

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Composite Materials

Composite material can be defined as a macroscopic combination of two or more distinct materials, having a recognizable interface between them. However, because composites are usually used for their structural properties, the definition can be restricted to include only those materials that contain a reinforcement (such as fibers or particles) supported by a binder (matrix) material. The constituents can be organic, inorganic or metallic (synthetic and naturally occurring) in the form of particles, rods, fibers, plates, foams, etc. Compared with homogeneous materials, these additional variables often provide greater latitude in optimizing, for a given application, such physically uncorrelated parameters as strength, density, electrical properties, and cost. Furthermore, the composite may be the only effective vehicle for exploiting the unique properties of certain special materials.[4-5]

2.1.1 Classification of Composite Materials

Composites can be divided into classes in many manners. One simple classification scheme is to separate them according to reinforcement forms.[4-7]

2.1.1.1 Particulate-Reinforced Composites

Particulate-reinforced composites consist of particle dispersed in a matrix. This type is considered to be a "particle" if all of its dimensions are roughly equal. Particulates may have any shape, configuration, or size. They may be powdered, beads, rods, crystalline, or amorphous. They may be metallic, ceramic, manmade, or natural materials. Concrete and wood particleboard are two familiar examples of particulate composites. Pieces of ceramic particles are placed in a metallic matrix and used as tough, abrasion resistant cutting tools. Metallic flakes have been added to improve electrical properties and provide some degree of radiation shielding in polymer composites. Generally, particles in polymer usually extend rather than reinforce the material. These are usually referred to as "filled" systems. Because filler particles are included for the aim of cost reduction rather than reinforcement, these composites are not generally considered to be particulate composites. Nonetheless, in some cases the filler will also reinforce the matrix material.

2.1.1.2 Fiber-Reinforced Composites

Fiber-reinforced composites are composed of reinforced fibers in a matrix. They contain reinforcements having lengths greater than their cross-sectional dimensions. They can be further divided into those containing discontinuous and continuous fibers. In discontinuous fibers case, the bond between the fibers and the matrix is broken at the fiber's ends, which thus carry less stress than at the middle part of the fiber. Therefore, continuous fibers can carry stresses along its length.

2.1.1.3 Laminar Composites

Laminar composites are composed of layers of materials held together by matrix binder, sandwich and honeycomb component as well as the term high-pressure laminates are included. Complicating the definition of a composite as having both continuous and discontinuous phases is the fact that in a laminar composite, neither of these phases may be regarded as truly continuous in these dimensions.

2.1.2 Theory of the Action of Fillers and Reinforcements

The action of active filler can be attributed to several mechanisms.[2] Some fillers form chemical bond with the material to be reinforced, such as carbon black produces crosslinking in elastomers by means of radical reaction.

Other fillers act mainly through the volume they take up. The chain molecules of the polymer to be reinforced cannot assume all the conformational positions that are basically possible. Moreover, it can be assumed that in certain zones around the filler particles the polymeric phase differs in structure and properties from the polymer matrix. The polymer segments attached to filler surfaces by primary or secondary valence bonds in turn cause a certain immobilization of adjacent segments and circumstances permitting, an orientation of the polymer matrix. The increase in glass transition temperatures observed in filled polymers, resulting from the limitations of mobility in the filler/polymer boundary zone, can be regarded as conformation of this theoretical concept.

The zone directly of filler surface, whose structure would appear to be ordered, thus causes a stiffening of the material as a whole. Lower deformability and higher strength are also due to this composite nature. Uniform distribution of fillers is especially important, so 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 the filler and the matrix are important factors in this regard.

Another mode of action of active fillers from the fact that when the polymer molecules are subject to mechanical stress with absorption of energy, they can slide off the filler surface. The impact energy can therefore be more uniformly distributed and impact strength increased as, for example, in the unplasticized PVC/calcium-carbonate system. In some cases, microcraze formation that destroys the impact energy at the filler/polymer interface is also facilitated.

2.1.3 Properties of Filled and Reinforced Plastic

The extensive range of fillers used nowadays indicates the main objectives which are to lower cost of molding compounds and to selective modification of the properties of a specific plastic. Inert fillers or extender fillers 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.[2]

The use of extender fillers can result in the following changes in the properties of thermoplastics: 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; and cost reduction.

Reinforcing fillers, on the other hand, produce the following improvement in thermoplastics: Increase in tensile strength and tensile stress at break, as well as in compressive and shear strengths; 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; and there is also a partial improvement in impact strength.

2.2 Matrix

Matrix is an essentially homogeneous resin or polymer material in which the fiber system of composite is embedded. Both thermoplastic and thermoset resin may be used. The purpose of the composite matrix is to bind the fiber together by virtue of its cohesive and adhesive characteristics, to transfer load to and between fiber, and to protect them from environments and handling. Nonetheless, the matrix resin provides many essential functions; in addition to those mentioned above, the matrix keeps the reinforcing in the proper orientation and position so that they can carry the intended loads, distribute the loads more or less even among the fiber, provide resistance to crack propagation and damage, and provide all of the interlaminar shear strength of the composite. Moreover, the matrix generally determines the overall service temperature limitations of the composite, and may also control its environmental resistance.[4]

2.2.1 Polypropylene

Polypropylene(PP), a thermoplastic polymer which entered to commercial production in 1957, was the first of stereoregular polymer. Polypropylene differs from polyethylene because there is a methyl group attached to every other carbon atom, which stiffens the chain. Unless the methyl groups are arranged in one position relative to the chain, the polymer doesnot crystallize until the stereospecific catalysts were developed (independently) by Natta and Ziegler. Crystallinity is responsible for the stiffness and solvent resistance of the commercial plastic. The most valuable property of polypropylene

is versatility. It can be tailored to many fabrication methods and applications. Some properties that are usually considered inherent advantages of polypropylene are: Low specific gravity (density); excellent chemical resistance; high melting point (relative to volume plastics); good stiffness/toughness balance; adaptability to many converting methods; great range of special purpose grades; excellent dielectric properties; and low cost (especially per unit volume).

Although polypropylene has many useful properties, it is not intrinsically tough, especially below its glass transition temperature. However, its impact resistance can be improved by adding elastomer, usually ethylene/propylene rubbers at 5 to 25%. [8-11]

2.2.2 Manufacture of Polypropylene Homopolymer

For the preparation of polypropylene, the C_3 fraction (propylene and propane) is the basic material and is produced by cracking of petroleum products such as natural gas or light oils. The C_3 fraction may be separated from the other gases without undue difficulty by fractional distillation. The separation of propylene from propane is rather more difficult and involves careful attention to the design of the distillation plant. For polymer preparation, impurities such as water and methylacetylene must be carefully removed. A typical catalyst system may be prepared by reacting titanium trichloride with aluminiumtriethyl, aluminium tributyl or aluminium diethyl monochloride in naphtha under nitrogen globe to form a slurry consisting of about 10 % catalyst and 90% naphtha. The properties of the polymer are strongly dependent on the catalyst composition and its

particle shape and size.

Propylene is transferred into the polymerisation vessel under pressure while the catalyst solution and the reaction diluent (usually naphtha) are metered in separately. In batch processes, it is carried out at temperatures of about 60°C for approximately 1-4 hours. In a typical process an 80-85% conversion to polymer is obtained. Since the reaction is carried out well below the polymer melting point the process involves a form of suspension rather than solution polymerisation. The polymer molecular weight can be controlled in a various ways, for example by the use of hydrogen as a chain transfer agent or by variations in the molar ratio of catalyst components, the polymerisation temperature, the monomer pressure or the catalyst concentration. At this stage of the process, the following materials are present in the polymerisation vessel: Isotactic polymer; atactic polymer; solvent; monomer; and catalyst.

The first step in separating these ingredients involves the transfer of the reaction mixture to a drum to remove the unreacted monomer which is purified (where necessary) and recycled. The residual slurry is centrifuged to remove the bulk of the solvent together with most of the atactic material which is soluble in the naphtha. The remaining material is then treated with an agent which decomposes the catalyst and dissolves the residue. A typical agent is methanol containing a trace of hydrochloric acid. The solution of residues in the methanol is removed by a centrifuging operation and the polymer is washed and dried at about 80°C. At this stage, the polymer may be

blended with antioxidants, extruded and cut into pellets. There are a number of variations in this basic process, many of which involve extra processes to reduce the atactic content of the polymer. A typical flow sheet for the manufacture of polypropylene is given in Figure 2.1. There have also been a number of quite substantial changes in the method of polymerisation over the years. For example newer catalyst systems, such as those containing magnesium compounds, give an appreciable improvement in the yield of isotactic material and this enables the washing stage to be dispensed with. Furthermore whilst the suspension process (in hydrocarbon) continues to predominate gas phase polymerisations, and polymerisation in liquid propylene are now being used. Thermal and chemical after treatments have also been developed to reduce the width of the molecular mass distribution.[10]

