# Building Composites Based on By-Products

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# ABSTRACT

## Building Composites Based on By-Products

Sahar Davoodi

This research program studies replacing part of PVC by a by-product material (lignin) in the plasticized PVC-wood flour composite formulation. Moreover, it studies and experiments different coupling agents to improve the interface between polymer matrix and wood flour.

For these purposes, series of PVC-wood flour control and blend formulations with different amount and type of lignins and wood flour were prepared. This process also included selecting the effective additives and adequate processing parameters for new formulation of PVC-lignin-wood flour composite to enrich the best properties. Tensile and thermal properties, as well as torque values are evaluated to choose the best formulation.

As a result, an effective heat stabilizer, lubricant and proper processing parameters were established. Although replacing part of PVC with large amount of lignin did not result in a composite with desired properties, significant improvements in tensile properties were attained when the concentration of alcell lignin in composite was of 1 and 2phr. Alcell due to its polar groups acts as an effective coupling agent and increases the interfacial adhesion between plasticized PVC and wood flour, so it improves the performance of the composite.

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# List of Notations

| | |
|---|---|
| 2-45 | Di-ethylene glycol dibenzoate/Benzoflex 2-45 |
| $\delta$ | Solubility parameter |
| ABAC | Abietic acid |
| AL | Alcell lignin |
| APHA | American public ealth association color index |
| Ba | Barium |
| ASTM | American society of testing materials |
| Ca | Calcium |
| Cd | Cadmium |
| CAS | Chemical abstracts service |
| CaSt | Calcium stearate |
| C-C | Carbon-Carbon bond |
| C=C | Carbon-Carbon double bond |
| Cl | Chlorine |
| C-O-C | Ether bond |
| C=O | Carbonyl |
| COH | Carboxyl |
| COO | Carboxylate |
| DOP | Di-ethyl hexyl phtalate |
| DSC | Differential scanning calorimetry |
| H | Hydrogen |

| | |
|---|---|
| HDPE | High density polyethylene |
| hrs | hours |
| IN | Indulin lignin |
| K | Fikentscher value (related to PVC viscosity) |
| LAC | Linoleic acid |
| LDPE | Low density polyethylene |
| Lindol | Tricresyl phosphate |
| MA | Maleic anhydride |
| MAPP | Maleic anhydride polypropylene |
| m.g | meter. gram |
| Min. | Minute |
| Mn | Number average molecular weight |
| MPa | Mega-Pascal |
| Mw | Weight average molecular weight |
| MW | Molecular weight |
| OH | Hydroxyl |
| PE | Polyethylene |
| pH | Potential of hydrogen |
| PHA | Phthalic anhydride |
| phr | parts per hundred parts resin |
| PMA | Poly (methyl methacrylate) |
| PMPPIC | Poly [methylene poly (phenyl isocyanate)] |
| PVC | Poly (vinyl chloride) |
| PP | Polypropylene |
| PS | Polystyrene |

| | |
|---|---|
| Tg | Glass transition temperature |
| T | Tomlinite lignin |
| VCM | Vinyl chloride monomer |
| WF | Wood flour |
| WFPC | Wood flour/fibre polymer composites |
| WPC | Wood polymer composites |
| Zn | Zinc |

# *Chapter 1 Introduction*

For over 20 years, natural organic fillers like lignocellulosic materials (wood flour (WF), hemp, flax, kenaf, jute, sisal, rice hulls, etc.) have pervaded into the North American plastics industry and markets with an impressive development. The North American demand for natural filler-plastic composites was 317.5 million tonnes in 2001, it is expected to be 396.9 billion tonnes in 2007 and to raise at least until 2010. 75% of these products will be manufactured by plastic-WF composites, and properties like environmental friendliness, recyclability, resistance to rot and fungus, less routine maintenance, and lower costs are their motivators. The most acceptable thermoplastics in the polymer-WF industry are polyethylene (PE) (83%), polypropylene (PP) (7%) and poly (vinyl chloride) (PVC) (9%) [based on North American market share in2002] [1].

Between these composites, the market for PVC-wood composites will increase 200% from 2003 to 2010, compared with 130% for PP-wood composites and 40% for PE-wood composites [1].

The main market for PVC-based wood composites is in building and construction applications like decking, fencing, and window and door profiles since they have satisfactory mechanical properties. The other realized markets are automotive, marine, consumer goods, etc.

The abbreviation "WPC" (wood polymer composite) most often represents wood thermoplastic composites which have a growing market today, especially PVC. WPCs have benefits of both wood and plastics. Some of these advantages are low density, low equipment abrasiveness, relatively low cost, good biodegradability, which are wood properties. Moreover, plastics contribute to WPCs good moisture and decay resistance. The demand for natural fibre/plastic composites are expected to increase 60% per year for building construction and 50% per year for automotive applications [2].

However, the low thermal stability of wood, and the difficulties in obtaining good filler dispersion and strong interfacial adhesion are strong limitations in this industry due to incompatibility between the hydrophilic, polar wood fibres and hydrophobic, non-polar thermoplastics which causes a weak interface between the wood filler and the matrix. Other negative factors are hydrogen bonding between wood components and physical entanglement of wood fibres which reduce the dispersion of the fillers in the viscous polymer matrix [3]. As mentioned above, the mechanical properties of PVC-WF composites like tensile, flexural and impact properties are decreased compared to the control PVC.

Many studies have been conducted regarding the use of effective coupling agents and compatibilizers to enhance the interfacial adhesion between WF and polymer matrix.

For PVC-Wood composites, the coupling effects of poly [methylene(polyphenyl isocyanate)], silanes, maleic anhydride, maleated polypropylene, and linoleic acid have been examined. None of them affected the mechanical properties of the composites. In the best conditions, the mechanical properties of PVC-WF went up to the same range as those of control PVCs [1].

The objective of the research program includes the development and evaluation of a new plasticized PVC-WF composite by replacing part of PVC with lignin and/or using lignin as a compatibilizer which is an original contribution for PVC-WF systems.

Utilization of lignin in PVC-WF composites was undertaken for several purposes:

- To develop more cost-effective materials with acceptable mechanical properties;
- To increase the strength of PVC-WF formulation to microbial attack;
- To develop a new market for lignin;
- To obtain a higher compatibility between the WF and PVC matrix;

Lignin, the second polymer used in this study, is a natural amorphous polymer with a cross linking structure. Normally, 25wt% of wood is lignin which, with cellulose, makes the fundamental components of most plants. Considering the large quantities of lignin produced annually by the pulp and paper industry and its functional characteristics in wood and plants, the idea of adding lignin to PVC-WF is entirely feasible.

Due to the complex structure of native lignin, interest in the development of lignin blends containing synthetic polymers was almost continuous in the past 20 years, but in most cases the resulting materials were brittle and weak.

Recently published data show that, generally, mechanical properties of the lignin-synthetic polymer blends are strongly influenced by the degree of associations of lignin components [4].

Studies done by Banu and colab [5] have demonstrated that it is possible to reduce Tg of lignin and consequently the degree of association between the individual molecular components through the use of specific plasticizers.

Having this observation in mind the PVC-WF- lignin composites were formulated with two of the best plasticizers found for lignin and also efficient for PVC, namely: diethylene glycol dibenzoate (2-45) and tricresyl phosphate (Lindol).

