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Synopsis

Comparison of the reinforcing effect of muscovite and phlogopite in thermoplastic composites

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The mechanical properties of particulate filled polymers are influenced significantly by interfacial interactions. The adhesion between the polymer and the filler depends on the area of the interface and the strength of the interaction. The former is related to specific area of the filler while the strength of the interaction can be modified by surface treatment. This study is focused on comparing the reinforcing ability of muscovite and phlogopite with and without surface treatment.

Muscovite and phlogopite are two common forms of mica. Mechanical properties such as Young's modulus, tensile strength, elongation and impact strength were used to compare the reinforcing ability of muscovite and phlogopite in EVA composites.

The Young's modulus of the surface treated and non-surface treated composites increased with an increase in filler loading. Composites reinforced with muscovite had similar moduli compared to composites reinforced with phlogopite. The tensile strength of phlogopite reinforced composites increased with an increase in filler content while that of muscovite reinforced composites remained constant. Surface modification by both silane and stearic acid reduced the tensile strength of phlogopite reinforced composites. The tensile strength of stearic acid treated muscovite reinforced composites improved but not to the same extent as the silane treated composites.

Both muscovite and phlogopite lead to a lowering of the impact strength at high filler loadings while the tensile impact strength of both muscovite and phlogopite reinforced composites improved when using silane and stearic acid. In non-surface treated systems, muscovite reinforced composites showed an initial increase in elongation while the elongation of phlogopite reinforced composites decreased with an increase in filler loading. Elongation at maximum load values, however, increased at low filler loadings, when using stearic acid. It can be concluded that stearic acid is not an effective coupling agent for mica/EVA composites and that the use of silane for phlogopite reinforced composites does not offer any improvement in mechanical properties.

Keywords: Phlogopite, muscovite, silane A-171, stearic acid, interfacial adhesion, Young's modulus, tensile strength, elongation at maximum load, impact strength, and surface treatment.

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Contents

LIST OF SYMBOLS

A_c	Area of the composite over which the tensile force acts
E_c	Young's modulus of the composite in the plane of orientation (Mpa)
E_m	Young's modulus of the reinforcement (mica) (Mpa)
E_p	Young's modulus of the polymer (Mpa)
G_p	Shear modulus of the polymer (Mpa)
MRF	Modulus reduction factor
v_f	Volume fraction reinforcement, associated with zero voidage
v_p	Volume fraction polymer, associated with zero voidage
α	Flake aspect ratio
σ_c	Tensile stress in the composite
σ_p	Tensile stress in the polymer
τ	Shear stress
φ	Porosity
φ_m	Fraction void volume per cubic meter particles
χ	Modified voidage (Voidage relative to polymer phase)
EVA	Ethylene vinyl acetate

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1. INTRODUCTION

Mineral filled polymers are utilized in large quantities in different applications [1]. The incorporation of these fillers is focused on the substitution of relatively costly materials and the improvement of mechanical properties such as strength, stiffness, dimensional stability and high temperature properties [2]. The degree of reinforcement depends on particle size and shape, the volume fraction of the filler and the nature of the interface between the polymer and the filler [3].

Mica is a generic name for a broad class of minerals of the phyllosilicate family [4]. They are characterized by a nearly perfect basal cleavage that permits the large crystal to be split or delaminated into thin, flexible flakes [5]. When suitably delaminated and oriented within the polymer matrix, it is capable of imparting a high degree of reinforcement [6]. The advantage of mica is that it is possible to use it at higher filler loadings than most other fillers. It is relatively inexpensive and quite abundant. [6].

Muscovite and phlogopite are the two primary types of mica used in polymers. Although there is extensive literature on the use of muscovite as a filler in many different compounds, studies dealing with phlogopite used as reinforcing filler are not as frequent.

It is the objective of this study to compare the reinforcing ability of phlogopite with that of muscovite in EVA. This will be accomplished by testing for the

Young's modulus, tensile strength, elongation and tensile impact strength. Non surface treated, silane treated and stearic acid treated phlogopite will be used in this study.

Results are based on laboratory scale experiments at an average particle size for phlogopite and muscovite of 60 mesh.

2.LITERATURE SURVEY

2.1. INTRODUCTION

The first ethylene copolymers, including EVA, were synthesized and patented in the 1930s at ICI in Great Britain in the same laboratories where polyethylene was discovered. Initially only low levels of vinyl acetate comonomer was used to produce modified polyethylene. During the late 1950s and continuing to the present day, the range of EVA copolymers has widened considerably, reflecting an appreciation for the versatility of the material [7]. Today the term EVA copolymer covers a divers family of materials. EVA copolymers are utilized in perhaps the broadest spectrum of applications of any synthetic polymeric material. EVA is also used by the cable industry for making heat shrinkable insulation [7].

Polymers have a low stiffness and strength compared to metals [8]. One of the methods used to overcome these deficiencies is the addition of reinforcing fillers to the resin to form a composite material. Fillers are gaining increasingly importance in compounds. Plastic producers and customers are now resorting increasingly to fillers for their development, not only for low costs, but also to obtain a specific property profile in the final product [9].

The performance of polymer composites depends largely on the interface between the polymer and the filler. Consequently, surface modification of fillers is an essential technology for composite materials [10]. The aim of the literature survey will be to define reinforcement and explain the factors that affect reinforcement.

2.2. FILLERS

Fillers are defined as additives in solid form that differ from the plastic matrix in respect to their composition and structure. They are generally inorganic by nature. Inert fillers or extender increase the bulk volume of the filler and therefore the price. Active fillers produce specific improvements in certain mechanical or physical properties and are therefore also known as reinforcing fillers [9].

2.2.1. Reinforcement

With reinforcements, the shape of the filler plays an important role [9]. There are five recognized shapes for fillers, summarized in Table 1.

Table 1 summary of filler shapes

	Group				
	3-D			2-D	1-D
Particle class	Sphere	Cube	Block	Flake	Fiber
Description	Spheroidal	Cubic Prismatic	Tabular Prismatic	Platy Flaky	Fiber
Examples	Glass,sphere ,microsphere	Calcite, feldspar	Silica,barite, nephelite	Kaolin, mica, talc,graphite	Wollastonite, wood flour

2.2.1.1. SPHERICAL FILLERS

Spherical fillers are generally made of glass. They can be either hollow or solid. The spherical filler increases stress distribution in the polymer. Shrinkage in materials reinforced with spheres is almost the same in all directions [11]. Reinforcement with spheres also leads to an increase in tensile, compressive strength, as well as flexural modulus [11].

2.2.1.2. FIBER FILLERS

Fiber reinforcing fillers are made from a wide variety of materials. These materials include glass, carbon, kevlar and fibrous minerals such as asbestos [9]. The orientation of the fiber reinforcements in polymer-filler system is important. As fibers are classified as one-dimensional particles, important physical properties associated with the strength of the polymer can only be altered in the direction of their orientation, unless randomly orientated [11].

Reinforcement with fibers leads to an increase in tensile and flexural strength in the direction of orientation [11]. The fiber aspect ratio also affects the reinforcement action. An increase in fiber length will result in an increase in surface area, thereby increasing the interaction between the polymer chains and the reinforcement.

2.2.1.3. FLAKY FILLERS

Flaky fillers include talc, kaolin, mica, silicon carbide, aluminum trihydroxide, graphite and metals (e.g. aluminum)[11]. The flaky shape of the fillers leads to modification of the polymer properties in two directions if not randomly oriented. Aspect ratio of the flake particles plays an important role. Aspect ratio is the ratio of the equivalent diameter to flake thickness. A wide variation in aspect ratio will cause the flakes not to align efficiently. The result is uneven stress distribution, which reduces properties such as strength and modulus [11].

A high aspect ratio is associated with large surface area. The increased surface area leads to better interaction between the polymer chains and the filler surface. Overall shrinkage of the composition is reduced, and is restricted to one direction. Reinforcement with flakes leads to an increase in tensile and flexural strength [12].

2.3. MECHANISM OF REINFORCEMENT

2.3.1. REINFORCEMENT THEORIES

The action of reinforcement can be attributed to three causes:

Chemical bond theory

- Some fillers form chemical bonds with the matrix, like carbon black [11]

Restrained layer theory

- Fillers act mainly through the volume that they take up. In the presence of the filler particles the polymer chains cannot assume all conformational positions thereby stiffening the polymer. It can be assumed that in a certain zone around the filler particles the polymer differs in structure and properties from the bulk polymer [11]. The polymer segments attached to the filler surface by secondary or primary valence bonds. Thus the polymer segments adjacent to the surface of the filler particles are immobilized due to the high degree of dimensional stability of the filler particle [11]. An increase in the glass transition temperature in filled polymers can be regarded as confirmation of the theoretical concept presented above. Lower deformability and higher strength are also explained by the restrained layer theory [11].

A homogenous distribution of filler in the matrix is required to enable as many polymer chains as possible to be bound to the free filler surface. In this regard the surface properties of the filler and polymer are crucial [11].

Debonding theory

- Another theory of reinforcement states that when polymer molecules are subjected to stress, they can slide off the filler surface. Energy can thus be uniformly distributed. This effect is demonstrated by an increased impact strength observed in unplasticized PVC/chalk system [11].

2.3.2. FACTORS INFLUENCING REINFORCEMENT

2.3.2.1. PARTICLE SIZE DISTRIBUTIION

Fillers are commonly classified in terms of the sieve opening through which a given percentage will pass or simply in microns. The particle size classification provides information as to the maximum particle size, but nothing as to the smallest or to the quantities of various sizes in between [13,14]. This information is given by the particle size distribution. It has been shown that a filler with a fairly wide particle size range will provide a compact arrangement requiring a minimum of resin to fill the space between the particles [13].

Performance of a composite depends on the mean size as well as the particle size distribution. For a given volume fraction filler, it can be expected that smaller particles, with a narrow distribution will be more effective at enhancing mechanical properties such as toughness [15,16].

Processing conditions may affect the particle size distribution. With dispersive mixing fracture of the filler particles can occur. This may change the mean particle size as well as the particle size distribution. Fracture of the filler during extrusion and injection moulding also may reduce the particle size distribution [17].

2.3.2.2. ORIENTATION

The way in which fillers are positioned or orientated in the polymer matrix will determine the direction and level of reinforcement. Oriented fillers normally result in greater reinforcement in the direction of orientation [17].

During extrusion and injection molding, the orientation of the filler is in the direction of the flow. A decrease in the degree of orientation of the filler increases with distance from the wall towards the centre. This may lead to inhomogenities with respect to the filler [17].

2.3.2.3. ADHESION

Reinforcement depends on the transmission of mechanical energy from the polymer to the filler through the interface [18]. An increase in the strength of the bond between polymer and filler leads to an increase in the reinforcing of the polymer [19]. The introduction of a filler into a resin creates an interface between two very dissimilar substances [20]. Water may accumulate at the interface, resulting in debonding of the filler thereby reducing the reinforcing action of the filler. Under a tensile force, the filler will "pull out" rather than accept the stress [18,20].

Coupling agents "compatibilise" the filler surface, resulting in better dispersion of the filler in the resin as well as a more intimate resin-mineral interface. Wetting out of the filler surface is an important factor in improving the properties of a composite, but true coupling requires the maintenance of this intimate bond in the presence of moisture [20].

