

## CHAPTER 2

### THEORY AND LITERATURE REVIEW

#### 2.1 Polyethylene

There is a large group of polymers formed by polymerizing monomers containing the C=C group. Since ethylene, containing the olefinic double bond  $\text{CH}_2=\text{CH}_2$ , is the simplest monomer that contains this structure, all other polymers having a substituted ethenic base could also be called ethenic polymers (2,3).

Although the chemical notation for the polymerization of ethylene indicates a simple reaction,



the properties of the polymer vary over a wide range, depending on molecular weight, the method of manufacture, and differences in structure. At one time these variations in structure were thought to be minor, but they are actually of such importance that entire areas of application are influenced.

The actual commercialization of polyethylene came as a result

of the research in 1933 by Dr. E. Fawcett and Dr. R.O. Gibson of the Imperial Chemical Industries (ICI) in England. Their discovery was a result of investigating the reaction of benzaldehyde and ethylene (obtained from coal) under high pressure and temperature. By 1954 two new production processes were developed for the production of polyethylene with densities of 0.91 to 0.97. One process developed by Karl Ziegler and associates in Germany permitted polymerization of ethylene at low pressures and temperatures in the presence of aluminum triethyl and titanium tetrachloride (catalysts). At about the same time the Phillips Petroleum Company developed a polymerization process using low pressures with a chromium trioxide promoted, silica-alumina catalyst.

The two most widely used grades of polyethylene are low density polyethylene, LDPE, which has branched chains, and high density polyethylene, HDPE, which is predominantly linear. Low density polyethylene is produced by a free radical initiated polymerization at high pressures while high density polyethylene is produced by a low pressure process with a metallic oxide catalyst of the Ziegler type.

Because of the intensity of polymerization conditions, the high pressure process tends to form molecules with side chains. These branches vary from one to five or more carbons in length and may be one to three in number for every 100 carbons in the main chain.

Any changes in the amount of branching in a polymer will affect the tendency to form crystallites and spherulites. In general, for a polymer which tends to crystallize, greater linearity (less branching) will increase the ratio of crystalline to amorphous regions. The percentage crystallinity will have a significant effect on properties. Greater crystallinity causes higher density, so more linear polymers are known as high density polyethylene.

### 2.1.1 Physical and chemical properties

The processes now used to produce polyethylene for plastics by no means cover the entire range of possible products. Oils and waxes may also be made by modifications of these polymerization processes. The molecular weight/crystallinity relationships allow the generation of a wide range of properties in both waxes and plastics.

The most important intrinsic properties of commercial polyethylenes indicating performance in principal applications are : (1) density, (2) melt index, and (3) molecular weight distribution.

#### (1) Density

The complete range of densities encountered in polyethylene extends from 0.910 to 0.965. The tremendous change of properties with density is reflected in the need to express densities



to three decimal places. A change of three in the third place produces appreciable property changes. In general, as density increases: (a) linearity increases, (b) stiffness increases, (c) tensile strength increases, (d) tear strength increases, (e) softening temperature increases (f) brittleness increases, (g) flex life decreases, and (h) tendency toward stress cracking increases.

In commercial practice, polyethylene is often classified into low-, medium-, and high-density groups to aid in predicting its properties. Low-density is below 0.925, medium extends from 0.925 to 0.940, and high from 0.94 to 0.965 gm/cm<sup>3</sup>.

## (2) Melt index

The most widely used correlation relating properties of polyethylene to average molecular weight is the melt index. The melt index is the weight of polyethylene extrudable in 10 minutes through a fixed orifice at 190°C, when a standard weight is applied to a piston operating in an extrusion chamber containing 3 grams of polyethylene. The melt index is roughly, but by no means exacty, inversely proportional to the melt viscosity, which in turn increases with average molecular weight.

Thus, a high melt index indicates greater fluidity at processing temperatures. Melt index was developed originally to indicate flow properties as a measure of extrudability.

In addition, as melt index increases, tensile strength decreases, and toughness decreases.

### (3) Molecular weight distribution

Molecular weight distribution affects the properties of polyethylene as well. As the  $M_w/M_n$  ratio increases, tensile strength decreases, brittleness increases, softening temperature decreases, tendency toward stress cracking increases, and toughness decreases.

Thus, there have three properties that are intrinsic for any particular grade of polyethylene: density related to linearity, melt index based on average molecular weight, and  $M_w/M_n$  proportional to molecular weight distribution. Since all of these variables affect some of the same mechanical properties, different combinations will generate a spectrum of properties, as can be seen in Table 2.1

Polyethylene has excellent resistance to both corrosive chemicals and solvents at room temperature. However, its resistance to solvents changes rapidly with temperature and exposed surface conditions, especially where elevated temperature may be encountered.



Polyethylene is subject to environmental stress-cracking. Some formulations are much more resistant than others. In addition to variations between polymer types, the resistance of any polyethylene to stress-cracking increases rapidly as the melt index of the material decreases below about 1. Whether or not a stress-cracking hazard exists in any particular situation involving contact of a liquid with polyethylene, therefore, depends upon the degree and type of stress on the polymer, the particular liquid involved, and the particular formulation.

Water and water solution of inorganic salts normally do not exhibit activity as stress-cracking agents, but water solution of detergents are very active in this regard. Some of the concentrated mineral and organic acids and concentrated aqueous solutions of the alkali hydroxides exhibit stress-cracking activity. Most organic liquids, under the proper conditions, are stress-cracking agents.

Although the mechanical properties of polyethylene vary widely, as discussed earlier, they are considered average or below average when compared to other plastics materials. The electrical properties of polyethylene, on the other hand, are outstanding. Polyethylene is free from taste, odor, and toxicity and, of course, is very lightweight. It is perhaps the easiest of the thermoplastics to process, being adaptable to all types of high-volume molding and extrusion. It can be molded in a wide range of sizes, thickness, and under a board range of molding conditions.

Table 2.1 Intrinsic Properties that Affect Polyethylene Resins.(3)

Physical properties	If Density Increases	If Melt Index Increases	If MWD Broadens
Melt viscosity	Higher	Lower	-
Vicat softening point	Much higher	Lower	Lower
Surface hardness	Higher	Slightly lower	Lower
Tensile strength			
Yield	Much higher	Slightly lower	Lower
Break	Slightly higher	Lower	Lower
Elongation	Lower	Lower	Higher
Creep resistance	Higher	Slightly lower	Higher
Flexural stiffness	Much higher	Slightly lower	-
Flexibility	Lower	-	-
Toughness	Lower	Lower	Lower
Low temperature brittleness	Lower	Lower	Higher
Stress crack resistance	Lower	Lower	Higher
Optical properties			
Transparency	Higher*	Higher	-
Freedom from haze	Higher*	Higher	-
Gloss	Higher*	Higher	-

Table 2.1 Intrinsic Properties that Affect Polyethylene Resins.  
(continued)

Physical Properties	If Density Increases	If Melt Index Increases	If MWD Broadens
Barrier properties			
MVT rate	Lower	-	-
Gas and liquid Transmission	Much lower	-	-
Grease proofness	Much higher	Slightly lower	-
Electrical properties	Slightly higher	No effect	-

\*Not true in the high-density range.