To achieve these purposes, different formulations of PVC-lignin blends filled with WF at different concentrations of lignin and WF were prepared, processed and tested.

## 1.2 Organization of the thesis

The next chapter of the present research reviews some theoretical background related to the research knowledge of PVC, WF, lignin, and additives which are used for PVC-WF formulation, as well as an introduction of thermoplastic-wood composites, processing procedures and standard tests.

Chapter 3 presents raw materials and their properties, as well as experimental procedures.

In chapter 4, all the experimental results are presented in the order of the different phases of the program. The analysis and explanation of the results of the materials' thermal properties, mechanical properties and processability are provided. The performance properties will aid in evaluating these formulations from a practical standpoint.

Finally, conclusions and suggestions for further research on this topic are provided in chapter 5.

# Chapter 2 Literature Review

It is accepted that the increase in the plastics market and growth of new and specialized applications are related to advances in the field of multi-component and multi-phase systems like composites, blends, alloys and foams. In these systems, fillers are the essential auxiliary components which are the minor dispersed phase in a major polymer matrix. The use of fillers has profitable effects on reducing the price of plastic compounds and favourable effects on some mechanical properties. There are different kinds of fillers, among which natural fibers have the perfect properties in plastic matrices. Natural fibers have low density and high specific properties which made them competitive to other reinforcements. In addition, they are biodegradable and nonabrasive unlike other reinforcing fillers.

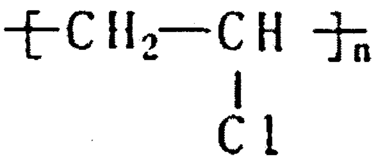
In contrast, incompatibility with the hydrophobic polymer matrix, tendency to form aggregates during processing, and their high moisture absorbability which are all results of hydrophilic and highly polar nature of their chemical structures make them inconvenient to be adopted as reinforcements in polymers.

As mentioned in Chapter 1, in this research, the attempt is to increase the compatibility of WF in PVC matrix by using PVC-lignin blends as the matrix as well as using different coupling agents.

## 2.1 Raw materials for PVC-WF composites

### 2.1.1 PVC

PVC is one of the most adjustable thermoplastic polymers which are known today. It is a chlorinated vinyl polymer which is made from vinyl chloride monomer (VCM).The number of repeating units (-$CH_2$-CHCl-) differs from 700 to 1500, so the theoretical molecular weight (MW) can change between 70,000-500,000(weight range) [6]. The chemical structure of PVC is presented in Figure 2.1.



$$\left[ CH_2 - \underset{\substack{|\\ Cl}}{CH} \right]_n$$

**Figure 2.1 Chemical structure of PVC**

PVC can be combined and designed to have certain properties. Therefore, it is presented in all zones of the modern life, such as homes, offices, and leisure centers. Some applications of PVC are as follows [7]:

- Construction (window frames and doors, pipes, wall coverings, sheets, panels, etc.)
- Medical (blood bags, plasma bags, tubing and infusion kits, etc.)
- Electrical (keyboards, computers, electrical cords, phone systems, cellular phones)

- Vehicles (sun visors, handbrake and gearbox lever parts, carpets, window encapsulations, dashboard skins, seat coatings, door panels, etc.)
- Packaging (food packaging, mineral water bottles, cosmetics and detergents containers, bottle caps)
- Cards (credit cards, smart cards, identity cards, telephone cards)
- Leisure and sports (toys, footballs, swimming rings, etc.)
- Clothing (raincoats, shoe soles, rubber boots, fashion, imitation leather)

This thermoplastic polymer has a series of significant characteristics. As mentioned above, PVC is a very versatile material. It is durable and is one of the longest lasting materials; 60% of its applications have a lifetime of more than 40 years and 85% of its products have medium to long-time applications. PVC is also hygienic safe and cost-effective. Around two thirds of all PVC production is used in the building and construction sector. Another sector using significant volumes of PVC is the packaging industry. Because of these outstanding properties, it has become one of the most thoroughly researched materials.

PVC is produced by polymerization of vinyl chloride mainly in suspension and emulsion techniques. In suspension polymerization, vinyl chloride monomer (VCM), initiators (monomer- soluble), catalysts, and other additives are fed into a large batch reactor. The name of the polymerization comes from a suspended droplets of liquid monomer ( monomer is dispersed in a liquid, usually water) by vigorous stirring and by addition of stabilizers which are gradually reacted together by the chain-growth polymerization mechanism to produce solid PVC granules $(\text{-CH}_2\text{-CHCl-})_n$. Non-reacted monomer is taken from the reactor, and water is separated by centrifugation. The polymer is then dried, typically in fluidized bed drying equipment. Suspension PVC can be used for extrusion, injection molding and film making.

In emulsion polymerization, VCM is fed to the batch reactor as an emulsion of very fine droplets in water. After polymerization, a stable emulsion or latex of PVC in water is produced. Water is taken from the system by evaporation in spray drying equipment after the un-reacted monomer is removed from the production. Applications of emulsion-PVC are as coating, dipping, or spreading, for which suspension-PVC cannot be used. A scheme of each polymerization is illustrated in Figure 2.2 and 2.3.

