Form	Liquid	
Viscosity	mPa.s	130
Density	g/cm3	1.08

Commercial calcite supplied from OMYA and fly ash supplied from Soma Thermic Central were used as fillers. Wet seiving was applied to fly ash samples to get -38 µm particles.

3.2. Methods

3.2.1. Preparation of PVC Plastisols and Test speciements

PVC plastisols were prepared using mechanical stirrer (Heidolph) for rheological measurements. For this purpose, all liquids, plasticizer (DINP), heat stabilizer, PVC powder and fillers were placed in a beaker and mixed at different rates (600 RPM, 1000 RPM, 1400 RPM) for 5 minutes.

PVC films were prepared on acetate sheets (using 500 µm applicator) and cured at $150^{o}C$ for 10 minutes to use for tensile strength tests. In addition, 6 mm samples were prepared using petri plates and cured at $150\ ^{0}C$ for 20 minutes to use for hardness and surface roughness tests.

The composition of PVC plastisols were given in Tables 3.4-3.7.

Table 3.4. Ingredients of standart PVC plastisol sample

Std PVC Plastisol	Sample	
	g	wt%
PVC	100.00	61.3
Plasticizer	60.00	37.04
Stabilizer	2.00	1.23
Total	162.00	100.00

Filler densities were used to determine the amount of filler ingredients in the plastisols. Volume fractions of the fillers were kept constant for the plastisols because of the difference between the densities of fillers used. $d_{Fly\ Ash} = 2.2$ g/cm^3 and $d_{Calcite} = 2.7$ g/cm^3. In Table 3.5 amount of fillers are given as PHR (Part Per Resin) and volume percentage.

Table 3.5. Amount of filler in volume % and PHR (Part Per Resin)

SAMPLE NO	PHR	vol %
SAMPLE 1	10.00	3.70
SAMPLE 2	20.00	7.41
SAMPLE 3	30.00	11.11

Table 3.6. Composition of PVC plastisol samples with Calcite as a filler

PVC + Calcite	Sample 1		Sample 2		Sample 3	
	g	wt%	g	wt%	g	wt%
PVC	100.00	58.14	100.00	54.95	100.00	52.08
Plasticizer	60.00	34.88	60.00	32.97	60.00	31.25
Stabilizer	2.0	1.16	2.00	1.10	2.00	1.04
Calcite	10.00	5.81	20.00	10.99	30.00	15.63
Total	172.00	100.00	182.00	100.00	192.00	100.00

Table 3.7. Composition of PVC plastisol samples with Fly Ash as a filler.

PVC + Fly Ash	Sample 1		Sample 2		Sample 3	
	g	wt%	g	wt%	g	wt%
PVC	100.00	58.78	100.00	56.09	100.00	53.64
Plasticizer	60.00	35.27	60.00	33.65	60.00	32.18
Stabilizer	2.00	1.18	2.00	1.12	2.00	1.07
Fly Ash	8.14	4.78	16.30	9.14	24.44	13.11
Total	170.14	100.00	178.30	100.00	186.44	100.00

3.2.2. Rheology Measurements

Brookfield DV III+ rheometer with ULA adapter was used to investigate the rheological behaviour of PVC plastisols. These measuremets were conducted to test the following conditions:

- Filler type: Calcite, Fly Ash
- Filler concentration: (vol %) 3.70, 7.41, 11.11
- Temperature : 25 ^{o}C, 30 ^{o}C, 35 ^{o}C
- Mixing rate : 600, 1000, 1400 RPM

Shear stress of the plastisols were measured at different speeds by using the following set conditions:

- Speed was set at minimum 0.01 RPM
- Speed was increased to 0.2 RPM by 0.01 RPM in every 30 second

The shear rate was adjusted to change between 0.01s^{-1} to 0.2 s^{-1} which seemed to be better condition for the system of this study.

3.2.3. Particle Size Distribution Measurements

The particle size distribution of fillers, fly ash and calcite, were measured using Malvern Mastersizer 2000 HD instrument. The working principle of this instrument is mie scattering (Figure 3.1).
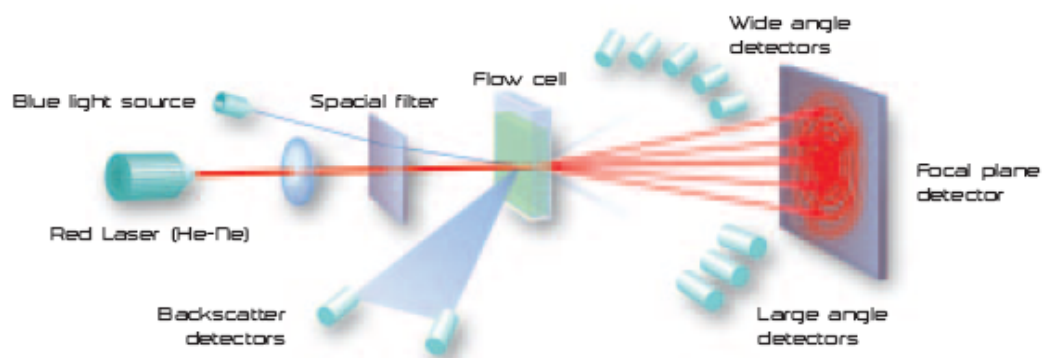

Figure 3.1. Working principle of Mastersizer 2000
(Source: Malvern 2005)

Particles are passed through a focused laser beam, scatter light at an angle, is inversely proportional to their size. The angular intensity of the scattered light is then measured by a series of photosensitive detectors as shown in Figure 3.1. The map of scattering intensity versus angle is the primary source of information used to calculate the particle size (Malvern 2005).

3.2.4. Surface Area Analysis

The total exposed surface area present in the powder samples is measured by the surface area analyzers.

- Specific Surface Area (SSA) → the surface area in a fixed mass of particles (m^2/g)
- Volume Spesific Surface Area (VSA) → the surface area in a fixed volume of particles (m^2/cm^3) (Dinger 2005).

The B.E.T. equation was used to measure of V_m, the volume of gas necessary to form a monolayer of liquid across a solid surface.

The equation is ;

$$\frac{x}{V(1-x)} = \frac{1}{V_m} + \frac{(C-1)x}{V_m} \qquad (3.1)$$

X → The relative pressure P/P_0, a gas of volume V (m^3 at S.T.P.) is absorbed

P → Pressure of the gas

P_0 → The saturated vapor pressure at the temperature

V_m → The volume of gas required to form a monolayer on the absorbent

C → Constant

Langmuir adsorption isotherm applied to multilayer adsorption is formulated in Equation (3.1). The theory is based on the establisment of an equilibrium between gas and adsorbed material involving the dynamic transfer of molecules betwwen the gas phase and the surface.

The B.E.T. method yields a value for the volume of a monolayer of adsorbed gas on the solid surface (McKay 1996).

The B.E.T. and Langmuir surface area, and pore size and volume of PVC powder and fillers were determined by Micromeritics Gemini 2380 model surface area analyzer.

3.2.5. Thermal Gravimetric Analysis (TGA)

The mass loss of the Soma fly ash was obtained previos studies. H_2O (free water molecules) was removed at a temperature around 200 °C and bound water was removed up to 400 °C point.

3.2.6. Mechanical Measurements

3.2.6.1. Measurement of Tensile Strength

The most general method is tensile strength to characterize the mechanical behavior of the material. The machine is used to be tested this property as shown in Figure 3.2.
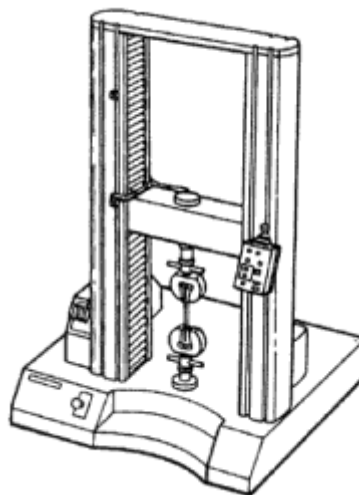

Figure 3.2. The machine for tensile strength test- including tension, compression parts

This type of machines should be constant-rate-of-crosshead movement and consisting one fixed and one movable parts. Extensiometer is used to measure the distance between two jaws. Tested materials are fixed by jaws. Speed of test is defined as the relative rate of motion.

Test speciements are cutted according to related standarts. This shape is called dogbone .Test speciements are shown in Figure 3.3.
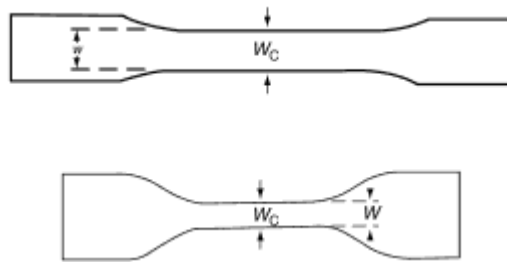

Figure 3.3. Test speciments for tensile strength shape

Two properties were determined, the first one is engineering stress:

$$\sigma = F/A_0 \qquad\qquad (3.2)$$

- F, applied force
- A_0, initial cross-sectional area

The True stres is based on the actual cross-sectional area, A, that change during the experiment.

The other important property is the engineering strain,

$$\varepsilon = (t - t_0)/l_0 = \Delta t/l_0 \qquad\qquad (3.3)$$

- l, current length of the speciment
- l_0, orginal length

Obtained quantities from tensile testing ;

- Tensile Strength: Maximum load divided by A_0.
- Percent Elongation: Percent elongation at yield is calculated, if the speciment gives a yield load bigger than the load at break.

- Modulus of Elasticity: E is the proportionality factor in Hooke's law :

$$\sigma = E.\ \varepsilon \hspace{4cm} (3.4)$$

It is also called Young Modulus. E is calculated from the initial linear portion of the load versus extension curve giving us the stress versus strain curve (Mark 2006).

In this study, samples for the mechanical measurement were prepared as 0.5 mm in thickness, 20 mm in width and 150 mm in lentgh.

3.2.6.2. Measurement Of Hardness

Hardness of the material is measured with durometer as shown in Figure 3.4. Hardness is measurement of depth of an indentation in the material created by a given force. The depth is related with the hardness, viscoelastic properties and the shape of the presser food. Durometer is used to measure of hardness of polymers, elastomers and rubbers. There are several types of durometer used for materials with different properties. ASTM D2240 type A and type D scales are common scales. The A scale is for softer plastics and the D scale is for harder ones (Wikipedia 2010).

Figure 3.4. Durometer , according to ASTM D 2240 standart.

According to ASTM D 2240 standart minimum thickness value should be 6.4 mm. Samples of this study was 6 mm in thickness.

3.2.7. Surface Roughness: Profilometry

Profilometry is used to study the topography of a material surface. Surface roughness is a critical parameter in various fields of materials science (Seitavuopio, et al. 2005). The basic principle of all instruments for physical profile measurement is based on a sensitive detection stylus that scans the substrate surface. The stylus consists of a fine tip that is fixed to a lever (Sinzinger and Jahns 2003). Profilometry is accurate, quantitative, flexible method and it can be used to study areas with diameters up to several centimeters (Seitavuopio, et al. 2005). All profilometers measure the physical depth of surface irregularities using some form of diamond or brush-type stylus attached to an arm that travels in a straight line for a specified cutoff or sampling length, typically 0.08 cm. Most profilometers allow for various cutoff lengths. The profilometer transforms the information from the stylus into an electrical signal and converts that signal into usable data.

Profilometry can be divided into two groups as stylus and optical. The stylus profilometer (SP), a powerful microscopic technique, has been developed to study the surface roughness of materials (Williamson 1967, Guenther, et al. 1984, Wiesendanger 1994). The stylus in the SP is used to scan surface, sense the variations of the sample. The stylus in the profilometer is carried by a cantilever beam and it rides on the sample surface. This means that a rough surface can be plastically deformed (Davis and Stout 1982). It is a technique in which a diamond stylus brought into contact with a sample and scanned over the surface. The surface profile causes an up-and-down movement of the lever which is detected (Sinzinger and Jahns 2003).
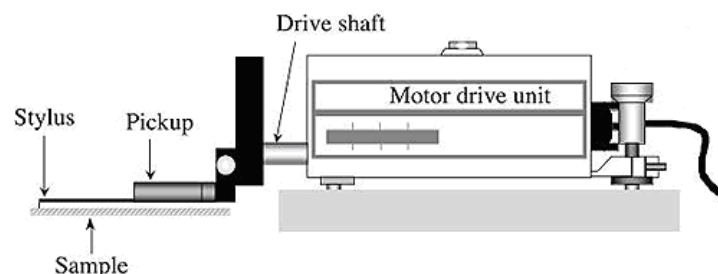

Figure 3.5. Schematic Configuration of a Profilometer and Its Units
(Source: Johnson 2000)

One well-established method for surface roughness measurement is non-contact laser profilometry or optical profilometry (Podczek 1998, Riippi, et al. 1998, Salako, et al. 1998, Ruotsalainen, et al. 2002, Seitavuopio, et al. 2003). The advantages of profilometry using a laser are the absence of contact, higher measurement speed, higher lateral resolution and greater depth range. Profilometry using a diamond stylus produces far better depth resolution. Laser profilometry has also been used in many different fields of material research like paper coating, dental materials and surgical prothesis (Wagberg, et al. 1993, Cho, et al. 2002, Chauvy, et al. 1998).