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### 2.1.2 Processing and production

Today, it is possible to produce polyethylene with branched chains or linear chains by either the high pressure (ICI) or low pressure (Ziegler, Phillips, Standard Oil) methods.

#### (1) High-Pressure Polyethylenes

The high-pressure process requires ultrahigh-purity ethylene (less than 0.2% CO, acetylene, O<sub>2</sub>, and moisture). Oxygen and peroxides act as catalyst. The ethylene is compressed to 1360 kg/cm<sup>3</sup> and heated to around 200°C. It is fed to a bank of autoclaves where the stagewise reaction takes place. Because catalyst concentration directly affects the average molecular weight, it is added at carefully controlled rates. The reaction is highly exothermic; thus, extremely good heat transfer is required to prevent runaway reactions.

From the reaction stages, the polymer/monomer mixture is sent to a series of separators, from which the monomer is recycled back to the compressors, and the overall system pressure is reduced to below atmospheric. The polyethylene is extruded into a continuous rod which is chopped to size for blending, compounding, and bagging.

## (2) Low-Pressure Polyethylenes

In the early 1950s, considerable interest in low-pressure (under 34 kg/cm<sup>3</sup>) process was stimulated by the development of the Ziegler catalysts in Germany. The lower-pressure methods, pioneered by Phillips and Du Pont in the U.S., are called Ziegler or "linear" process, in contrast to the high-pressure, or conventional, processes. Low-pressure polymerization produces a polyethylene having remarkably different properties, due to the greater linearity of the polymer and differences in molecular weight distribution.

There are two basic low-pressure processes: the Ziegler (suspension) method and the Phillips (solution) method. In the former process, catalyst made from the reaction of titanium tri- or tetrachloride with aluminum alkyls are used. The monomer is added to a well-stirred dispersion of catalyst in a liquid hydrocarbon. Reaction conditions are less than 100°C and 100 atms. As the polymer forms from the catalyst, it produces a slurry which is sent to a flash drum from which the remaining monomer is removed for recycling. The polymer is freed of solvent and catalyst through a series of filtrations, extractions, and washings, after which it is dried, extruded, chopped, compounded, and bagged.

In the solution process, a solvent such as cyclohexane is added to a reactor. Then monomer and catalyst are

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added. The reaction condition range from 130 to 160°C and 13.6 to 34 kg/cm<sup>3</sup>. A typical catalyst is a composition of chromium oxides on an activated silica-alumina base. The reactor is a two-zone continuous unit which has a well agitated reaction zone and a quiescent separation zone for catalyst settling. The polymer solution still has some remaining catalyst; therefore, the solution is passed through a flash drum (removes and recycles monomer), centrifuge (removes catalyst), and cooler/precipitator (removes polymer). The polymer is then dried, extruded, chopped, compounded, and bagged as in the other processes.

Both processes require exceptionally efficient catalyst removal, particularly if the polymer is to be used in electrical applications.

In 1977 a low-pressure gas-phase process for the manufacture of low-density polyethylene was announced. The process is reported to require half the capital investment, one quarter of the energy, and 10% of the plant space now needed to produce equal amounts of conventional polyethylene by the high-pressure processes.

In this new process, gaseous ethylene, comonomer (when required), and catalyst are continuously fed to a fluidized-bed reactor. The reaction pressure is 6.8-20.4 kg/cm<sup>3</sup>, which is about one-hundredth of the pressure used in high-pressure production. The reaction temperature is controlled at less than 100°C, which is



roughly a third of that used in high-pressure operation.

Because of the low-pressure reaction zone, energy use is cut by 75%. Less and much thinner piping is required. The first reactor, a 110,000 ton/year unit, consists of a single 14-foot-diameter tank. The reactor stage required to produce an equivalent amount of polymer in a conventional plant requires one mile of heavy wallpipe. The new process eliminates or sharply reduces complex pumping and recovery systems, refrigerated ethylene streams, and heat- and noise-producing rotary and reciprocating equipment. Simplified instrumentation also makes possible servicing without reactor shutdowns.

### 2.1.3 Applications

Polyethylene may be easily processed by every method devised for thermoplastics. Probably the largest use is in the manufacture of containers and film consumed by the packaging industry. Film thickness vary from under 0.05 mil to 8 mils, and may run as high as 20 mils sheet. Variation in clarity are possible, maximum transparency being desired for display wrapping.

Flat-die extrusion into water baths or onto chilled rolls produces higher clarity in the film and, coupled with variations in the polymers and copolymers, make polyethylene competitive with traditional cellophane as well as many newer films. The principal

uses for film are food, soft goods (sheets, shirts, etc.) and hardware packing, garment bags, drum liners, temporary building closures for protection during construction, moisture barriers under concrete slabs and on foundations, soil mulching, green houses, automobile seat covers, tarpaulins, and temporary decoration displays.

Electrical insulation was the first, and to this day, still is a major use of polyethylene. Low power factor and dielectric constant at high frequencies make it particularly valuable for communication wire and TV lead-ins. Because of its excellent electrical resistance and its high chemical inertness, it finds prime use as buried power-cable jacketing.

Polyethylene pipe is another major application for this polymer. Drums and drum liners, containers for chemicals, labwares, and tubings are other important industrial applications.

Polyethylene powder has been added to thermoplastic and thermoset resins to improve various properties of the matrix resin. In vinyls, the polyethylene powder improves flow and impact strength. In polystyrenes, a slight improvement in flow and apparent improvement in processing smoothness is achieved. However, impact strength and clarity decrease.



## 2.2 Fillers

### 2.2.1 Type and properties

Fillers are defined as additives in a solid form that differ from the plastics matrix in respect to their composition and structure. Fillers may best be classified according to their chemical and physical characteristics. They may be divided initially into organic and inorganic groups, and each of these two groups may be subdivided into fibrous and non-fibrous types; in addition, protein fillers are included with organic

Many of the fillers mentioned may be further subdivided within any one group, depending on differences in physical characteristics such as particle-size distribution, particle size, particle shape, bulk density, and so on.

Although most fillers are solids, a few silicate types contain air voids to reduce effective filler density. Inert fillers or extender filler increase the bulk and lower the price, active fillers produce specific improvements in certain mechanical or physical properties and are thus also known as reinforcing fillers. The term reinforcement is not specifically defined, since reinforcement is understood to mean, for example, both an increase in tensile strength and an increase in flexural modulus.