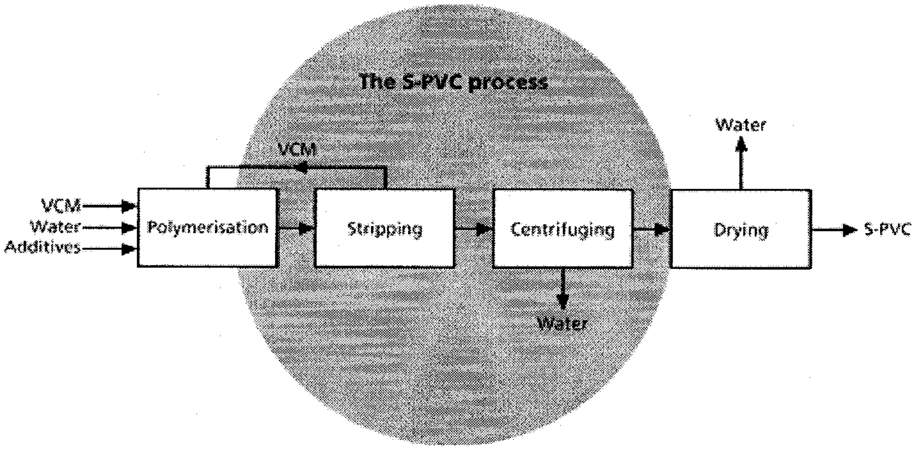


**Figure 2.2 Scheme of suspension-PVC polymerization [8]**

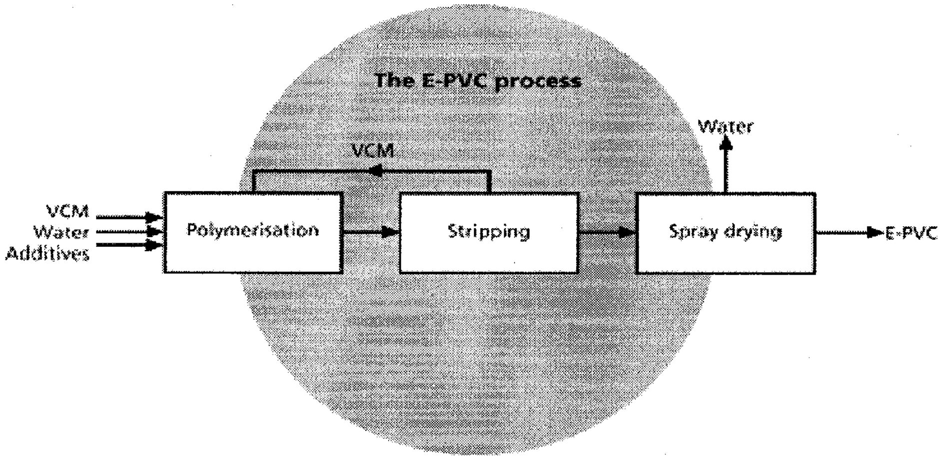


**Figure 2.3 Scheme of emulsion-PVC polymerization [8]**

## 2.1.2 Additives

To produce the desired products, other additives should be mixed with wood and PVC. Some of these additives are plasticizers, coupling agents, lubricants, foaming agents, light and heat stabilizers and fungicides which are added in small amounts to the compound. The kind and amount of these additives depend on the properties of the products [9].

### 2.1.2.1 Plasticizers

A plasticizer is usually a liquid material added in plastics to develop the processability and serviceability of the end product [10].

The roles of plasticizers are to help the processing of PVC by reducing the intermolecular forces as well as the glass transition temperature of the polymer, which enables the formation of a product that possesses flexibility and softness. Moreover, a plasticizer may reduce the melt viscosity, or lower the elastic modulus of the melt.

PVC is a low crystalline polymer which has around 2-10% crystallites surrounded by amorphous areas. These amorphous areas are tightly bonded by hydrogen bonds. Plasticizer's molecules, in proper conditions (compounding, heat and shear), can penetrate the amorphous areas of PVC and disturb intermolecular attractions. When enough plasticizers have entered the matrix, a general relaxation and partial mobility are imparted to the polymer chains [10].

PVC has good compatibility with a lot of plasticizers and can accept different concentrations of plasticizers, thus it can be changed from a rigid and brittle material to flexible and rubber-like product.

The characteristics of a good plasticizer are solvency, compatibility, permanence, low migration and extraction.

Three main plasticization theories have been proposed for the main effect that plasticizers produce [11]:

1) Lubricating theory of plasticization: this theory states that as the system is heated the plasticizer molecules surround the polymer macromolecules, weaken their interactions mostly Van der Waals forces, thus preventing the formation of a rigid network. This reduction in Van der Waals forces increases the flexibility, softness, and elongation of the polymer [11].

2) Gel theory: in this theory, the plasticized polymer is counted as a viscoelastic material in which a three-dimensional network of secondary bonding forces hold molecules together and lets them easily flex in case of external stresses [11].

3) Free volume theory: adding plasticizers increases internal space available with in a polymer providing easier movement of macromolecular chains. The free volume theory builds on both the lubricating and gel theory of plasticization [11].

Effective plasticizers for PVC have to contain polar and non-polar groups on their molecular structures. The polar part of the plasticizer molecule bonds with the PVC molecule, and the non-polar portion provides free volume at the other polar sites of the polymer chain. To have a good compatibility between PVC and the plasticizer, there should be a balance between the polar and non-polar parts of the plasticizer molecules [11].

The addition of plasticizer to PVC changes its mechanical properties and that depends on the amount of plasticizer. Small quantities of plasticizer (up to 20%) to a PVC blend increase modulus and tensile strength of the blend, and reduce its impact strength and elongation at break. However, increasing amount of plasticizer results opposite behaviour which is normally expected of a plasticizer. As illustrated in Figure 2.4, after adding 17% of di-ethyl hexyl phthalate (DOP) impact strength went down, and then it started to go back up, also tensile strength increased until 8% of DOP and then decreased [12]. The behaviour of PVC blends due to small amount of plasticizer is known as antiplasticization effect, which Robeson and Fauche [12]considered it was attributable to the filling of the polymer free volume and hence the restriction of the molecular motion.

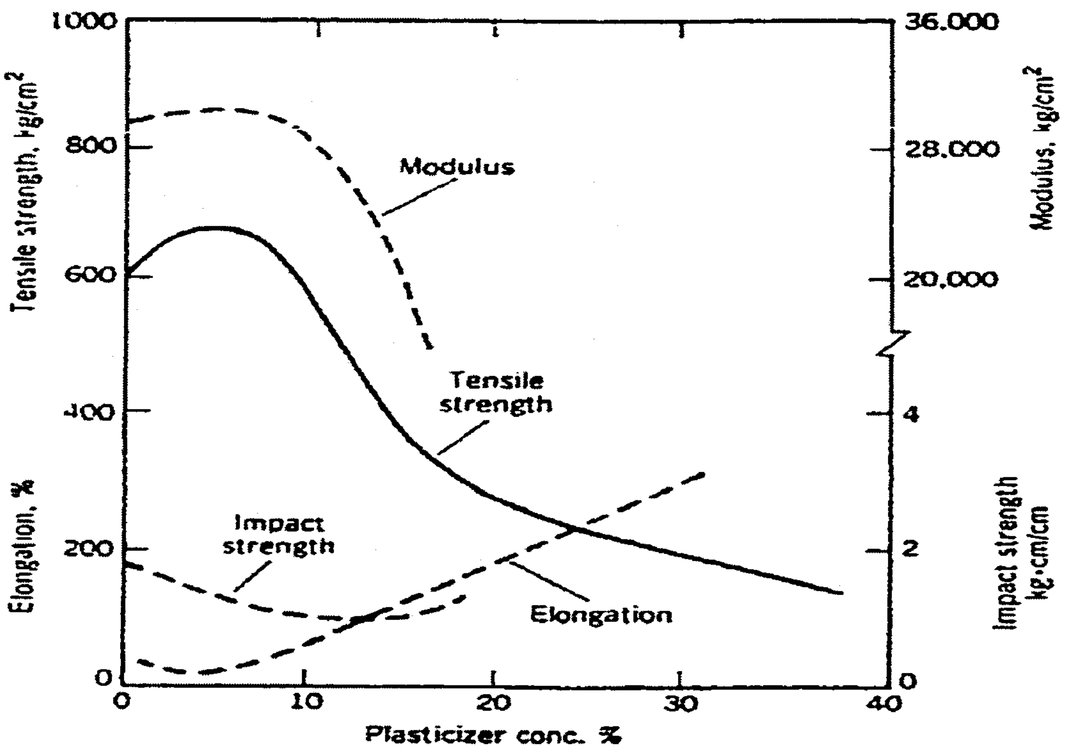


Figure 2.4 Mechanical properties of PVC plasticized with various concentrations of DOP [12]

## 2.1.2.2 Heat stabilizers

Heat stabilizers are used to inhibit thermal degradation of PVC during processing. At elevated processing temperatures, PVC is subject to dehydrochlorination which leads to depolymerization and degradation. In addition, the HCl given off during dehydrochlorination acts as catalyst to further dehydrochlorination. Consequently, PVC heat stabilizers should play two functions. Initially, they prevent the dehydrochlorination. Secondly, the stabilizers react with HCl given off to slow down the autocatalytic effect.