Roughness is commonly calculated using one of four methods: Ra (roughness average), RMS (root mean square), Rz (a 10 point average), and Rt or Rmax (maximum between peak and valley). Surface roughness is calculated by a profilometer using any of four common methods: Ra, RMS, Rz, and Rt (Rmax).

a) Ra or roughness average is the average of peak and valley distances measured along the centerline of one cutoff length (usually 0.08 cm).

b) RMS or root mean square is an older method, not common today, averaging only the heights of all points measured in one cutoff length. Readings are similar to Ra but about 10% higher.

c) Rz, a 10-point average, is an average of the five highest peaks and the five lowest valleys measured in one cutoff length.

d) Rt (Rmax), maximum height between peak and valley, is the value of the vertical distance between the highest peak and lowest valley measured along one cutoff length.
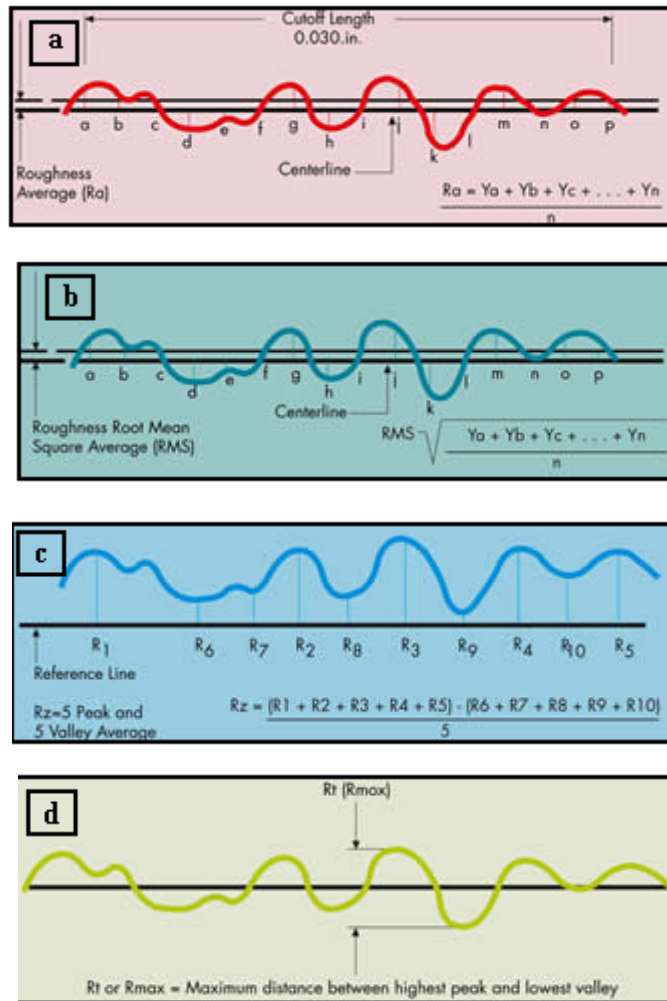
Figure 3.6. Four Ways to Calculate Roughness
(Source: Hebert 2009)

In the study surface roughness of the polymer films was measured with a stylus profilometer (Mitutoyo Surftest SJ-201P, Japan) which scans surface roughness between 0.01 – 100 μm with 2μm-diameter diamond stylus and 0.01μm resolution. The roughness of the surfaces, R_a, was determined with 0.8 mm sampling length and three sampling scans. For each film at least ten measurements were done.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Characterization of Materials: PVC Powder, Fly Ash, Calcite

4.1.1. Morphology

Scanning electron microscope (SEM) was used to take pictures of the powder materials to determine the general look of particles such as shape. These pictures are presented in Figure 4.1 and Figure 4.2 for both calcite and fly ash materials. As it is seen from Figure 4.1 that the shape of fly ash is not regular and uniform. There are large and small particles. There are some perfectly sphere fly ash particules. This is expected due to the mixed compositon of ash content. Figure 4.2 gives the general morphology of calcite particles. As it is seen from the figure that the shape of calcite particles are quite different from the that of fly ash particles. In deed, this difference was one of the main reasons that the fly ash was chosen as an alternative filler material in this study.

Morphology is used to determine the possibility of processing. PVC morphology is affected during two stages of its producing: in polymerization and during drying (Wypych 1988).
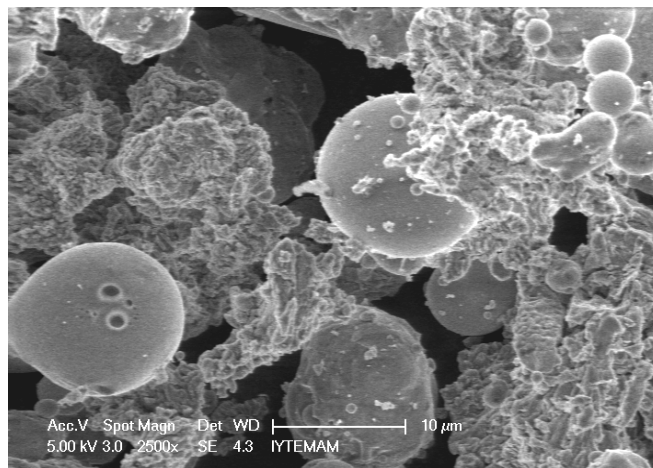
(a) (2500x)
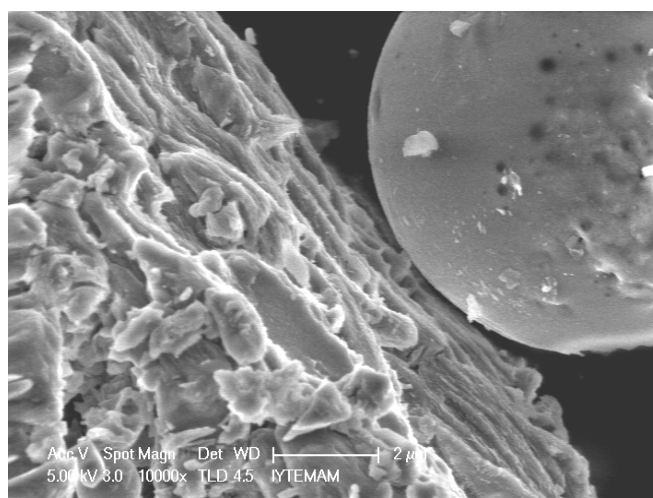
(b) (10000x)

Figure 4.1. SEM Pictures of sieved fly ash powder (-37 µ)
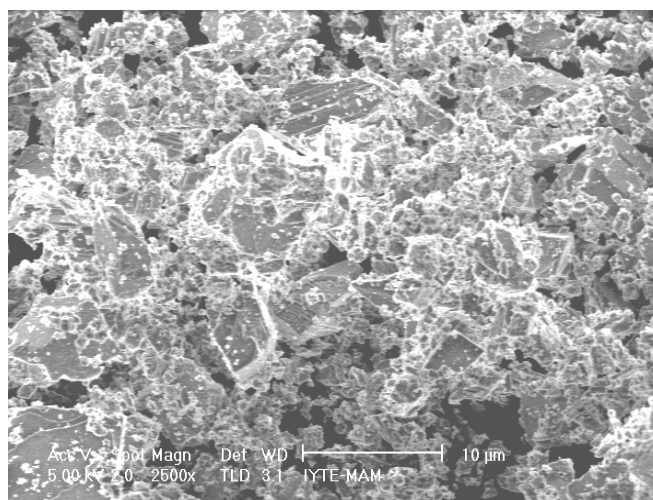(a) (2500x) (b) (10000x)

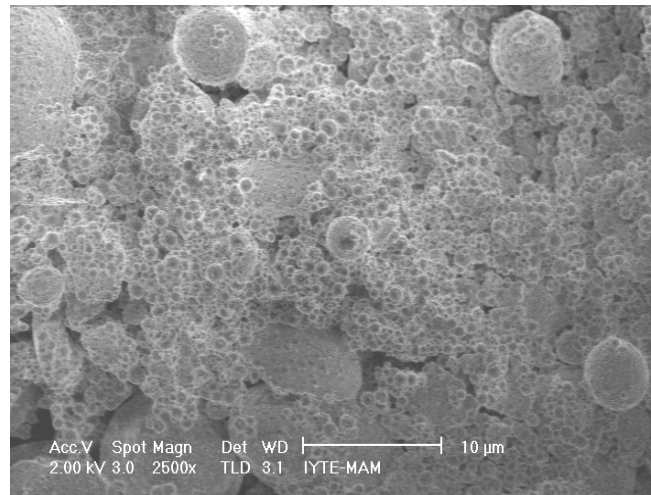Figure 4.2. SEM Picture of commercial calcite (5 µm) (2500x)

Figure 4.3. SEM Picture of commercial product PVC powder (2500x)

The morphology of the PVC particules that are known to affect the migration of the plasticizer into the PVC particles (which suppose to happen during the preparation of PVC plastisols) and change some properties of the flexible PVC plastisols such as viscosity, process rate, curing time, were also investigated. Therefore, the general morphology of PVC powder (SEM picture) is presented in Figure 4.3. PVC powder particles seem to all have spherical shapes as shown in the figure. However, there is a size distribution. That is the size of spheres are not uniform.

4.1.2. Particle Size Distribution Measurements

Particle size distributions of calcite and fly ash powders were obtained using Malvern Mastersizer 2000 HD and presented in Figures 4.4-4.6. The size distribution of PVC powder, on the other hand, could not be obtained with this system due to the distribution problems observed in water. Therefore, the particle size information of PVC powder was obtained using the SEM picture given in Figure 4.7. It is seen that the size of PVC particles were in nanometers and have some distribution also.
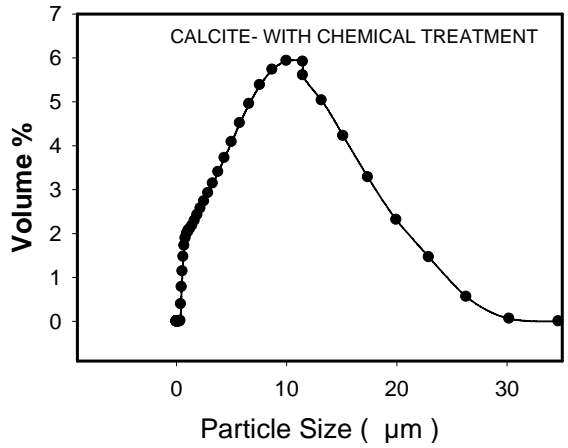
Figure 4.4. Particle size distribution of calcite (Malvern Mastersizer 2000 HD)
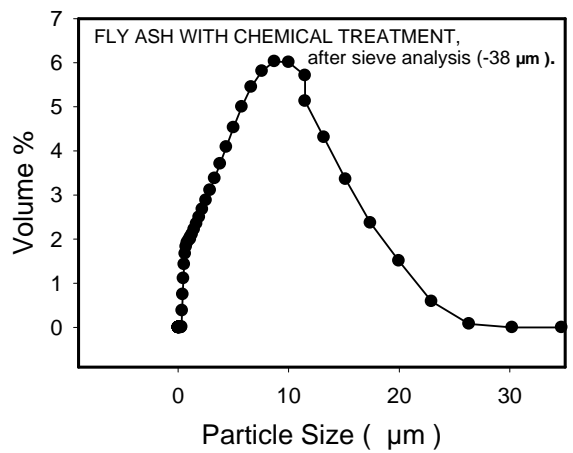

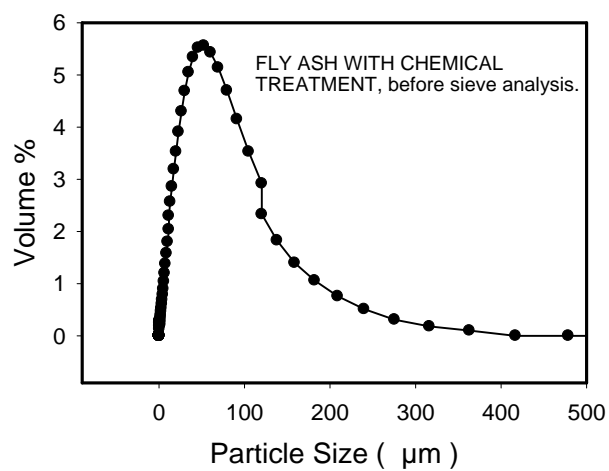Figure 4.5. Particle size distribution of fly ash, after sieve analysis

Figure 4.6. Particle size distribution of Soma fly ash, before sieve analysis

Figure 4.4 gives the size distribution of -38 μm fly ash material which is one used in this study as filler while Figure 4.6 gives the size distribution of all material before sieving. The Figures 4.4 and 4.5 shows that the size distributions of fly ash and calcite powders are so similar to each other. This is good in terms of comparison of these materials. The coarse particles were separated from fly ash since these are expected to affect the surface and mechanical properties of the PVC films.
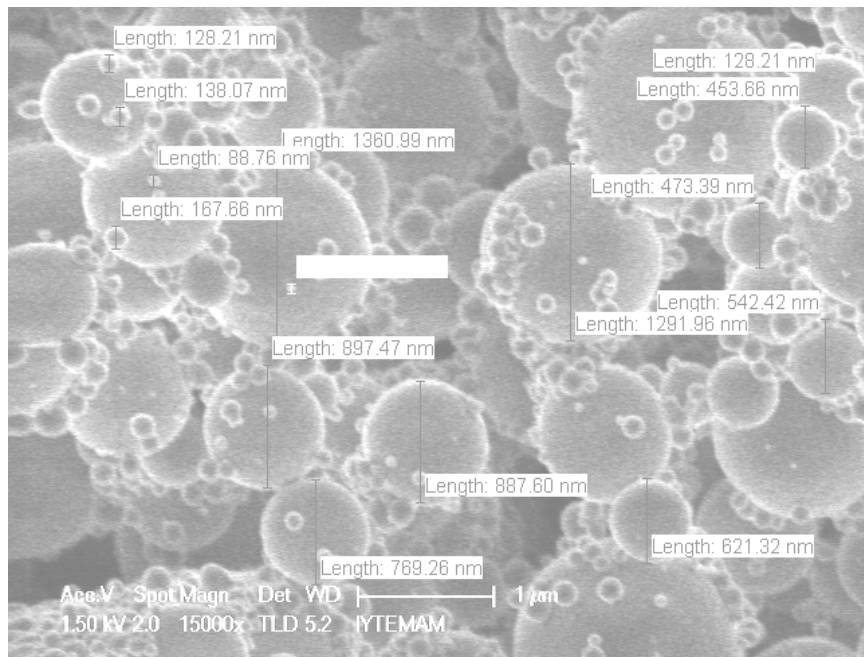
Figure 4.7. Particle size distribution of Soma fly ash, before sieve analysis

4.1.3. Thermal Gravimetric Analysis (TGA) of Fly Ash

The TGA results are presented in Figure 4.8 as a % mass loss percent as a function of temperature. It is seen that there is no considerable change in mass loss after 700 °C. The total mass losses from the ash is between 2 to 4 % when it is heated to 1000 °C.
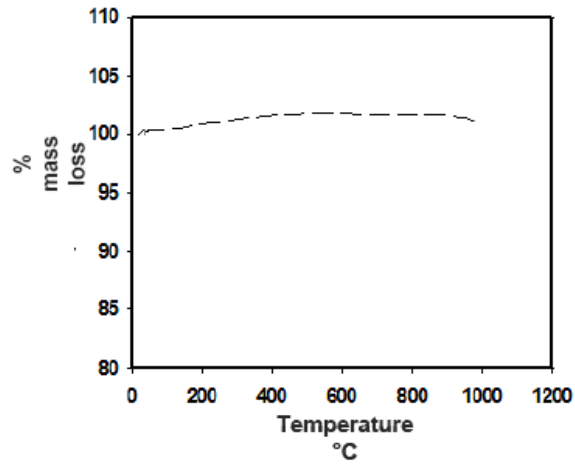
Figure 4.8. TGA graph of the Soma fly ash