Table 2.2 General classification of fillers (4,5,6).

organic		Inorganic	
<i>Fibrous</i>	<i>Non-fibrous</i>	<i>Fibrous</i>	<i>Non-fibrous</i>
Cottonseed hulls	Carbon black	Asbes	Silica
Sisal	Graphite	Glass fibre	Talc
Wood flour	Walnut-shell flour		Calcium silicate
Cotton flock	Coconut-shell flour		Mica
Cotton linters	Cork dust		Clays
Purified wood cellulose			Slate
			Kieselguhr
			Antimony trioxide
			Barium sulphate
			Calcium carbonate

The use of extender fillers can result in the following changes in the properties of thermoplastics (4):

- increase in density,
- increase in modulus of elasticity, as well as in compressive and flexural strength (stiffening),
- lower shrinkage,

- increase in hardness and improvement in surface quality,
- increase in heat deflection temperature and lowering of the temperature dependence of the mechanical properties, there being generally no improvement in mechanical and physical properties compared with unfilled polymers,
- cost reduction.

Reinforcing fillers, on the other hand, produce the following improvements in thermoplastics:

- increase in tensile strength and tensile stress at break, as well as in compressive and shear strength,
- increase in modulus of elasticity and stiffness of the composite material, increase in heat deflection temperature and lowering of the temperature dependence of the mechanical values,
- lower shrinkage,
- improvement in creep behavior and bend-creep modulus, reduction in the viscoelastic yield under load; there is also a partial improvement in impact strength.

(1) Disadvantages of the reinforcing fillers are mainly attributable to the generally anisotropic (directional) effect of the reinforcement.

Two discrete 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 plastics phase should possess higher elongation at break than the filler. For this reason, fibers are particularly suitable as reinforcing agents. When fiber reinforced material is subject to tensile load, local tensile stresses are transferred to the plastic/fiber interface by shear forces and distributed over the fiber surface. For this purpose, the fiber must adhere well to the polymer and possess a specific length, since otherwise it slips out of the matrix material. The higher the modulus of elasticity of the matrix, the smaller can be the minimum length of fiber. Adhesion can be considerably increased by coupling mechanisms between filler and plastic.

### 2.2.2 Theory of the action of fillers and reinforcements

The action of active fillers can be attributed to three causes (4). Some fillers form chemical bonds with the material to be reinforced, carbon black, for example, produces cross-linking in elastomers by means of radical reactions.

Other fillers act mainly through the volume that they lie up. In the presence of the filler particles, the chain molecules of the material to be reinforced cannot assume all the conformational positions that are basically possible. Moreover, there are a number of basic reasons for assuming that in a certain zone



around the filler particles the polymer material differs in structure and properties from the polymer matrix on its own. The polymer segments attached to the filler surface by secondary or primary valence bonds in turn cause a certain immobilization of adjacent segments and a possible orientation of the polymer matrix.

The reason for this immobilization lies in the high degree of dimensional stability of the filler particles. The increases in the glass transition temperature observed in filled polymer - resulting from the limitations on mobility in the boundary zone of the polymer material can be regarded as confirmation of the theoretical concept presented above.

The zone directly at the filler surface, whose structure would appear to be ordered, thus causes a stiffening of the material as a whole. The lower deformability and higher strength are also due to this composite nature.

A homogeneous distribution of fillers in the matrix is basically important, in order that as many polymer chains as possible can be bound to the free filler surface. The free surface energy and the polarity of the bond between filler and matrix are also important factors in this regard.

The third mode of action of active fillers results from the fact that when the polymer molecules are subject to stress

with absorption of energy, they can slide off the filler surface. The impact energy can thus be more uniformly distributed and impact strength increased as in the unplasticized PVC/chalk system. In some cases, microcraze formation that destroys the impact energy at the filler/polymer interface is also facilitated.

### 2.2.3 Calcium Carbonates

Calcium carbonates are popular nonmetallic minerals fillers for plastics because of their combination of low cost, high brightness, and ability to be used at high filler loadings. They generally are categorized as extenders since they are used for cost reduction and provide little reinforcement (4,5,6).

Calcium carbonates are supplied in five forms: water-ground, dry-ground, ultrafine-ground, precipitated, and surface-treated carbonates. Naturally occurring calcium carbonates are sedimentary rocks of marine origin. A rough distinction is made between:

chalk: loosely coherent, consisting of fine calcite crystals and fragments, originating from shells and skeletons of nanofossils.

limestone: more highly coherent consisting of macrofossils of sea shells.

marble: formed by metamorphosis of a sedimentary rock, i.e. recrystallization in the earth's interior at high pressures and temperature of 600°C. The resultant rock is relatively hard with dense, coarse-grained structure.

### (1) Natural Calcium Carbonates

Natural carbonate is mainly calcite, a rhombohedral crystal (sp.gr. = 2.70-2.72, Mohs hardness = 3.0, pH = 9-10). Commercial deposits contain less than 3 % magnesium carbonate and traces of other impurities, such as iron and sulfur. Naturally occurring calcium carbonates in the form of chalk, limestone or marble for use in thermoplastics should show typical properties in Table 2.3

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Table 2.3 Typical properties of natural calcium carbonates (4).

Description	Unit
CaCO <sub>3</sub>	98.5 to 99.5%
MgCO <sub>3</sub>	up to 0.5%
Fe <sub>2</sub> O <sub>3</sub>	up to 0.2%
Al-silicate (colloidal)	up to 1.0%
Loss on ignition	43.3 to 43.8%
Moisture content	up to 0.2%
(DIN 53198, ISO/DIS 787/2-1979)	
Density	up to 2.7 g/cm <sup>3</sup>
Mohs hardness	3
Degree of whiteness	85 to 95%
(Elrepho green filter, MgO = 100%)	
pH (DIN 53200, ISO/DIS 787/9-1979)	9.0 to 9.5
Oil absorption (DIN 53199)	9 to 21 g/100 g powder
DOP number (ASTM D 281-31)	9 to 33 g/100 g powder
Specific surface	1 to 15 m <sup>2</sup> /g

## (2) Use of Natural Calcium Carbonates in Thermoplastics

In terms of weight, ground calcium carbonate is the most important filler used in plastics. Ultrafine ground chalks

are frequently employed. The inert filler calcium carbonate plays an important role in the search for a balance between a low price and the retention of physicomechanical values. High-quality carbonate fillers are distinguished by the following properties:

- High chemical purity, no heavy metal ions that can catalyze the aging process in polymers,
- no tendency to form agglomerates,
- calcitic structure with relative low specific surface, without any great absorptive effect on plasticizers and other additives,
- high degree of whiteness, hence the possibility of partial substitution of expensive white pigments,
- coloration in pastel shades is possible, also at high filler contents,
- non-abrasive, gentle on machine parts (Mohs Hardness ~ 3),
- good dispersibility (in particularly coated grades) with only slight influence on the mechanical and electrical properties of the final products,
- increase in stiffness and modulus of elasticity,
- reduced shrinkage, higher color fastness,
- improvement in the surface of the article,
- lower plate-out (deposition of mixture ingredients),
- increased impact strength, in particular through

coated grades,

- improvement in stability and aging resistance, particularly when using coated grades,
- non-toxic, odorless, tasteless, heat-resistant up to 600°C,
- low price, cheaper than precipitated calcium carbonate, hence beneficial increase in weight and volume.