Some stabilizers perform both functions with a single product while others are made of two or more components to do the entire task.

Acceptable heat stabilizers for PVC are: mixed metal systems consisting of barium-cadmium (Ba-Cd) barium-zinc (Ba-Zn) or calcium-zinc (Ca-Zn), lead-based systems and organotin compounds. The stabilizers most commonly used in vinyl flooring are soaps of barium, calcium, zinc, and certain organotin compounds [7].

### 2.1.2.3 Lubricants

Lubricants are used to prevent the sticking of polymer compounds to metallic surfaces of processing equipments. They affect inter-molecular friction and adhesive properties of plastics during processing and service.

There are two kinds of lubricants: internal and external. Internal lubricants are usually soluble in PVC reducing viscosity and improving the flow of melt; they act like plasticizers. External lubricants have limited compatibility to PVC such that they will sweat out during processing to form a film between the compounds and the processing equipments like calcium stearate [13].

### 2.1.2.4 Lignins

Its name came from lignum meaning wood in Latin. It is a main part of vascular plants after cellulose. 24-33% and 19-28% of softwoods and hardwoods, respectively, are made of lignin. Lignin, as can be seen from figure 2.5, represents main functions in wood structure plants. It acts like an adhesive between wood cells and performs strength and stability to the wood structure. Also, lignin does not permit passage of water through the cell walls; therefore, it plays an important role in the internal transportation of nutrition and water. Moreover, it contributes as a resistant factor to biological degradation [14].

Lignin is a natural amorphous, polyphenolic material produced from dehydrogenation of three phenylpropanoid monomers: coniferyl alcohol, sinapyl alcohol and p-coumaryl alcohol. The chemical formulas of these alcohols are shown in Figure 2.6. These monomers bond together by ether bonds (C-O-C) and carbon-carbon bonds (C-C); these bonds and functional groups of monomers impart a high polarity to the resulted cross-linked polymer.

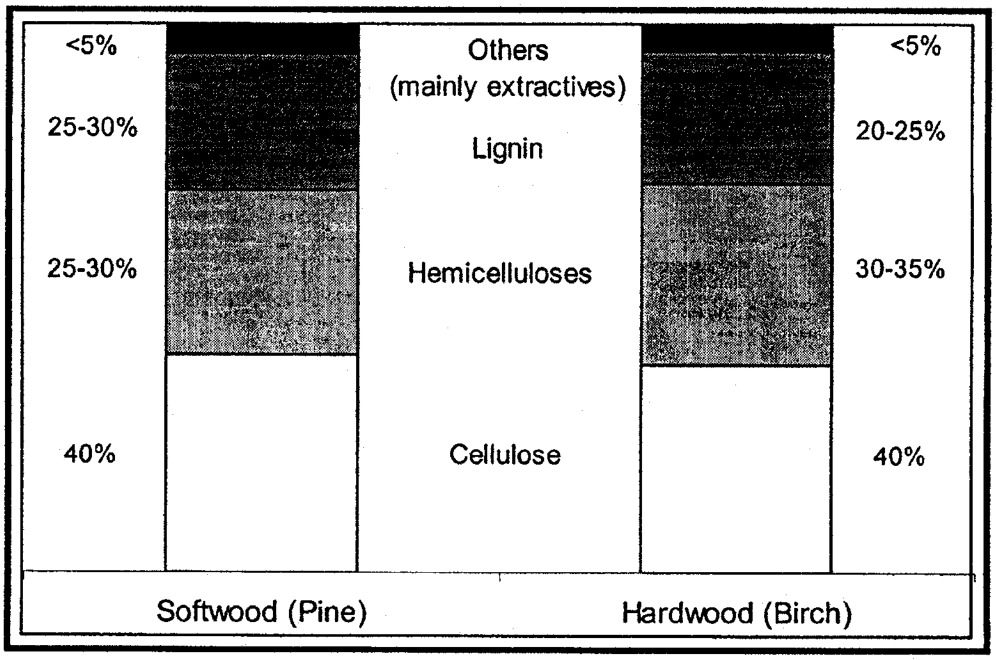
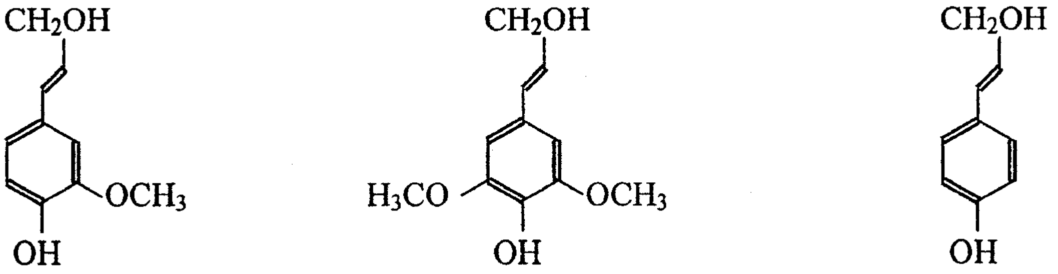


**Figure 2.5 Average chemical compositions of softwood and hardwood as a percentage of dry solid wood [15]**

Softwood lignin is made of 90% trans-coniferyl alcohol and 10% trans-p-coumaryl alcohol, and lignin in hardwood is composed of 50% trans-coniferyl alcohol and 50% of trans-sinapyl alcohol [15].



Trans-coniferyl alcohol Trans-sinapyl alcohol Trans-p-coumaryl alcohol

**Figure 2.6 The building units ($C_6C_3$) of lignin [15]**

Lignin as a natural polymer has very positive and effective properties which make it a proper resource in polymer industry. Some of its properties are its availability and chemical composition and its annually huge amount production (it is a by-product of pulp and paper industry (~50 x $10^6$ tonnes)).

Although these excellent properties make lignin a perfect nominate to participate in polymeric compounds, some difficulties like its variability, polydispersity, low solubility, high glass transition temperature, its chemical complexity, macromolecular structure, and the presence of different chemicals from the wood processing industries arise[16].

Lignin is produced industrially as a by-product of pulp and paper industry through a series of processes which extract cellulose from wood and clear away lignin. This lignin is different from natural lignin (known as native lignin) because it is subjected to a series of chemical changes and named as technical lignin [17].

The technical lignin is a free-flowing brown powder with densities ranging from 1.3 to1.4 g/cm$^3$. Although the molecular weight ranges from 1000 to 12000, its glass transition temperature (Tg) is between 100°C and 180°C which is high compared with Tg's of most synthetic materials.

According to Yoshida et al., [18], the high Tg values of lignins are due, in large part, to the degree of association by hydrogen bonding caused by the presence of phenolic hydrogen groups in the main chain.