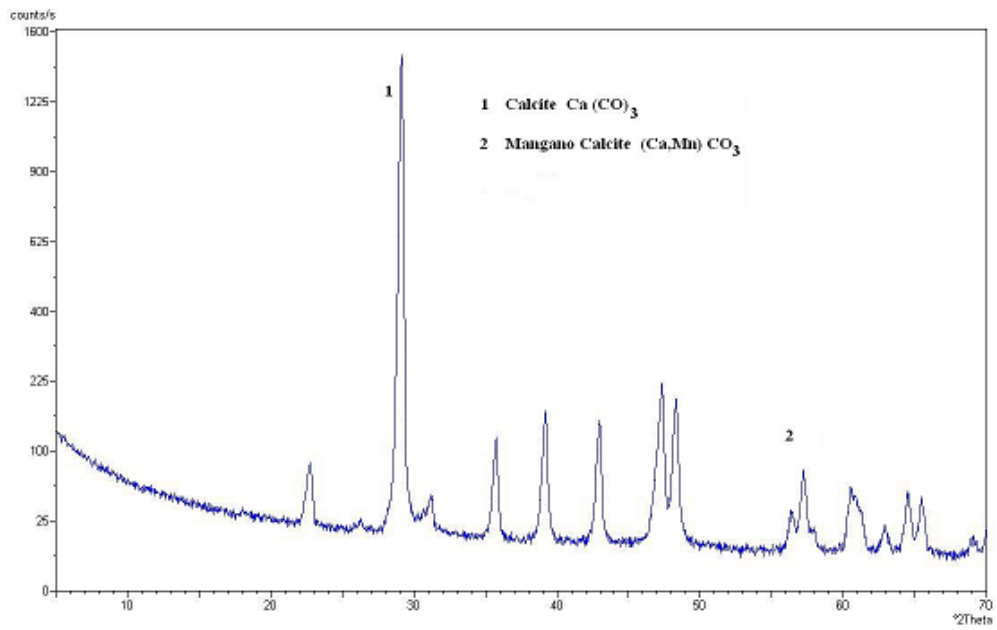## 4.1.4. XRD Analysis of Fillers

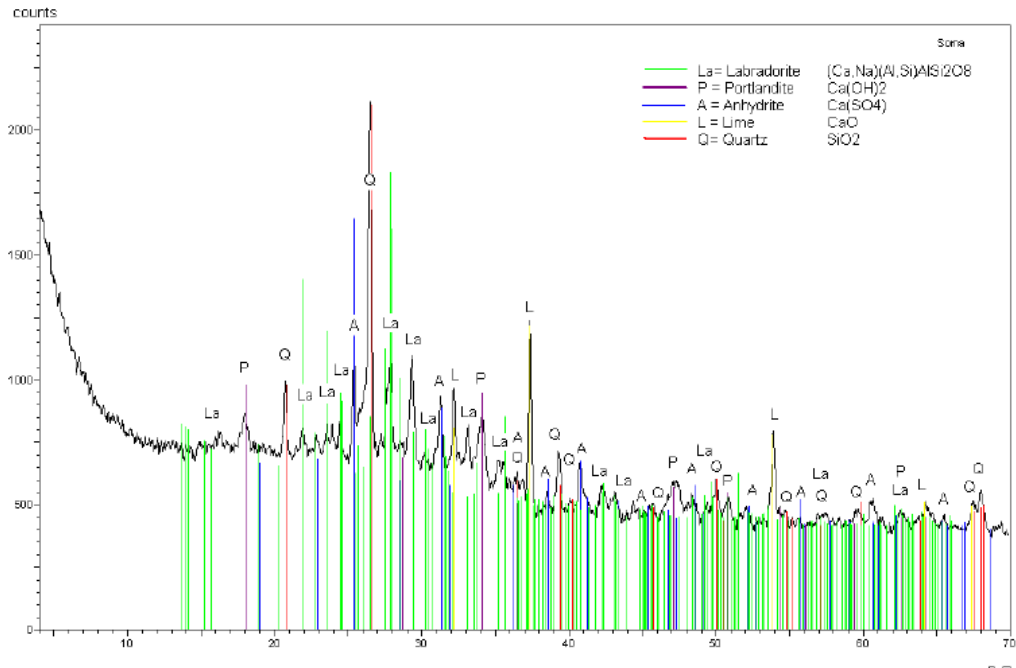Figure 4.9. XRD analysis of calcite

Figure 4.10. XRD analysis of Soma fly ash

The identification of fillers were also done by XRD analyses. The graphical representations explain that calcite is highly rich in $Ca(CO)_3$,. Soma fly ash is mainly rich in amounts of Al, Si, Ca compounds.

4.1.5. Surface Area Analysis

Surface area property of fillers affect the surface and mechanical properties of the polymers. Some additives in plastisols interact with particle surfaces and affect interparticle repulsive and attractive forces in the interparticle fluid. Therefore surface area measurements of calcite and fly ash samples was done and the results are presented in Table 4.1. According to Table 4.1 PVC particles have higher surface area than fillers. However, fly ash powder seems to have higher surface area than calcite. The average pore size is also little higher in the case of fly ash compare to the other materials.

Table 4.1. Surface area results of powders used in this study

Material	Surface Area		BJH Adsorption Average Pore Witdh (4V/A)
	BET Surface Area	Langmuir Surface Area	
	m²/g	m²/g	Å
PVC(KValue=75)	5.7224	23.0932	29.453
Calcite	3.528	14.5911	29.453
Soma Fly Ash	4.07	16.62	33.21

4.1.6. XRF Analysis of Fly Ash

XRF analysis is one of the elemental analysis for the fly ash. Spectro IQ II instrument is used for analysis. Table 4.2 shows that fly ash sample contains Ca, Si and Al at highest concantration values.

Table 4.2. XRF analysis result of fly ash sample

Z	Symbol	Element	Concentration
12	Mg	Magnesium	1.50%
13	Al	Aluminum	11.74%
14	Si	Silicon	19.56%
20	Ca	Calcium	17.19%
26	Fe	Iron	3.41%

4.1.7. ICP-MS Metal Analysis of Fly Ash

The elemental determinations obtained by ICP-MS analyses were shown in Table 4.3.

Table 4.3. ICP-MS results of fly ash

Metal	Concentration (μg/L) ICP-MS
Li / 7	595.100
B / 11	4.051
Na / 23	179800
Mg / 24	31.060
Al / 27	14.730
K / 39	34380
Ca / 43	344100
Cr / 53	121.800
Fe / 56	4.975
Co / 59	1.750
Ni / 60	13.280
Cu / 63	7.783
Zn / 66	62.360
Ga / 69	21.830
Sr / 88	3963
Ba / 137	789.00
Bi / 209	5.360

ICP-MS analyses shows that obtained fly ash from Soma Thermic Central contains very high concentrations of Ca and Na metals. Other high level of metals are; K, Sr and Ba. The amount of metals in the fly ash describes us production type of the fly ash and type. But used fly ash in this study could not be match with any type. Because metal concentration values were found different from desired values.

4.2. Rheology Measurements of the PVC Plastisols

Rheology is important for the processing of PVC plastisols due to their effect on the surface characteristics and process parameters such as process rate, time and therefore the quality and cost of final product. PVC Plastisols are known to show different type of rheological properties according to PVC type. But, the common rheological behaviour is supposed to be Pseudoplastic especially in the case of PVC plastisols used in leather and conveyor belt production.

In this study, the rheological behaviour of PVC plastisols with different compositions were tested. These studies were conducted using the test procedure given in Chapter 3. The following parameters were tested.

- Type of filler
- Concentration of fillers
- Mixing rate of PVC plastisols
- Temperature of PVC plastisols

Figure 4.11 presents the rheological behaviour of standart PVC plastisols as a function of temperature (25, 30 and 35 ^{o}C). This samples do not contain any filler material. Therefore they will be used as reference results during this study. These measurements are conducted at different mixing rates.

It is seen from Figure 4.11 that, the shear stress seems to increase slightly with temperature increase at 600 and 1000 RPM mixing rates. This might be due to the following reason. When the temperature gets higher, plasticizer, the mobile phase, may diffuse into the PVC plarticules easily and therefore diminish from the system. This will make more PVC particules swell and increase the viscosity of PVC plastisol. At high shear rate, on the other hand, this effect disappears.
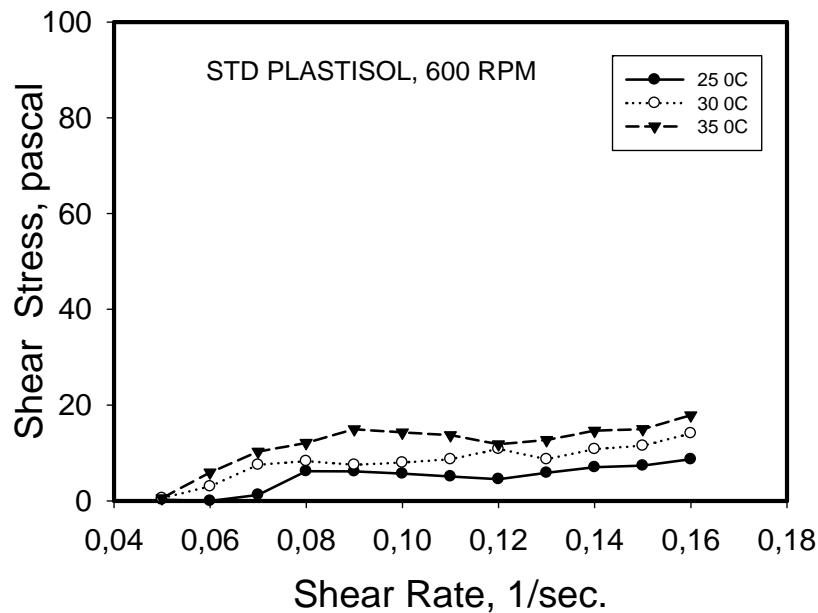
(a)

Figure 4.11. Effect of temperature change on rheological behaviour of standart PVC plastisol mixtures after different mixing rates: (a) 600 RPM, (b) 1000 RPM, (c) 1400 RPM (cont. on next page)
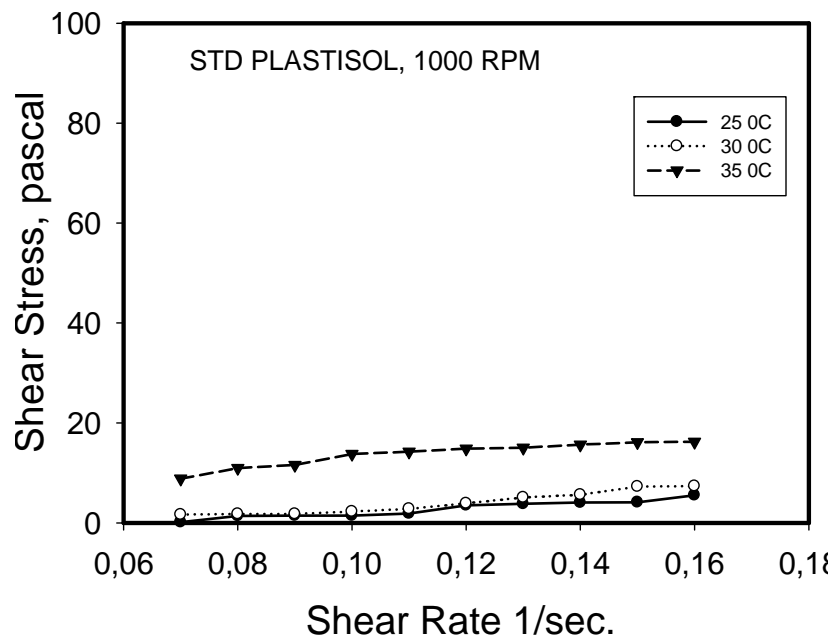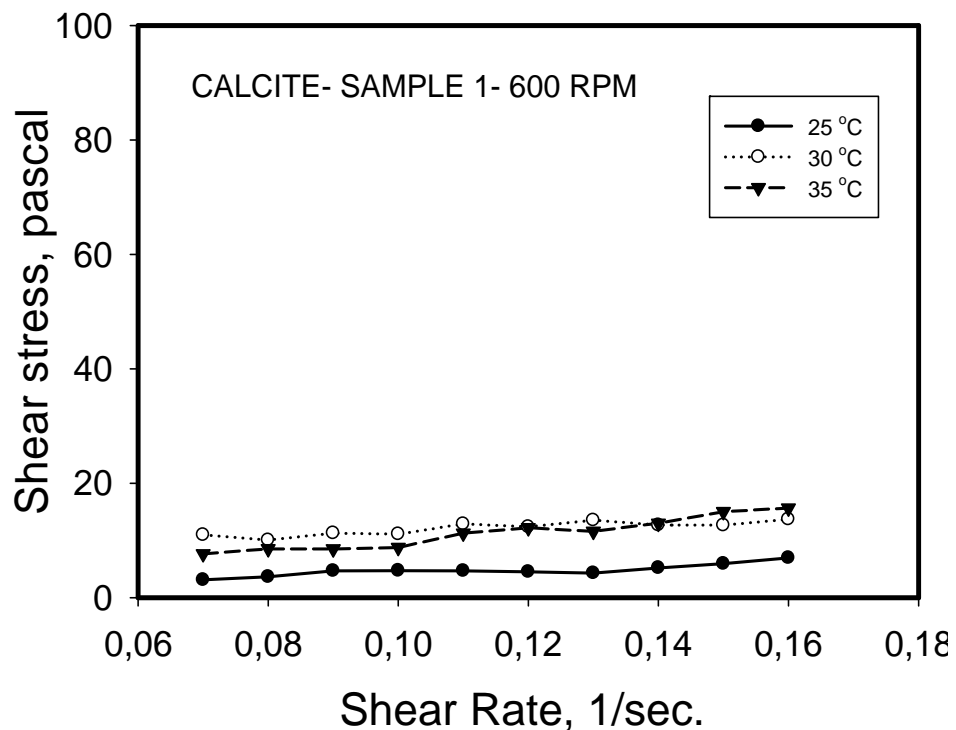
(b)
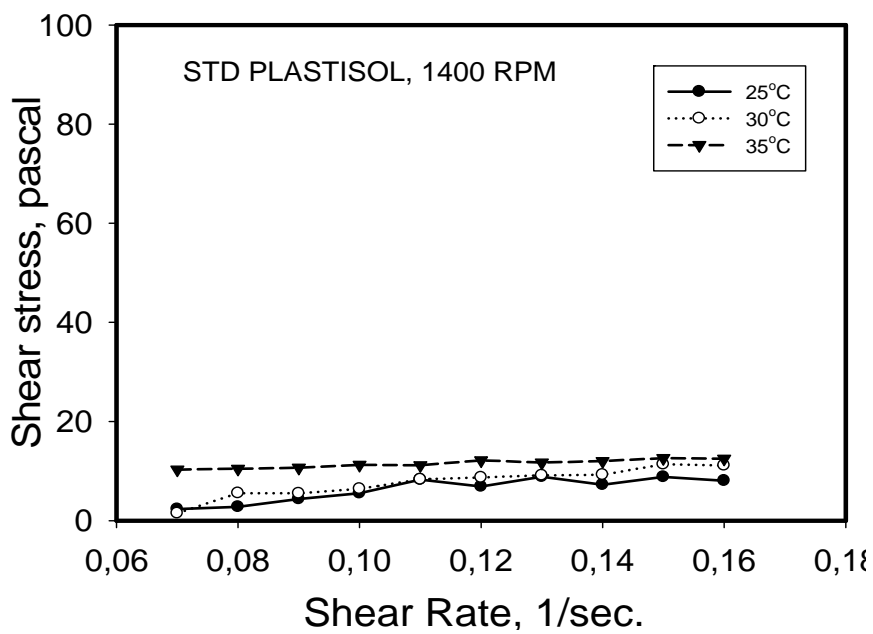
(c)

Figure 4.11. (cont.)

Figure 4.12 presents the rheological behaviour of PVC plastisols with a filling material, calcite, as a function of temperature (25, 30 and 35 ^{o}C). These measurements are conducted at different mixing rates for sample 1. It is seen from Figure 4.12 that, the shear stress seems to increase with high temperature 35°C in the

case of 1000 RPM mixing rate. At high mixing rate (1400 RPM), however, the rheological behaviour of the suspension changes from newtonian to the presudoplastic.