2.4. COUPLING AGENTS

2.4.1. INTRODUCTION

Bonding between polymers and inorganic surfaces is an important science [20]. The need for new bonding techniques arose in 1940 when glass fibers were first used as reinforcements. The specific strength to mass ratio of early glass-resin composites was higher than those of aluminum or steel, but they lost much of their strength during prolonged exposure to moisture. This loss in strength was attributed to the debonding of resin from hydrophilic glass by the intrusion of water [20].

Preparation of glass-resin bonds under dry conditions did not produce composites that were more water-resistant. Even bonds of resin to fresh glass surfaces, did not withstand the action of water [20]. Clearly, the interface between such dissimilar materials did not allow the formation of a water-resistant bond. This necessitated the use of an intermediate material to hold the two dissimilar materials together. Such materials are called coupling agents [20].

2.4.2. DEFINITION OF A COUPLING AGENT

Coupling agents also called wetting agents, dispersion aids or processing aids, are used to improve the interaction between a polymer and a filler surface [21]. Complete dispersion of the filler in the resin is necessary to eliminate voids or clumps that will act as weak points in the composite [22]. Treatment of the filler protects it against abrasion and cleavage during mixing and production of the final composite [22]. The treatment promotes optimum alignment of polymer segments at the interface and overcomes inhibitory catalytic effects the filler may have on the polymer. The treated filler should remain chemically inert during mixing, but combine with the polymer during molding [22].

Good coupling agents will improve the following properties of the filled system:

- The wettability of the filler surface by the polymer
- The shock absorbing and stress releasing properties of the interface between the filler and polymer
- The mechanical strength of the interfacial layer

Although coupling agents may perform several useful functions, several simple laboratory tests are recommended to evaluate any new potential coupling agents. More extensive and sophisticated methods may then be used to refine the application for optimum performance [11].

2.4.3. THEORIES OF BONDING THROUGH COUPLING AGENTS

A small quantity of coupling agents at the interface may have a great effect on the performance of a composite [20]. Various theories of adhesion exist, which contribute to the understanding of the mechanism of adhesion through coupling agents [20].

2.4.3.1. THE CHEMICAL BONDING THEORY

Coupling agents contain chemical functional groups that can react with a given surface. Attachment to the surface can therefore be made through covalent bonds. In addition, coupling agents contain at least one other functional group, which could react with the resin. The coupling agent may therefore act as a bridge to bond a surface to a resin with a chain of primary bonds. This could be expected to lead to the strongest interfacial bond [20].

2.4.3.2. WETTING AND SURFACE ENERGY EFFECT

It has previously been concluded that good wetting at the surface by a liquid resin is of prime importance in the preparation of composites [20]. Physical adsorption of a resin on a high-energy surface would result in adhesive strengths far more than cohesive strengths if complete wetting is obtained [20].

In order to obtain complete wetting of a surface, the adhesive must initially be of low viscosity and have a surface tension lower than the critical surface tension of the filler surface [20]. Although all solid surfaces have very high critical surface tensions, many hydrophilic minerals in equilibrium with atmospheric moisture are covered with a layer of water. Hence, in a humid atmosphere, poor wetting and spreading of a nonpolar adhesive would occur with the moist surface of a polar adherent. Polar additives on the other hand may be able to either absorb the water or displace it through surface-chemical reactions.

2.4.3.3. THE MORPHOLOGY THEORY

I) THE DEFORMABLE LAYER THEORY

There has been considerable confusion over which morphology would be desired in a resin adjacent to the treated filler. A flexible, deformable phase seems desirable to accommodate stresses at the interface [20].

II) THE RESTRAINED LAYER THEORY

At the other extreme, it has been proposed that the resin in the region of the filler should have a modulus somewhere between that of the mineral and the matrix [20]. This theory suggests that the coupling agent functions by tightening up the polymer structure in the interface region. The restrained layer is required at the interface for maximum bonding and resistance to hydrolytic cleavage [20].

III) TOUGH COMPOSITES FROM RIGID RESINS THEORY

Maximum toughness of composites is obtained with a deformable layer while maximum chemical resistance is obtained with a restrained layer at the interface. Tough, water-resistant composites may be prepared from rigid resins by bonding a thin elastomeric interlayer to the mineral surface through a cross-linkable silane. Elastomeric interlayers are selected that bond to the matrix resin by inter-diffusion or some related mechanism [20]. SBS block copolymer interlayers bond well to polyolefins while elastomeric urethane bonds well to polycarbonates, polyterepthalates, and polyamides [20].

2.4.3.4. ACID-BASE REACTIONS

It is common practice to modify polymers with carboxy groups for improved adhesion to metals. Bolger [23] pointed out that various metal oxide surfaces have different isoelectric points in water and therefore might be considered as more or less acidic or basic [20]. Adding suitable acid or basic solvents to the system could further modify acid-base reactivity between filler and matrix [20]. It is also known that acid –base reactions may be important in aligning coupling agents on a filler surface [20].

2.4.4. TYPES OF COUPLING AGENTS

2.4.4.1. SILANE COUPLING AGENTS

I) Structure

Silane coupling agents are bifunctional molecules, which improve the bond between organic polymers and siliceous fillers [20]. Typical fillers are glass or minerals such as navoculite, kaolin clay, mica, wollastonite and alumina trihydrate [14]. Silanes have the highest consumption among the various groups of coupling agents [21,24]. The properties of organofunctional silanes are due to their molecular structure and reactions. The general chemical structure of silanes is:

$$\mathbf{Y\text{-}\ (CH_2)_n - Si\ X_3 \qquad n = 0 - 3}$$

The silicon as central unit of a silane is combined with two different functional groups:

- Organofunctional group **Y**

This is strongly bound to the silicon via a stable unreactive carbon chain. The adhesion to the polymer occurs via this organofunctional group. The most common organofunctional groups are amines, methacrylates, epoxy, vinyls, alcoholic, acids and chlorinated groups [21,24].

- Siliconfunctional group **X**

These include mostly alkoxy groups, which are directly attached to the silicon. It reacts through hydrolysis with active centers on inorganic substrates or by condensation with other silicon compounds [21,24].

II) Mechanism

The mode of action of organofunctional silanes can be explained by the following steps:

1. Reaction of the siliconfunctional group
    - Hydrolysis
    - Bonding to the inorganic surface
    - Condensation
2. Reaction of the organofunctional group
    - Bonding to the polymer

HYDROLYSIS

Silanes react with water in the presence of a catalyst (acid or base) to form silanols and the corresponding alcohol, which is illustrated in Figure1. Aminosilanes are hydrolyzed without addition of a catalyst (the basic amino group acting as catalyst) and the formed aminosilanol is stable. Other functional silanes are hydrolyzed preferably in the presence of an acid (e.g., acetic acid), but the formed silanol has limited stability [24].

The rate of hydrolysis is influenced by:

- Concentration
- pH- value
- Type, quantity of hydrolysis catalyst
- The organofunctional group
- The siliconfunctional group

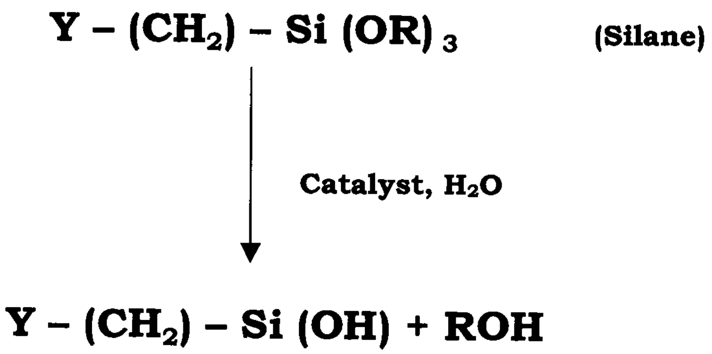


Figure 1. Acid catalyzed hydrolysis of silane to form silanol

BONDING TO THE INORGANIC SURFACE

This is in particular due to the formation of hydrogen bonds and chemical bonds between silanols and OH- groups of the inorganic substrate [21,24]. The efficiency of the bond between the silanol and the inorganic substrate is influenced by:

- The siliconfunctional group which affects the wetting properties and the reaction rate
- The organofunctional group which affects the wetting and film forming properties
- Drying. This is done after pretreatment and is advantageous to remove excess water and to complete the condensation of unbonded OH-groups of the silanols. The formed film improves the hydrophobic properties and protects the inorganic surface.
- The substrates itself: various inorganic materials have different surface activities with respect to silanes
- Additives which affect silane bonding and rate of reaction

CONDENSATION

The silanols can also undergo self-condensation. The reaction rate of the condensation depends on the silane concentration, type and quantity of hydrolysis catalyst, pH-value and additives [24].

BONDING TO THE POLYMER

The organofunctional group of the silane interacts with the functional group of the resin by chemical bonds or secondary bonds to establish a bridge between the polymer and the substrate. The organofunctional group has to be chosen as to ensure compatibility with the resin [20,24].

2.4.4.2. TITANATE COUPLING AGENTS

Titanate and zirconate coupling agents have been developed for use with particulate fillers rather than fibers [21]. They can be effective in preventing or reducing the agglomeration of particles, promoting adhesion, changing the degree of hydrophobicity, altering the rheology of a system, increasing the maximum filler loadings, and reducing the ageing rate of filled plastics and plastic coated metals [26,27].

I) Structure

As with silanes, a hydrolyzable component provides bonding with the filler, while a miscible or reactive component orientates toward the polymer portion of the composite. Titanates have the general structure:

$$(X)_m\text{-Ti-}(O\text{-}Y\text{-}R\text{-}Z)_n$$

- The **X** component

It is a hydrolyzable functional group, which bonds to a proton bearing substrate (the filler) [21,28].

- The **Y** group

This may be an alkylate, carboxy, sulfonyl, phenolic, phosphate, pyrophosphate or phosphite group which imparts specific properties not associated with the coupling ability of the additive, such as oxidation or corrosion resistance [21].

- The **R** group

It provides compatibility with the resin and other properties such as lubricity impact improvement and plastication [21].

- The **Z** component

The component is reactive with the resin, and is generally a methacrylate or amine functional group [21].

- Various combinations of m and n provide diversity in application and processing of the titanate coupling agents. Where m=1, n=3, the titanate is a monoalkoxy, recommended for thermoplastics and organic based systems. The chelates, m=4, n=2, are recommended for epoxies, urethanes, polyesters and alkyds [21,26].

II) Mechanism

The coupling mechanism is strongly dependent on the nature of the titanate and the exact nature of the substrate. The following categories can be identified as part of the general mechanism:

1. Alcoholysis (solvolysis)
2. Surface chelation
3. Coordination exchange
4. Coordination to salt formation
5. Polymer ligand exchange catalysis
6. Organic ligand interaction

2.4.4.3. MISCELLANEOUS COUPLING AND WETTING AGENTS

Various other chemicals are used as wetting agents for fillers [21]. These include esters, organosilicon compounds and chlorinated paraffins [21]. Most of the materials are proprietary and therefore have undisclosed chemical compositions. Whether or not these materials act as true coupling agents (i.e. bonding to both the filler and the resin) is unknown [21].

Many are thought to act by wetting the material surface and causing it to be hydrophobic, allowing better dispersion between the polymer and the filler. Characteristically, anionic wetting agents are used with acidic fillers, while cationic agents work best with acidic fillers [21]. There may be a synergistic effect between two or more coupling and wetting agents. For example, the chlorinated paraffins in conjunction with silanes improve coupling between glass fibers and polypropylene [21].