### (3) Synthetic, Precipitated Calcium Carbonates

These carbonate fillers known as CCP (calcium carbonicum praecipitatum) show the following properties in Table 2.4:

Table 2.4 Typical properties of precipitated calcium carbonates (4).

Description	Unit
Mean particle diameter	approx. 0.004 to 0.07 $\mu\text{m}$
Degree of whiteness (Elrepho green filter, MgO = 100%)	95 to 96 %
Oil absorption	35 to 40 g/100 g powder
Specific surface	32 to 40 $\text{m}^2/\text{g}$



The special properties of precipitated, surface-treated calcium carbonates result from their small partical size, their high degree of purity, their aragonite structure. As a consequence of the surface treatment in question, good dispersibility in the polymer matrix is thereby obtained.

Like the ground carbonates, precipitated calcium carbonates are frequently used in the thermoplastics and make possible the following improvements in their properties:

- Increased impact strength
- high surface gloss in the finished products,
- good elongation at break, tear propagation resistance and tensile strength,
- higher modulus of elasticity,
- reduced plate-out,
- good weathering resistance.

Compared with the natural, ground calcium carbonates, the synthetic, precipitated calcium carbonate fillers, do, however, possess the following disadvantages:

- More expensive than ground chalk,
- due to the larger surface, the shearing forces during processing are appreciably higher; high filler additions are thus not possible,
- greater absorptive effect on plasticizers, stabilizers, lubricants etc.

#### (4) Use of Calcium Carbonate in HDPE

Because of the high degree of crystallization of HDPE, the strength of the material at low temperatures is more strongly influenced by fillers than is the case with LDPE (4). As with all non-polar polymers, the critical factor is the adhesion between filler and matrix. Appreciably better adhesion and markedly higher mechanical values (modulus of elasticity, impact strength) can be achieved simply by using a vented extruder.

The use of mineral fillers was until recently confined to paperlike films. However, blown articles are now also produced with calcium carbonate as filler. Here the advantages lie in higher stiffness and higher production outputs, resulting from the lower specific heat and improved thermal conductivity (more rapid cooling). Moreover, all the advantages obtainable with calcium carbonate in LDPE, e.g. better printability, are also achieved in HDPE.

Compared with most other fillers, the use of surface-coated calcium carbonate results, in particular, in higher impact strength. Melt index, elongation, tear propagation strength, shrinkage, stress cracking and cold flow are reduced by the filler.

#### 2.2.4 Carbon black

Essentially, carbon black depends for its properties on its fine state of subdivision, the particles ranging from 50 to 5000 Å. The differences in properties shown by different types of carbon black is due largely to differences in average particle size. Carbon blacks are manufactured by either the partial combustion or thermal decomposition of gaseous or liquid hydrocarbons, and the method of preparation has been the principal method of classification (1,4).

##### (1) Channel blacks.

Impingement blacks, or gas blacks, are obtained by the impingement of small natural-gas flames on cool metal-channel surfaces. The carbon black deposited is scraped from the channels and separated from impurities by the use of high-velocity air streams. Channel blacks range in particle size from 50 Å to a maximum of 350 Å.

##### (2) Furnace-combustion blacks.

Furnace-combustion blacks are produced by the partial combustion of essentially gaseous hydrocarbons in closed furnaces. The process is essentially the same as the channel black process, but instead of using a large number of tiny impinging flames, a large volume of gas and air undergoes combustion and cracking in



furnaces. The carbon black, which is suspended in the spent reaction gases, is collected by electrostatic precipitation and centrifugal force. The furnace blacks are larger in size than the channel blacks, a typical range being 500-800 A.

### (3) Furnace thermal blacks.

Furnace thermal black is produced by thermal decomposition rather than partial combustion of hydrocarbons. There are two types of carbon black in this category, one produced from natural gas by an endothermic process, and one produced from acetylene by an exothermic process. In this process air and gas insulated furnace to a temperature of 900-1400°C. The furnace is then charged with gas alone, and thermal decomposition in the gas phase occurs. The carbon blacks obtained by this method are of the coarsest type and average 4000 A in diameter. The most intense blacks are the channel blacks, which also have the highest oil-absorption, owing to their large surface area and small particle size.

### (4) Graphite.

Natural graphite is a mineral form of carbon crystallised in a regular hexagonal system with rhombic geometry. Because of its diverse properties graphite is an extremely versatile material. It marks easily, burns slowly, it is almost inert chemically, operates satisfactorily over a wide temperature range,

and is a good conductor of heat and electricity.

In industry, graphite is classified as disseminated flake, vein graphite, and amorphous graphite. The main sources of natural graphite occur in Canada (flake), Mexico (amorphous), Ceylon (vein graphite), and Madagascar (flake). In these and other smaller areas the mining techniques vary from a selection of the ore by hand to more sophisticated operations such as drilling and blasting. Grinding of the ore followed by flotation (liquid or air) is used to concentrate the graphite.

In plastics systems graphite is used in those applications where its properties of heat stability, lubricity, and electrical conductivity are of value. In consequence it finds application generally in industrial plastics such as nylon or polytetrafluoroethylene (PTFE), and in those plastics where good electrical conductivity is required, such as in electroplating applications.

Although perhaps a little out of context here, mention should be made of the graphite fibres and whiskers obtained by the pyrolysis of existing synthetic fibres such as polyacrylonitrile. Such fibres have high strength, e.g., tensile strength up to 400,000 psi, and are capable of operating in air without a binding resin at up to 450°C and, in the absence of air, up to 2,000°C or even higher. Resistance to oxidation can be

improved by coating with silicon carbide. These graphite fibres are still extremely expensive and will only be used for very specific requirements.

#### (5) Use of carbon black in thermoplastics

As regards their use in plastics, carbon blacks are classified according to their particle size and color intensity. Carbon blacks with small particle size are usually more difficult to disperse than coarser types.

Carbon black is also used to achieve volume conductivity and to improve heat deflection temperature. In the record industry, carbon black serves as a filler, in foams, use is also made of hollow carbon black spheres.

Carbon black is frequently utilized as a protection against UV radiation and as a black pigment in thermoplastics.



### 2.2.5 Fiber glass

The engineering trend towards lightweight constructions calls for the use of materials with high strength, combined at the same time with low weight and corrosion resistance. Although plastics as such possess many advantages, their strength properties and especially their stiffness are often inadequate. In order, in such case, to be able to obtain a solution that is acceptable both from the technical and economic aspects, it is necessary to switch to composites and to incorporate materials such as reinforcing fibers in the plastics. Glass fibers have thus attained major importance as reinforcements for thermoplastics (1,4).