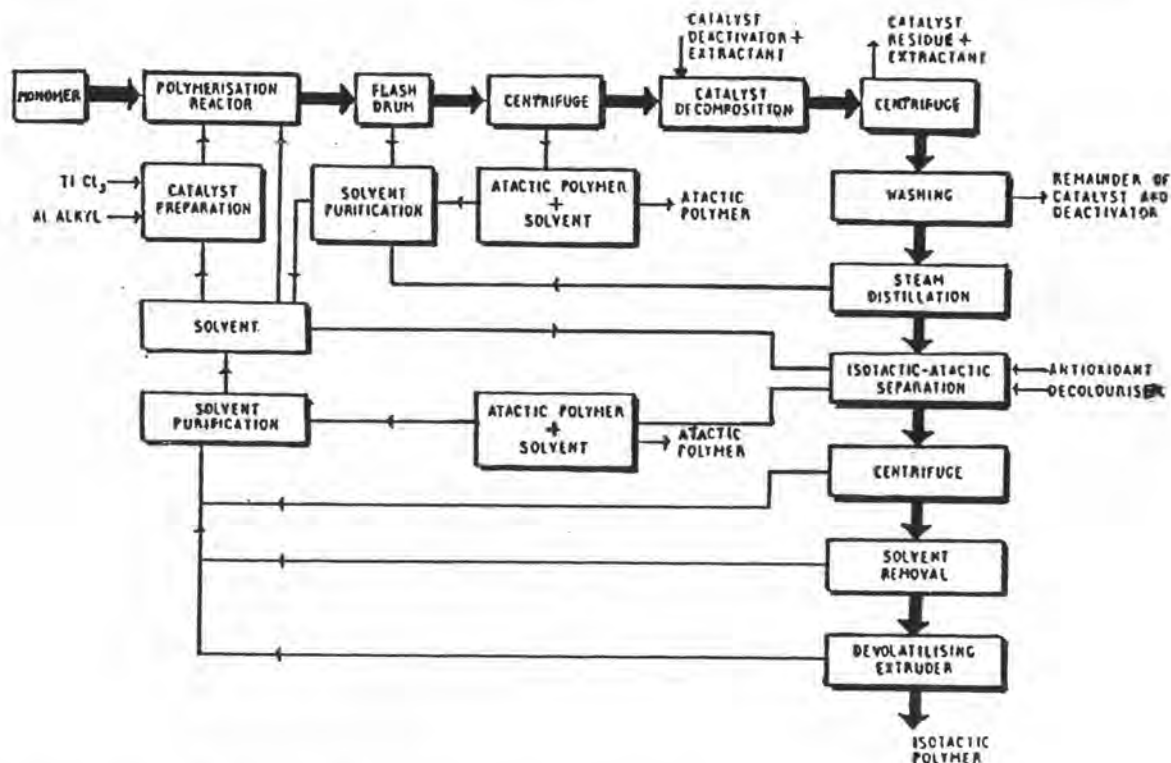


Figure 2.1 Typical flow sheet for polypropylene manufacture.

2.2.3 Classification of Polypropylene Polymer

2.2.3.1 Polypropylene Homopolymer

Polypropylene is synthesized by placing propylene monomer under controlled conditions of heat and pressure in the presence of organometallic, stereospecific catalysts (Ziegler-Natta type). Depending on the catalyst and polymerization process used, the molecular structure of the resulting polymer consist of three different types of stereochemical configurations in varying amounts. These are referred to an isotactic, syndiotactic, and atactic, for which their structures are shown in Figure 2.2. [11]

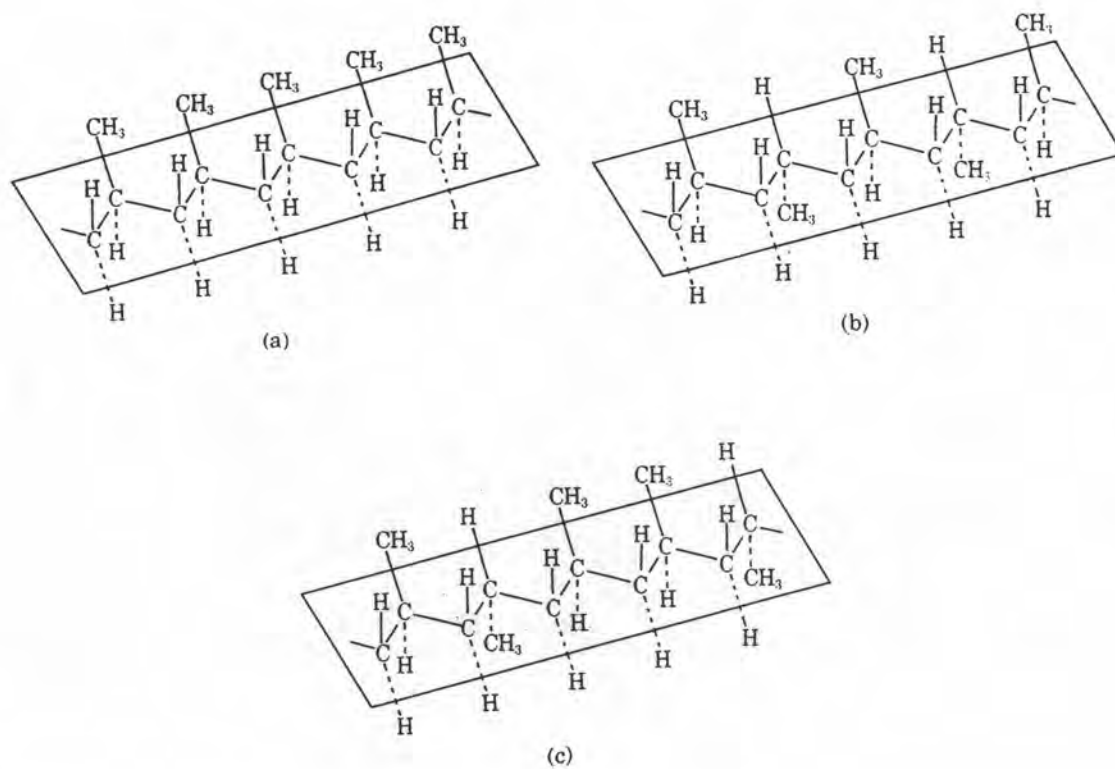


Figure 2.2 Polypropylene structures

a) isotactic b) syndiotactic c) atactic

In isotactic polypropylene (the most common commercial form), the methyl groups are all on the same side of the polymer backbone, providing a structure which readily allows crystal formation. The crystalline nature of the isotactic form gives it good solvent and heat resistances. Catalyst technology implemented during the last decade, which minimizes the formation of the non-isotactic isomers, has eliminated the need for separation of the less-valued atactic fraction, thus reducing the number of processing steps. The two processes primarily used to produce polypropylene are a vapor phase and a slurry in liquid propylene.

By comparison with high density polyethylene and low density polyethylene, polypropylene homopolymer has lower densities, significantly higher melting temperatures, and a higher flexural modulus, i.e., stiffness. These property distinctions lead to differences in end-uses. Stiffness and ease of orientation make polypropylene homopolymers suitable for numerous fiber and stretched tape applications, while their higher heat resistance makes them useful in rigid, autoclavable containers and in molded parts for appliances and autos.

Variables that have primary influence on the processing and physical properties of polypropylene homopolymer include molecular weight (normally expressed in term of flow rate), molecular weight distribution (MWD), stereospecificity, and additives. The average molecular weight ranges from about 200,000 to 600,000. The MWD is usually expressed as ratio of the weight average molecular

weight of the polymer (\bar{M}_w) to the number average molecular weight of the polymer (\bar{M}_n), or \bar{M}_w/\bar{M}_n . This relationship is also known as the polydispersity index. The MWD of a significant effect on its processability and end-use properties. A polypropylene composition having a broad MWD is more shear-sensitive than one with a narrow MWD. As a result, broad MWD materials process more readily in injection moulding applications. MWD is a function of both the catalyst system and the polymerisation process.

Polypropylene homopolymers are used in a variety of processes to produce a wide range of products. Extrusion is the largest market, with textile fibers and filaments the largest segment within the market. Polypropylene has long been a major raw material for making fibers because of its colorability, wear, and chemical resistances; and its favorable economics. Injection moulding, the next largest market for homopolymer, includes containers and closures, automotive applications, housewears, toys, and many other consumer and industrial end-uses.

2.2.3.2 Polypropylene Copolymer

Polypropylene copolymer preparation, isotactic polypropylene homopolymer is made by polymerising propylene in the presence of Ziegler-Natta catalyst systems. The ethylene/propylene rubber fraction is either synthesized in the presence of homopolymer in a second, gas-phase reactor or is purchased beforehand and then blended with the homopolymer in the extruder. The resulting impact polypropylene copolymer is pelletized and sold as such.

Impact polypropylene copolymer, one of the lightest thermoplastics, has a density less than 1, and is less expensive per pound than PET, PBT, HIPS, and ABS. Based on specific volume, the cost per cubic unit of impact polypropylene is less than these resins and PVC. Only HDPE is competitive by this measure. The effect of the elastomer is that amorphous rubber particles distributed throughout the semicrystalline homopolymeric matrix provide stress concentration point at the interface, which initiate local deformation instead of allowing cracks to propagate. So, impact polypropylene copolymer has excellent notched impact energy; Izod impact strength range from 1.5 to 15 ft-lb/inch, and also excellent in Gardner impact properties at low temperatures; Gardner impact strength at -40°F range from 15 to over 300 inch-pound. Furthermore, it is highly resistant to chemicals and environmental stress cracking. The rubber fraction that lended polypropylene its impact resistance does, however, decrease stiffness and lower the heat distortion temperature of impact polypropylene relative to the homopolymer.