In the absence of calcite, an increase in temperature increased the viscosity of plastisols due to the increase in diffusion of plastiser (diminish from the system) in to the PVC particles and therefore the swell of PVC particles. In the presence of calcite, however, at moderate mixing rates, the shear stress seems to increase with high temperature most probably due to the same reason given above and then the the rheological behaviour of system changed form newtonian to pseudoplastic.

(a)

Figure 4.12. Effect of temperature on the rheological behaviour of PVC – CALCITE plastisol, sample 1 mixtures after different mixing rates: (a) 600 RPM, b)   1000 RPM, (c) 1400 RPM (cont. on next page)
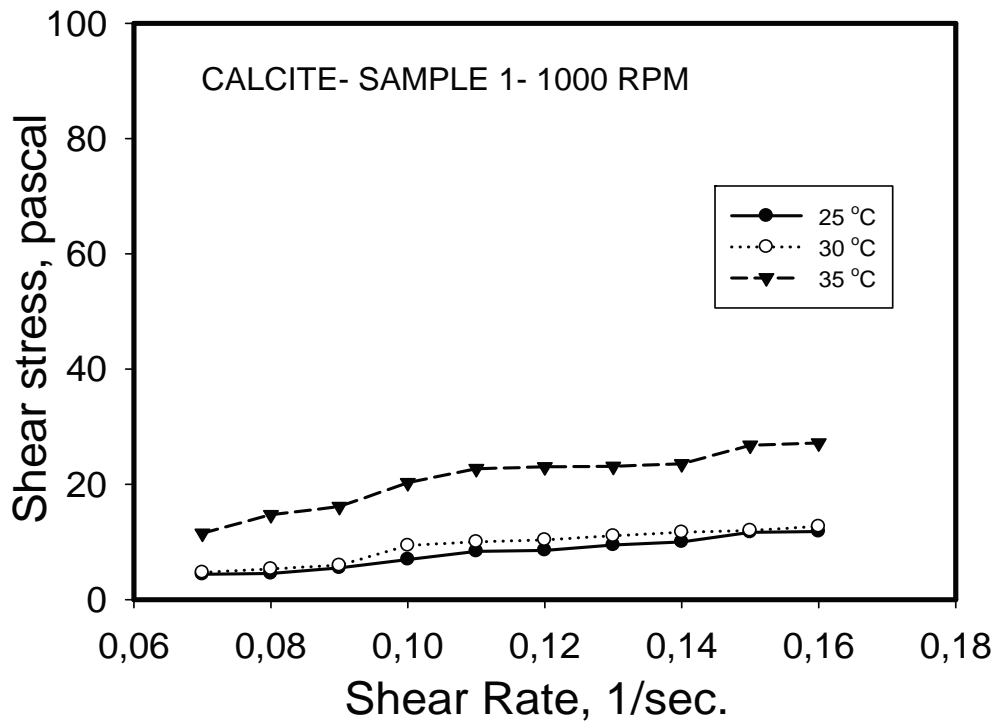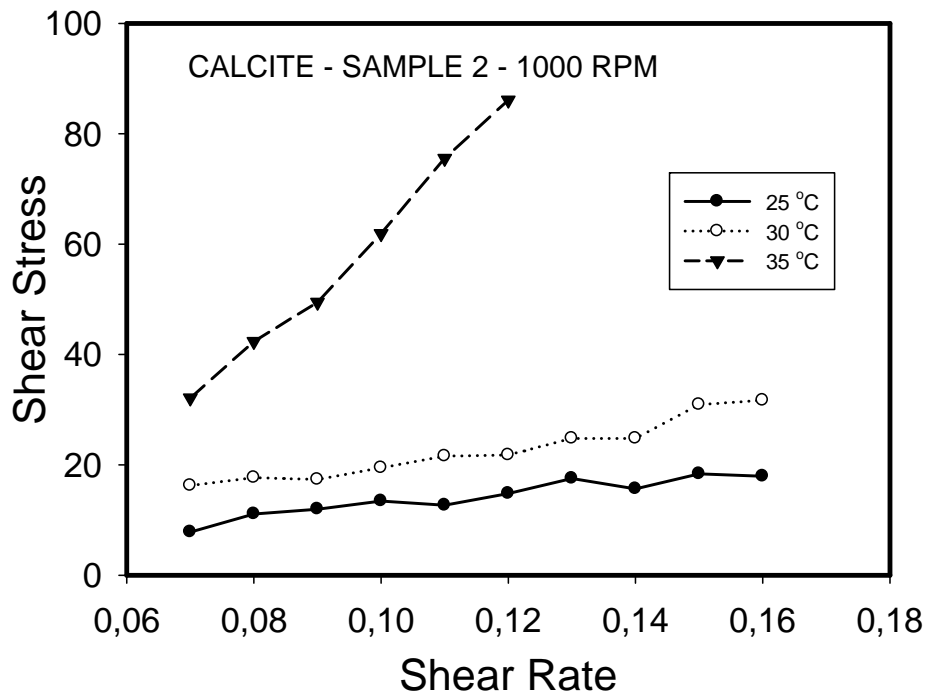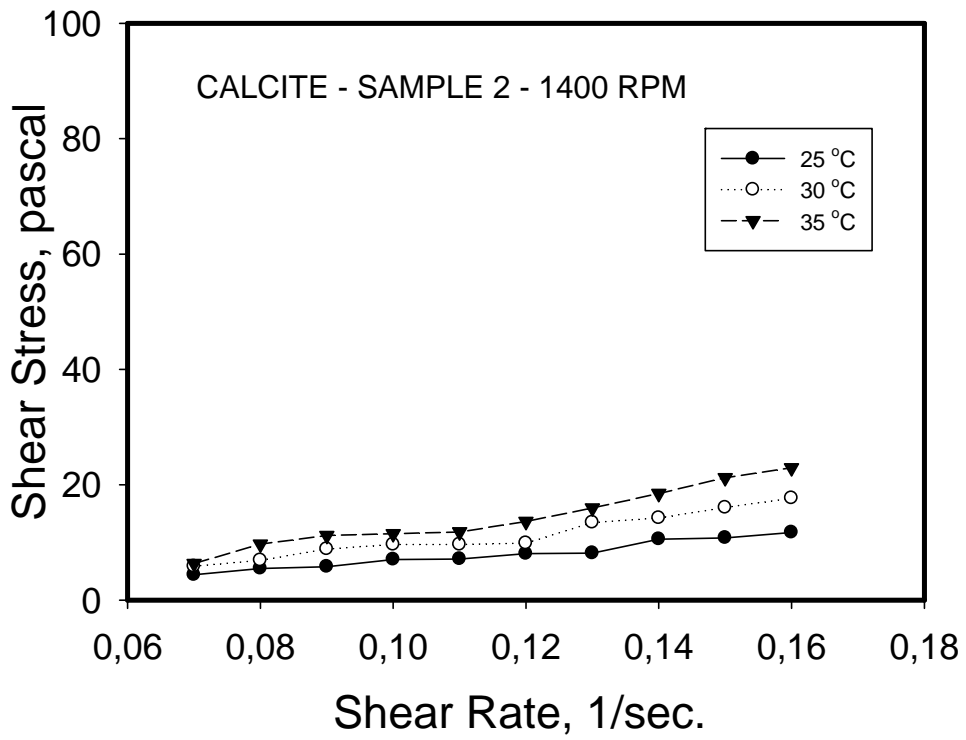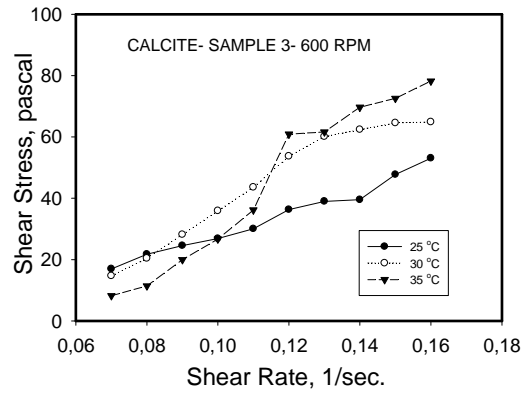
(b)
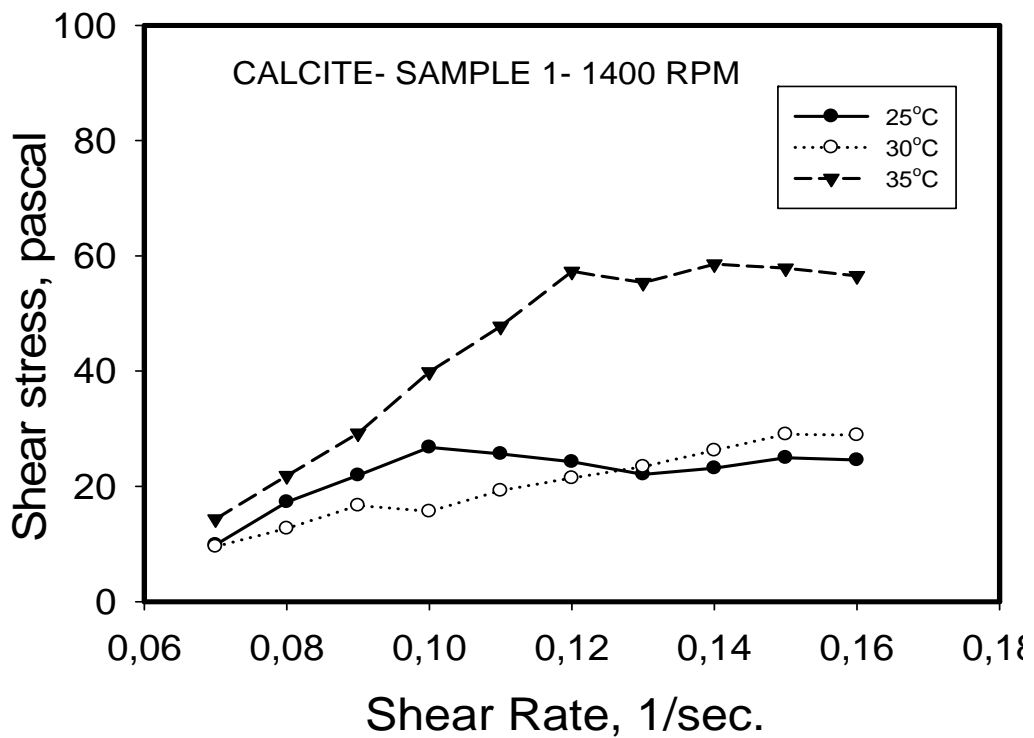
(c)

Figure 4.12. (cont.)

Figure 4.13 presents similar type of results for the rheological behaviour of PVC plastisols with a filling material, calcite, sample 2. It is seen from Figure 4.13

that, the shear stress seems to increase at high temperature, 35 $^{\circ}$C, in the case of both 600 and 1000 RPM mixing rates. This is most probably due to the same reason given above. The high mixing rate (1400 RPM), however, destroys this effect and decreases shear stress down to its original value. The rheological behaviour of the suspension also stays newtonian.
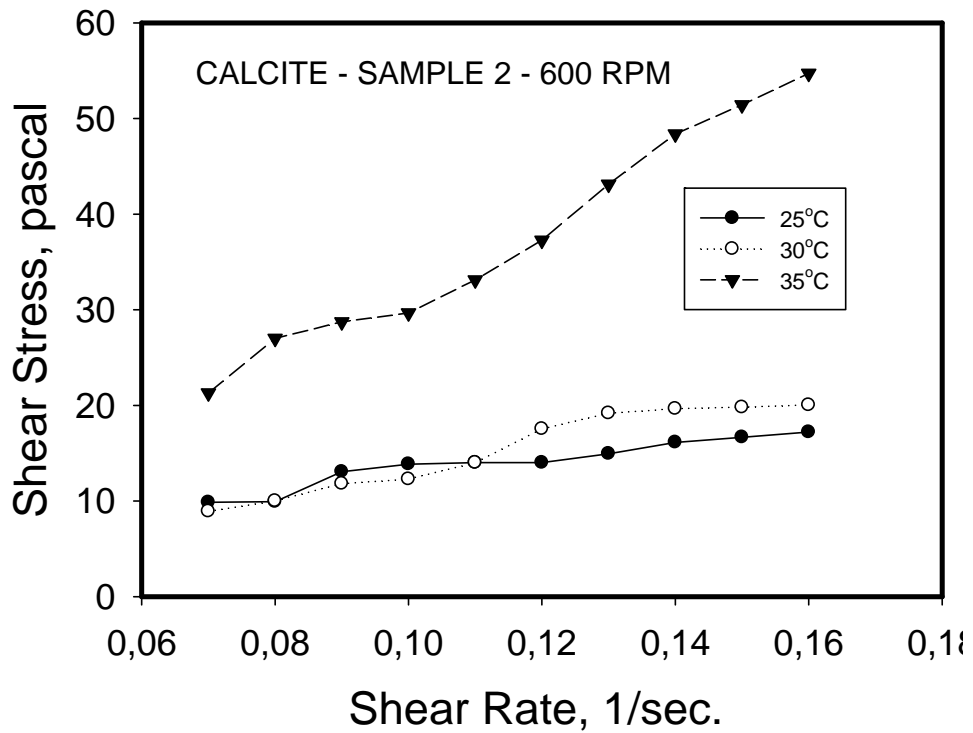
(a)

Figure 4.13. Effect of temperature change on the rheological behaviour of PVC-CALCITE plastisol, sample 2 mixtures after different mixing rates: (a) 600 RPM, (b) 1000 RPM, (c) 1400 RPM (cont. on next page)
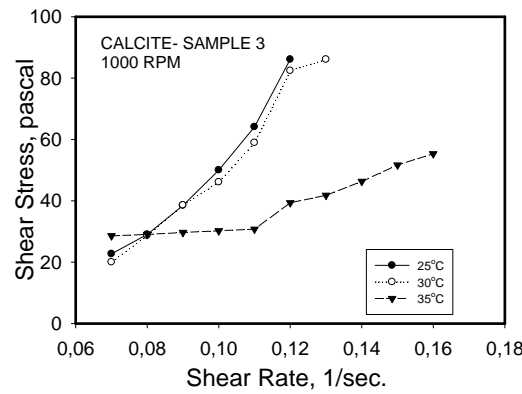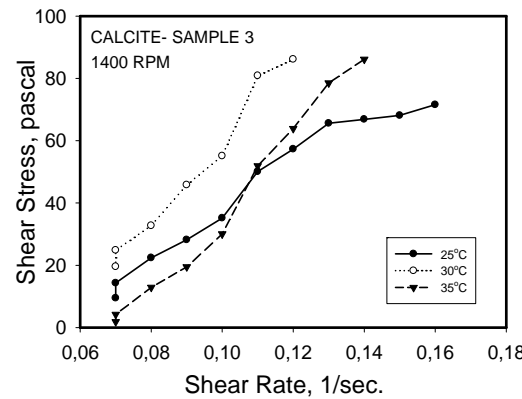
(b)

(c)

Figure 4.13. (cont.)