#### (1) Textile glass

Glass grades for technical applications consist of oxidic network formers and silicon, boron or aluminum oxide as skeleton substances. From the melts of these naturally occurring minerals, textile glass fiber mainly 10 to 20  $\mu\text{m}$  in diameter are produced by means of the mechanical drawing method for continuous-filament glass fiber and the rod or blast drawing processes for staple fiber. The fibrous products include:

- Strands : Approximately aligned continuous strands of 100 to 400 single filaments without twist. They are gathered together into rovings of 30 to 60 strands.

- Filament yarns : Spun from continuous filament with twist.
- Staple fibers : They consist of randomly oriented, comparatively short monofilaments (textile fibers) with a fleecy handle.
- Staple yarns : Yarns produced with low-twist fibers.

The two-dimensional structures are subdivided into fiber fleeces, mats, coverings, fabrics, felts and sheets.

## (2) Glass grades

- A glass : Alkali-containing, with and without additions of boron, moderately soluble in alkalis, used in articles not greatly subject to stress and exposed neither to the action of weathering nor moisture. Use in engineering apparatus etc.
- D glass : Dielectric grade, limited to electrical insulating materials.
- E glass : Most commonly used grade, aluminum-boron-silicate glass. The alkali oxide content must not exceed 0.8%, highly soluble in acids, moderately soluble in alkalis, used in the electrical industry etc.
- M glass : High modulus glass for products subject to extremely high stress.
- R glass :  $\text{SiO}_2/\text{Al}_2\text{O}_3/\text{MgO}$  system with high strength and good thermal stability.

- S glass : High strength for aircraft and rocket construction.

Glass fibers differ according to density, refractive index and chemical resistance. E glass possesses the lowest dielectric constant and  $\tan \Delta 9.10^{-4}$  the lowest dissipation factor. The most important properties of the different types of glass fiber are compiled in table 2.5

Table 2.5 Properties of different types of glass fibers (4).

Property	E glass	A glass	A glass with boron addition	R glass	S glass	M glass
Density ( $g/cm^3$ )	2.54	2.48	2.5	2.5	2.49	2.89
Strength of monofilament ( $N/mm^2$ )	3500	2450	2900	4750	4900	3500
Modulus of electricity ( $N/mm^2$ )	73000	45000	60000	83000	87000	124000



Glass fibers are rot-resistant, reasonably resistant to aggressive chemicals, heat-resistant up to 650°C, possess high tensile strength and good elasticity. The greatest drawback to the use of glass fibers as reinforcement lies in their very high brittleness.

### (3) Fiber glass in thermoplastics

Glass fiber-reinforced thermoplastics are manufactured by two different processes. In the first process, glass fiber strands are impregnated with the melt of a thermoplastic and after solidifying, the strands are cut into rodlike granules. The fibers are, therefore, of the same length as the rods and oriented in the latter's longitudinal direction. In the second process, the thermoplastic in a powdery form is blended with the ready-cut short fiber glass, extruded and granulated. In Europe, the major proportions of glass-reinforced plastics are sold as granules in a ready-to-process form. Only in a few instances are glass fiber and plastic brought together in the feed hopper of the machine and mixed there in accordance with American practice.

The material mainly used for the reinforcement of thermoplastics and thermosetting plastics is the alkali-free E glass, which in comparison with the alkali A glass is noted for its good electrical properties also in damp surroundings. The lower brittleness of E glass additionally contributes to the fact that the

original length of the fibers is retained during manufacture of the granules.

Short fibers are more readily dispersible. The spures can be more easily removed during injection molding. This is of importance in the case of single-gating and multi-gating. Moreover, short-fibered granules are cheaper than long-fibered material. The advantages of the short fibers are opposed by a number of disadvantages. Impact strength, for example, does not match the values of the long-fibered product, heat deflection temperature is 5 to 6°C lower. Flexural strength and flexural modulus are also lower than with the products reinforced with long fibers.

The reinforcing action of glass fibers is so great that an addition of 30% generally results in a doubling of tensile strength, modulus of elasticity is trebled, coefficient of linear thermal expansion and shrinkage are reduced to a third. At the same time, however, a limited decrease in notched impact strength and a somewhat more pronounced directional dependence of shrinkage in injection moldings occur.

#### (4) Reinforcing action of fiber glass

The reinforcing action of fiber glass is decisively influenced by the following properties:



- The length/diameter ratio of the reinforcing fibers should be large,
- the fiber should, where possible, be oriented in the direction of the force profile,
- optimum adhesion between fiber and matrix is desirable (size, coupling agent),
- intimate wetting of the fiber surface can be achieved by intensive blending operations, however, this may have an unfavorable influence on fiber length, the fibers become shorter and assume the character of a filler.

Strength and stiffness increase to a maximum level as the glass content rises and then fall again. This maximum is reached when the plastics matrix no longer suffices to transfer the forces between the fibers and to fill cavities. This influence is much greater with tensile and flexural stress than with compressive stress. In thermoplastics, short-fibered reinforcement additionally results in an appreciable lowering of elongation at break. Apart from the glass content, glass distribution has a decisive influence on the properties. This applies in particular to long-fibered reinforcement. Basically speaking it can be stated that the longer the fibers, the higher are the mechanical values.

Glass fiber-reinforced thermoplastics combine the good properties of the plastics with those of the inorganic glass and in their property values approach the level of metals. Glass fibers



metallized with aluminum are also supplied for the purpose of increasing electrical conductivity.

(5) Property improvement through glass fiber reinforcements (20 to 40% fiber glass)

- Increase in tensile, compressive and flexural strength, as well as in the modulus of elasticity,
- appreciable increase in stiffness and flexural modulus; this property is of major importance, especially for technical applications,
- increase in tensile stress at break in the case of brittle based polymers and in notched impact strength at low temperatures, which usually drops sharply in non-reinforced thermoplastics,
- reduction in the coefficient of linear thermal expansion and in shrinkage, dimensional stability is considerably improved,
- resistance to cold flow is increased and creep lowered (smaller bend-creep modulus),
- improvement in heat deflection temperature,
- less noise development, also in the case of vibration,
- flexibility in design,
- material savings are possible, since as a result of the improved mechanical properties, many parts can be

reduced in size or made thinner.

(6) Disadvantages of fiber glass reinforcement

- A slight reduction in impact strength can be expected in thermoplastics which by nature are impact-resistant,
- surface finish of the finished part is usually somewhat rougher than that of non-reinforced molding compounds,
- higher abrasion in processing machinery.