2.5. PROPERTIES OF FILLED AND REINFORCED POLYMERS

2.5.1. INTRODUCTION

Both extenders and reinforcing fillers normally increase the modulus of elasticity of the polymer, whereas tensile strength can only be improved by reinforcing fillers. Heat deflection temperature, that is, stiffness at elevated temperatures, cannot be increased to the same extent by extender fillers as by reinforcing fillers [11].

Extender fillers typically induce the following changes to thermoplastics:

- Increase in density
- Increase in modulus of elasticity
- Lower shrinkage
- Increase in hardness
- Improved surface quality
- Increase in heat deflection temperature
- Lowering of temperature dependence of the mechanical properties

- Cost reduction

Reinforcing fillers may normally produce the following additional changes to thermoplastics:

- Increase in tensile strength
- Increases compressive and shear strength
- Improves creep behavior

Two discreet phases are always present in reinforced plastics. The discontinuous filler phase should exhibit higher tensile strength and a higher modulus of elasticity than the polymer matrix, whereas the continuous plastic phase should possess a higher elongation at break than the filler. When a reinforced material is subjected to a tensile load, local tensile stresses are transferred to the plastic/fiber interface by sheer forces and distributed over the filler surface. For this purpose the filler must adhere well to the polymer. Coupling mechanisms between filler and plastic can considerably increase adhesion [11].

Various composites have different requirements. Table 2 summarizes the filler properties needed to meet these requirements.

Table 2. **Influence of filler/reinforcement properties on composite properties [11]**

Requirements to be met by the composite	**Filler/reinforcement properties required**
Manufacture of the composite	
Storage of the filler before compounding.	Low moister absorption, high bulk density
Optimum compounding	Mean particle size, good wettability by the polymer matrix, no static charges, good dispersion behavior, no shortening of the reinforcing fibers.
Low viscosity during compounding	Particles as round as possible, with small specific surface and low absorptivity, low surface energy.
High compounding speed	Low specific heat, high thermal conductivity
Processing of the composite	
Low shrinkage, low internal stresses, no cracks, quicker demoulding.	Low specific heat, high thermal conductivity, low thermal expansion, uniform filler distribution in the matrix, good adhesion between reinforcement and plastic
No abrasion problems in the processing machine.	Low hardness, small, round particles, good thermal stability of any surface treatment used.
Properties of the composite	
Mechanical properties:	
High tensile strength and elongation	High strength in comparison to the matrix, high aspect ratio and good fiber/matrix adhesion in case of reinforcing fibers, good distribution in matrix
High flexural strength	Same requirements as for high tensile strength, it is important to obtain a smooth surface in the finished article.
High compressive strength	Low compressibility, small, round filler particles for partly crystalline polymers
High modulus of elasticity (high stiffness)	High length/diameter ratio in fibrous or lamellar reinforcements, high modulus of elasticity in comparison to the matrix, high orientation, good adhesion to matrix

Table 2. Influence of filler/reinforcement properties on composite properties [11] continued.

Requirements to be met by composite	**Filler/reinforcement properties required**
High degree of hardness	High degree of hardness, particle size distribution suited to a high packing density, nucleating properties in partly crystalline polymers
Low abrasion	Low degree of hardness
Thermal properties	
Low thermal expansion	Small coefficient of thermal expansion, anisotropic, hard particles, good adhesion to matrix
Good flame and glow resistance	Favorable chemical composition, good thermal conductivity, high thermal stability
High heat deflection temperature	Good thermal stability
High resistance to thermal shock	High thermal conductivity
Electrical properties:	
Low dissipation factor, favorable dielectric constant, good insulating properties	Low moisture and plasticizer absorption, good adhesion to matrix, suitable electrical properties, insulating properties, nucleating action in partly crystalline polymers
Chemical properties:	
High chemical resistance	Suitable chemical composition
Good weathering properties	High U.V. resistance, good chemical resistance, water resistance, permanent bond with the matrix
Low water absorption	Low moisture absorption, permanent bond with the matrix
Optical properties:	
Good transparency	Suitable refractive index
Good shade	Suitable chemical composition
Good surface quality	Small, round or lamellar filler particles
Cost:	
Maximum possible degree of filling	Shape, size and distribution of the particles, low filler cost per unit volume

2.5.2. COMPOSITES CONTAINING MICA

Good chemical resistance, excellent weather resistance, low thermal conductivity, excellent dielectric properties and stability at high temperatures generally characterize micas. The properties of composites containing mica are highly dependent on the type of resin, the type of mica, method of fabrication, processing conditions, mica volume fraction, and degree of interfacial bonding [29].

The addition of mica increases the heat deflection temperature and modulus of a polymer. It may also increase the tensile and flexural strength of the composite although these properties are sensitive to the presence of coupling agents and flake orientation. Mica also improves the notched impact strength of some polymers while the unnotched impact usually decreases [29,30]. Table 3 illustrates the properties of mica filled HDPE [31].

Table 3. **Influence of mica on the properties of HDPE**

MECHANICAL PROPERTIES	CHANGE IN MATERIAL PROPERTIES
Tensile strength	When 25% silane coated mica was used, a 50% improvement in tensile strength was reached over the unfilled system. A reasonable increase in this property was also observed with uncoated mica
Bending strength and modulus	The bending strength of treated and untreated mica increased significantly as mica was incorporated into the system
Impact strength	The impact strength was reduced with the inclusions of mica. Silane treatment further reduced the impact strength.

2.5.2.1. PROPERTIES OF MICA

Mica is the group name for a broad class of aluminosilicate minerals of the phyllosilicate family. They are characterized by nearly perfect basal cleavage that permits the large crystals to be split or delaminated into thin, flexible flakes [5,29]

Flakes are a special class of discontinuous reinforcing fillers. They have an advantage over fibers because they can reinforce in a plane instead of along a single axis. In flake- reinforced composites, properties such as modulus, strength, thermal expansion and shrinkage are considered planner isotropic. Glass and mica are among the lower cost inorganic flake reinforcements. The Young's modulus of glass flakes and mica are 1.05x10^7 psi and 2.5x10^7 psi respectively [30].

Mica has been traditionally used as a filler primarily in phenolic and epoxy resins imparting dielectric, thermal and mechanical improvements [30]. The various micas, although structurally similar, may vary widely in chemical composition. However within any one variety, the compositions does not vary greatly. The prominent types of mica are muscovite and phlogopite [5]. The properties of the two prominent micas are given in Table 4.

Table 4. Properties of the two most prominent forms of mica

	Muscovite	Phlogopite
Formula	$K_2Al_4(Al_2Si_6O_{20})(OH)_4$	$K_2(Mg,Fe)_6(Al_2Si_6O_{20})(OH,F)_4$
Young's modulus	21 000 Mpa	21 000 MPa
Tensile strength	25 X 10^6 psi	25x10^6 psi
Ultimate tensile strength	37,000 – 43,000 psi	37,000 – 43,000 psi
Mohs hardness	2,8 – 3,2	2,5 – 3,0
Density	3.0 g/ml	2,9 g/ml
Bound water	4,5%	3,0%
Maximum use temp	600°C	1000°C
Acid resistance	Excellent	Decomposed by H_2SO_4
Color	Colorless, yellow, silver, green	Reddish-brown, brown, black

I) PHLOGOPITE

Phlogopite is a rarer member of the mica group and is not well known even by mineral collectors [32]. It is being mined for its heat and electrical insulating properties, which are considered superior to other micas [14]. The typical light brown color of phlogopite is characteristic although it is difficult to distinguish brown biotite from dark brown phlogopite. The two are actually end members in a series that is dependent on the percentage iron [32].

Phlogopite, like other micas, has a layered structure of magnesium aluminum silicate sheets weakly bonded together by layers of potassium ions. These potassium ion layers produce the perfect cleavage [32].

II) MUSCOVITE

Muscovite is the most widely used mica owing to its natural occurrence in large sheets. It is dioctahedral, with a theoretical composition 11.8% K_2O, 45.2% SiO_2, 38.5% Al_2O_3 and 45% H_2O [32,35]. Two thirds of the possible octahedral positions are filled and the octahedral sheet is populated with aluminum only. Muscovite is the most widely used mica [5].

2.5.2.2. EVALUATION OF MECHANICAL PROPERTIES

I) TENSILE PROPERTIES

Tensile test measurements are among the most important indications of strength in a material and are the most widely specified properties of plastic materials. Tensile strength, in the broad sense, is a measurement of a materials ability to withstand forces that tend to pull it apart and to determine to what extent the material stretches before breaking. Tensile modulus is an indication of the relative stiffness of a material. Different types of plastic materials are often compared on the basis of tensile strength, elongation and tensile modulus data [33].

II) FLEXURAL PROPERTIES

The stress- strain behavior of polymers in flexure is of interest to a designer as well as a polymer manufacturer. Flexural strength is the ability of the material to withstand bending forces applied perpendicular to its longitudinal axis. The stresses induced due to the flexural load are a combination of compressive and tensile stresses [33].

Flexural properties are reported and calculated in terms of the maximum stress and strain that occur at the outside surface of the test bar [33]. Many polymers do not break under flexure even after a large deflection. This makes determination of the ultimate flexural strength impractical for many polymers. In such cases, the common practice is to report flexural yield strength when the maximum strain in the outer fiber of the specimen has reached five percent. For polymeric materials that break easily under flexural load, the specimen is deflected until a rupture occurs in the outer fibers [33].

III) IMPACT PROPERTIES

The impact properties of polymeric materials are directly related to the overall toughness of the material. Toughness is defined as the ability of the polymer to absorb applied energy [33]. Impact resistance is the ability of a material to resist breaking under a shock loading or the ability to resist the fracture under stress applied at high speed, while impact strength is a measure of toughness [33].

The molecular flexibility is important when determining the relative brittleness or toughness of a material. For example, in stiff polymers like polystyrene, the molecular segments are unable to disentangle and respond to the rapid application of mechanical stress and the impact produces brittle failure. On the other hand, flexible polymers have high impact strengths due to the ability of the large segments of molecules to disentangle and respond rapidly to mechanical stress [33].

2.6. MODELS PREDICTING THE MECHANICAL PROPERTIES OF REINFORCED POLYMERS

2.6.1. YOUNG'S MODULUS

As discussed earlier, the incorporation of particulate fillers in polymers improves the modulus of the composites [9]. The modulus of such composites results from the interplay between the properties of the resin, the filler, and the interfacial region [34,35]. The modulus is affected by a number of parameters including the volume fraction, aspect ratio, shape, and orientation of the filler and the porosity in the composite [36]. A number of theories have been developed to describe how the above parameters affect the behavior of particulate filled polymers. These are discussed below.