Figure 4.14 presents similar type of results for the rheological behaviour of PVC plastisols with a filling material, calcite, sample 3. It is seen from Figure 4.14 that, the effect of temperature seems complex.
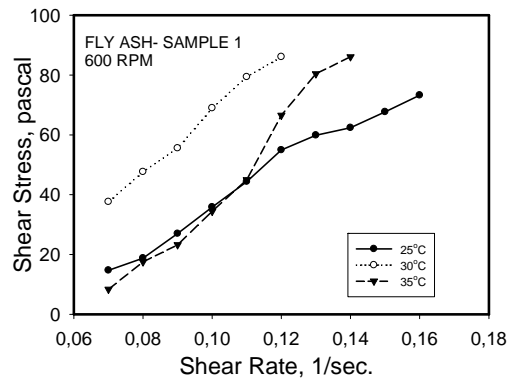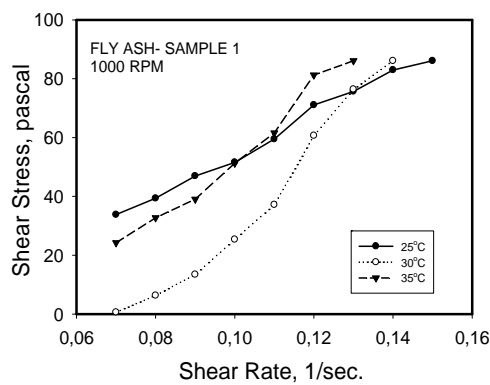

(a)

(b)

(c)

Figure 4.14. Effect of temperature change on the rheological behaviour of PVC-CALCITE plastisol, sample 3 mixtures after different mixing rates: (a) 600 RPM, (b) 1000 RPM, (c) 1400 RPM
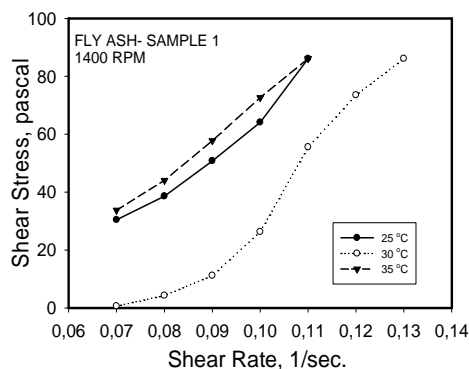
Figures 4.15, 4.16, and 4.17 present similar type of results for the rheological behaviour of PVC plastisols with a filling material, fly ash. It is seen from the figures that the effect of temperature seems complex in the case of fly ash. However, the results also show that the rheolgoy of PVC plastisol changes. It becomes harder system.
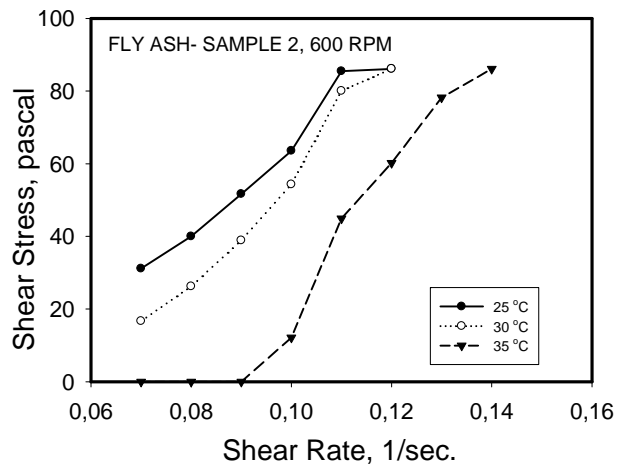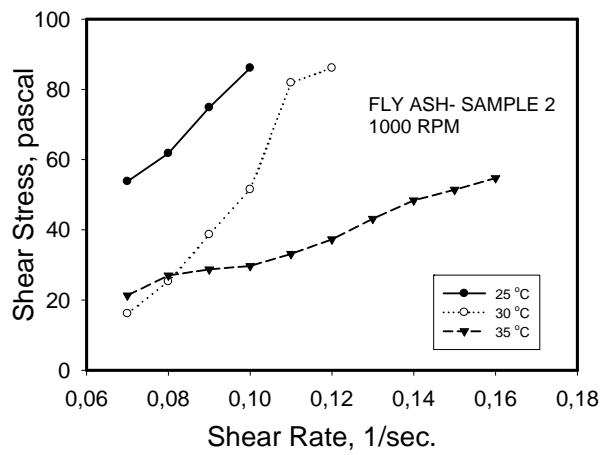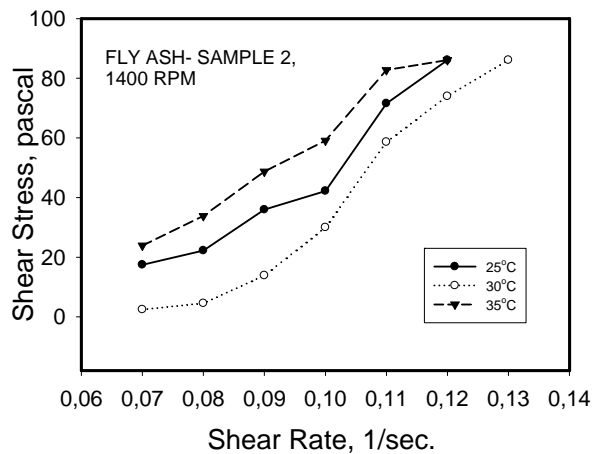

(a)

(b)

(c)

Figure 4.15. Effect of temperature change on the rheological behaviour of PVC–FLY ASH plastisol, sample 1 mixtures after different mixing rates: (a) 600 RPM, (b) 1000 RPM, (c) 1400 RPM

(a)

(b)

(c)

Figure 4.16. Effect of temperature change on the rheological behaviour of PVC–FLY ASH plastisol, sample 2 mixtures after different mixing rates: (a) 600 RPM, (b) 1000 RPM, (c) 1400 RPM
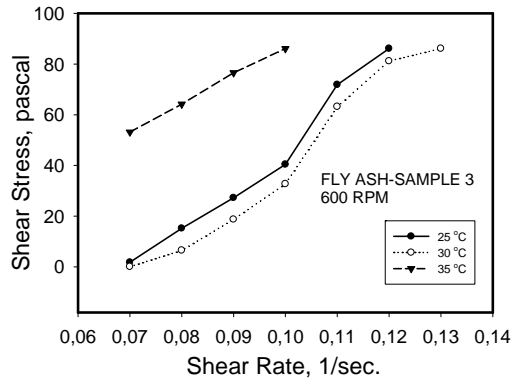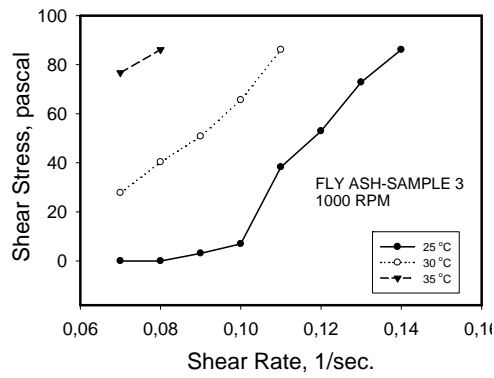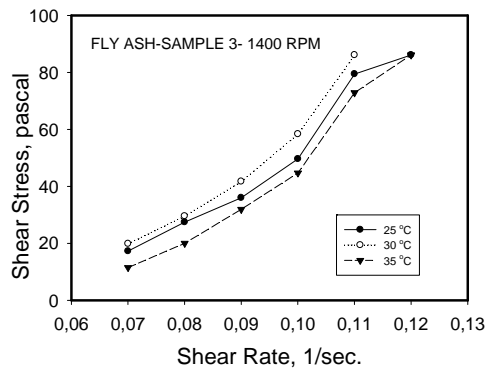
(a)

(b)

(c)

Figure 4.17. Effect of temperature change on the rheological behaviour of PVC–FLY ASH plastisol, sample 3 mixtures after different mixing rates: (a) 600 RPM, (b) 1000 RPM, (c) 1400 RPM

Figures 4.18- 4.20 present the rheological behaviour of standart and other PVC plastisols with calcite and fly ash as a function of mixing rate (600, 1500 and 1400 RPM) for different temperatures. The sample type used in these studies were type 1. It is seen from the figures that, the rheology of the standart PVC plastisol does not change with the change in mixing rate. However, in the case of filling materials

calcite and fly ash, the rheology of the PVC standart changes. This change seems complex.
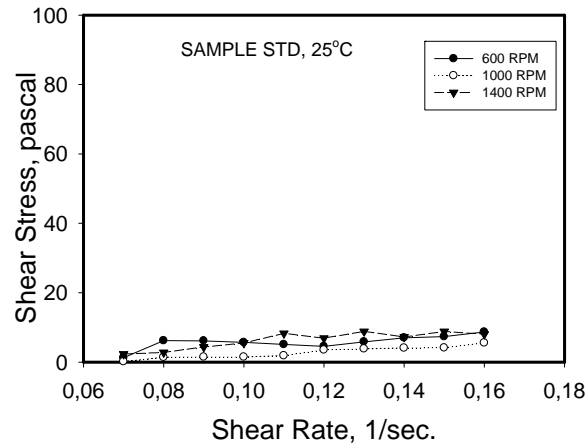
(a)
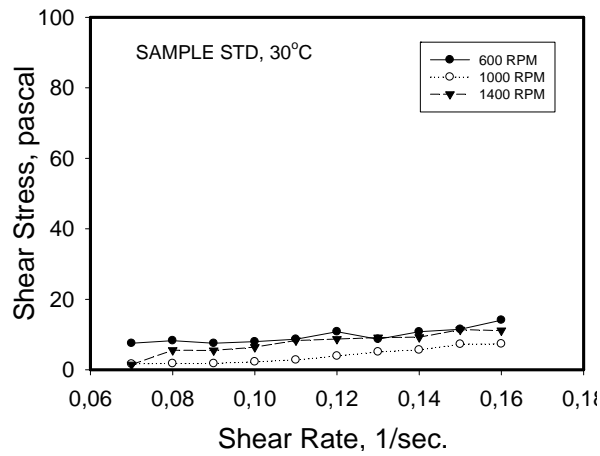
(b)
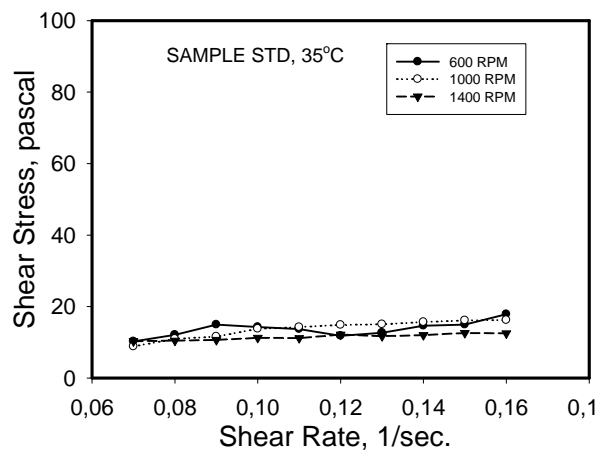
(c)

Figure 4.18. Effect of mixing rate on the rheological behaviour of standart PVC plastisol mixtures at different temperatures : (a) 25 ^{0}C, (b) 30 ^{0}C, (c) 35 ^{0}C

(a)

(b)

(c)

Figure 4.19. Effect of mixing rate on the rheological behaviour of PVC – CALCITE plastisol mixtures at different temperatures : (a) 25 ^{0}C, (b) 30 ^{0}C, (c) 35 ^{0}C
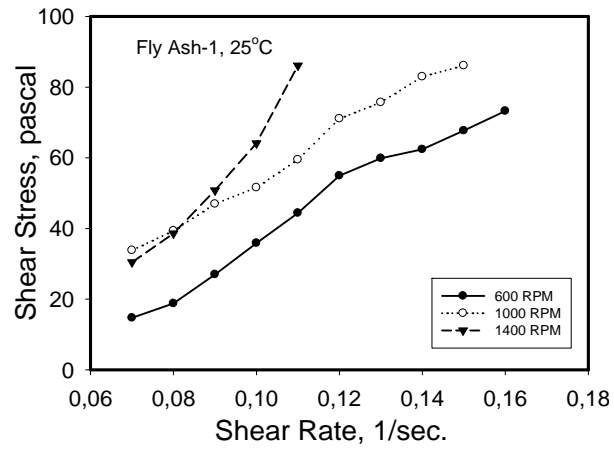
(a)
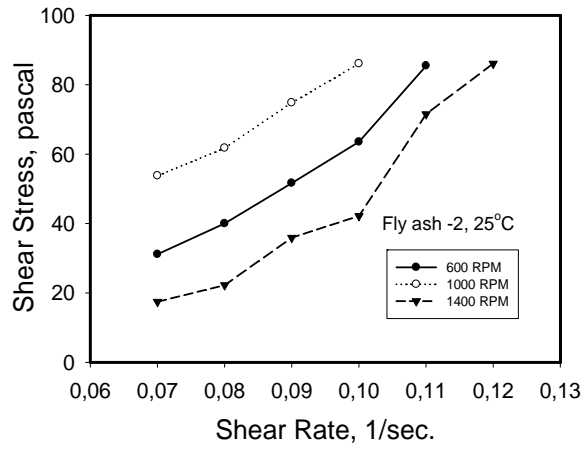
(b)
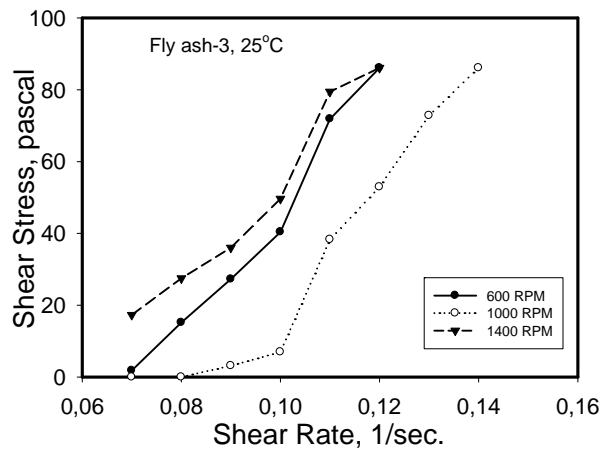
(c)

Figure 4.20. Effect of mixing rate on the rheological behaviour of PVC –FLY ASH plastisol mixtures at different temperatures : (a) 25 ^{0}C, (b) 30 ^{0}C, (c) 35 ^{0}C

4.3. Surface Characterization

4.3.1. SEM（Scanning Electron Microscope）

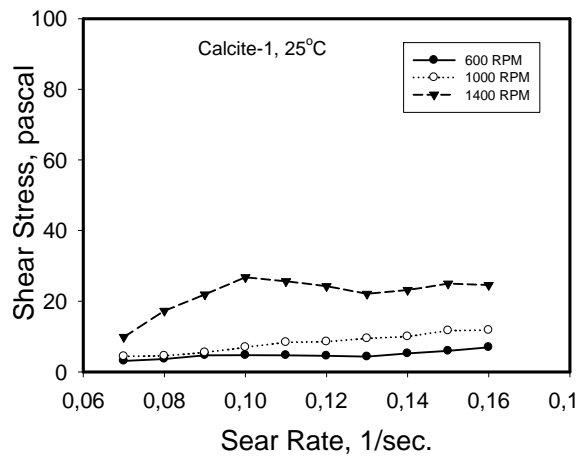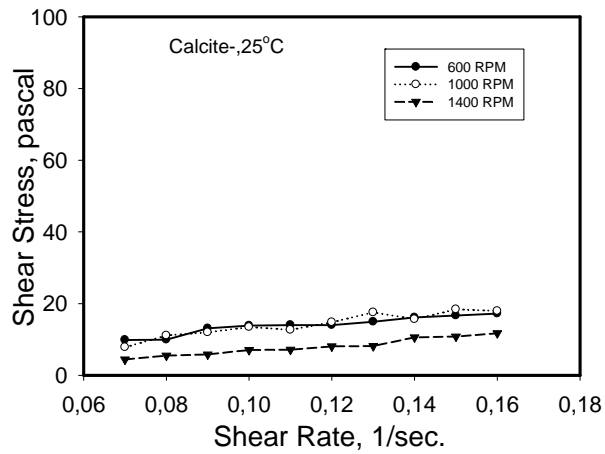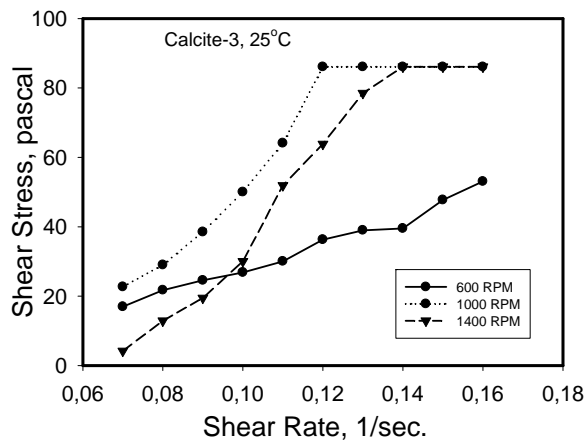Representative SEM images were collected randomly at 1000 magnification to have an idea about the appearance of the PVC films. These SEM images are in good agreement with the profilometer results. That is, there are enough changes in the surface roughness which are visible to the eye at these magnifications as a function of filler (calcite and fly ash) concentration.