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### 2.3 LITERATURE REVIEW

In the field of polymer compounding, many investigators studied the compounding in different ways. The polymer is compounded with additive such as flame retarding agent, modifiers, fillers and reinforcements and colorants. In this literature survey, the work of polymer filled with fillers and reinforcements are summarized as follows:

In 1989, V. Malpass and J. Kempthorn (8) used notched Izod and falling-weight impact tests to study the effect on toughness of adding 30 percent by weight by extrusion compounding of untreated 3- $\mu\text{m}$  average particle size  $\text{CaCO}_3$  or 15- $\mu\text{m}$  talc to general purpose polypropylene homopolymer, high-impact polypropylene copolymer, and high molecular weight HDPE. The study suggested that extrusion compounding  $\text{CaCO}_3$  or talc into the resins increased polyolefin rigidity while reducing tensile elongation to break (Table 2.6) and increasing notch sensitivity at high impact-strain rates. The authors concluded that mineral-filled polyolefins could compete with ABS and other engineering resins especially when rigidity and impact resistance at low temperatures were required.



Table 2.6 Tensile properties for PP, HDPE filled and unfilled, and for ABS polymer (8).

Compound	Tensile modulus, psi	Tensile strength, psi	%elongation	
			Yield	Break
PP homopolymer	140,000	4900	10	319
30% CaCO <sub>3</sub>	230,000	4100	8	60
30% talc	280,000	4900	7	10
PP copolymer	100,000	2900	12	396
30% CaCO <sub>3</sub>	150,000	2300	7	392
30% talc	180,000	2600	6	43
HDPE	130,000	4100	12	162
30% CaCO <sub>3</sub>	180,000	3700	10	102
30% talc	210,000	4300	9	58
ABS	180,000	6400	5	9

In 1989, A. Adur, R. Constable and J. Humenik (9) had reported that untreated fillers could be competed with treated fillers by using the coupling agent. To test the polypropylene compound with treated and untreated mica and an acrylic-acid-modified polypropylene as the coupling agent, the properties, tensile strength, flexural modulus, heat deflection temperature and Izod impact were measured. Melt compounding was conducted in Banbury and powder blending was performed in a twin cone blender (for the resin in flake form). The test pieces were produced on an injection molding machine. After tested all required properties, they had concluded that the addition of acrylic-acid-modified polypropylene to mica-filled polypropylene composites yields composites with higher physical and thermal properties. (Figure 2.1 and Table 2.7). The acid-modified polypropylene acted as a coupling agent for micas. Optimum level was 10 to 15 percent by weight of the compound at a mica loading of 40 percent. The increase in physical properties was observed with both large and small-particle-size micas, (Figures 2.2 and 2.3) but the method of compounding affected the physical properties (Figure 2.4 ), if the compounding breaks down the aspect ratio of the mica flake, lower physical properties were obtained.

Table 2.7 Heat deflection temperature values of mica-filled polypropylene system (9).

Mica type	Type of blending	HDT no coupling agent, deg C	HDT at optional level of coupling agent, deg C	HDT increase at 1820 kPa, %
Mica 1 <sup>a</sup>	Powder	86	115	25
Mica 2 <sup>a</sup>	Powder	75	114	34
Mica 1 <sup>a</sup>	Banbury	99	110	12
Mica 2 <sup>a</sup>	Banbury	87	109	22
Mica 3 <sup>a</sup>	Powder	68	95	16
Mica 4 <sup>a</sup>	Powder	76	91	28
Mica 5 <sup>b</sup>	Powder	86	104	17
Mica 6 <sup>b</sup>	Powder	78	99	28

<sup>a</sup>Phlogopite mica.

<sup>b</sup>Muscovite mica.



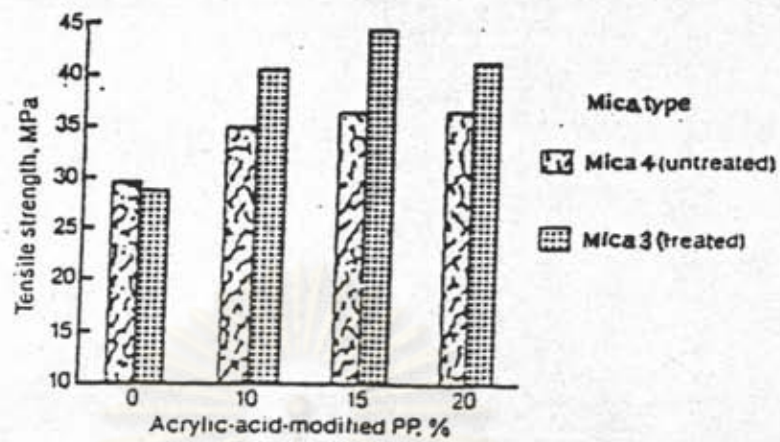


Figure 2.1 Effect of surface treatment and coupling agent level on tensile strength; phlogopite Micas 3 and 4.

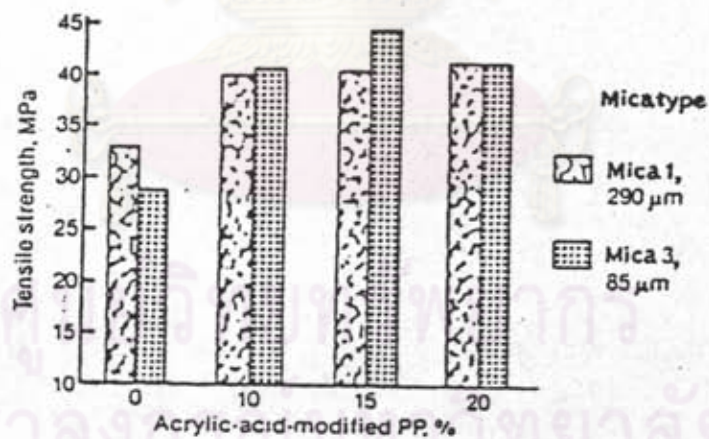


Figure 2.2 Effect of particle size and coupling agent level on tensile strength; Micas 1 and 3.

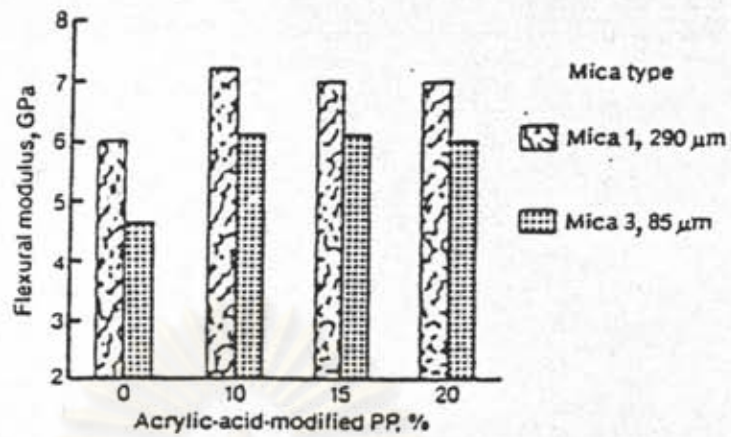


Figure 2.3 Effect of particle size and coupling agent level on flexural modulus; Micras 1 and 3.