I. The series and parallel models

In a two-phase material, different values of overall stiffness are obtained when components are in parallel or series, yielding Voigt and Reuss average moduli respectively (see Figure 2). For the case of parallel arrangement uniform strain is assumed in the two-phase. The effective moduli is given by

$$E_C = E_P V_P + E_M V_M \qquad (1)$$

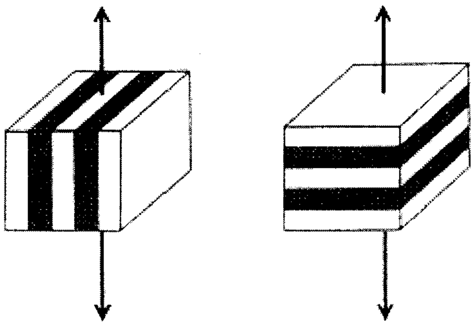
In the series arrangement the stress is assumed to be uniform in the two-phases. The effective modulus is given by

$$E_C = \frac{E_P \; E_M}{E_P \, V_M + E_M \, V_P} \tag{2}$$

For Equation 1 it is assumed that the Poison's ratios of constituent phases are equal, whereas for equation 2 v_C is given by

$$v_C = \frac{(v_P \, V_P \, E_M + v_M \, V_M \, E_P)}{(V_P \, E_M + V_M \, E_P)} \tag{3}$$

These equations are seldomly able to represent experimental data. This implies that the assumption of either a state of uniform strain or uniform stress in the individual phases of filled system is not sufficient to describe the modulus nor the tensile strength [35,36].



A: Isostrain (Voight)

B: Isostress (Reuss)

Figure 2: Mixing rule condition for layered composites

II. The Hirsh model

In this model the effective modulus is a summation of Equation 1 and 2

$$E_C = x\,(E_P V_P + E_M V_M) + \frac{(1-x)\quad E_P\ E_M}{E_P V_M + E_M V_P} \tag{4}$$

The parameters *x* and 1-*x* are the relative proportions of the material conforming to the upper and lower bound solutions respectively. When *x* is zero, Equation 4 reduces to Equation 2. For the perfectly bonded filler, when *x* equals one, the equation reduces to Equation 1[36].

III. The Takayanagi model

Takayanagi devised a series-parallel and parallel-series model as an aid to understand the viscoelastic behavior of a blend of two isotropic polymers in terms of the properties of the individual components [36]. In the series-parallel model the modulus is given by a combination of Equation 1 and 2

$$1/E_C = \frac{\alpha}{(1-\beta)E_M} + \frac{(1-\alpha)}{\beta_E P} \tag{5}$$

In the parallel-series model the modulus is given by

$$E_C = \beta(\alpha + \frac{(1-\alpha}{E_M} + \frac{1-\alpha)^{-1}}{E_M})\frac{(1-\beta)E_P}{E_P} \tag{6}$$

where α and β represent the state of parallel and series coupling in the composite respectively.

IV. The Counto model

Counto obtained the modulus for the two-phased media by assuming perfect bonding between the matrix and the particle [36]. The modulus of the composite is given by

$$1/E_C = \frac{(1-V_P^{1/2})}{E_M} + \frac{1}{(1-V_P^{1/2})/V_P\,E_M + E_P} \qquad (7)$$

V. The Paul model

Paul assumed that the constituents are in a state of macroscopically homogeneous stress. Adhesion is assumed to be maintained at the interface of a cubic inclusion embedded in a cubic matrix [36]. When a uniform stress is applied at the boundary the elastic modulus of the composite is given by

$$E_C = \frac{E_M\ (1+(m-1)V_P^{\ 2/3})}{1+(m-\ 1)(V_P^{\ 2/3}\ \ V_P)} \qquad (8)$$

in which $m = E_P/E_M$

VI. The Cox model

This model predicts the modulus for short fiber composites. It is assumed that the load transfer to the fibre from the matrix is by shear. The Young's modulus is given by

$$E_C = E_M\,(1-V_F\,) + E_F V_F\,(1-\frac{\tan h\,z}{z}) \qquad (9)$$

Where

$$Z = \frac{L}{2r}\ [\frac{2G_M}{E_F In(\frac{R}{r})}]^{1/2} \qquad (10)$$

L is the fibre length, *r* the radius and *2R* the center –to-center distance between the fibres. The filler shape was characterized by the aspect ratio, *p=l/2r* where *p>>1*.

VII. Verbeek 's model

He considered a system where the reinforcements are rectangular platelets aligned parallel to the applied force. The stress in the polymer layer is transferred to the flakes via shear mechanism [37]. Since the plates are discontinuous the shear force will be a maximum at the edges of the individual particles. Stress transfer occurs progressively along the platelet length and the shear approaches lower values at the middle of the platelet. For flakes within a infinite aspect ratio the modulus of the composite is given by the isostrain mixing rule [37]. This model takes into account that the modulus of the composite will approach zero as the volume fraction polymer approaches zero.

$$E_C = v_f\ E_M\ \mathrm{MRF} + v_P E_P \qquad (11)$$

Where the modulus reduction factor (MRF) is given by

$$\mathrm{MRF} = 1 - \frac{\tanh k}{k} \qquad (12)$$

$$k = \alpha \sqrt{\frac{(1-x)^3}{E_m} \frac{\nu_f}{(1-\nu_f)}} \tag{13}$$

$$x = \frac{\phi}{\nu_p(1-\phi)+\phi} \tag{14}$$

$$\phi = \frac{(1-\nu_p)^2 \varphi_m}{1-\nu_p \varphi_m} \tag{15}$$

Limitations of the theoretical models

- In the series and parallel model it is assumed that the individual phases are under uniform strain or uniform stress respectively. Practically filler particles may not be completely separated from one another and the reinforcement element may effectively be an aggregate of smaller particles. The applied stress will therefore not be distributed evenly between the particle and the aggregates and the assumption of either uniform stress or strain will not be valid [36,37].
- The elastic modulus depends on the volume fraction of the filler not the particle size. Lewis and Nielsen [38] showed that the modulus increased as the particle size decreased. This is due to the fact that the surface area increased providing a more efficient interfacial bond (36).
- Perfect adhesion is assumed between the filler and the polymer matrix. Sato and Furukawa [39] discussed the case of non-perfect adhesion. They

assumed that non-bonded particles act as holes and therefore there is a slight reduction in modulus [35,36].

- It is normally assumed that particles have uniform width and thickness and are uniformly distributed. The particle shape, size and distribution may in actual fact not be uniform. Polydispersed particles pack more densely than monodispersed particles. Densely packed particles may yield a higher modulus at the same volume fraction [36].

2.6.2. TENSILE STRENGTH

Models used for the prediction of tensile strength in filled systems are less developed than those for the modulus [36]. In the power law it is assumed that the strength of the particulate composite is determined by the effective available area of load bearing matrix due to the presence of the filler [36]. In the case of poor adhesion, there is no load transfer to the filler and the total load is carried by the matrix.

$$\sigma_C = \sigma_p(1 - av_f^b) \tag{16}$$

where σ_c and σ_p are the ultimate tensile strength of the composite and the matrix respectively, υ_f the volume fraction of the filler, a and b are constants depending on the assumed particle shape and orientation.

Fillers, which are irregular, turn to weaken the composition due to high stress concentration factors around their sharp edges. A stress concentration factor is introduced which takes into account the reduction in strength due to stress concentration caused by irregular shapes:

$$\sigma_C = \sigma_P(1 - av_f^b)K \tag{17}$$

In the Padawer and Beecher model, it is assumed that failure will be due to flake pull-out if the maximum calculated shear strength in the matrix exceeds the shear strength of the particle . This situation is described by

$$\sigma_C = v_P\sigma_P + K'_3\,\tau_P \mathrm{MPF} \tag{18}$$

where

$$\mathrm{MPF} = v_m\left(\frac{\alpha}{u}\right)\left(\frac{1}{\tanh(u)} - \frac{1}{u}\right) \tag{19}$$

$$u = \alpha\left(\frac{G_P v_f}{E_m(1 - v_f)}\right)^{1/2} \tag{20}$$

All models presented so far suffer the same drawback. This is because they all predict the modulus and strength to be that of the reinforcement at zero volume fraction polymer. This implies a monolithic filler.

Verbeek argued that the modulus and strength of composite is also strongly influenced by the porosity. In his model the strength and modulus of the composite is zero when no polymer is present [36]. He argued that the porosity of the composite influences the effective available area of load bearing matrix. He proposed that the composite modulus be reduced by the factor (1-χ). χ is determined from the porosity of the composite, as mentioned earlier.

$$\sigma_C = (\nu_P + K'_3 \tau_P \mathrm{MPF})(1 - \chi) \tag{21}$$

EXPERIMENTAL

3.1. MATERIALS

Table 5: List of materials

Material	Supplier
Ethylene vinyl acetate (EVA) (ELVAX), 18% vinyl content, MFI 2	Du Pont
Organofunctional silane A-171 (vinyl trimethoxy)	Union carbide supplied by Southern Chem.
Stearic acid	Merk (PTY) LTD. South Africa
Muscovite, particle size between 180 - 250μm(mesh 60)	Affirm Marketing Services. LTD
Phlogopite, particle size between 180 - 250μm(mesh 60)	Foskor LTD. South Africa

3.2. METHOD

Figure 3 depicts the general procedure followed for the preparation of the composite.

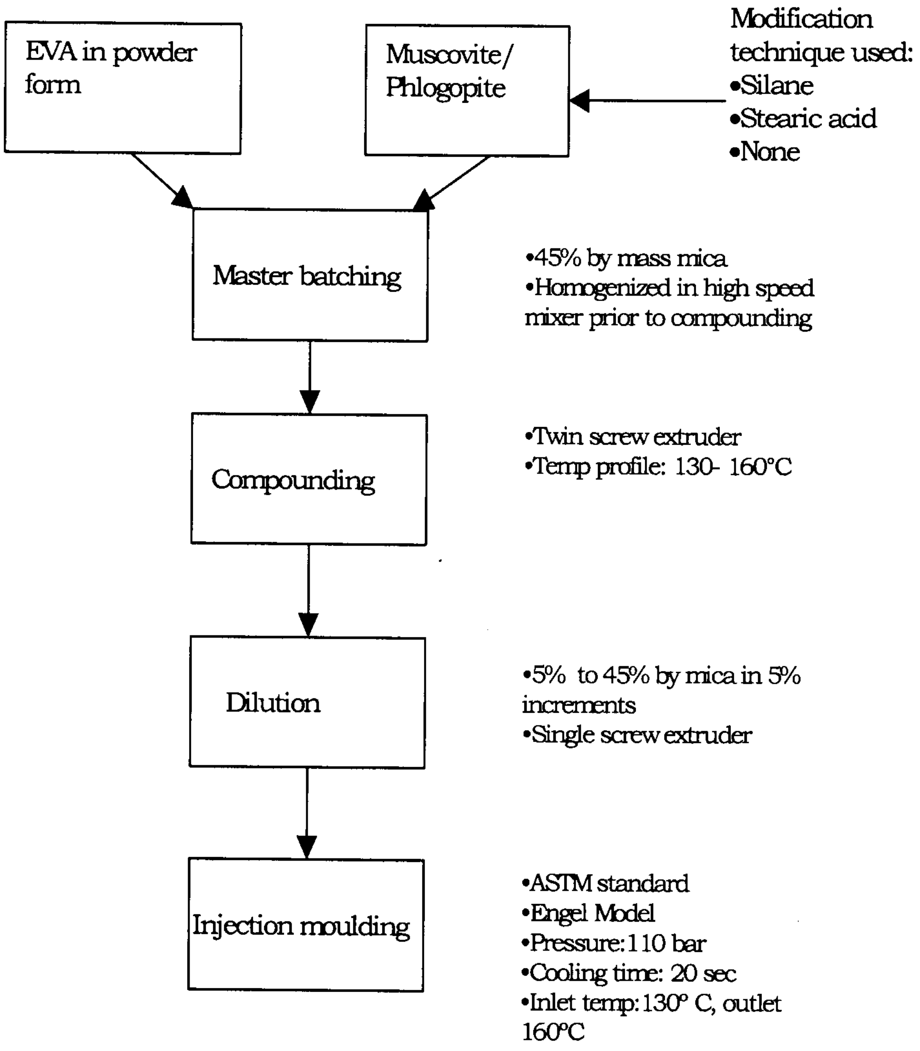


Figure 3: General procedure followed for the preparation of the composites

3.3. EQUIPMENT USED

High speed mixer :Jones industrial mixer, model HS25

Single screw extruder :Single screw extruder from Rapra technology.