The chief commercial application of impact polypropylene is injection moulding of articles used in automotive applications, housewears, and appliances. The impact resistance, low density, colorability, and processability of impact polypropylene make it ideal for such applications. More applications for extruded sheeting made from impact polypropylene copolymers, extruded sheets can be thermoformed into large, thick parts. Good examples are fender and trunk liners in the automotive industry. Sheet extruded from impact polypropylene also can be used in stamping processes in which

small, odd-shaped parts are stamped from a large sheet.

Some properties of isotactic polypropylene and polypropylene copolymer are compared in Table 2.1. [10]

Table 2.1 Some Mechanical and Thermal Properties of Commercial Polypropylenes.

Properties	Test method	Homopolymers			Copolymers	
Melt flow index	(a)	3.0	0.7	0.2	3.0	0.2
Tensile strength						
(lb _f /in ²)	(b)	5000	4400	4200	4200	3700
(MPa)		30	34	29	29	25
Elongation at break(%)	(b)	350	115	175	40	240
Flexural modulus						
(x 1000 lb _f /in ²)	-	190	170	160	187	150
(MPa)		1310	1170	1100	1290	1030
Brittleness temperature	ICI/ASTM					
(°C)	D476	+15	0	0	-15	-20
Vicat softening point	BS 2782					
(°C)		145-150	148	148	148	147
Rockwell hardness						
(R-scale)	-	95	90	90	95	88.5
Impact strength						
(ft-lb _f)	(c)	10	25	34	34	42.5
(J)		13.5	34	46	46	57.5

(a) Standard polyethylene grader: load 2.16 kg at 230°C.

(b) Straining rate 18 in/mim.

(c) Falling weight test on 14 in diameter moulded bowls at 20 °C.


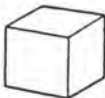
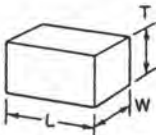
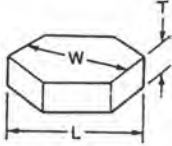

2.3 Fillers

A filler is a finely divided solid that is added to a liquid, semisolid, or solid composition to modify the composition's properties and reduce its cost. Fillers are usually classified according to their source, function, composite, or morphology (see Table 2.2). [12] However, none of these classification schemes is entirely adequate owing to overlap and ambiguity of their categories. Filler can constitute either a major or a minor part of a composition. The structure of the filler particles can range from irregular masses to precise geometrical forms such as spheres, polyhedrons, or short fiber as shown in Table 2.3.[14] An understanding of physical properties of filler and associated functions is most important in applying filler technology. Mineral fillers represent over 80% of the filler market primarily because of their low cost.

Table 2.2 Classification of Fillers

Method of classification	Examples
Source	Natural (mineral); synthetic
Function	Opacification, reinforcement
Composition	Carbonate, silicate, lignin
Morphology	Hollow, sphere, fiber, platelet

Table 2.3 Particle Characteristics

Idealized shape class					
Particle Class	Sphere	Cube	Block	Flake	Fiber
Descriptor ^a	spheroidal ^b	cubic ^c prismatic rhombohedral	tabular prismatic pinacoid irregular	platy flaky ^d	acicular elongated fibrous
Shape ratios;					
length (L)	1	~1	1.4-4	1	1
width (W)	1	~1	1	<1	<1/10
thickness (T)	1	~1	1-<1	$\frac{1}{4}$ -1/100	<1/10
Examples	glass spheres microspheres	calcite feldspar	calcite feldspar silica barite nephelite	kaolin mica talc graphite hydrous alumina	wollastonite tremolite wood flour

^a Preferred to particle class since this is based on relative surface area. First descriptor is preferred.

^b In the sense that a spheroid approaches a true sphere.

^c Generally distorted cubes; more nearly prismatic.

^d Generally having the nature of hexagonal platelets, as illustrated.

In the plastics industry, the term filler refers to particulate materials that are added to plastic resins in relatively large (over 5%) volume loadings. At present, the performance specifications for most compounded plastic products are less strict than for other filled products, such as elastomers and paints, and cost reduction is the primary objective. Hence, plastic compounders tend to compound with the objective of optimizing properties at minimum cost rather than maximizing properties at optimum cost. Table 2.4 lists typical plastic fillers and their uses.[12]

Table 2.4 Typical Plastic Fillers and Their Uses

Filler	Specific gravity	Typical compatible resins	Uses
Alumina trihydrate	2.4	polyesters	fire resistant filler
Carbon black	0.2-2.3	epoxies	electrical goods
Calcium carbonate			
mineral	2.7	most resins	tile, molded goods
precipitated	2.6	most resins	pipe, putty
Clays	2.6	most resins	flooring tile
Feldspar	2.6	thermoplastics	plasticols
Metal	2.5-11.5	epoxies	radiation shields, solders
Mica	2.82	most resins	sheet molded goods
Polymers			
solid spheres	1.1-1.3	most resins	molded goods
hollow spheres	0.2-0.5	thermosets	molded goods
Silica			
diatomite	2.0-2.4	polyethylene	films
novaculite	2.65	thermosets	electrical goods
quartz flour	2.65	thermosets	molded goods
tripolite	2.65	thermosets	molded goods
wet process	1.9-2.2	thermoplastics	sheets, films
vitreous	2.18	epoxies	electrical goods
Silicate glass			
solid spheres	2.5	most resins	molded goods
hollow spheres	0.22	thermosets	molded goods
flakes	2.01	thermosets	electrical goods
Talc	2.7-2.9	PVC, polyalkenes	extruded and molded goods
Wood and shell flour	0.19-1.6	most resins	molded goods.

2.3.1 Organic Fillers

Initially, these additives were of natural origin, and were abundantly available at low cost. Most of them, like wood flour, cotton, and vegetable fibers, are fibrous in structure, and are composed largely of cellulose, with lesser amounts of lignin and other compounds. However, some are not fibrous in nature, and some are of animal origin. At present, synthetic organic materials, chiefly fibers, are also being used as plastic additive, principally for reinforcement of physical properties. Like fillers and reinforcements generally, the organic material additives affect many properties of the compounds into which they are incorporated. The natural materials are generally less expensive than the resins with which they are compounded, and this is the most important reason for their use. However, both natural and synthetic organic additives have important functional effects, including improvement in processability and desirable modification of the properties of the final compound. Organic fillers are shown in Table 2.5. The more important specifications of the common organic fillers are generalized as shown in Table 2.6. [14]

Table 2.5 Organic Material that have been Used as Fillers for Plastics.

NATURAL MATERIALS		
Wood flour	Shell fiber	Miscellaneous materials
Soft woods	almond shell	beer hops, spent
pine, ponderosa	apricot pit shell	coal, anthracite fines
pine, white	Brazil nut shell	coca bean material
Norway fir	candle nut shell	coke
Douglas fir	coconut nut shell	cork, granulated
spruce	filbert shell	corn, cobs
redwood	peanut shell	citrus pulp, dried
Hard woods	pecan shell	flax shives
ash	walnut shell	furfural process residues
beech		hemp hurds
birch	Cotton fibers	keratin
maple	cotton flock	chicken feathers
oak	cotton fabric, chopped	cattle hooves
Bark, fir	cotton cord, chopped	hog bristles
Sawdust, shavings, chips	cotton linters	leather
Sawdust, rubber-coated	cotton seed hulls	milkweed products
	cotton seed fibers	peat moss
Vegetable fibers	cellulose fibers	soybean meal
hemp		strach, corn, potato, rice
coconut(coir fiber)		wheat straw
jute		wool fibers
ramie		
sisal		
SYNTHETIC MATERIALS		
Regenerated cellulose		
rayon fabric		
Cellophane, finely cut		
Polyacrylonitrile fibers		
Polyamide, aliphatic(nylon) fibers		
Polyamide, aromatic(aramid) fibers		
Polyester fibers		
Polytetrafluoroethylene fibers		
Polyvinyl alcohol finers		
Rubber dust, hard		
- rubber dust, vulcanized		

Table 2.6 Properties of Common Organic Fillers

Detail	Wood flour	Cotton flock, Chopped cotton fabric	Cellulose flock	Sisal flock
Ash content	0.3%	0.5-1.5%	0.15%	0.3% max.
Acetone sol.	8.5% max.	2.0-3.0%	-	-
Oil absorption (cm ³ /10 grams)	15-30	20-30	-	-
Ether extract	5.0% max.	2.0% max.	0.24%	0.5-1.5%
%Insolubles	0.0%	1.5-2.5%	0.0%	0.0%
Color	softwood (light cream) hardwood (light tan)	bleached (white colored)	bleached (white) unbleached (tan)	light tan
Appearance	fibrous	fibrous/macerated	fibrous	fibrous
Moisture	5.0-8.0%	5.0-8.0%	5.0-8.0%	12.0% max.
Bulk density (ml/50 grams)	softwood (190-260) hardwood (160-200)	180-300	135-400	140-330
Weight/cu ft	softwood (6-10 lb) hardwood (11-16 lb)	7-11 lb	5-18 lb	4-16 lb
Particle size	5-140 mesh	10-200 mesh	10-200 mesh (10-100 mesh) precision cut. (1/32-1 inch)	random cut.