(a)　　　　　　　　　　　　　　　(b)

(c)　　　　　　　　　　　　　　　(d)
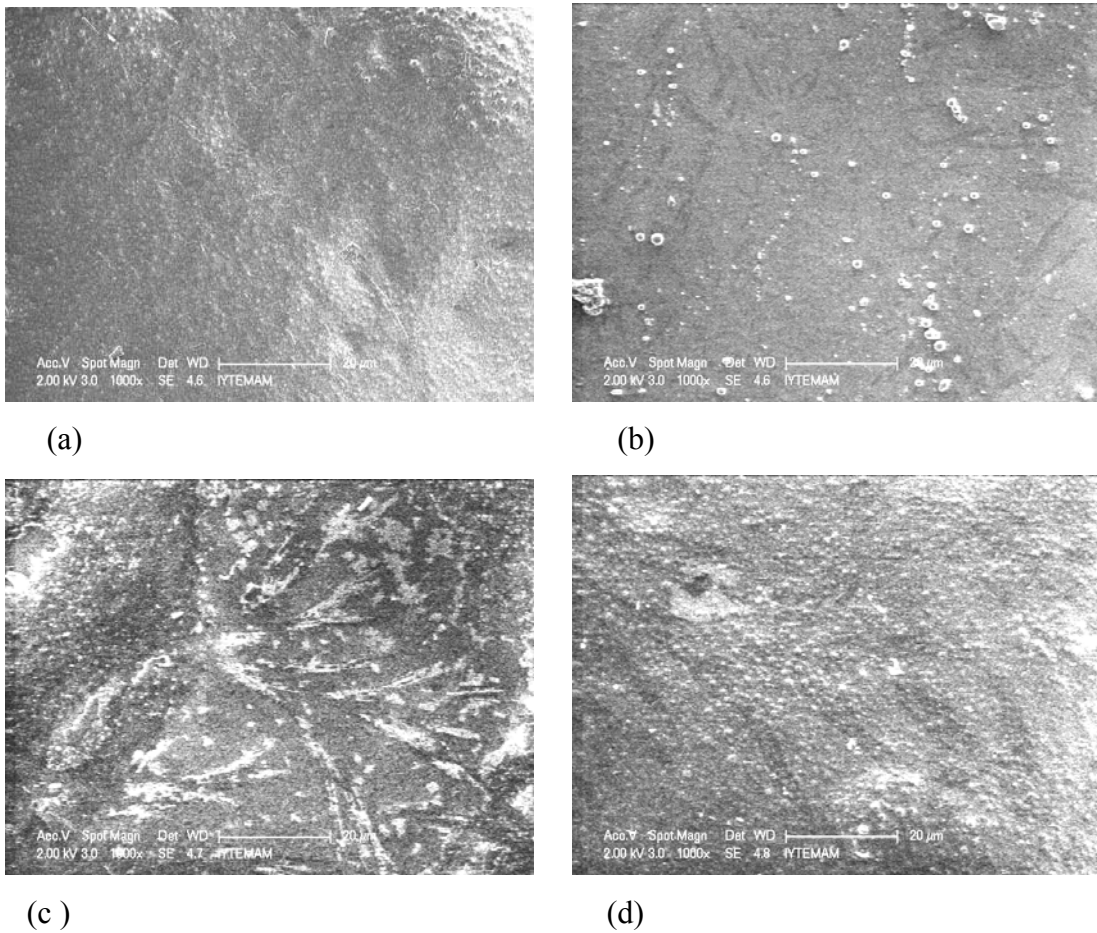
Figure 4.21. SEM photographs of the PVC films, included diffrent concentration of calcite. (a) Std sample surface, (b) Calcite-Sample 1, (c) Calcite-Sample 2, (d) Calcite-Sample 3

Figure 4.21 shows the calcite filled PVC film surfaces, PVC film without filler and maximum level of calcite loaded films seem similar, sample-1 and sample-3 seem different. Especially, there is a particules on the surface of the calcite-sample 2. These particules may be PVC powders which were not swelling and wet by plasticizer because of a inadequate mixing.

(a)

(b)

(c)

(d)
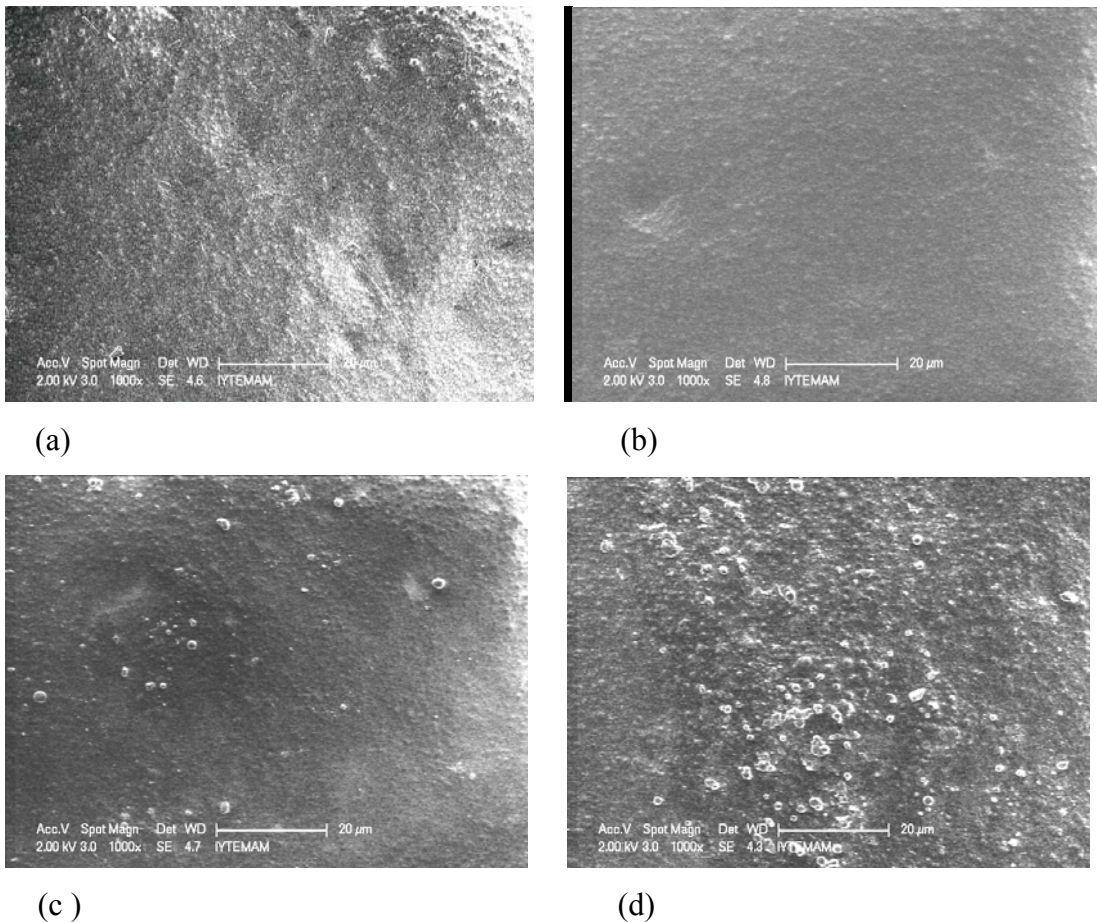
Figure 4.22. SEM photographs of the PVC films, included different concentration of fly ash (a) Std sample surface , (b) Fly Ash–Sample 1, (c) Fly Ash–Sample 2, (d) Fly Ash–Sample 3

Figure 4.22 shows fly ash filled PVC film surfaces, (b,c and d) and PVC film without filler (a), Sample 1, which was loaded minimum concentration of fly ash and standart PVC films seem similar, but at higher concentrations, there are corruption on the surfaces.

4.3.2. Surface Roughness Measurements

Surface roughness measurements were conducted using a profilometer mentioned in Chapter 3 in detail. The effect of both filler type and concentration were tested. The results of these measurements are presented in Figures 4.23 and 4.24 for calcite and fly ash concentrations respectively. It is seen from the figures that using a filler (calcite or fly ash) increases surface roughness. However, this increase is more in the case of fly ash. In the absence of any filler, the surface roughness was found to be approximately 0.2 μm. Increasing calcite concentration from 6% to 18% increased the surface roughness value from 0.2 to 0.8 μm. This might be simply due to the larger size of calcite particles (see also Figures. 4.4, 4.5 and 4.7). However, the roughness is more (from 0.2 to 1.5 μm) in the case of fly ash even though it has very similar size distribution to calcite. This might be due to the complex composition of fly ash and interparticle relations.

As a conclusion, the roughness of PVC plastisol will be depend the type and concetration of filler material. Therefore, one has to optimize the type and concentration of filler material depending on the purpose of PVC plastisol application and the demand of surface roughness.
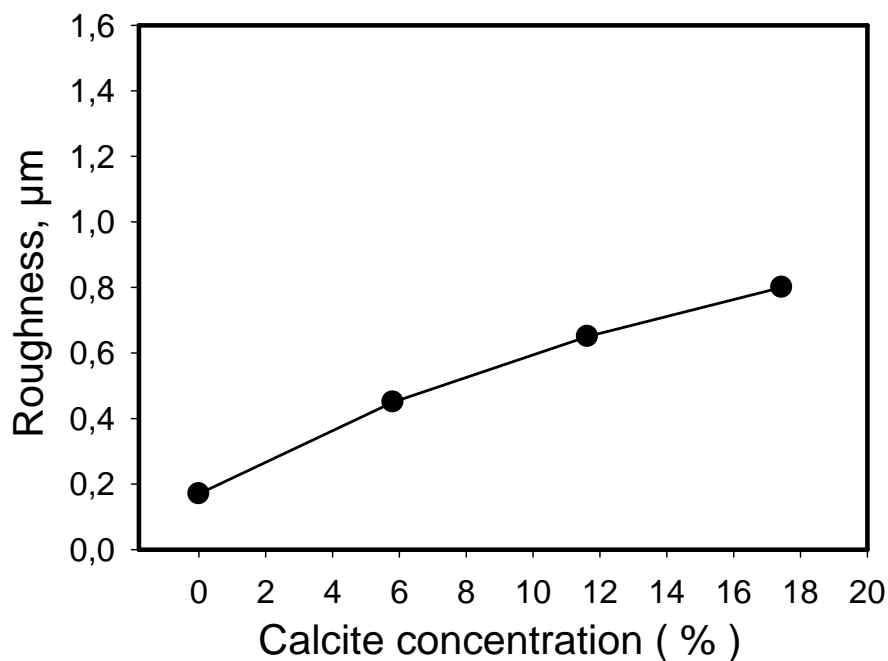
Figure 4.23. Profilometer surface roughness graph for calcite filled PVC films
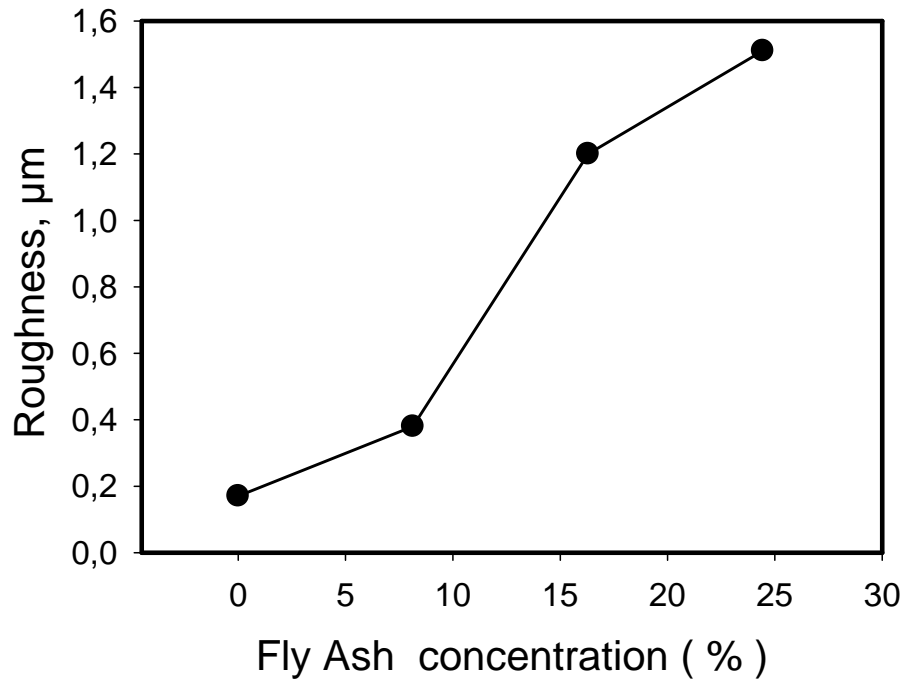
Figure 4.24. Profilometer surface roughness graph for Fly Ash filled PVC films

4.4. Mechanical Tests

4.4.1. Hardness Measurements

Hardness of polymer material filled with fly ash is very different from calcite filled and no filled materials. At some industries, harder materials are choosen for their usage, such as belts on the treadmill. Soft conveyor belts are choosen to be able to transform boxes or goods for slopped systems. According to their hardness values all metarials filled with filler, used in this study, can be used in conveyor belt as cover materials according to usage of materials. Hardness may be caused due to hardness of the filler material.