The CTM :Self-driven CTM from Rapra Technology Ltd. and the extruder are used in conjunction to prolong the available residence time

Twin screw extruder :twin screw extruder from Berstorff with a capacity of 30 kW. The screw configuration includes kneading block to improve mixing.

3.4. EXPERIMENTAL OUTLAY

Table 4 provides a summary of all experiments performed with a brief description below.

Table 6. A summary for the description of the experiments performed

				Percentage polymer						
				5	10	15	20	30	40	45
Surface modification	None	Type of mica	Muscovite							
			Phlogopite							
	Stearic acid		Muscovite							
			Phlogopite							
	Silane		Muscovite							
			Phlogopite							

3.4.1. NON - SURFACE TREATED SYSTEMS

Experiment 1: To compare the reinforcing effect of muscovite and phlogopite in EVA

This experiment investigates the reinforcing effect of muscovite and phlogopite in injection moulded EVA. This is directed towards the improvement in mechanical properties such as tensile strength, Young's modulus, elongation at break and impact strength.

3.4.2. SURFACE TREATED SYSTEMS

Experiment 2: Influence of silane coupling agents on the mechanical properties of mica reinforced EVA.

In mineral filled composites, the important thing is to disperse the particle individually in the matrix. The issue is to separate the particle from aggregates and to promote wetting of the particles by the polymer. This experiment investigates the effect of surface modification of mica on the mechanical properties of EVA. The surface treatment will be done using siliquest A-171.

Experiment 3: To compare the reinforcing ability of phlogopite and muscovite in EVA using stearic acid.

A cheaper non-reactive coupling agent (surfactant) can also be applied in the surface modification of mineral fillers. One such material is stearic acid. The aim of this experiment is to determine the surface modification of stearic acid on mica by evaluating the mechanical properties of stearic acid treated mica filled EVA.

3.5. MECHANICAL TESTING

Equipment

Table 7: list of equipment used for mechanical testing

Analysis	Equipment
Tensile strength	Instron 1122 Capacity 5kN
Young's modulus	Instron 1122 Capacity 5kN
Elongation at break	Instron 1122 Capacity 5Kn
Scanning Electron Microscopy	Joel 840 scanning electron microscope
Tensile impact test	Zwick Impact Tester

Analytical methods

All experiments were repeated once and the values repeated are therefore an average of 5 specimens per sample (i.e. 10 specimens in total).

Tensile testing

Tensile properties were measured using an Instron testing machine. Tests were conducted in accordance with ASTM D 638. A crosshead speed of 50mm/ min was employed and the average value of 5 specimens were taken for each sample.

Tensile impact testing

The tensile impact test was done on a Zwick Impact Tester. It was determined according to ASTM D 1822. A 40kpcm hammer was used. A total of five specimens were tested for each sample at room temperature to obtain the average impact value.

SEM

Scanning electron microscopic studies of fractured samples were carried out on a Joel 840 scanning electron microscope. The accelerated voltage was 5kV. Samples were sputter coated with Polaron E5200, using gold to increase surface conductivity.

4. RESULTS AND DISCUSSION

4.1. YOUNG'S MODULUS

The Young's modulus is the tensile stiffness of the material. Generally the Young's modulus of a composite will increase with an increase in filler loading. Classical models used for predicting the Young's modulus also predict an increase in modulus with filler loading. Newer models, however, also predicts a decrease in modulus, approaching zero as the volume fraction polymer approaches zero. One such model also suggests that a maximum modulus will be reached at about 50% by volume filler [34].

Figure 4 shows the Young's modulus of non-surface treated muscovite and phlogopite reinforced EVA. It can be seen that the Young's modulus for phlogopite and muscovite reinforced EVA increases as the filler loading increases. It can also be seen that muscovite yielded similar results to phlogopite. The results are not surprising as the modulus of phlogopite and muscovite are very similar.

Figure 5 and 6 show the Young's modulus of silane treated and stearic acid treated muscovite and phlogopite reinforced EVA respectively. As expected the Young's modulus increased with an increase in filler loading. The Young's modulus for muscovite and phlogopite treated with stearic acid and silane, respectively, yielded similar results compared to those of the non-surface treated EVA. This similarity is due to the fact that the Young's modulus is measured at small deformation. Consequently, the strength of the interfacial interaction, which may be influenced by coupling agents, does not play a role in the actual value of the modulus.

Also shown in the Figures are the curves for the prediction of the modulus calculated using equations 2 and 11. The predicted values using equation 13 are very close to the experimental values as opposed to the prediction using equation 2.

The poor correlation of equation 2 could be due to the increase in porosity as the volume fraction of the filler is increased. In equation 2 it is assumed that the filler and the polymer phase are under equal stress, which is clearly not the case, since the phases are oriented parallel to the applied force. The voids will lower the modulus of the composite, as they cannot carry any load.

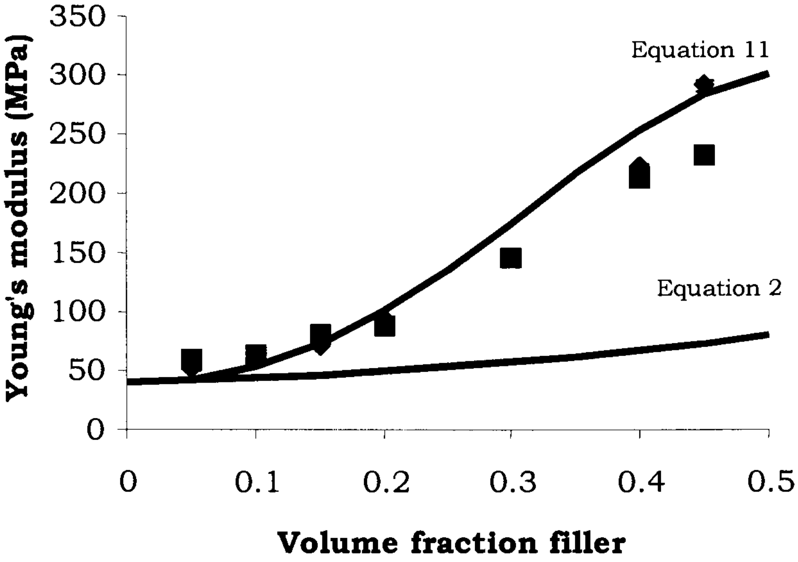


Figure 4: Young's modulus of EVA reinforced muscovite and phlogopite. ◆ - Phlogopite ; ■ - Muscovite

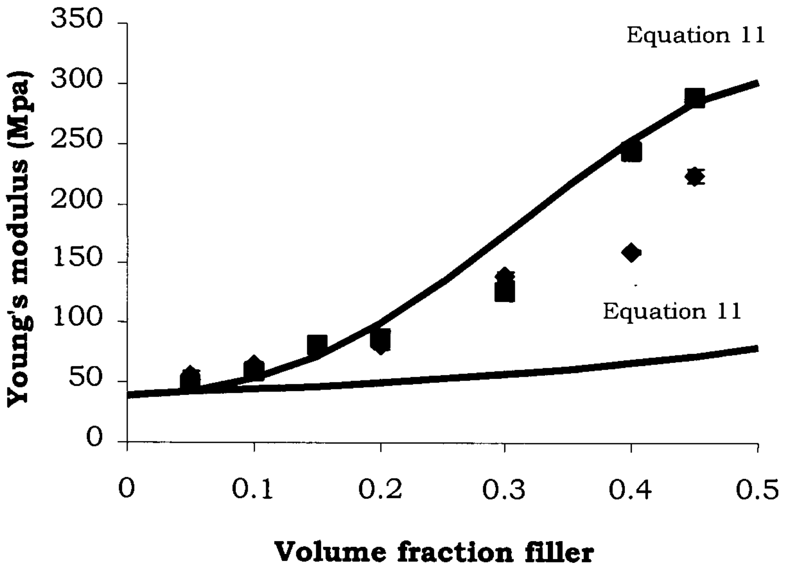


Figure 5: Young's modulus silane treated muscovite and phlogopite of reinforced EVA. ♦ - Phlogopite ; ■ - Muscovite

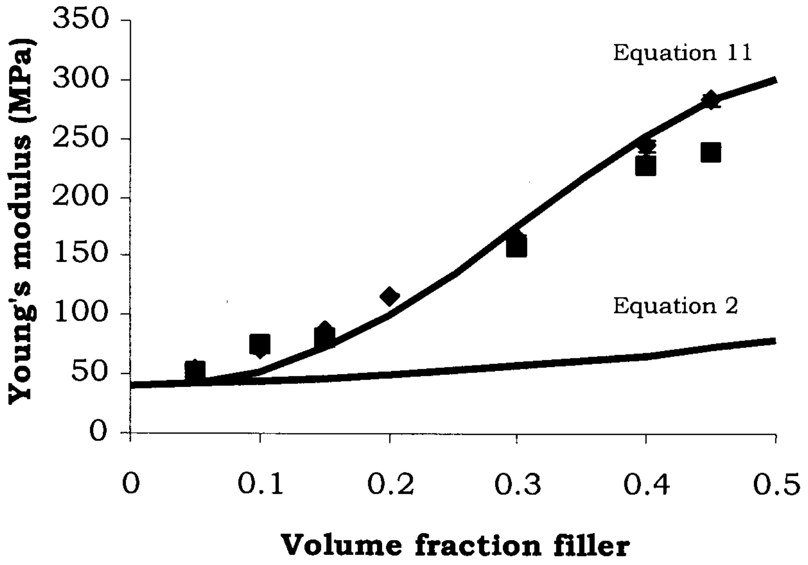


Figure 6: Young's modulus stearic acid treated muscovite and phlogopite of reinforced EVA. ♦ - Phlogopite ; ■ - Muscovite

4.2. TENSILE STRENGTH

The tensile strength of filled polymers is much more sensitive to factors such as interfacial adhesion, filler agglomeration and particle size. Figure 7 shows the tensile strength of muscovite and phlogopite reinforced EVA composites as a function of volume fraction filler. The tensile strength of the muscovite reinforced composites remained relatively constant at 8MPa, while the tensile strength of the phlogopite reinforced composites increased to about 12MPa.

Poor adhesion will usually lead to a reduction in tensile strength of polymers. The increase in tensile strength of phlogopite could be an indication of better interfacial adhesion between the EVA and phlogopite. Based on the chemical nature of muscovite (iron poor) and phlogopite (iron rich) [27] it might be possible that the adhesion between the phlogopite and EVA is slightly better than that of muscovite and EVA, given the slight polarity of EVA.