2.3.2 Wood Flour

Wood flour is a finely ground, dried wood product, fibrous in structure, that acts as reinforcing material for plastics. It is made mostly from softwood, chiefly pine and spruce, but hardwood maple or ash flour are used where no wood resin content is desired. Woods containing essential oils, such as cedar, are not suitable. Wood flour is made from sawdust, chip and shavings by grinding in a buhrstone mill, and has the appearance of wheat flour. Wood flour is composed largely of cellulose in content. Cellulose structure can be shown below.

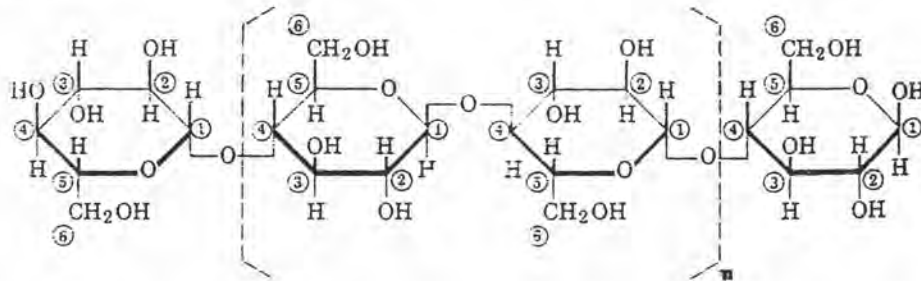


Figure 2.3 Structure of cellulose

Compared to inorganic fillers, cellulose fillers offer many advantages [15-17]:

- a) Lower cost.
- b) Little damage during processing.
- c) Lower abrasion of processing equipment.
- d) Thermoformability into shaped products.
- e) No health hazard.
- f) Lower density.
- g) Abundant renewable resource.
- h) Biodegradable in nature.

Particle sizes commonly used for plastics fillers are 40, 60 and 80 mesh, with sizes as fine as 140 mesh available. Wood flour may absorb some resins or gums when mixed with some plastics, and mineral fillers may also be combined to vary the properties of the molded product. Wood flour is already being employed in thermoplastic on an industrial scale. Its use results in the following advantages: Cheap filler; improved shrinkage behavior; increase in modulus of elasticity and stiffness, fall less rapidly at elevated temperatures; and tensile strength and tensile stress at break are scarcely affected.

2.4 Coupling Agents

Coupling agents have been used as a "molecular bridge" to produce a bond between polymer and filler or reinforcement particles. Coupling agents are defined primarily as materials that improve the adhesive bond of dissimilar surfaces. It must involve an increase in true adhesion, but it may also involve better wetting, rheology, and other handling properties. The coupling agents may also modify the interphase region to strengthen the organic and inorganic boundary layers. Modification of the interface may produce other changes in composites that are very desirable. Surface treatment of a mineral may improve wetout with a polymer, as well as dispersion of fillers in liquid polymers. The treatment protects the mineral against cleavage and may even heal flaws in the surface. The polymer layer may be strengthened by interface modification that promotes alignment of polymer segments and interdiffuses with the polymer, possibly forming interpenetrating polymer networks (IPNs). Many types

of coupling agents such as chromium complexes, phosphorus esters, titanate ester are also useful, but the best known coupling agents are the silane materials.[18-19]

2.4.1 Organofunctional Silanes

Silane coupling agents are chemical tools for the plastic compounder, they can increase filler loading, higher reinforcement levels and improve processing and end-product properties. Silane coupling agents, used in a wide range of composite products, enable the plastics compounder to maximize, as economically as possible, the contributions of individual components to the properties of the composites. When components of differing chemical nature and physical form are combined, problems originate in the interfacial region where the organic resin phase must wet and spread over the inorganic filler or reinforcement surface. Silane coupling agents provide significant benefits by modifying the interfacial region. Their unique chemistry permits reaction with organic as well as inorganic materials.[13,20]

2.4.1.1 Structure and Chemistry

The generic composition of a silane coupling agents has a chemical structure as follows [13]:



where X is a hydrolyzable group on silicon such as chloride, methoxy, ethoxy, or acetoxy.

Y is an organofunctional group.

R is a nonhydrolyzable carbon that links between the silicon atom and the organofunctional group.

Si is a silicon atom.

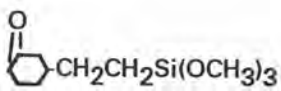
The chemistry of preparation of this family of materials has been extensively studied in detail from both the formation of Si-C bond and the modification of Si-X groups. Most commercially available organofunctional silane are the alkoxy silane derivatives :



For many composites, a silane is chosen in which Y has maximum reactivity with the matrix resins. Table 2.7 shows a line of commercially available silane coupling agents, their structures and suitability for use with various matrix resins.[20]

Silane coupling agents provide chemical bonds between organic polymers and mineral surfaces. Methoxy silanes may react directly with hydroxyl groups on a mineral surface to form oxane bonds. The silane may also be prehydrolyzed to form silanetriols, which condense with surface hydroxyl groups and with each other to form an organosilicon-bonded surface. The fiber-glass industry invariably applied silanes from aqueous solution to deposit about 0.5% by weight of siloxane on the fibers [20], as shown in Figure 2.4.

Table 2.7 Silane Coupling Agents: Structure and Recommended Polymer Systems.

Silane	Description	Structure	End-Use Polymer
A-151	Vinyltriethoxysilane	$\text{CH}_2=\text{CHSi}(\text{OC}_2\text{H}_5)_3$	
A-172	Vinyl-tris(2-methoxyethoxy)silane	$\text{CH}_2=\text{CHSi}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_3$	Unsaturated polyester,
A-174	gamma-Methacryloxypropyltrimethoxysilane	$\begin{array}{c} \text{CH}_3 \quad \text{O} \\ \diagdown \quad \parallel \\ \text{CH}_2 = \text{C} - \text{C} - \text{OCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3 \end{array}$	DAP, polyolefin
A-1100	gamma-aminopropyltriethoxysilane	$\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OC}_2\text{H}_5)_3$	Epoxy, phenolic,
A-1120	N-beta-(aminoethyl)-gamma-aminopropyltriethoxysilane	$\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$	melamine, polyamide, polyester,
A-1160	gamma-Ureidopropyltriethoxysilane	$\begin{array}{c} \text{OH} \\ \parallel \\ \text{NH}_2\text{CNCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OC}_2\text{H}_5)_3 \end{array}$	polycarbonate
A-186	beta-(3,4-Epoxycyclohexyl) ethyltrimethoxysilane		Epoxy, phenolic,
A-187	gamma-Glycidoxypropyltrimethoxysilane	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_2 - \text{CH} - \text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3 \\ \diagup \quad \diagdown \\ \quad \quad \text{O} \end{array}$	polyester
A-189	gamma-Mercaptopropyltrimethoxysilane	$\text{HSCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$	Epoxy, polysulfides

Coupling agents may also be added to resins to obtain unprimed adhesion to mineral surfaces. Silanes may be formulated into primers by partial hydrolysis or by modification with polymer precursors. Primers on massive mineral surfaces are related to coupling agent applied to fiberglass or particulate minerals but are often applied in much thicker layers. Commercial applications of silane coupling agents are not as simple as shown in Figure 2.4. From practical tests it has been determined that good adhesion of polymers to minerals often requires much more than a monolayer of coupling agent. It is common practice to put up to a hundred monolayer equivalents, or more, of silane on the surface. Furthermore, it has been observed that silane primers are very effective in bonding certain polymers to minerals where no chemical reaction between the organofunctional group Y and the polymer is observed. Bonding through silane coupling agents by other than simple chemical reactivity is explained by interdiffusion and IPN formation in the interphase region. Interdiffusion and cross-linking of silane adhesion promoter were recently identified as the mechanism of adhesion of poly(vinyl chloride) plastisols to silane treated mineral surfaces [19], as shown in Figure 2.5.

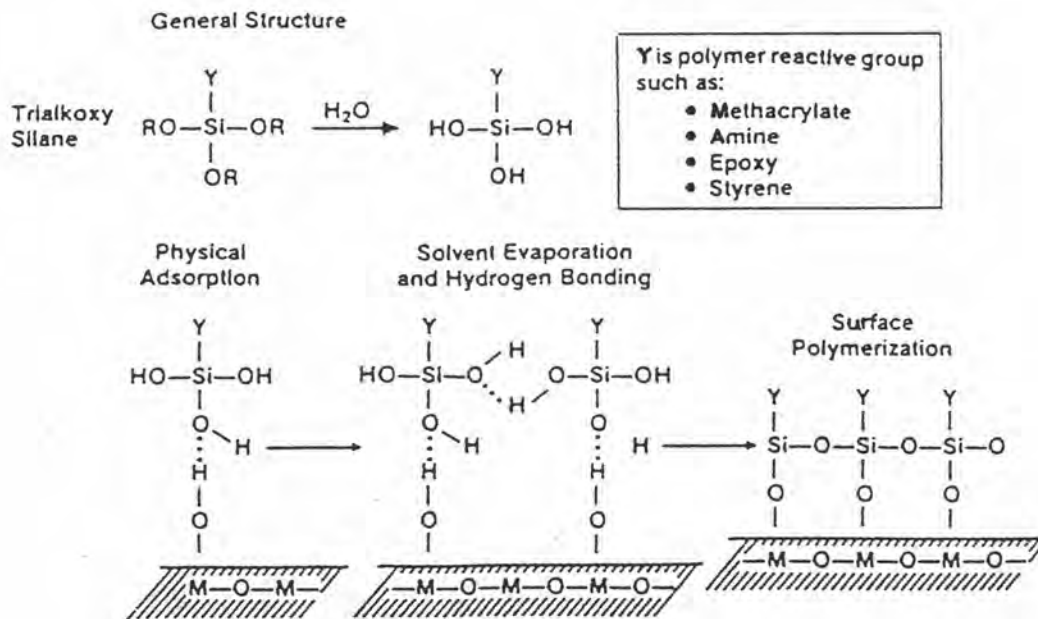


Figure 2.4 Monolayer model for bonding in mineral-polymer composites.