There are different kinds of technical lignins, depending on the chemical processes used for delignification of wood. Lignosulfonate is derived from sulfite pulping of wood, Kraft lignin is obtained by treating wood with alkali, whereas organosolv lignins are obtained from the delignification of wood with organic solvents (mainly alcohol).In this new delignification process (organosolving), hardwood chips are batch cooked and after treated with steam of (aqueous ethanol or methanol liquor) solvents at high temperature. The resulted lignin changes a lot less than the other types of lignin, and is free from sulphur. Also, it is not soluble in water at neutral or acidic pH [19]

### 2.1.2.5 Wood flour

Wood is a heterogeneous, anisotropic, natural polymer composite which is classified as either softwood (from conifers) or hardwood (from broad-leaved trees). These both kinds are composed of cellulose fibres in an amorphous matrix of hemicelluloses and lignin and also a small percentage of extractives, and the differences between hardwood and softwood are in their components concentration.

Cellulose, which is the main component of wood, has the most defined chemical structure. Cellulose is a polysaccharide derived from beta-glucose units [20]. It is a crystalline, linear polymer, and its high polarity due to its many hydroxyl groups provides the strength and stability of the wood structure.

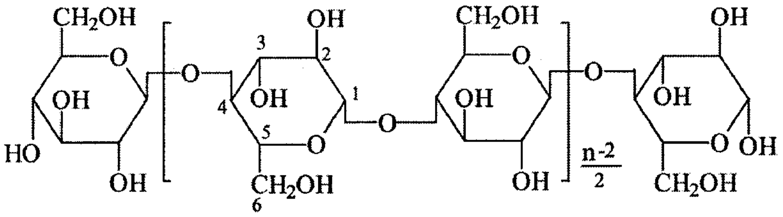


**Figure 2.7 Chemical structure of cellulose [21]**

Hemicelluloses, as the second main component of wood, are branched polymers which their made units contain five or six carbon atoms. They do not have one defined chemical structure. Their molecular weights are much less than that of cellulose.

Lignin as another component of wood is discussed in previous section, and its structure is presented in Figure 2.8.

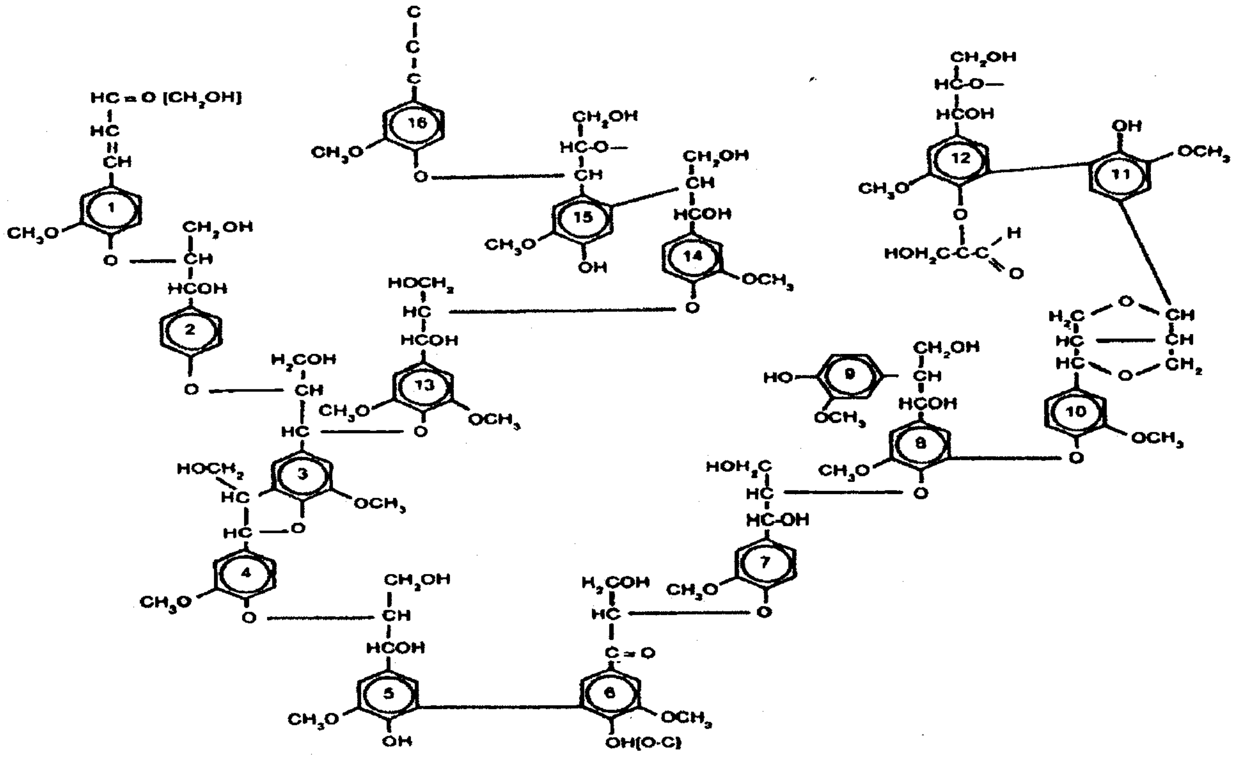


Figure 2.8 A partial softwood lignin structure [22]

WF has been produced industrially since 1906. It is a by-product from companies which make lumber and furniture, window, door, etc. Its price ranges between \$0.11–0.22/kg in the United States and it depends on particle size and its distribution, availability and shipping distance [9].

## 2.2 Thermoplastic-wood composites

Plastic sector was one of the first users of WF which was utilized as a proper filler in producing plastic-WF composites like railings, window and door profiles, and especially decking as can be seen from Figure 2.9. In North America, production of these composites was increased from 50000 in 1995 to around 600000 tonnes in 2002. The demand for wood fibre-plastics increases about 60% per year for building construction products [22].