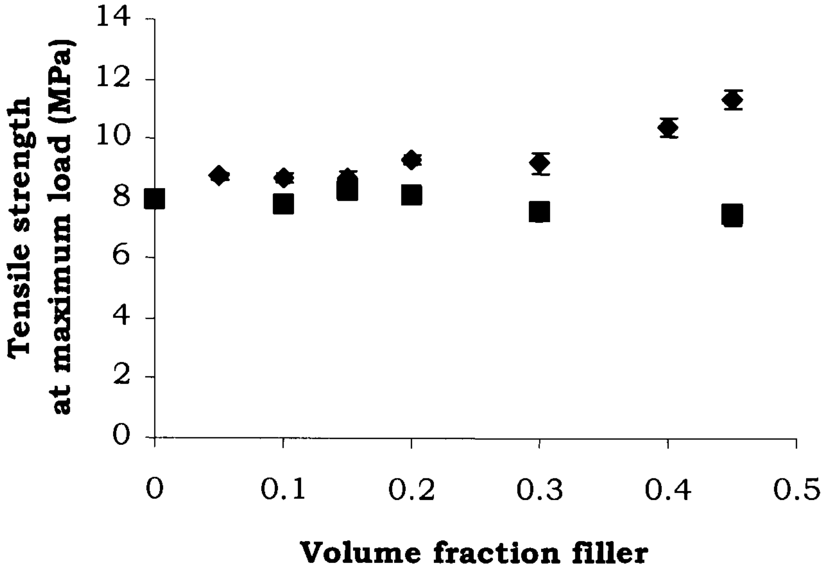


Figure 7: Tensile strength of EVA reinforced muscovite and phlogopite. ♦ - Phlogopite ; ■ - Muscovite

It can be expected that the inclusion of a coupling agent should improve the tensile properties of the composite under consideration. As can be seen from Figure 8, silane treated phlogopite reinforced EVA showed similar results as acompared to the non-surface treated system. Surface treatment is only one of the remedies for poor mechanical performance. It can therefore be concluded that the inclusion of a silane coupling agent does not offer any additional advantage for phlogopite reinforced composites. Silane did, however, improve the tensile strength of the muscovite reinforced composites at higher filler loadings.

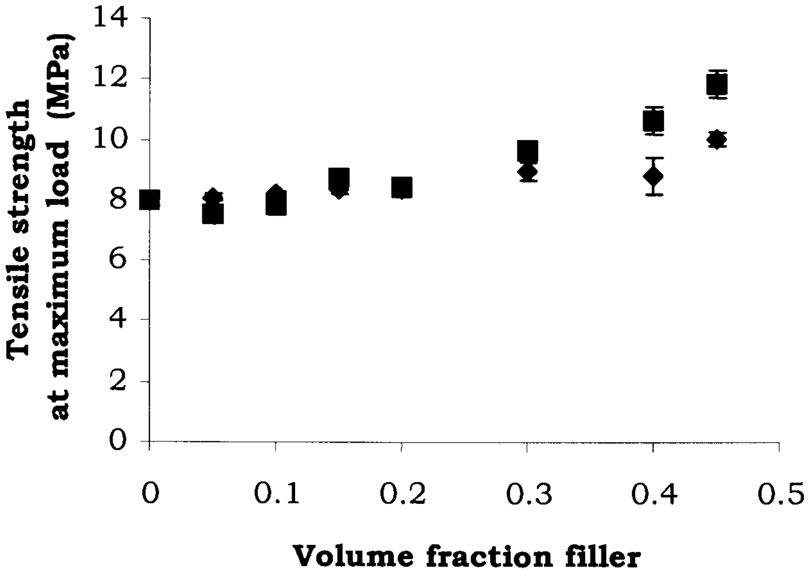


Figure 8: Tensile strength at maximum load of silane treated muscovite and phlogopite of reinforced EVA. ♦ - Phlogopite ; ■ - Muscovite

For comparative purposes, it was also decided to test the performance of a non-reactive surface modifier such as stearic acid. The results from Figure 9 show that, although the tensile strength of the phlogopite reinforced composites was higher than pure EVA, it was lower than the non surface treated system. Furthermore, the scatter in the data for the muscovite reinforced system suggest that stearic acid does not improve the tensile properties for this system. These results therefore suggest that stearic acid is not an effective coupling agent for mica and EVA.

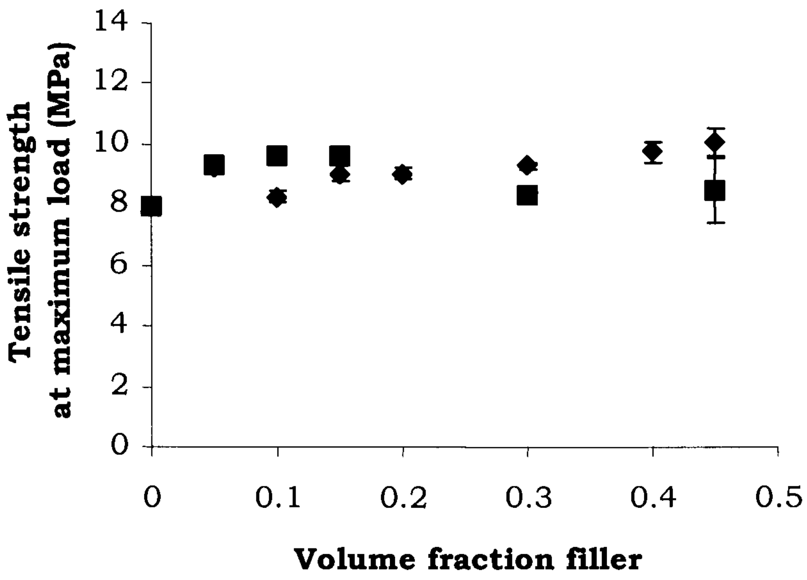


Figure 9: Tensile strength at maximum load of stearic acid treated muscovite and phlogopite of reinforced EVA. ♦ - Phlogopite ; ■ - Muscovite

4.3. ELONGATION AT MAXIMUM LOAD

Elongation for composites will be influenced by the mobility of the polymer chains. As the amount of filler in the composite is increased, one would expect that the mobility of the chains would decrease. This results in a composite with lower elongation values compared to that of the virgin polymer.

In figure 10, 11 and 12 one can clearly see the lower elongation values for all the systems tested at high filler loadings. An important observation, however, is that the stearic acid treated composites and the non-surface treated systems show an initial increase in elongation at lower filler loading. This effect may be due to filler-matrix which debonding exaggerates the effect of the elongation of the polymer chains. At higher filler loadings the chains are simply too restricted for significant elongations. This effect, however, is not present when silane is used as a surface modifier. This indicates better adhesion and therefore less filler-matrix debonding. This can also be seen, to a lesser extent, for the non-surface treated phlogopite composites.

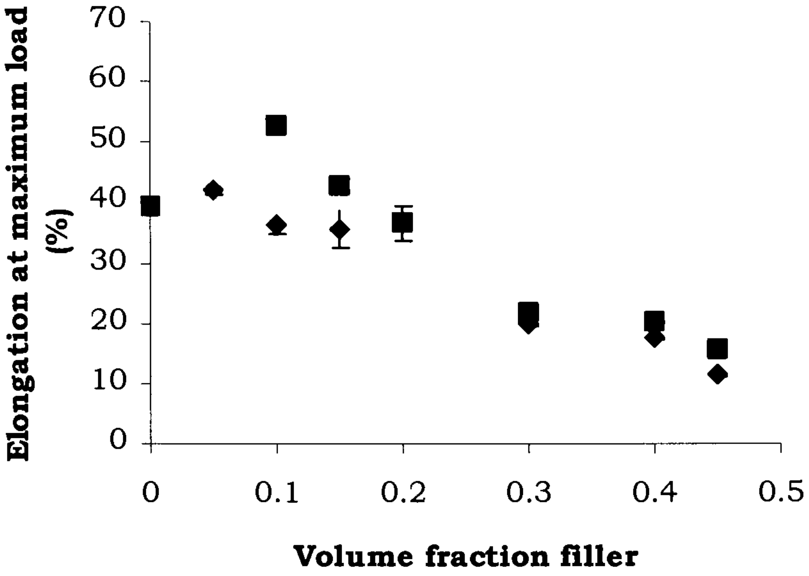


Figure 10: Elongation at maximum load of EVA reinforced muscovite and phlogopite. ♦ - Phlogopite ; ■ - Muscovite

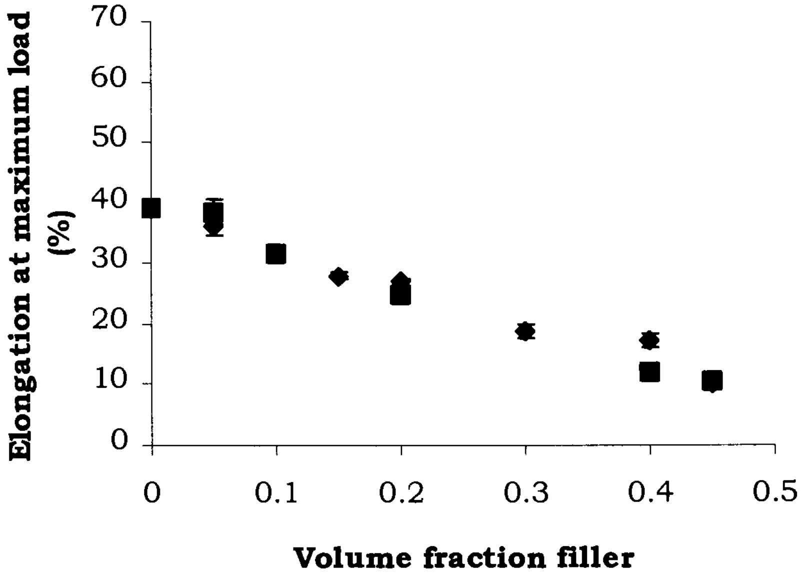


Figure 11: Elongation at maximum load of silane treated muscovite and phlogopite of reinforced EVA. ♦ - Phlogopite ; ■ - Muscovite

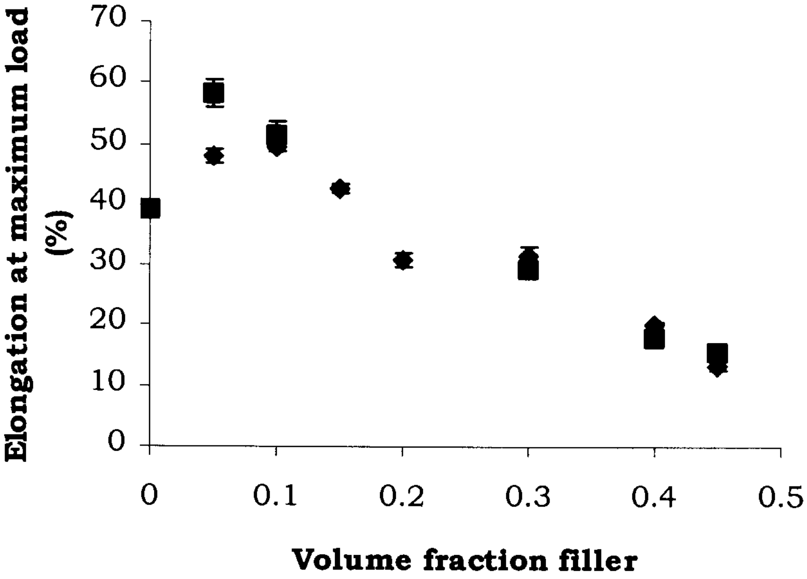


Figure 12: Elongation at maximum load of stearic acid treated muscovite and phlogopite of reinforced EVA. ♦ - Phlogopite ; ■ - Muscovite

4.4. TENSILE IMPACT STRENGTH

Impact strength is a complex interplay between the degree of adhesion between the filler and the polymer as well as the size and shape of the filler. It is generally known that most flaky mineral fillers will decrease the impact strength of polymers.