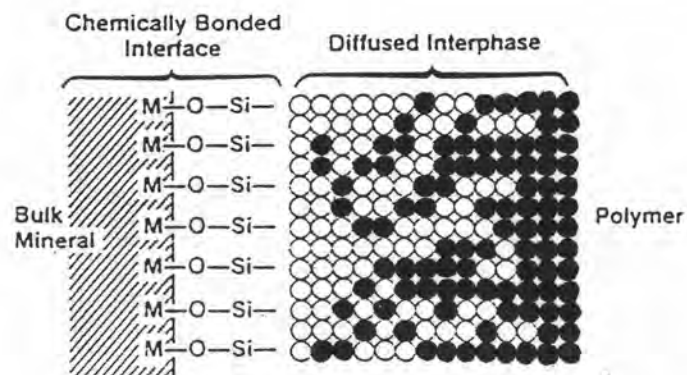


Figure 2.5 Bonding through silanes by interdiffusion:
 open circles indicate regions of coupling agent;
 solid circles indicate regions of polymer.

2.4.2 Epolene Waxes

Epolene waxes are medium to low molecular weight polyethylene or polypropylene waxes which are useful as processing aids, mould release agents, dispersion aids, and coupling agents in the plastics industry.[21] Since numerous types of Epolene waxes are available, properties can be to fit various processing operations. Classification of various Epolene waxes is shown in Table 2.8.

Table 2.8 Classification of Epolene Waxes

Name	Type
Epolene C waxes	Highly branched, medium molecular weight polyethylene waxes.
Epolene C-16, C-18 waxes	Chemically modified polymers of ethylene.
Epolene N-waxes	Low molecular weight polyethylene waxes (except N-15).
Epolene N-15 wax	Low molecular weight polypropylene wax.
Epolene E waxes	Oxidized low molecular weight polyethylene waxes (except E-43).
Epolene E-43 wax	Chemically modified polymer of propylene.

Epolene polyolefin waxes find wide use as plastic additives. Depending on the end use involved and the specific wax selected, it can enhance processability and performance of composites.

In this work, Epolene E-43 wax is chosen as a coupling agent for wood/polypropylene composite. It has been suggested that it can function as a coupling agent for many filled or reinforced plastic such as glass, mica, talc, CaCO_3 , wood flour in polypropylene and high density polyethylene. Moreover, it improves processability and surface characteristics. Epolene E-43 wax can replace more expensive silane treatments in composites.

Epolene E-43 wax is the low molecular weight maleated polypropylene. Preparation of maleated polypropylene, polypropylene has been reacted with maleic anhydride by free radical grafting reaction. The reaction product apparently contains succinic anhydride moieties, which are located within the polypropylene chains or at chain ends.[22-23] Two properties of maleated polypropylene which could influence their effectiveness are (a) molecular weight, which could affect entanglement with the resin, and (b) acid number, which indicates the amount of functionality present in the coupling agent[24]. The effectiveness of maleated polypropylene may be related to its ability to penetrate the wood and form a strongly held hydrophobic layer that is attractive to the polypropylene, thereby increasing both the effective bonding area and mechanical interlocking. That is a result of reaction of its anhydride groups with the wood and of the compatibility of its polypropylene segments with the polypropylene matrix.[25-26]

2.5 Literature Review

The use of cellulose and lignocellulosic composites appears to gain in importance, at least, judging from the increasing number of research works in this area. The applications of such materials range from simple filling to more elaborate structures like laminates and chemically modified systems. Despite the large number of literature references, systematic studies of the various aspects of this area appear to be relatively rare. This is also the case with cellulose and various types of lignocellulosic materials used as fillers for thermoplastics. In this literature survey, the work of polymer filled with natural fillers and reinforcements is summarized as follows:

Klason, C., Kubat, J. and Stromvall, H.E. [27] reported on the processing and properties of composites consisting of thermoplastics and cellulose-based filler. In the work, processing aids or coupling agents were not added. The plastics used were HDPE, PP, PS, SB, PA6, and PA12. The fillers were wood flour (WF, white spruce), cellulose flour (CF, bleached-sulphate, pine) and cellulosic fiber (bleached-sulphate, birch). The mixtures were homogenized by kneader or single screw extruder before injecting into tensile test bar mold. The modulus increased with the filler content as shown in Figure 2.6, while the yield and breaking stress remained relatively unaffected. The elongation at rupture (Figure 2.7) and the impact resistance (Figure 2.8) fell sharply when the filler content was increased. The compounding method had no influence on the modulus. Kneader compounding, producing a higher homogeneity, gave higher strength and

impact values (Figures 2.7, 2.8) than compounding in a single-screw extruder. At processing temperatures in the excess of 200 °C, severe discoloration was noted.

Myers, G.E., Chahyadi, I.S., Coberly, C.A. and Ermer, D.S.[28] studied the mechanical properties of wood flour filled polypropylene composites which improved by using coupling agents to enhance the bonding between filler and matrix. The effectiveness of a commercially available additive, Epolene E-43, was examined. The effect of Epolene E-43 was studied alone and in combination with three other variables: the weight ratio of wood flour to polymer in the composites (45/55 or 55/45), size of wood flour particles (20 or 40 mesh), and extruder residence time (one or three extrusions). Of all the variables, Epolene E-43 had the greatest effect on strength. This effect was somewhat enhanced by using the 40-mesh wood flour and three extrusions; for this combination of variables, wood flour/polymer ratio and 40 mesh wood flour resulted in the largest values of flexural and cantilever-beam modulus. Addition of Epolene E-43 slightly decreased notched impact energy but possibly increased unnotched impact energy. None of the variables had a significant effect on melt viscosity. Average wood flour particle size was decreased by processing, particularly in the presence of Epolene E-43. Overall, these findings indicate that Epolene E-43 exerts some degrees of coupling action. The higher cost of Epolene E-43 can be compensated by increasing the ratio of wood flour to polypropylene.

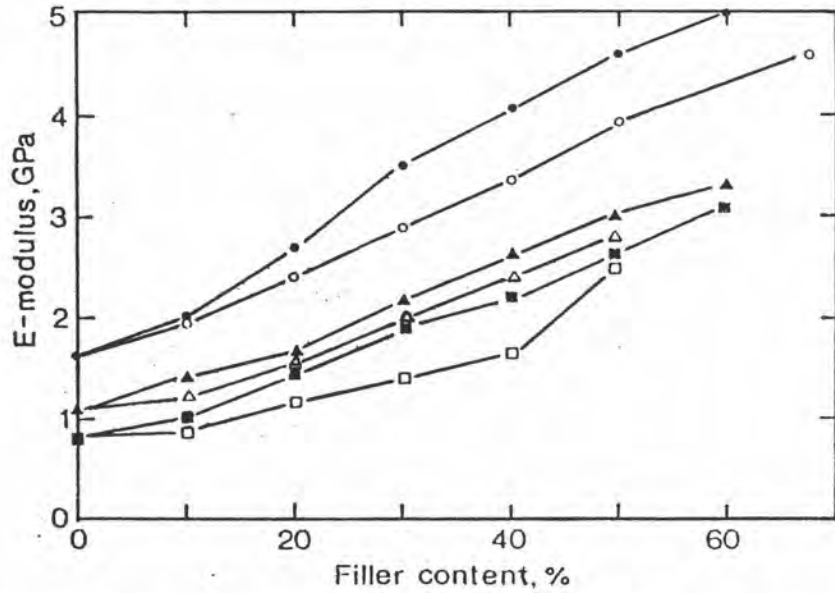


Figure 2.6 Modulus vs. filler content (mix in Buss-Kneader) for HDPE (■), PP (▲), and SB (●). Open symbol, CF; Filled symbol, WF.

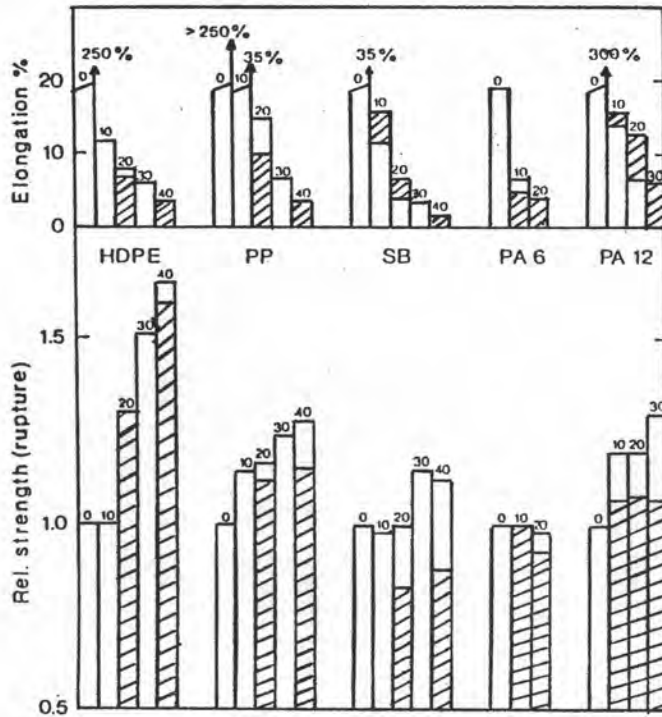


Figure 2.7 Tensile strength and elongation at rupture for various matrixe filled with WF. Compounding: Single-screw extruder (dash areas), Buss-Kneader (open areas).