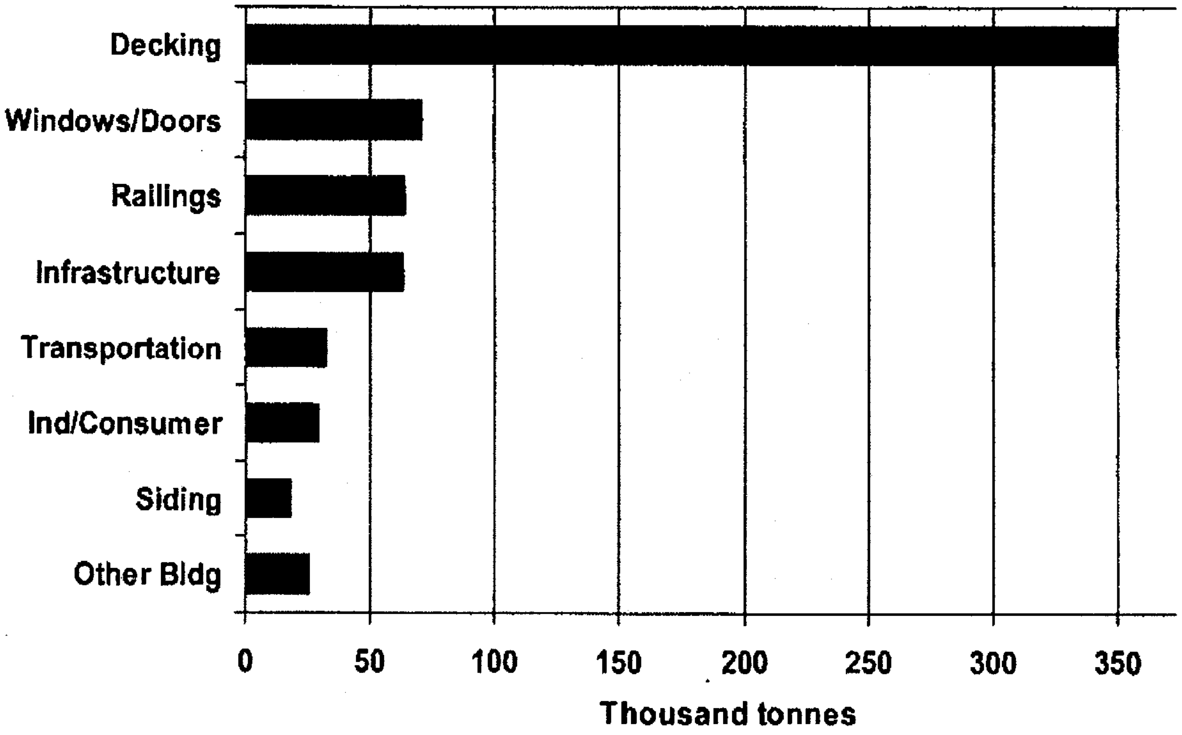


**Figure 2.9 The applications and market size of plastics with wood flour [22]**

WF is used with thermoplastics for two main reasons. The first is to enhance the mechanical properties of the plastics like stiffness, flexural and tensile modulus. However, in the absence of a proper coupling agent, tensile and flexural strength usually decrease. The second reason is environmental preference and biodegradability of WF. Other advantages are its low density, low cost and low equipment abrasiveness. Furthermore, plastics provide WPCs with good moisture and decay resistance [22].

Although there are a lot of positive aspects of using this natural filler in plastics, some restrictions are applied too. First, thermoplastics with processing temperatures lower than 200°C can be chosen because of WF's low thermal stability. Accepted polymers which are used for manufacturing WPC are high and low density polyethylene (HDPE, LDPE), polypropylene (PP), PVC, polystyrene (PS) and poly (methyl methacrylate) (PMMA). The percentage of each polymer in manufacturing these composites is illustrated in Figure 2.10.

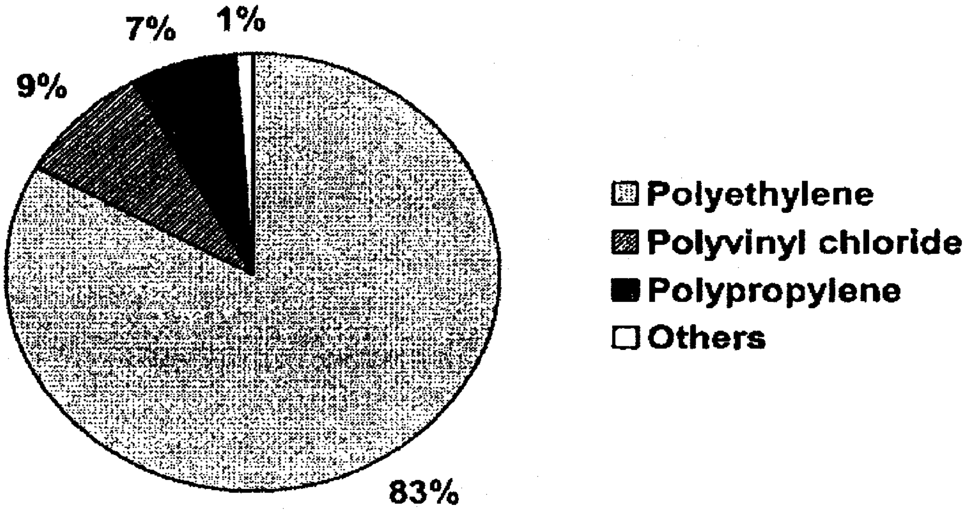


**Figure 2.10 Plastics used in plastic-wood composites [22]**

Another restriction is the low dispersing and low adhesion of this polar filler in hydrophobic matrix of plastics [22].

## 2.2.1 Manufacturing of thermoplastic-wood composites

There are two-steps in processing thermoplastic composites. The first step is compounding, in which all the raw materials like plastic pellets, additives and fillers or reinforcing materials are mixed together and they are heated. In most cases, thermoplastic polymer is heated before it is melted and then other additives are added to the compound.

In the second step, melted mixture is shaped or pressed by different techniques to the final product, or just the pellets are formed and final products get ready in additional other steps. Such techniques are injection molding, calendaring, thermoforming, compression molding [23]. These techniques are proper when the second step is a batch process and final shape of the product is not complicated.

There are two main issues regarding processing of WF-thermoplastic composites. First is the intermolecular bonding between the wood flour or wood fiber particles which causes the agglomeration of wood particles in matrix and consequently decrease the mechanical properties of the composite. Another issue is the decomposition of lignocellulosic materials whose rate is increasing with increasing processing temperature. At the usual processing temperature (180-200°C) some decomposition are reported. The gases produced from these decompositions made a lot of voids in the final product, which cause a decrease in mechanical properties.

### 2.2.2 Coupling agents and compatibilizers

In composites, interface between components plays an important role in mechanical properties. This phase is responsible for transferring stresses from matrix to the fibers or fillers, so it's the main factor in composites' strength. In a polymer composite system, mechanical properties such as tensile strength and elongation are lower than those of unfilled composites when no coupling agents or compatibilizers are used. In other words, coupling agents are necessary for making a good interface between different components in a composite system especially when fillers like polar WF are used in a low polar matrix of PVC.

Over forty coupling agents have been used in production and research of wood fibre polymer composites (WFPC).These agents are classified as organic, inorganic, and organic-inorganic groups [24].

Organic coupling agents include isocyanates, anhydrides, amides, imides acrylates, chlorotriazines, epoxides, organic acids, monomers, polymers and copolymers. They have bi- or multifunctional groups in their molecular structure. These functional groups react with (-OH) groups of cellulose and lignin and form covalent hydrogen bonding [25].

Only a few inorganic coupling agents, such as silicates, are used in WFPC. Inorganic coupling agents possibly act as dispersing agents to counteract the surface polarity of WF and improve the compatibility between WF and polymer [26].

Organic-inorganic coupling agents include silanes and titanates. The functionality of the organic part in these agents determines their coupling effectiveness on WFPC. Their functionality is between organic and inorganic coupling agents [26].

The most popular coupling agents currently being used include anhydrides, isocyanates, silanes [24].

### 2.2.2.1 Acids and anhydrides

The most, acids and anhydrides were used as coupling agents in plastic-WF composites. Acids are expected to coat WF to decrease the density of OH groups in the composite; most utilized acids are: stearic acid, abietic acid (ABAC), and linoleic acid (LAC). Anhydrides such as phthalic anhydride (PHA) which have carboxylate groups

(-COO-) were assumed to react with hydroxyl groups from wood by esterification or hydrogen bonding, and therefore decrease the hydrophilic characteristic of wood [24]. Maleic anhydride (MA) contains one carbon-carbon double bond (C=C) and two carboxylate groups (-COO-); this structure increases the graft reactivity of the carbon-carbon double bonds with the polymer matrix through the addition of a radical initiator, resulting in crosslinking or strong adhesion at the interface [27]. However, the molecular chain of MA is much shorter than that of polymer matrix and WF, so it is not so effective to improve the interfacial adhesion [26]. Consequently, its grafted polymer, such as MA-grafted PE and MA-grafted PP are used as coupling agents. Interaction between MA-grafted PP and OH groups in wood is illustrated in Figure 2.11. However, regarding tensile tests of PVC-WF composites containing 30% wood dust only tensile modulus was increased by using stearic acid or MA. Other tensile properties which are tensile strength, ultimate elongation and elongation at break did not change effectively [1].