In Figure 13 the impact strength of phlogopite and muscovite reinforced composites are shown as a function of volume fraction filler. In the previous section it was suggested that the adhesion between phlogopite and EVA is slightly better than between muscovite and EVA. The results presented in Figure 13 show that the addition of phlogopite to EVA decrease the impact strength as expected. The difference between the adhesion of muscovite and EVA phlogopite and EVA is once again evident from the impact properties of the muscovite reinforced systems at low volume fractions.

If it is assumed that flake pull out is the predominant stress absorbing mechanism, then the very strong adhesion between a filler and a polymer may result in weaker impact properties. Optimal impact properties can be obtained when maximum energy is absorbed by the flake pull out process. Flake pull out will therefore lower the impact properties.

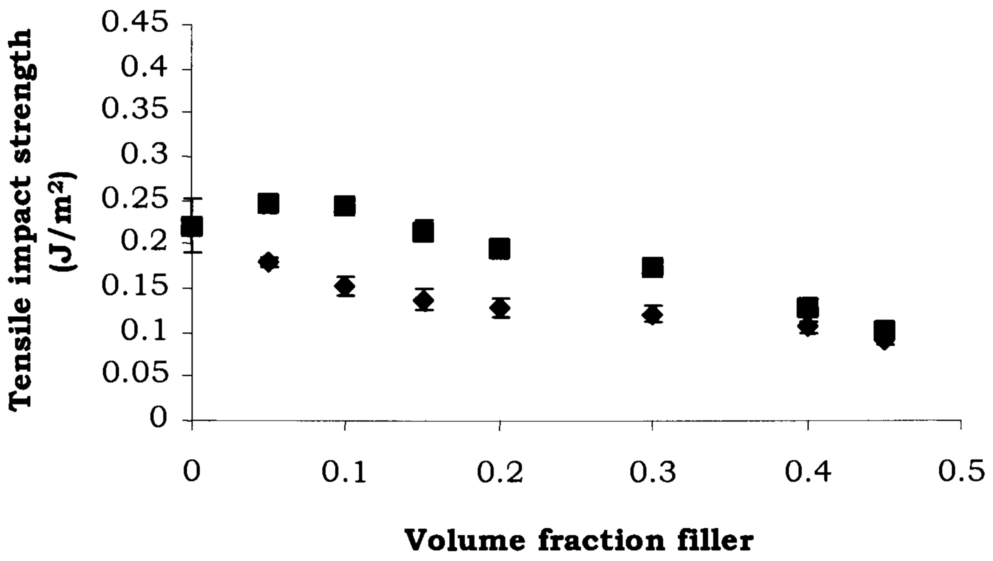


Figure 13: Tensile impact strength of EVA reinforced muscovite and phlogopite. ♦ - Phlogopite ; ■ - Muscovite

From Figure 14 it can be seen that the impact properties of the muscovite composites remains relatively unchanged despite the silane treatment. This indicates that although the adhesion might have improved it is still not a strong adhesion. In Figure 14 it can also be seen that the impact properties of the phlogopite composite increased in the lower volume fraction region, indicating that the adhesion is now weaker, compared to the untreated system.

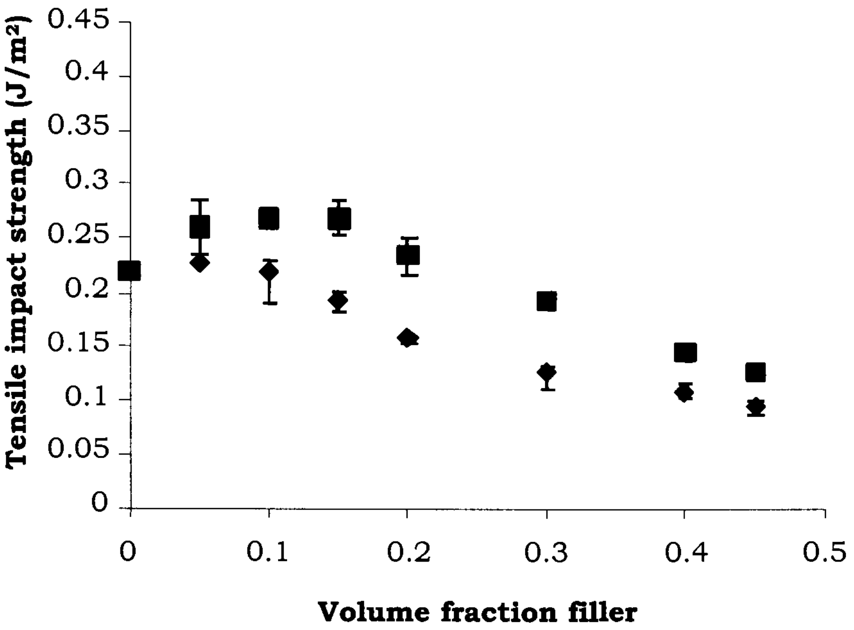


Figure 14: Tensile impact strength of silane treated muscovite and phlogopite of reinforced EVA. ♦ - Phlogopite ; ■ - Muscovite

These results correspond well to that of the stearic acid treated systems where it was said earlier that treatment with stearic acid actually decreases the adhesion for muscovite and phlogopite. In Figure 15 it can be seen that the muscovite composites showed a great increase in impact strength and phlogopite composites behaved similarly to that of the silane treated systems.

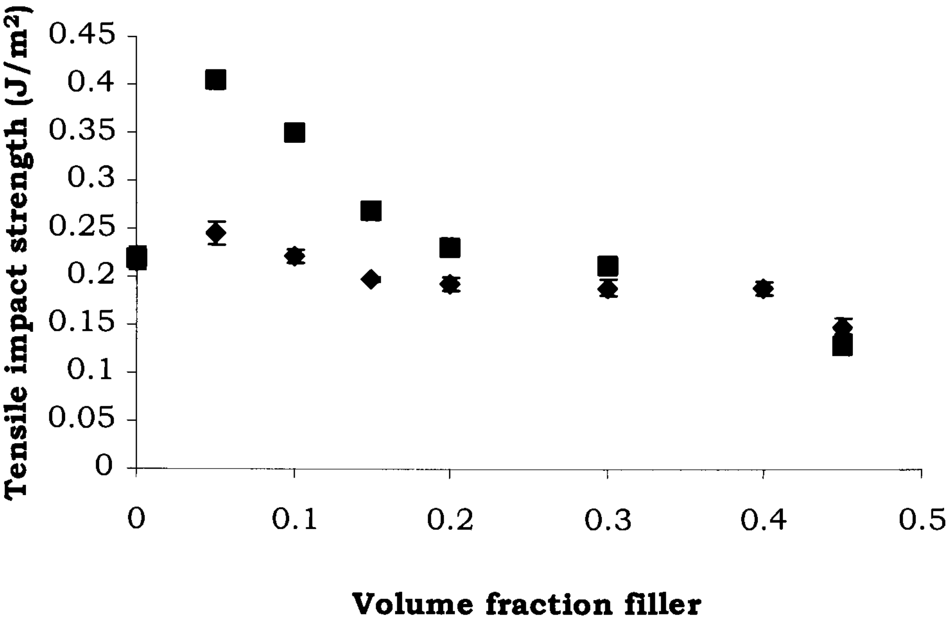


Figure 15: Tensile impact strength of stearic acid treated muscovite and phlogopite of reinforced EVA. ♦ - Phlogopite ; ■ - Muscovite

4.1.5. SEM

Adhesion between the filler and the matrix is not the only factor that can contribute to poor mechanical performance. Flake miss-alignment, flake irregularities, porosity and filler agglomeration can cause a great reduction in the mechanical properties. SEM photomicrographs of the fractured surface of the muscovite (Figure 16) and phlogopite (Figure 17) reinforced EVA show possible flake agglomeration, which indicated the need for coupling agents. Also evident from these photos are the streaky protrusions formed at the edges of the phlogopite composites. This is normally an indication of good adhesion.

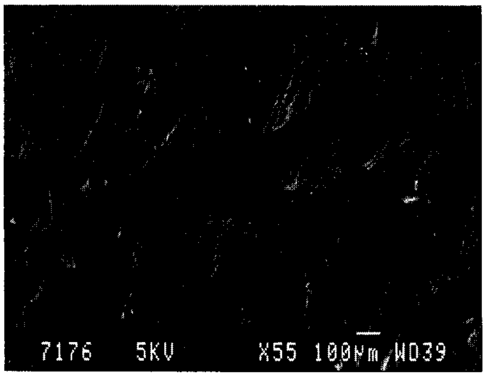


Figure 16: SEM of EVA fractured composite containing muscovite

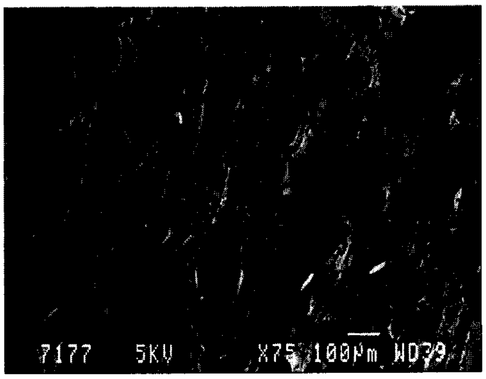


Figure 17: SEM of EVA fractured composite containing phlogopite

4. CONCLUSIONS

The reinforcing ability of muscovite and phlogopite were compared by evaluating the mechanical properties of the EVA/mica composites. The Young's modulus increased as the amount of filler content increased. It is, however, not unexpected that the Young's modulus of the composite increases with filler content. Surface treatment had no effect on Young's modulus. It is known that the Young's modulus is relatively unaffected by the degree of interfacial adhesion and therefore the composite modulus will simply increase as stiffer material is added to the matrix [15].

Interfacial adhesion does, however, influence the tensile strength of reinforced composites. It was found from the experiments performed that the adhesion between phlogopite and EVA is better than that of muscovite and EVA. This was evident from the improved tensile strength of phlogopite reinforced EVA compared to that of muscovite reinforced composites from the non-surface treated composites. Muscovite yielded better results in terms of elongation and tensile impact strength when compared to the non-surface treated phlogopite, which further supports the better adhesion of phlogopite when compared to muscovite.

Treatment by silane did not offer any additional advantage on the tensile properties for phlogopite reinforced composites. Silane did, however, improve the adhesion between muscovite and EVA. This was evident from the improved tensile strength, lower impact strength and lower elongation when compared to the non-surface reinforced composites.

It was also found that the stearic acid has limited success as a coupling agent. The tensile strength for both phlogopite and muscovite was reduced; the elongation and tensile impact strength were increased when compared with the non-surface treated reinforced composites.

Based on the information given above it can be concluded that phlogopite is only slightly superior to muscovite as a reinforcing agent in EVA. However, for most properties, the reinforcing ability of muscovite and phlogopite are similar.