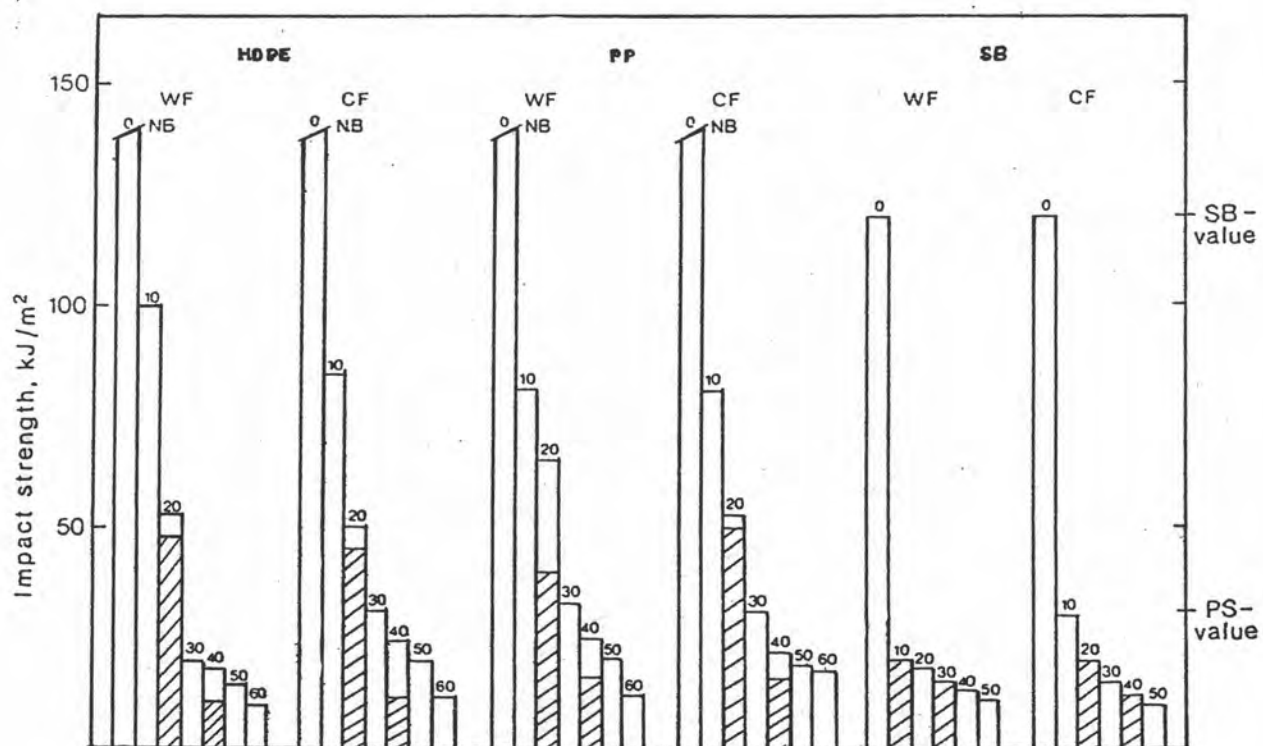


Figure 2.8 Impact strength (unnotched charpy) for HDPE, PP and SB filled with WF and CF.

Compounding : Single-screw extruder (dash areas),

Buss-Kneader (open areas). NB, no break.

Myers, G.E., Chahyadi, I.S., Gonzalez, C., Coberly, C.A., and Ermer, D.S. [17] investigated the effects of the concentration of a maleated polypropylene additive (0 to 5 percent by weight) and of extrusion mixing temperature (190 to 250 °C) on the mechanical properties of extruded and injection-moulded polypropylene-wood flour composite. The effects of maleated polypropylene additive on similarly processed polypropylene-wood flour and high density polyethylene-wood flour composites were also compared. The results of experiment can be shown in Figures 2.9 and 2.10. In this work, both the additive and the high extrusion temperature led to some wood degradation and to less polar wood surface. The additive led to greater reinforcement of the composite, as indicated by moderate but useful increases in heat deflection temperature, strength, and modulus. The major portion of those improvements were achieved by adding 1 to 2 percent additive. However, both the additive and the high extrusion temperature decreased impact energy, presumably as a consequence of increased reinforcement by the particles and wood degradation. Heat deflection temperature, and modulus of the polypropylene-wood flour system were marginally better than the high density polyethylene-wood flour system as shown in Figures 2.10a,b,c; while the impact resistance was marginally poorer (Figure 2.10d).

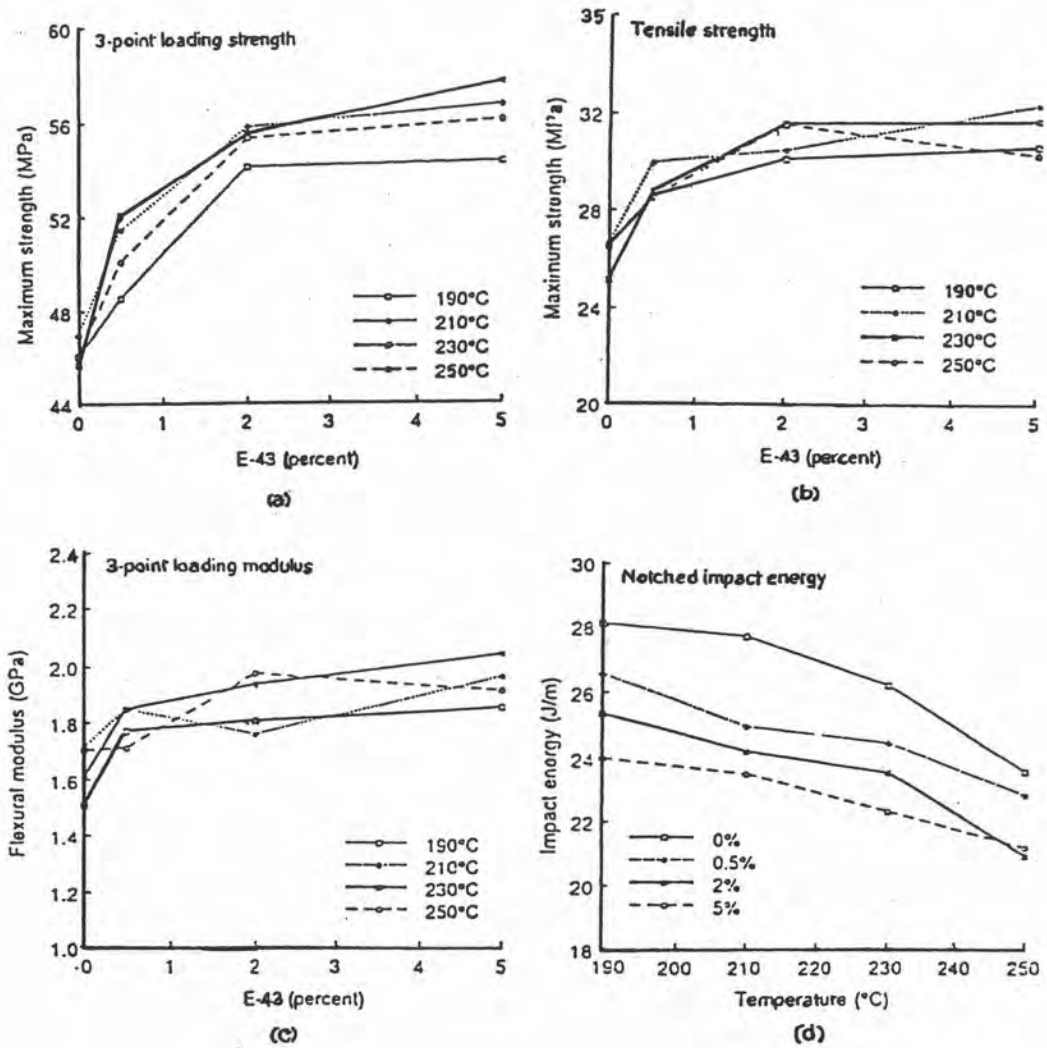


Figure 2.9 Mechanical properties of PP-WF composites as a function of extrusion temperature at different Epolene E-43 concentrations

- Flexural (three point loading) strength.
- Tensile strength.
- Flexural (three point loading) modulus.
- Notched impact energy.