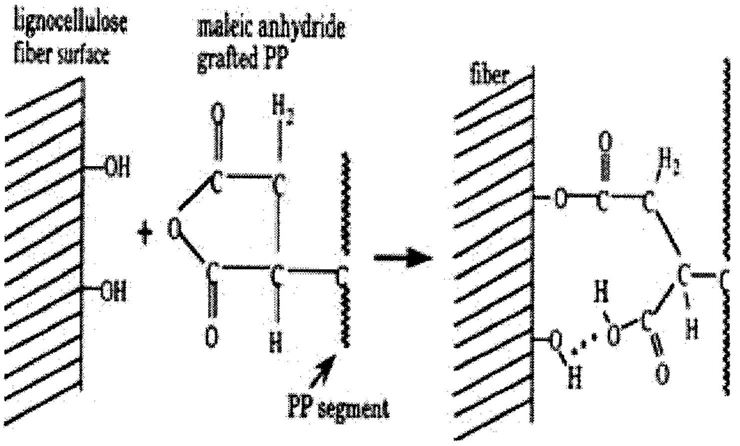


**Figure 2.11 Reaction of an anhydride end group on MAPP with a cell wall hydroxyl group [9]**

### 2.2.2.2 Polyisocyanates

Poly [methylene poly (phenyl isocyanate)] (PMPPIC) is the most functional coupling agent in different polymer systems. It forms strong covalent bonds with –OH groups of wood, producing urethane structures through hydrolysis reaction:

$$R\text{-}N{=}C{=}O + HO\text{-}wood \rightarrow R\text{-}NH\text{-}CO\text{-}O\text{-}wood$$

Polar PMPPIC may interact with PVC, which has electronegative chlorine and electropositive carbon and hydrogen. In conclusion, at interface, PVC and treated wood with PMPPIC reacts. The drawback of this coupling agent is the urethane bonds which are not healthy to human body [1].

### 2.2.2.3 Silanes

Silanes are important coupling agents in polymer blends and composite field. They are silicon-based chemicals having two kinds of active groups (inorganic and organic) in the same molecule. $YSi(OR)_3$ is a general chemical structure of a molecule of silane where OR is a hydrolyzable group (alcoxy) such as methoxy, ethoxy or acetoxy, and Y is an organofunctional group such as amino, methacryloxy, epoxy, etc.

It acts like a bridge between inorganic fillers and polymers because of its two inorganic and organic functional groups. To be effective, silane should first hydrolyzed and form an organic silanol, which reacts with the hydroxyl groups of cellulosic fibers to form a silane layer on the fiber surface. Many factors, such as hydrolysing time, organofunctionality of silane, temperature, pH of the solution and so on, influence the formation of silanol groups during hydrolysis, and subsequently affect the effectiveness of coupling agent. In addition, special attention should be paid to the concentration of silane in solution so that monomeric dominates, since oligomeric silanols are known to be less effective as a coupling agent [28].

Ishida [29] reported that the concentration of silane in water should be in the range of 0.01% to 2% by weight in order to ensure dominancy of monomeric silanols.

The main disadvantage of treating the particulate fillers as WF with a water solution of silane is the difficulty of drying the aqueous slurry. A hard cake formed after drying, requires an additional effort to finally crush the aggregated particles.

Hydroxyl groups of silanols make hydrogen bonds with hydroxyl groups of wood. R groups of silanes make weak Van der Waals links with polymers. However, studies demonstrated that these weak bonds did not affect mechanical properties positively; moreover, most of the mechanical properties of WF-polymer composites were less than that of primary polymer's system.

To produce effective chemical bonds at the interface of WF and polymers proper processing conditions as mentioned above should be applied.

Silane could be used also as a dispersing agent; it leads to an effective dispersing of fillers and pigments. This improvement results from displacement or modification of the moisture layer, giving reduced clumping particles and improved wetability by polymer [30].

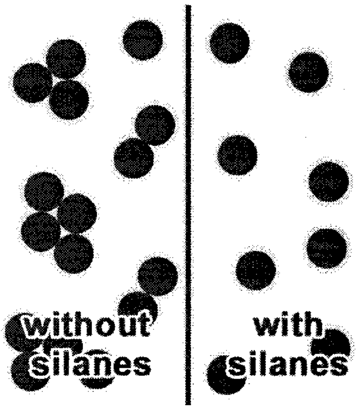


**Figure 2.12 Effect of silane as a dispersing agent [30]**

## 2.2.2.4 Copper-amine treatment of WF

Recent studies demonstrated that the treatment of WF with aqueous solutions of copper- ethanol amine which their copper concentration range between 0.2 to 0.6 wt% of WF could improve the mechanical properties of PVC-WF composites due to an improved PVC-WF interfacial adhesion [31].

## 2.2.2.5 Chitin

As it was discussed earlier, to enhance the interfacial adhesion between wood particles and PVC matrix, the second largest plastic used in manufacturing wood-plastic composites, several investigators have assessed the effect of various fibre treatments, including different types of isocyanates, maleic anhydrids, silanes, etc., as coupling agents. Most mechanical properties of the composites were improved by these chemical treatments compared to those of composites with untreated fibres. However, the properties of composites were inferior to those of unfilled PVC, suggesting that, unlike polyolefin-WF composites, the well known claim of converting the hydrophilic surface of wood fibre to a hydrophobic one is not effective in enhancing the adhesion of PVC to WF. The use of aminosilane modified in some cases the wood surface, and facilitated the interaction between wood and PVC. In spite of these benefits, gamma-aminopropyltriethoxysilane was not been extensively used as a coupling agent for PVC-wood composites, mainly due to its high cost but also due to the difficulty in evenly coating the surface of WF, owing to the sensitivity of the silane to hydrolyze and self-condense [32].

A natural polymer chitin was recently used as a coupling agent for rigid PVC-WF composites as well as in other polymers. It is one of the most abundant natural polymers and is extracted from the shells of crustaceans.

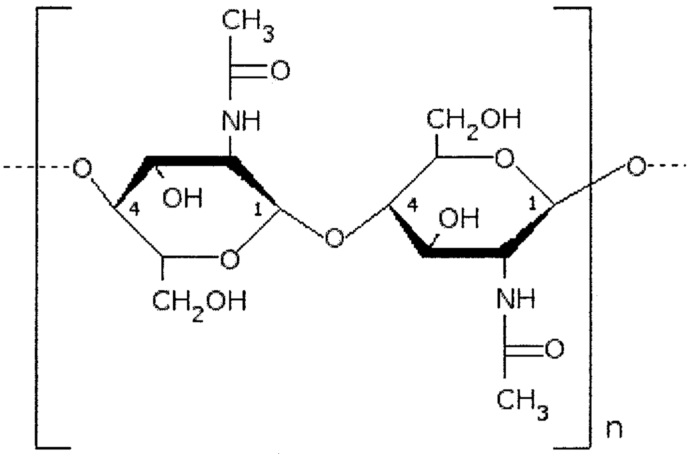


**Figure 2.13 Chemical structure of chitin [33]**

It is believed that the acetyl amine functionality of chitin should permit to it to interact with wood and PVC in a manner similar to amino silane [32].