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7. Appendix

7.1. SURFACE TREATMENT

A1. Application of Organofunctional silane A-171

Both phlogopite and muscovite were coated with a silane-coupling agent in the following manner: it was applied by immersing either filler (100g) in 1% solution of ethanol (1g silane in 100ml of ethanol). The filler was then allowed to mix with the coupling agent. Excess ethanol was then filtered off. The filler was then left overnight so that the ethanol can evaporate. To insure that the coupling agent adhered tightly to the filler surface, the air-dried filler was placed in an oven at 110°C for three hours.

A2. Application of stearic acid

Surface treatment of phlogopite and muscovite was carried out in solution. 100 g of either filler was immersed in butanol solution containing 1% stearic acid (1g stearic acid in 100 ml of butanol). The filler was then allowed to mix with the solution. The suspension was then left standing for three days, and then the butanol was removed by filtering it off. The filler was air-dried.

A.3. Preparation of samples

Compounding of EVA and either of the two fillers i.e. phlogopite and muscovite was done using a high-speed mixer. The mixing of EVA with both fillers was done using the following steps

- The samples of EVA and muscovite/ phlogopite were weighed.
- Both the EVA and the filler were poured into a high-speed mixer. This was done in order to homogenize the dry blend.

The homogeneous dry blend was then compounded in a twin extruder to melt-mix the compound.

7.2. Mechanical testing and Conditioning

Conditioning (ASTM D 618)

A true material comparison is possible only when property values are determined by identical test methods under identical conditions. Temperature and humidity affect physical and electrical properties of plastics and electrical insulating materials. Plastics tested above room temperature will yield relatively higher impact strength and lower tensile strength and modulus. In order to make reliable comparison of different materials and test result obtained by different laboratories, it is necessary to establish standard conditions of temperature and humidity.

Conditioning is defined as a process of subjecting a material to a stipulated influence or combination of influences for a stipulated period of time. Three basic reasons for conditioning of a specimen are:

- To bring the material into equilibrium with normal or room conditions
- To obtain reproducible results regardless of previous history or exposure
- To subject the material to abnormal conditions of temperature and humidity in order to predict its service behavior

STANDARD LABORATORY TEMPERATURE: this is defined as 23°C with a standard tolerance of ±2°C

STANDARD LABORATORY ATMOSPHERE: this is defined as an atmosphere having a temperature of 23°C and a relative humidity of 50 percent with a standard tolerance of ±2°C and ±5 percent, respectively.

DESIGNATION FOR CONDITIONING

Conditioning of a test specimen is designated as:

A/B/C

Where A= a number indicating duration of conditioning (hrs); B= a number indicating conditioning temperature (°C); C= a number indicating relative humidity (percentage or a word) to indicate immersion in a liquid.

A sequence of conditioning is denoted by use of a plus (+) sign between successive conditions.

Methods for mechanical testing and equipment selection

Tensile test (ASTM D 638).

A. Apparatus

The tensile testing machine of a constant-rate-of-crosshead movement is used. It has a fixed or essentially stationary member, carrying one grip and a movable member carrying a second grip. Self-aligning grips employed for holding the test specimen between the fixed member and the movable member prevents alignment problems. A controlled velocity drive is used. Some of the commercially available machines use a closed loop servo-controlled drive mechanism to provide a high degree of accuracy. A load- indicating mechanism capable of indicating total tensile load with accuracy of ±1 percent of the indicated value or better is used. An extension indicator, commonly known as the extensiometer, is used to determine the distance between two designated points located within the gauge length of the test specimen.

B. Test procedures.

Tensile strength

The speed of testing is the relative rate of motion of the grip or test fixtures during the test. There are four different testing speeds specified in the ASTM D 638 standard. The most frequently employed speed of testing is 0.2 in/min. The test specimen is positioned vertically in the grips of the testing machine. The grips are tightened evenly and firmly to prevent any slippage. The speed of testing is set at the proper rate and the machine is started. As the specimen elongates, the resistance of the specimen increases and is detected by a load cell. The instrument records this load value (force). The elongation is continued until a rupture of the specimen is observed. Load value at break is also recorded. The tensile strength at yield and tensile strength at break is calculated [13].

Tensile modulus and elongation

Tensile modulus and elongation values are derived from a stress-strain curve. An extensiometer is attached to the test specimen. The extensiometer is a strain gauge type of device that magnifies the actual stretch of the specimen considerably. The simultaneous stress-stain curve is plotted on graph paper. A given procedure is followed to carry out the calculation [13].

Tensile impact test (ASTM D 1822)

The tensile impact strength was developed to overcome the deficiencies of flexural (izod and charpy) impact tests. Unlike izod-charpy-type pendulum impact tests, which are limited to thick specimens only, the tensile impact test allows the user to determine the impact strength of very thin and flexible specimens.

A. Apparatus

The tensile impact testing machine consists of a rigid massive base with a suspending frame. The pendulum is specially designed to hold the dumbbell-shaped specimen so that the specimen is not under stress until the moment of impact.

B. Test procedure

The thickness and width of the test specimen are measured with a micrometer. The specimen is clamped to the crosshead while the crosshead is out of the pendulum. The whole assembly is placed in the elevated pendulum. The other end of the specimen is bolted to the pendulum. The pendulum is released and the crosshead is allowed to strike the anvil. The tensile impact energy is measured and recorded from the scale reading

7.3. Parameter values used in models

Table 8: Parameter values used in models

	Polymer (EVA)	Muscovite	Phlogopite
Density	0.939 kg/m³	2.900 g/cm³	3 g/cm³
Plate aspect ratio		18	18
Maximum packing density		0.5	0.5
Young's modulus	40 Mpa	21000 Mpa	21000 Mpa
Shear strength	14.815 Mpa		
Tensile strength		25 X 10^6 psi	25 X 10^6 psi

7.4. Results

Table 9. Mechanical properties of EVA/muscovite composites

Volume fraction filler	Elongation at break(%)	STDV	tensile strength (Mpa)	STDV	Young's modulus (Mpa)	STDV	Tensile impact strength	STDV
0	38.724		8.073		48.93		0.22	
10	52.87	0.96192	7.8012	0.23121	63.72	2.16689	0.24377	0.01116
15	42.9	1.22867	8.2515	0.08358	80.1187	1.20255	0.2156	0.00349
20	36.66	2.91068	8.11566	0.02558	88.9433	1.02660	0.19538	0.01324
30	21.95	0.68589	7.57366	0.29797	146.587	2.07876	0.17456	0.00349
40	20.1225	0.31436	9.02533	0.01150	213.083	4.86535	0.1274	0.00849
45	15.7266	0.48757	7.4845	0.48154	232.166	3.78439	0.1029	0.00349

Table 10. Mechanical properties of EVA/phlogopite composites.

Volume fraction filler	Elongation at break(%)	STDV	tensile strength (Mpa)	STDV	Young's modulus (Mpa)	STDV	Tensile impact strength	STDV
0	38.724		8.073		48.93		0.22	
5	42.028	0.77921	8.75062	0.10933	52.1321	2.00890	0.17885	0.00464
10	36.44	1.52561	8.69216	0.17024	59.5545	0.90109	0.15251	0.01154
15	35.4825	2.99753	8.68575	0.23794	72.0075	2.34809	0.1372	0.01154
20	21.452	0.81591	9.31888	0.15432	93.7608	2.05816	0.12801	0.01091
30	20.0022	0.60871	9.20788	0.36073	146.457	2.33422	0.12127	0.00908
40	17.7837	0.41757	10.4036	0.31516	223.416	5.19259	0.10596	0.00635
45	11.4266	0.17374	11.356	0.29194	291.383	11.8263	0.09003	0.00349

Table 11. Mechanical properties of EVA/muscovite composites.(silane treated)

Volume fraction filler	Elongation at break(%)	STDV	tensile strength (Mpa)	STDV	Young's modulus (Mpa)	STDV	Tensile impact strength	STDV
0	38.724		8.073		48.93		0.22	
5	38.4787	2.14774	7.53402	0.18491	47.9936	0.9596	0.26092	0.01174
10	31.7425	0.81330	7.8718	0.28798	60.1066	1.45627	0.2695	0.00718
15			8.7734	0.22222	81.785	1.85819	0.2695	0.00306
20	24.99	1.00264	8.41715	0.19444	86.874	1.68812	0.23397	0.00705
30			9.6796	0.10137	126.5	0.98994	0.19355	0.00792
40	12.1744	0.65718	10.6247	0.44992	244.783	6.96862	0.14455	0.00663
45	10.6097	0.29317	11.8685	0.43480	288.275	3.07055	0.12678	0.00827

Table 12. Mechanical properties of EVA/phlogopite composites. .(silane treated)

Volume fraction filler	Elongation at break(%)	STDV	tensile strength (Mpa)	STDV	Young's modulus (Mpa)	STDV	Tensile impact strength	STDV
0	38.724		8.073		48.93		0.22	
5	35.975	1.17525	8.0824	0.12905	56.5575	2.99748	0.22723	0.02538
10	31.7152	0.87717	8.20231	0.09188	64.9154	1.30358	0.21988	0.00792
15	28.012	0.67598	8.37653	0.12814	79.4725	1.13474	0.19355	0.01611
20	26.9226	0.43243	8.35525	0.19331	81.0441	2.21793	0.1568	0.01611
30	18.802	1.29028	8.9612	0.30673	139.685	3.50299	0.12495	0.00792
40	17.347	1.25967	8.8491	0.60401	160.383	2.44574	0.10718	0.00792
45	10.0159	0.38383	10.0548	0.24757	223.45	5.33463	0.09371	0.00556

Table 13. Mechanical properties of EVA/muscovite composites. (Stearic acid)

Volume fraction filler	Elongation at break(%)	STDV	tensile strength (Mpa)	STDV	Young's modulus (Mpa)	STDV	Tensile impact strength	STDV
0	38.724		8.073		48.93		0.22	
5	59.0767	2.01315	9.28997	0.24056	53.1766	0.50991	0.40425	0.36443
10	47.628	1.78828	9.64522	0.23202	75.5883	1.68598	0.34912	0.36443
15	42.2775	1.58745	9.6306	0.16390	80.7433	1.97305	0.2695	0.27256
20	0	0					0.23091	0.22662
30	27.7758	0.91496	8.31370	0.17612	157.858	3.83144	0.21253	0.21743
40	17.2741	0.48648			227.8	4.35698		
45	15.61	1.08752	8.45125	1.05629	239.9	7.03775	0.12923	0.13475

Table 14. Mechanical properties of EVA/phlogopite composites. (Stearic acid)

Volume fraction filler	Elongation at break(%)	STDV	tensile strength (Mpa)	STDV	Young's modulus (Mpa)	STDV	Tensile impact strength	STDV
0	38.724		8.073		48.93			
5	47.842	1.22446	9.2026	0.09777	54.506	1.82544	0.24561	0.22662
10	45.534	0.84695	8.25192	0.18896	70.8271	1.05350	0.22111	0.22968
15	35.1016	0.75272	9.03685	0.25006	87.7232	0.85826	0.19722	0.18681
20	32.498	1.04540	9.02829	0.20222	116.545	1.41768	0.19355	0.18681
30	28.4206	1.08889	9.51	0.11199	165.462	2.26522	0.18865	0.18068
40	19.2687	0.86400	9.73483	0.33932	244.8	5.31836	0.18803	0.18068
45	14.37	0.53839	10.0645	0.48477	283.866	5.21376	0.14822	0.14393