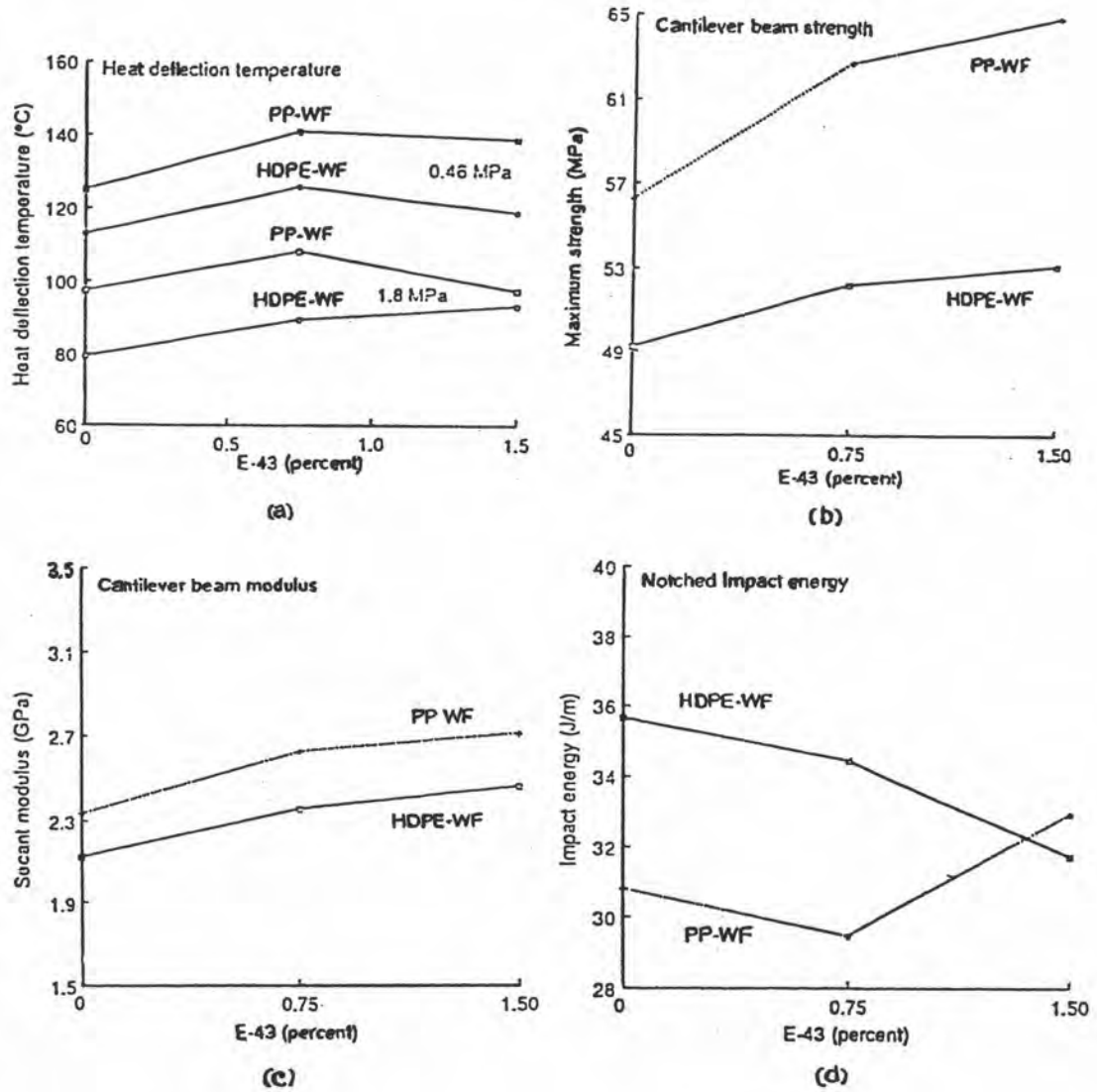


Figure 2.10 Effect of Epolene E-43 concentration on mechanical properties of PP-WF and HDPE-WF composites.

- a) Heat deflection temperature.
- b) Cantilever beam strength.
- c) Cantilever beam modulus
- d) Notched impact energy.

Raj, R.G. and Kokta, B.V. [15] studied silane-coated wood fibers as filler in LLDPE. Chemithermomechanical pulp (CTMP) of aspen was pretreated with various silane coupling agents (silane A-172, A-174 and A-1100) having different functional groups. The properties of composites are shown in Figure 2.12. The results also indicate that silane A-174 (methacryl functional group) performed better as a coupling agent than silane A-172 or A-1100. Vinyl groups in silane A-172 and A-174 may react with the matrix through radical reaction, whereas this may not be the case with aminopropyl groups in silane A-1100. LLDPE filled with silane A-174 pretreated wood fiber (50% filler weight) produced a 31% increase in tensile strength and 124% increase in tensile modulus compared to unfilled LLDPE. The researcher expected that a possible coupling mechanism of polymer-coupling-wood fiber could be shown in Figure 2.11.

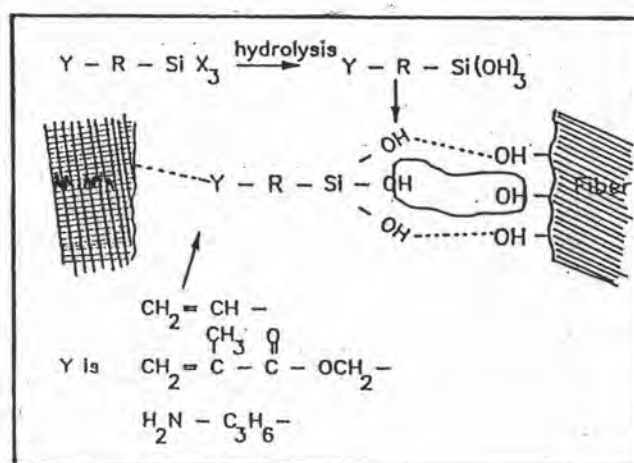


Figure 2.11 Possible coupling mechanism at the fiber-matrix interface.

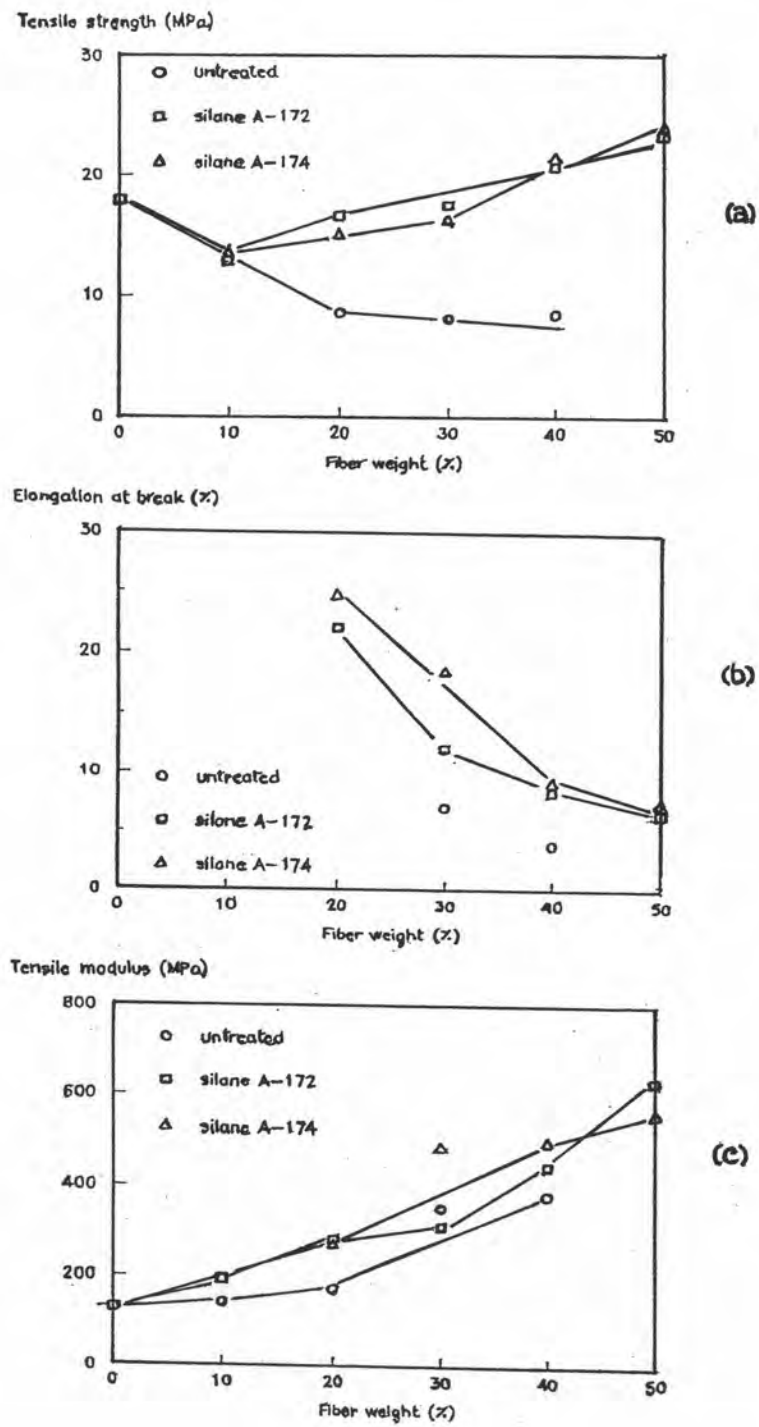


Figure 2.12 Effect of silane pretreatment on mechanical properties of LLDPE-Wood fiber composites.

a) Tensile strength. b) Elongation at break.

c) Tensile modulus.