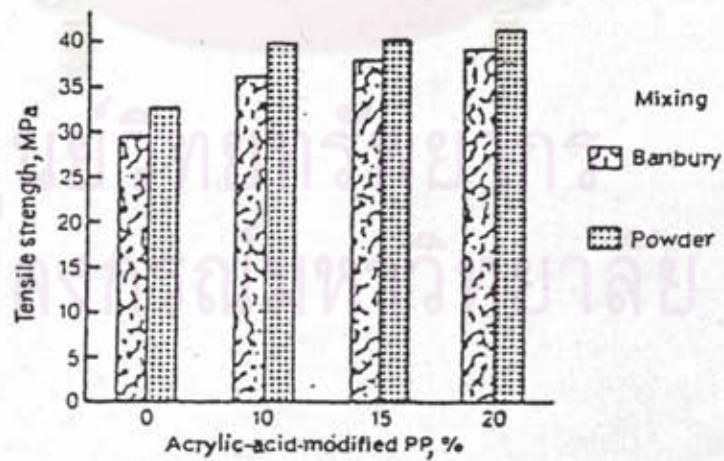


Figure 2.4 Effect of mixing procedure and coupling agent level on tensile strength; Micras 1.

V.E. Malpass, J.T. Kempthorn and A.F. dean (10) had reported about thermoforming behavior of mineral-filled polypropylene, using 10% and 30% by weight of small-particle-size  $\text{CaCO}_3$  as filler. They used "hot" tensile properties to evaluate the thermoforming behavior. The specimens were mixed by Banbury ( $150^\circ\text{C} - 165^\circ\text{C}$ ), milled ( $182^\circ\text{C}$ ), to form the 60 mil milled sheet from compression molded ( $196^\circ\text{C}$ ) then cut to strips, 2-inch long and 0.5-inch wide for tensile test. The tensile testing was done on Instron tensile tester with strain rate approximately 3,500% per min. They had concluded that the hot tensile property that was most affected by the addition of  $\text{CaCO}_3$  was elongation (strain) to break. The 30% loading gave a significant reduction in total elongation capability of the homopolymer (Figure 2.5) but the presence of mineral filler profoundly affected cycle time for thermoforming by increasing heating and cooling rates. The reasons were first, heat capacity value was decreased; second, thermal conductivity was increased. So, up to 30% by weight of  $\text{CaCO}_3$  could be incorporated into polypropylene homopolymer with relatively minor effects on hot tensile properties. This mineral filler could improve room temperature moduli and heat deflection temperatures of polypropylene.



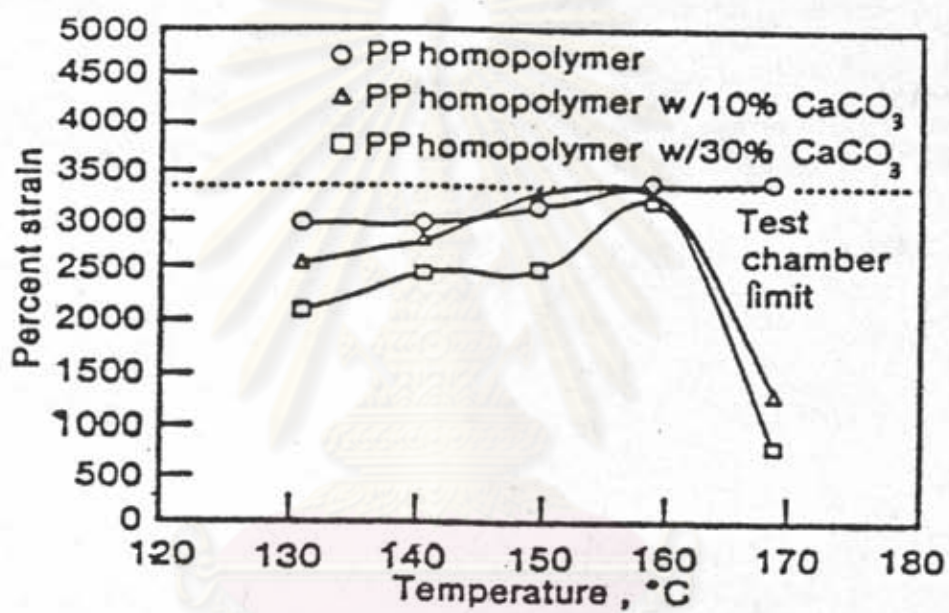


Figure 2.5 Dependence of total elongation up to 3360% on test temperature for PP homopolymer.

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J. Kubat and H.E. Stromvell (11) studied about the natural filler, lignosulphonates, for polystyrene and polyethylene. Three grades of lignosulphonates were used as fillers. The maximum filler content was 70% (by weight). The thermoplastic and the filler were blended in a tumble mixer prior to homogenization in a mixing extruder. The tensile test specimens were produced by injection moulding and test was done on Instron tensile tester. The other mechanical property was unnotched impact resistance (Charpy). The result could be concluded that tensile modulus of these thermoplastic were increased (Figure 2.6) but the tensile strength, elongation at break, impact strength, were greatly decreases (Figures 2.6 and 2.7). In general, the tensile strength decreased with an increasing amount of filler. Some interested point of this report was this filler-polymer system unsuitable for normal applications but it was water-degradable materials which may be suitable for some special application.

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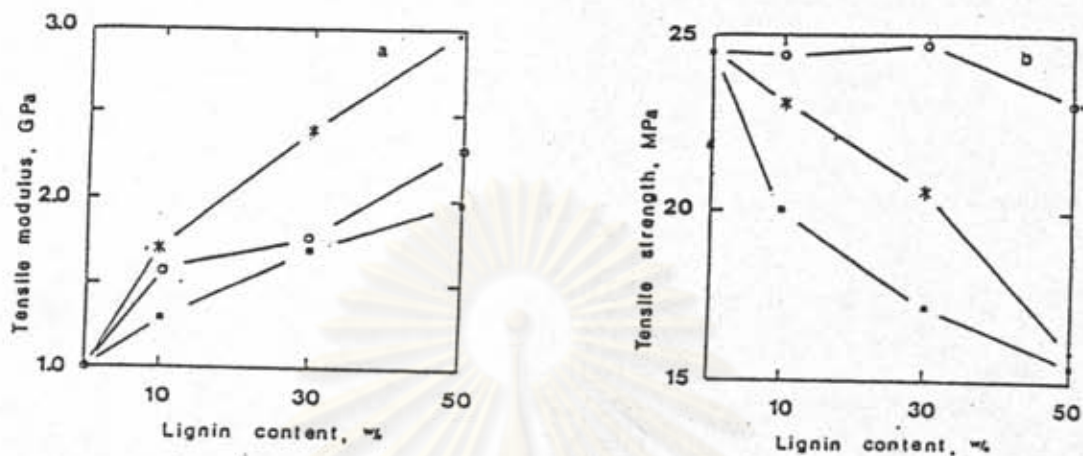


Figure 2.6 Tensile modulus and tensile strength versus filler content for HDPE base materials.