Table 4.4. Hardness values of the PVC films

Sample	Hardness
	Shore A
Std PVC Film	76
Calcite 1	77
Calcite 2	78
Calcite 3	78
Fly Ash 1	77
Fly Ash 2	82
Fly Ash 3	82

4.4.2. Tensile Strength Measurements

4.4.2.1 Effect of Filler Concentration to the Mechanical Properties

Tensile strength measurements are conducted as a function of filler concentration. The results of these measurements are presented in Figures 4.25 a-b for fly ash and Figures 4.26 a-b for calcite. It is seen from Figures 4.25 a-b that the effect of fly ash concentration is important. The stress increases with an increase in fly ash concentration first reaches a maximum value, 6 N/mm^2 at 8% fly ash and then decreases with a further increase in concentration for all the stirring speeds tested. However, this is not the case for calcite. The stress does not change significantly with an increase in calcite concentration except the highest concentration tested at 600 RPM mixing rate. As a result, both the filler concentration and mixing rates of the PVC plastisols affect the mechanical properties of the PVC films formed. At low concentration of fly ash, 4%, PVC film had better mechanical properties than calcite filled PVC films. At higher concentrations, on the other hand, the stress values decreased. This is the indication of weaker mechanical properties.

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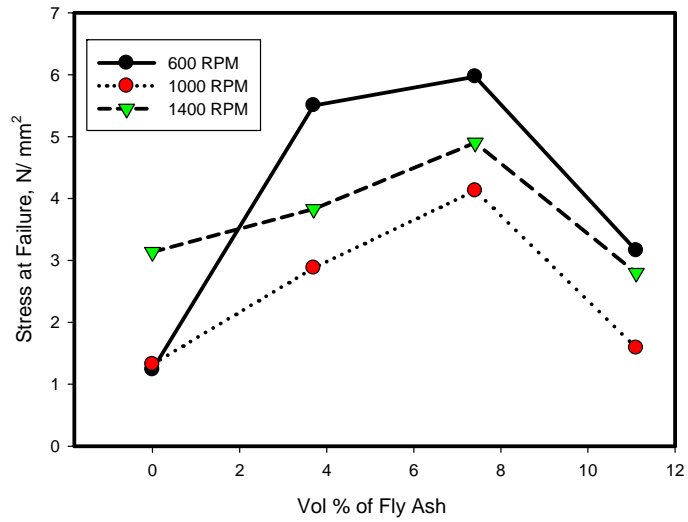
(a)
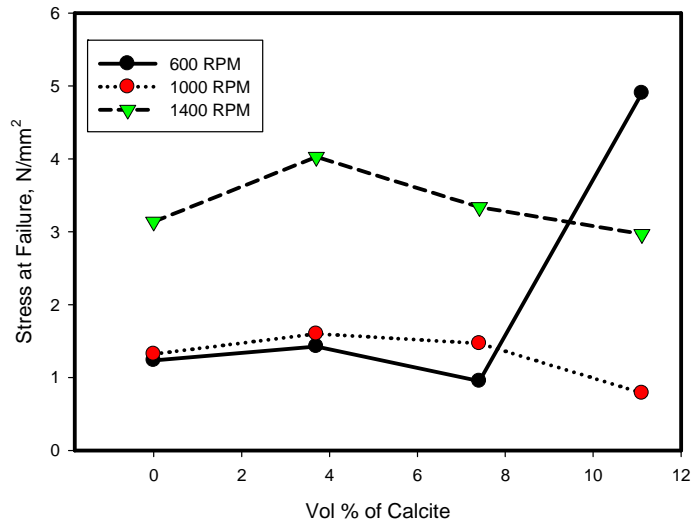
(b)

Figure 4.25. Filler concentration (Vol %) versus stress at failure graphs (a) Fly Ash
(b) Calcite

In addition, the Figures 4.26 a,b and c are given to compare the stress at failure results of fly ash and calcite as filling materials.

4.4.2.2 Comparison of Filler Types
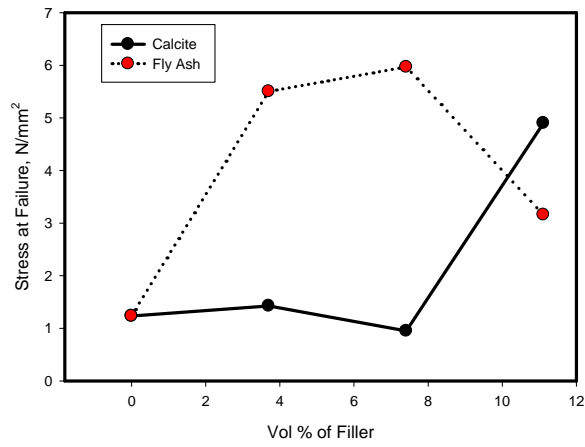
(a)   600 RPM
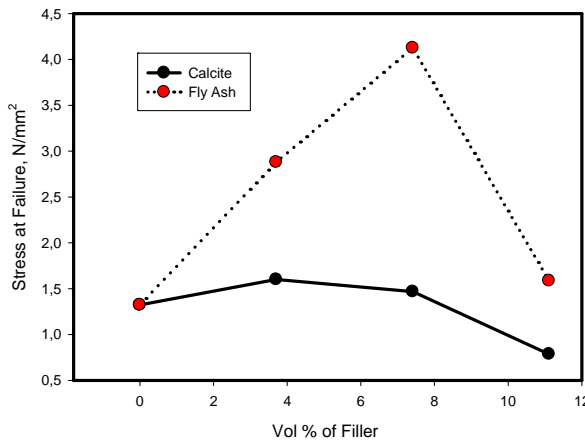
(b) 1000 RPM
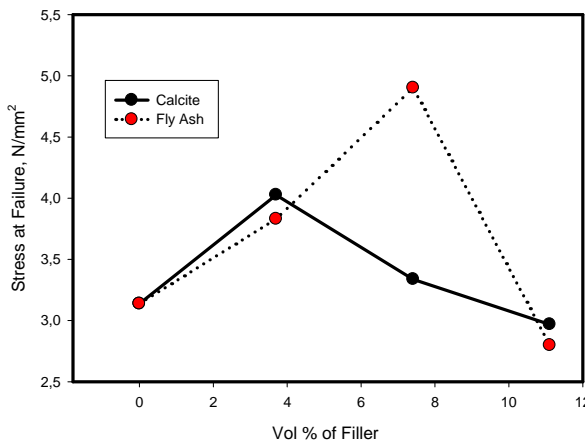
(c) 1400 RPM

Figure 4.26. Filler concentration (Vol %) versus stress at failure graphs (a) 600 RPM
(b) 1000 RPM (c) 1400 RPM

As in general results are taken from Figure 4.25 and Figure 4.26, filler concentration and mixing rates of the PVC plastisols affect the mechanical properties of the PVC materials. At low concentration of fly ash films have better mechanical properties than calcite filled PVC films. At highest concentration values of filler, stress values decreases means mechanical behaviours of the materials become weaker.

As mentioned before, 1% elongation property is very important for the conveyor belts, if higher force is loaded than required force for 1 % elongation to the conveyor belt during assamblage to the conveyor system, belt undergoes plastic deformation and pull out. In Figure 4.27, the effect of filler concentration on stress at 1% elongation values are represented as a graph.
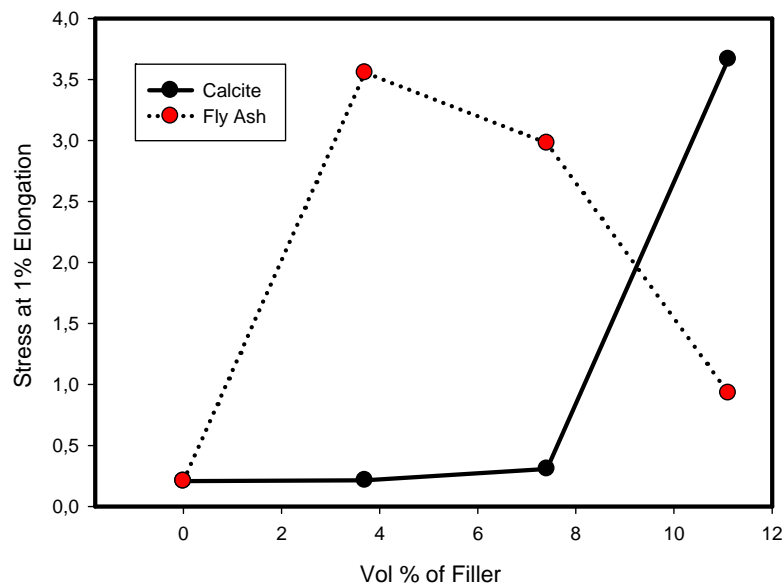
(a)
Figure 4.27. Filler concentration (Vol %) versus stress at 1% elongation graphs (a) 600 RPM (b) 1000 RPM (c) 1400 RPM (cont. on next page)
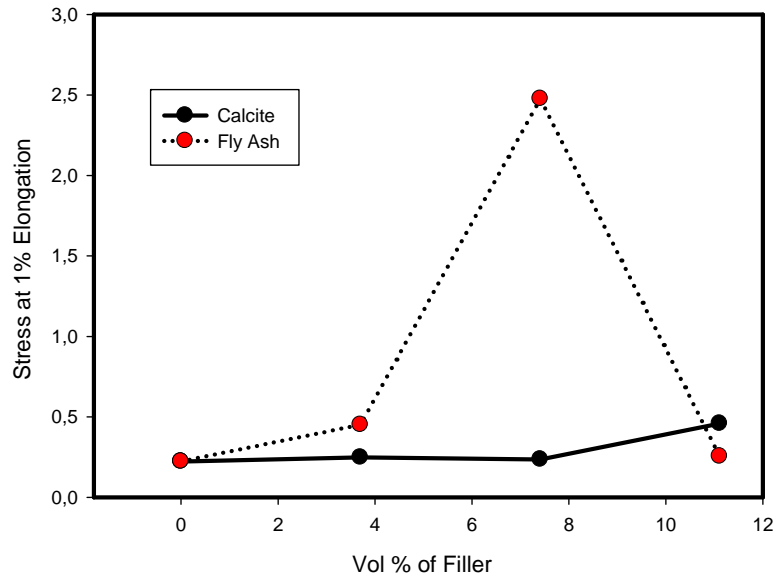
(b)
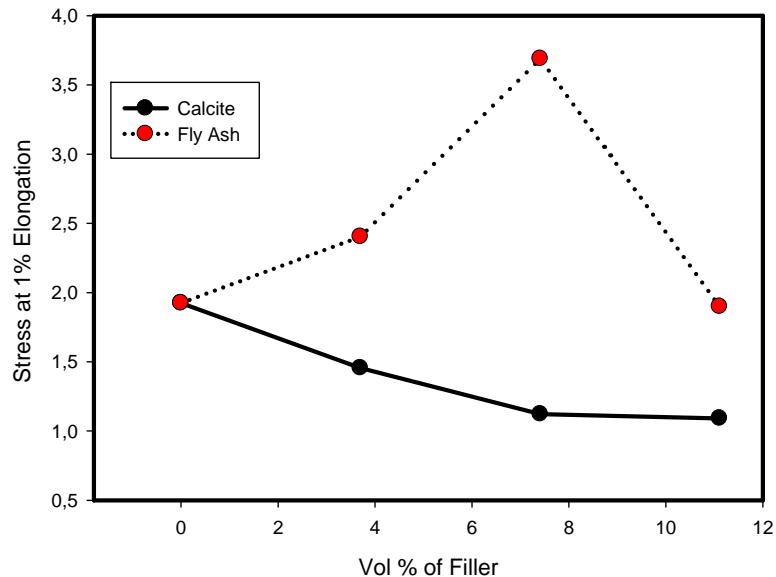
(c)

Figure 4.27. (cont.)

As in Figure 4.27 when the volume of fly ash is inrecased, the amount of force inreases to stretch the film as 1% in length up to 8 % (amount of filler as in volume percentage), after this concentration mechanical property of the fly ash loaded films become weaker. For calcite, PVC films which were prepared with 600 and 1000 RPM mixing rates, only at highest concentration of calcite, the amount of force is required for the 1% elongation increase. At low concentrations, the change is a little. As seen in Figure 4.27 (c), when calcite filled PVC plastisols mixed at 1400 RPM, prepared films from this plastisols, shows different mechanical property. The stress

value decreased as concentration of calcite was increased. This result may be caused again inadequate curing of the PVC films.

4.4.2.3 Effect of Mixing Rates of The PVC Plastisols To The Mechanical Properties

Mixing rate of the PVC Plastisol affects the mechanical properties of the prepared PVC film as seen in Figure 4.28.
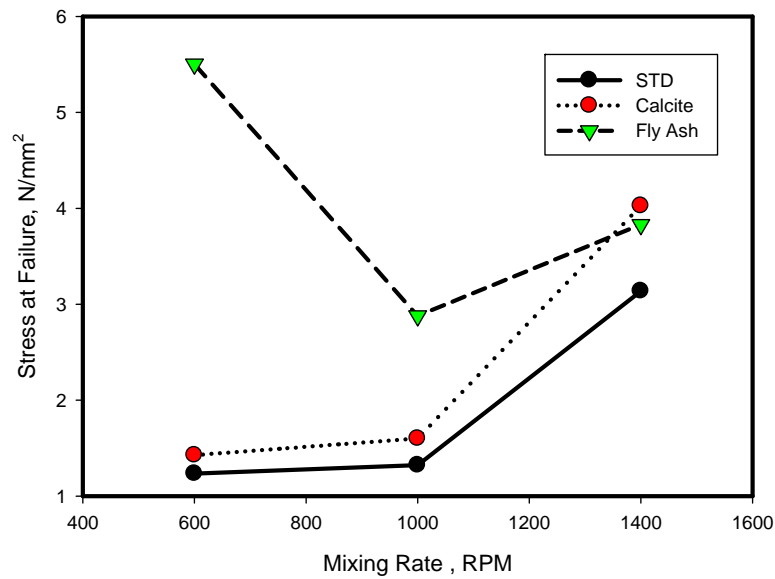
(a)