Raj, R.G., Kokta, B.V., Grouleau, G., and Daneault, C. [16] studied the influence of coupling agents on mechanical properties of composites containing cellulosic filler. Three different cellulosic fibers were mechanical pulp, wood flour and cellulose pulp. The polymer-wood fiber was homogenized in a single screw extruder. The amount of wood fiber was varied from 0 to 40% by weight of fiber. The extrudate was ground to 20 mesh and then molded in a Carver laboratory press (temperature 150 °C, pressure 3.3 MPa) into dog-bone-shaped tensile specimens. The addition of wood fibers in HDPE increased the stiffness of the composites while the tensile strength decreased. To improve the adhesion between the filler and the polymer matrix, wood fibers were pretreated with a silane coupling agent/polyisocyanate before compounding with the polymer. Tensile strength increased from 18.5 MPa (untreated fiber) to 35.2 MPa in isocyanate-treated fiber composites. To compare the cost/performance of mica and glass fiber with the cellulose fiber at 30% fiber weight, the data of these composites were compared in Tables 2.9 and 2.10. From these data, it indicated the advantage of wood fiber over glass fiber and mica.

Table 2.9 Comparison of Tensile Properties of Wood Fiber, Glass Fiber and Mica HDPE.

Fiber (wt%)	Tensile strength (MPa)			Elongation (%)			Tensile modulus (GPa)		
	10	20	30	10	20	30	10	20	30
Wood fiber ^a	27.8	31.7	35.2	8.9	7.6	6.0	1.01	1.34	1.63
Glass fiber	28.4	33.9	37.6	9.8	8.7	7.5	1.17	1.48	1.84
Mica	23.6	21.8	19.7	7.1	4.8	3.4	1.29	1.57	1.93

^a3.0% PMPPIC treated.

Table 2.10 Cost Analysis of HDPE Reinforced with Different Fillers

Polymer	Filler		Starting material (\$/ton)	Composite (\$/ton)
	Type	Wt%		
HDPE	—	—	1070	—
HDPE	CTMP aspen	10	350	998
	Mica	10	750	1038
	Glass fiber	10	3200	1283
HDPE	CTMP aspen	30	350	854
	Mica	30	750	974
	Glass fiber	30	3200	1709

Takase, S., and Shiraishi, N. [26] studied on composites from wood and polypropylene. Composites of polypropylene(PP) or maleic-anhydride-modified polypropylene (MPP) with refiner ground pulp(RGP) were prepared under various kneading conditions(mixing temperature, rate of rotation, and mixing time) and then the kneaded samples were molded into films by hot-press for testing to evaluate their tensile strength, elongation at break and Young's modulus. Furthermore, the effect of modifiers of PP on the properties was evaluated in this study. Modified PP that can be grafted or can have affinity to RGP was proved to improve the tensile strength of the molded composites as the RPG content increased, while the strength was decreased for PP-RGR composite without the modifier. MPP was also evaluated as a compatibilizer for PP-RGP composites, and a tremendous improvement of tensile strength was achieved with MPP addition of only 2.5%, indicating that MPP can act as compatibilizer in its system.

Xanthos, M. [30] studied the effects of processing conditions and coupling agents on properties of extruded and injection moulded polypropylene composites containing 30 and 40% by weight of wood flour.

Wood flour was obtained from reed plants. The properties of injection moulded composites are comparable with those of composites containing calcium carbonate or talc, with the additional advantage of low specific gravity. Processing of these composites requires the use of low temperatures and adjustments in extrusion and injection moulding conditions. Defects resulting from the thermal degradation of wood are thus minimized. Some extrusion data suggest that properties improve with increasing melt temperature. A methacryloxysilane and dimaleimide(m-phenylenedimaleimide) were evaluated as coupling agents. The performance of these additives as adhesion promoters improved in the presence of free radical sources. Results obtained with the maleimide suggest that an interesting method of improving adhesion be the use of maleimide modified polypropylene as the base resin for compounding with wood flour. In spite of the low aspect ratio of the wood flour and its limited thermal stability, it appears to be a potential reinforcing filler for polypropylene.

Woodhams, R.T., Thomas, G. and Rodgers, D.K. [31] investigated the mechanical properties of wood pulp fiber compared favorably with glass fiber. Softwood pulp fibers with fiber aspect ratio near 100 were being dispersed into high density polyethylene or isotactic polypropylene with the aid of carboxylic dispersing agents to form mixture containing 50% weight wood pulp which could be readily injection moulded. Comparisons of the stiffness/weight efficiencies revealed that pulp composites equal or exceed the stiffness of most traditional materials of construction including steel, aluminum, glass fiber composites, and talc filled polyolefins, while retaining a

major material cost advantage. Wood fibers are non-abrasive so that relatively large concentrations may be incorporated into polyolefins without causing serious machine wear during mixing and fabrication.

Kubat, J., and Stromvell, H. E.[32] studied the properties of injection moulded lignin-filled polyethylene and polystyrene. Three grades of lignosulphonates were used as filler. The maximum filler content was 70% (by weight). The thermoplastic and filler were blended in a tumble mixer prior to homogenization in a mixer extruder. The tensile test specimens were produced by injection moulding and the test was done on Instron tensile tester. The another mechanical property was unnotched impact resistance (Charpy). The results could be concluded that tensile moduli of these thermoplastics were increased (Figure 2.13a) but the tensile strength, elongation at break, and impact strength were greatly decreased with the increasing of lignin content (Figures 2.13b,c,d).

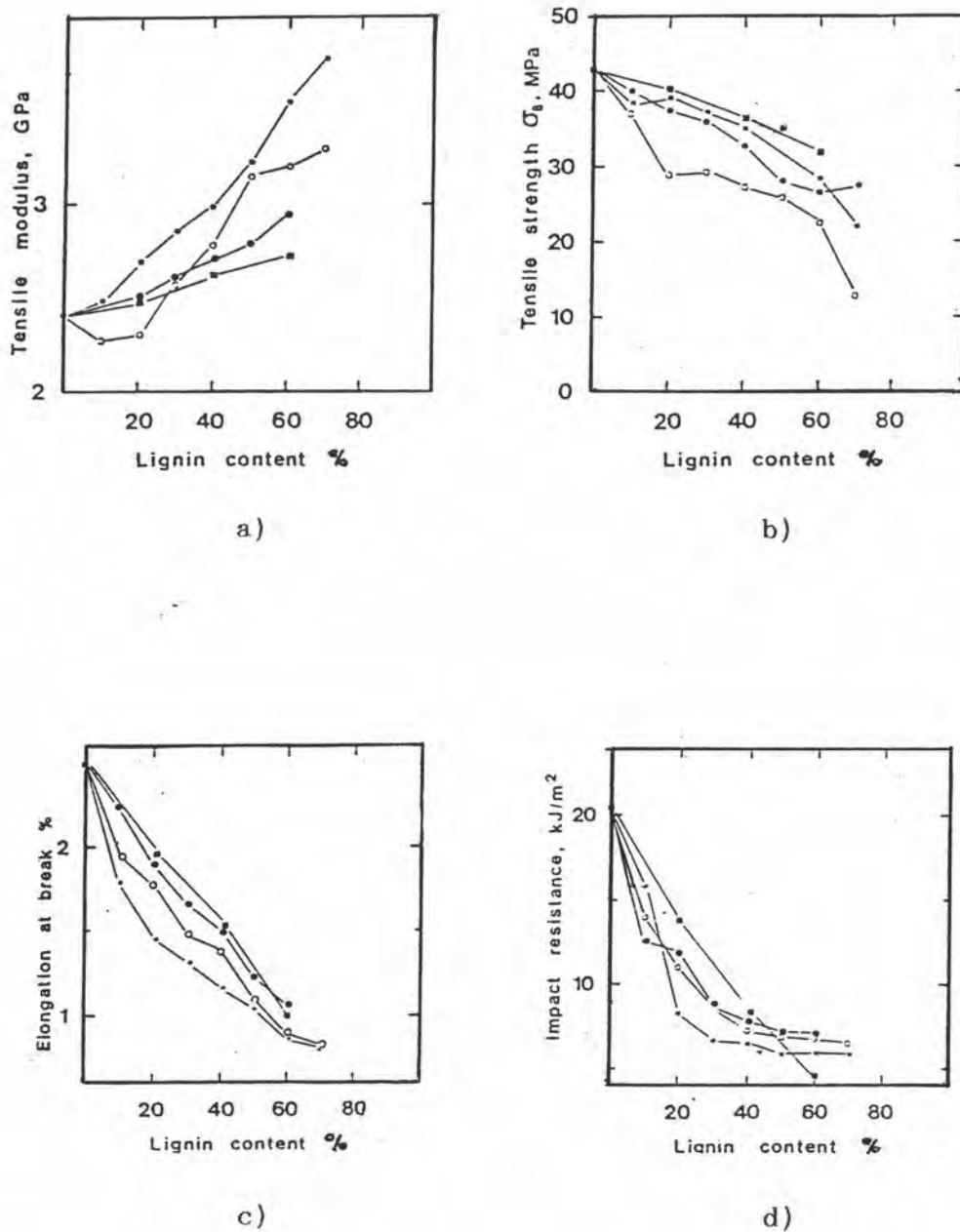


Figure 2.13 Mechanical properties of PS-Lignin composites.

a) Tensile modulus. b) Tensile strength.

c) Elongation at break. d) Impact resistance.

*, Wanin S.; O, Wanin SR.; ●, Ultrazine Na; ■, Indulin AT