(a) Tensile modulus versus filler content

(b) Tensile strength at break versus filler content

\*, Wanin S; o, Wanin SR; ■, Indulin AT.

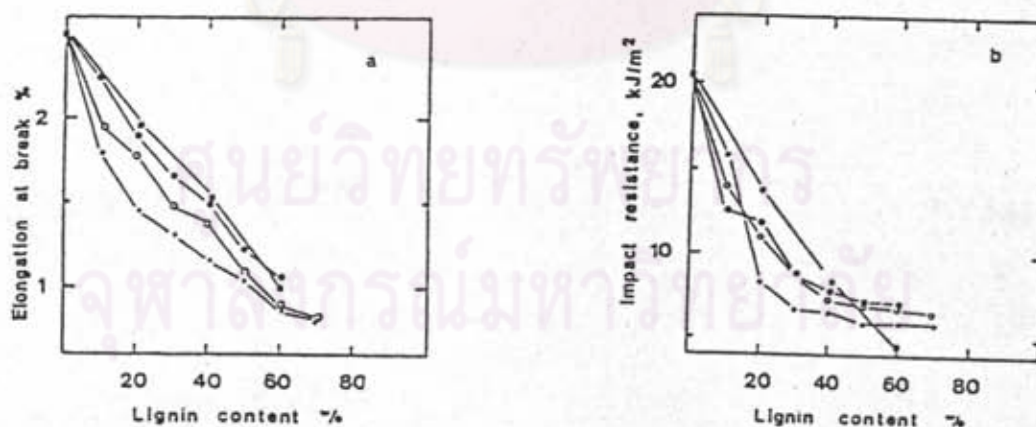


Figure 2.7 Elongation at break and impact resistance versus filler content for PS base materials.

(a) Elongation at break versus filler content

(b) Impact resistance versus filler content

\*, Wanin S; o, Wanin SR; ■, Indulin AT.



C. Busigin, R. Lahtinen, G.M. Martinez, G. Thomas and R.T. Woodhams (12,13) had reported about the properties of mica-filled polypropylene, using two types (Phlogopite, Suzoritic) of mica, 40% by weight, as a filler with and without using the dispersing agents or coupling agents. The polypropylene powders were mixed with the filler by several different methods eg. a laboratory-scale Banbury, a Brabender twin screw, a Brabender Roller-Blade mixer, a one-litre Gelimat and a larger 50-litre production-scale Gelimat. The compounded mixes were then pelletized and formed by an injection molding machine. The test properties were tensile strength, flexural strength, and notched Izod impact strength. Some specimens were reground and repeated to test the mechanical properties to assess the influence of recycling on the retention of properties. The results were, the more aspect ratio, the increase in modulus, both tensile and flexural. The mixing conditions have an important influence on the tensile and flexural strength. The use of coupling agent reduces the Izod impact values approximately 10% and the Izod values were appear to be independent of the particle diameter but depended upon the mica concentration. Mica-filled thermoplastic could be reprocessed several times without drastic reduction in mechanical properties.

L.C.B. Davies, K.A. Hodd and G.R. Sothern, Department of Non-metallic materials, (14) had studied about the use of pulverized fuel ash (PFA) as a filler for polyolefins. PFA is a mineral filler which comprises fine aluminosilicate glass beads. The compounds of PFA and polypropylene ranging from 0 to 60 percent by weight were prepared by heated two roll milling and followed by granulation. The test specimens of compounds were prepared by injection molding. The melt flow index, tensile and impact strengths were measured. Talc and limestone-filled polypropylene were studied in the same manner with PFA filled polypropylene. Although, all properties were not so good but in compare with talc-filled polypropylene, the mechanical properties were found to be closely, with the same weight percent loading of filler.

E.E. Berry, R.T. Hemmings, and J. Leidner (15), investigated about the spherical filler. They used subbituminous fly ash, talc, calcium carbonate and glass sphere as fillers for polypropylene, nylon, and PVC. The concentrations of filler to be compounded were 20, 30, 40 % by weight, compounding in a Brabender twin screw extruder for polypropylene and nylon, in a Gelimat machine for PVC and granulation in a Wiley mill. The test specimens were formed by injection molding and the Izod impact, flexural modulus, tensile properties were measured. It was found that the flexural modulus was the most pronounced effect, which the larger-particle size fillers were more effective in increasing the flexural modulus than the finer fractions, especially at the higher loading. The impact and tensile



strength usually decreased with introduction of fillers. The same as elongation, all of the fillers reduced elongation in each resin, with no definite indication of an effect associated with particle size of filler type. In conclusion, the ash filler behaved as a nonreinforcing filler, with mechanical properties similar to those of calcium carbonate, but it showed improved mechanical properties when compared with synthetic glass spheres.

In 1985, Kazuta Mitsushi, Soji Kodama and Hitishi Kawasaki, (16), studied about the mechanical properties of polypropylene filled with calcium carbonate in terms of the effects of filler content, filler size, surface modification of filler and strain rate. They used unmodified and modified polypropylene (with a phosphate coupling agent), mixed in a two-roll mill with  $\text{CaCO}_3$  in 1.6, 3.2, 6.4, 9.0, 14.5, and 21.0 volume percent. The compounded was pressed to a molded plate by a compression mold. The test specimens were drawn by a tensile test machine with various strain rates. The results showed that the tensile modulus and tensile yield stress of unmodified systems were increased with an increase of filler content and strain rate, and with a decrease of filler size. The yield strain was decreased with an increase of filler content and with a decrease of filler size, but did not depend on the strain rate. By using the phosphate coupling agent as a modifier, the dependence of elastic modulus on the filler size was maintained, but the dependence on strain rate and filler were lowered. The yield stress was decreased by the surface modified fillers.



Ashok M. Adur and Stephen R. Flynn, BP Performance Polymers, Inc. (17), studied about the coupling agent for talc filled polypropylene. Small particle size (average  $1.5 \mu\text{m}$ ), both treated and untreated, large particle size (average  $9.0 \mu\text{m}$ ), and an amino-silane surface treated talc with particle size between  $1.5$  to  $1.8 \mu\text{m}$  were used as fillers. Polypropylene base used in this study was an unmodified polymer. Tensile properties, flexural modulus, heat deflection temperature and notched Izod impact strength were measured.

The results showed the improvement in adhesion between polymer and filler and the increase of the above mechanical properties but no effect on notched Izod impact strength. The application of these systems gives the opportunity to formulate more cost-effective composites.



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