Figure 4.28. Mixing Rate of PVC Plastisols versus stres at failure graphs (a) Sample 1 (b) Sample 2 (c) Sample 3 (cont. on next page)
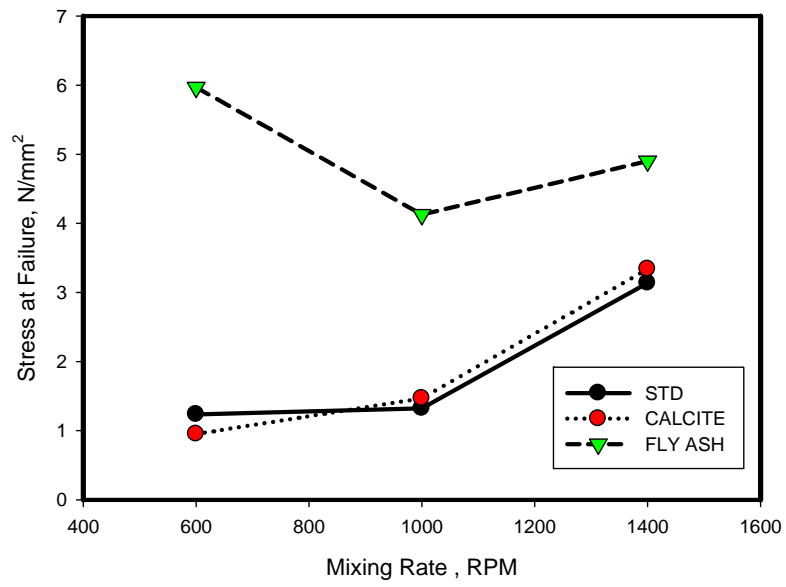
(b)
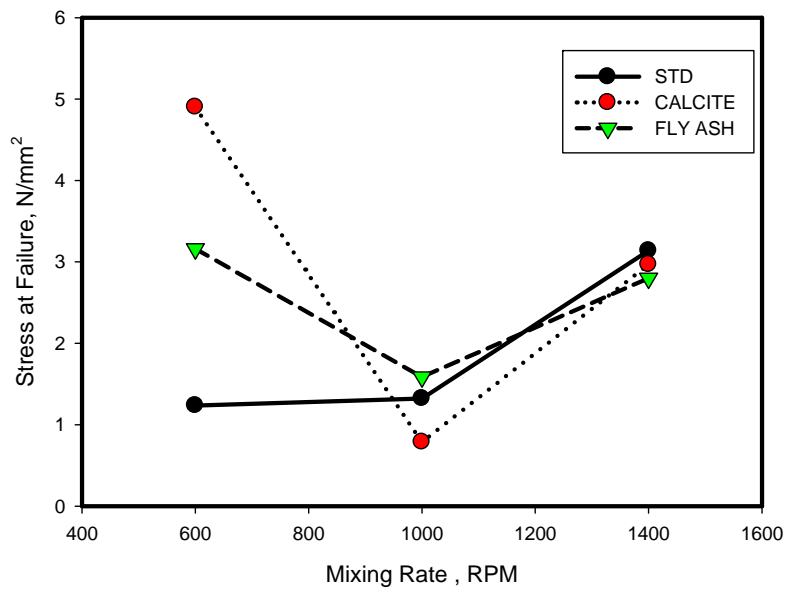
(c)

Figure 4.28. (cont.)

Films which were prepared with the fly ash had different mechanical property than calcite filled and no filled materials, when the lowest concentration of filler was loaded to the PVC plastisol. Highest stress values were obtained at lowest mixing rate, at 600 RPM. After this rate, stress value was decraeasing up to 1000 RPM, then was increasing again. But for the calcite filled and no filled materials, stress value was increasesing, when mixing rate of the PVC plastisol was increased. The most efficient mixing rate was 1400 RPM for calcite filled and no filled PVC plastisols. In general fly ash filled films showed better mechanical property than calcite filled and no filled films.

Same results are said for samples number 2, 7.41 % in volume, but for the highest filler concentration, 11.11 % in volume, calcite filled and fly ash filled films shows the same mechanical properties.
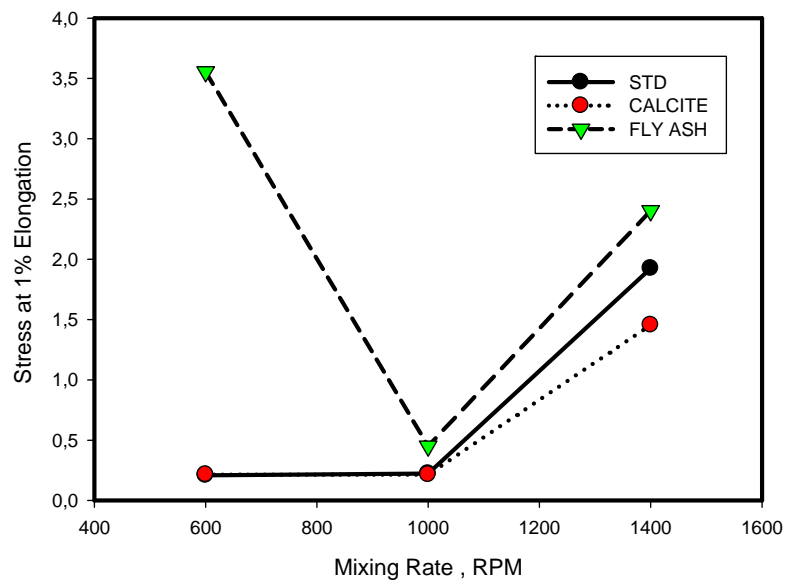
(a)

Figure 4.29. Mixing rate of PVC Plastisols versus stress at 1% elongation graphs (a) Sample 1 (b) Sample 2 (c) Sample 3 (cont. on next page)
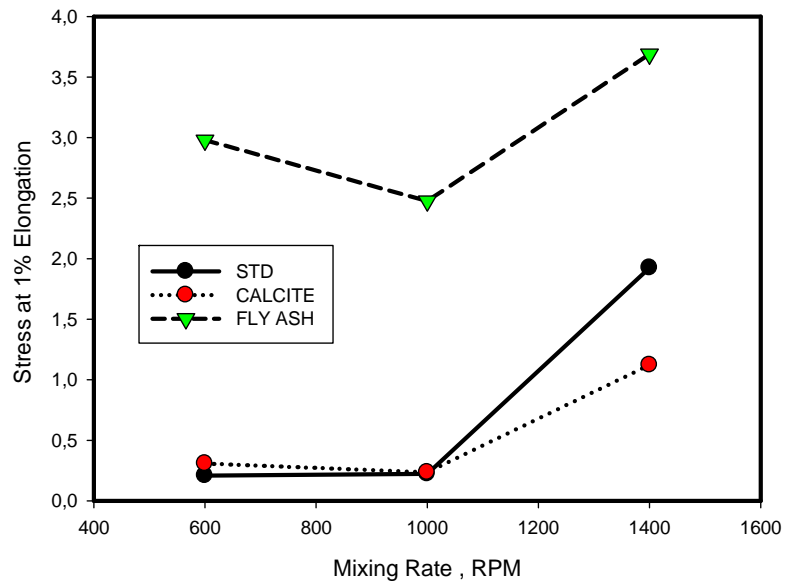
(b)
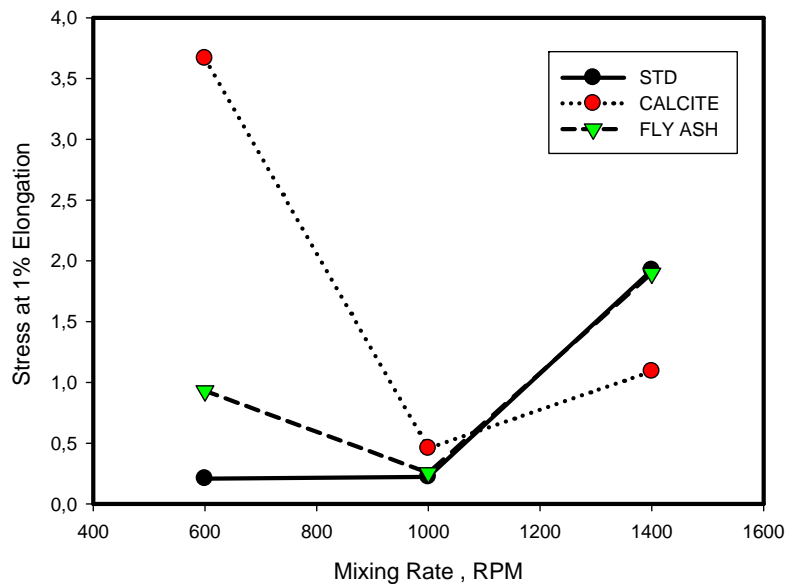
(c)

Figure 4.29. (cont.)

When the volume percentages of fillers were 3.7 % and 7.41 in PVC plastisols, calcite filled material and no filled standart material exhibits similar mechanical behaviour as shown in Figure 4.28 and Figure 4.29. There is no much changing between mixing ratio 600 RPM and 1000 RPM for them, but increasing of the force is required for the 1% elongation at 1400 RPM is observed But also fly ash filled material needs much more force for 1% elongation than others.

At highest concentration value, mechanical properties of the fly ash filled material becomes weaker than calcite and similar with no filled PVC films.
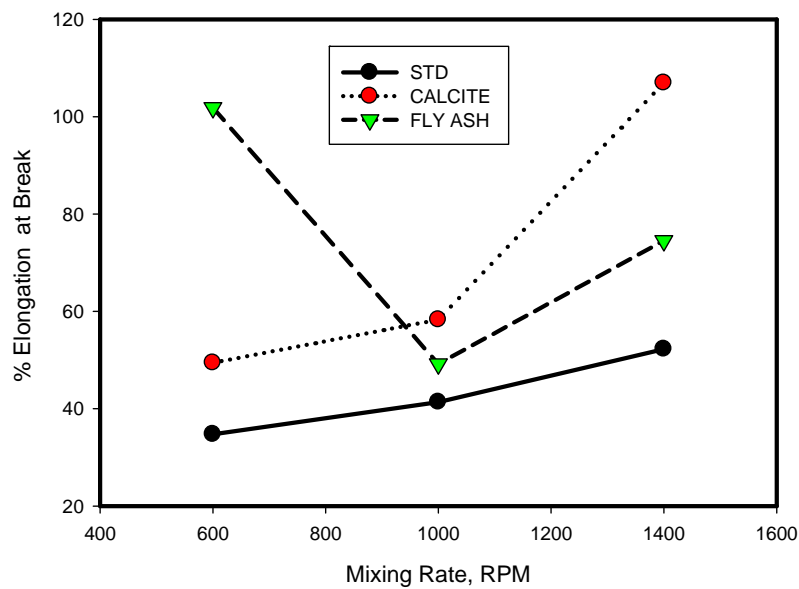

(a)

Figure 4.30. Mixing rate of PVC Plastisols versus % elongation at break graphs (a) Sample 1 (b) Sample 2 (c) Sample 3 (cont. on next page)
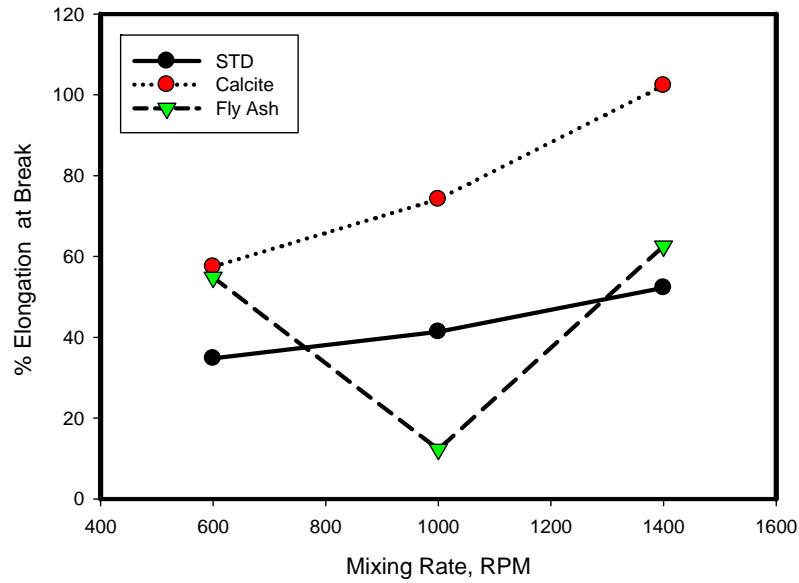
(b)
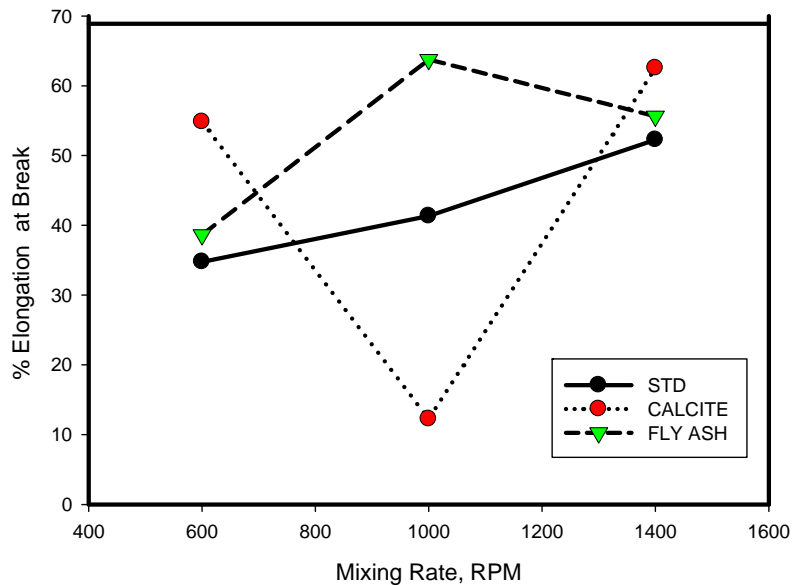
(c)

Figure 4.30. (cont.)

As a result, fly ash filled materials have better mechanical properties. The reason should be morphological properties of the used filler in the PVC plastisols. Fly ash powder, used in this study included sphere particles, but calcite particles have different morphology but not any sphere particules.

Xie was conluded that pure PVC is brittle, but $CaCO_3$ nanoparticles are loaded to the PVC matrix, the nanocomposites show ductile behaviors (Xie, et al. 2004).

CHAPTER 5

CONCLUSION

In this study, rheological behaviour of the fly ash filled PVC plastisols and mechanical properties of the end products were investigated. Different concentration calcite and fly ash were loaded to the PVC plastisols as fillers. Rheology is important property for a coating technologies. Because it effect the surface properties of the polymers. Fly ash caused difficult morphology than calcite. Calcite is used common filler in coating technologies. But using concentration is important for processing. At higher concentrations, plastisols have very high viscosity levels and this situation make difficult to proccesing.

As a conclusion fly ash can be used as a filler instead of calcite in the plastisols, but not same filler concentrations as calcite because of difficulty of rheology.

Temperature changing affects the rheological behaviour as, or the standart plastisols and for the calcite filled plastisols; when the temperature is increasing, shear stress is increasing. For the fillers, there is no exact relation with temperature and rheology.

Mixing rate of the PVC plastisols affect the rheological behavior, but there is no regular increasing or decreasing according to this changing.

Standart PVC plastisols and calcite filled plastisol show the similar rheological behaviour at minimum concentrations. But fly ash filled PVC plastisols have more difficult rheology than others. Concentration of the fly ash affect the rheological behaviour. When the concentration is increased, shear rate is increasing and rheological behaviour becomes difficult.

The surface roughness of the PVC films, filled with fly as have higher values than others. High concentration of fly ash becomes worse the surface quality.

Hardness values are increasing as;

Std PVC film < Calcite filled PVC Film < Fly Ash filled PVC film.

Mechanical properties of the fly ash filled PVC films are better than others. When the concentrations of all filler type were increased, mechanical behaviours get weaker than before.

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