Around 7% weight to WF addition of chitin affects the flexural strength and flexural modulus of PVC-WF composites; they increased about 20% and the storage modulus about 25% compared to the neat PVC-WF composites [32].

# *Chapter 3 Research Program*

This research program includes the preparation and testing plasticized PVC-WF composites by replacing part of PVC with different lignins and utilizing different coupling agents as silanes, chitin and Alcell lignin. Selection of an efficient heat stabilizer and of adequate processing parameters were also included into the research program.

## 3.1 Materials

### 3.1.1 PVC

The synthetic (suspension polymerization) polymer used is PVC homopolymer (Oxy Vinyls $^{TM}$ 185), in a white powder form for flooring, calendaring and injection molding supplied by Oxy Vinyls LP, Dallas, Texas. Its characteristics as indicated by the producer are presented in the Table 3.1.

**Table 3.1 PVC (Oxy Vinyls 185) resin properties [34]**

| | |
|---|---|
| K-Value | 56 |
| Mw | 38000 |
| Specific gravity | 1.4 |
| Bulk density, g/cm$^3$ | 0.59 |
| Glass transition temperature (Tg)* | 85.5 °C |
| Particle size | 40 Mesh, 0%<br>100 Mesh, 20%<br>Thru, 200 Mesh, <3% |

* As determined by DSC in the material laboratory of BCEE department.

### 3.1.2 Lignin

Three kinds of lignin were used in this study: Alcell (AL), Indulin AT (IN) and Tomlinite (T). However, the main lignin which was used for the rest of the study was AL. It is an organosolv hardwood lignin produced by Alcell Technologies Inc (Miramachi, New Brunswick). IN is a kraft softwood lignin. It does not have any hemicelluloses, and its physical form is a brown powder. It is produced by Westvaco Chemicals (Charleston Heights, USA). T is a kraft hardwood lignin. Properties of all three lignins are presented in Table 3.2 [1].

**Table 3.2 Properties of different lignins [35]**

| Characteristics | AL | IN | T |
|---|---|---|---|
| Number molecular weight [Mn] | 800-900 | 1858 | 650 |
| Weight molecular weight [Mw] | >2000 | 7050 | 2800 |
| Polydispersity [Mw/Mn] | 2.22 | 3.79 | 4.3 |
| Specific gravity | 1.27 | 1.3 | 1.3 |
| Average particle size [μm] | 16 | 8 | 16 |
| pH value | 4 | 6.5 | 6 |
| Glass transition temperature, Tg[°C] | 97 | 142 | 133 |

## 3.1.3 Wood flour

The Maple Hardwood WF 8010 was from American Wood Fibres Company (AWF) (Columbia, MD). Its characteristics as indicated by the producer are shown in Table 3.3.

**Table 3.3 Properties of Maple hardwood 8010 WF [36]**

| | | |
|---|---|---|
| Moisture content [%] | Max 6 | |
| Typical acidity [pH] | 5 | |
| Typical ash content [%] | 0.7 | |
| Specific gravity | 1.41* | |
| Mesh size | 60 Mesh | <0.36 |
| | 80 Mesh | 0-15 |
| | 100 Mesh | 0-45 |
| | 120 Mesh | 0-40 |

* As determined in the material laboratory of BCEE department.

## 3.1.4 Plasticizers

The main plasticizers used in this research were diethylene glycol dibenzoate/Benzoflex 2-45 from Velsicol, Rosemont, IL supplier and tricresyl phosphate/Lindol from Akzo Nobel, Dobbs Ferry, NY. Their abbreviations in the text will be 2-45 and Lindol, respectively.

### 3.1.4.1 Diethylene glycol dibenzoate (2-45)

The chemical structure of 2-45 is presented in Figure 3.1, and its physical properties according to the producer are presented in Table 3.4.

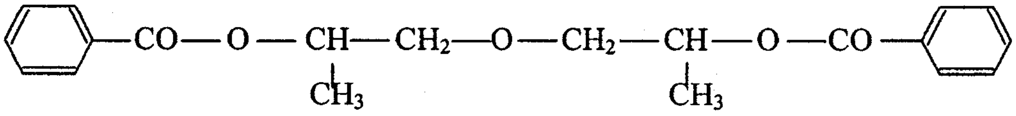


**Figure 3.1 Chemical structure of 2-45 plasticizer**

**Table 3.4 Properties of 2-45 plasticizer [37]**

| Characteristics | 2-45 |
|---|---|
| Molecular formula | $(C_6H_5CO_2CH_2)_2O$ |
| Molecular weight | 314.3 |
| Physical state | Liquid |
| Color | Clear colorless |
| Odor | Mild ester |
| Specific gravity | 1.178 |
| Viscosity [mPa.s at 25 °C] | 65-66 |
| Boiling point [°C at 5 mm Hg] | 240 |
| Pour point (°C) | 28 |
| Glass transition temperature, Tg [°C]* | -52 |

* As determined by DSC in the material laboratory of BCEE department.

### 3.1.4.2 Tricresyl phosphate (Lindol)

Lindol is used as a flame-retardant plasticizer in vinyl and cellulosic thermoplastics. Its chemical structure is illustrated in Figure 3.2 and its principal properties according to the producer are indicated in Table 3.5.

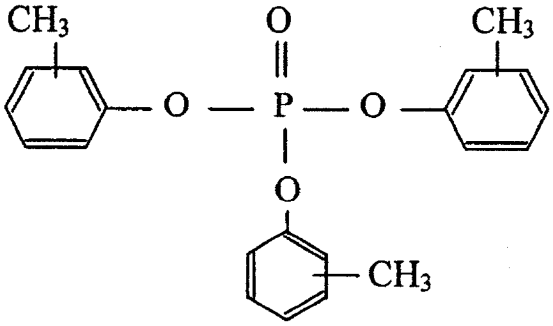


**Figure 3.2 Chemical structure of Lindol plasticizer**

**Table 3.5 Properties of Lindol plasticizer [38]**

| | |
|---|---|
| Physical appearance | Clear, transparent liquid |
| Phosphorus content, wt.% | 8.4 |
| Specific gravity, 20°C /20°C | 1.170 |
| Viscosity [mPa.s at 25 °C] | 65 |
| Acidity, mg KOH/g | 0.10 |
| Water content, wt.% | 0.10 |
| Color, APHA | <75 |
| Glass transition temperature, Tg [°C]* | -57.6 |

* As determined by DSC in the material laboratory of BCEE department.

### 3.1.5 Lubricants

#### 3.1.5.1 Calcium stearate

Calcium stearate (CaSt) was used as an external lubricant and it was supplied by Blachford Canada Ltd under the name of L-155 having characteristics shown in Table 3.6.

**Table 3.6 Properties of L-55 calcium stearate [39]**

| | |
|---|---|
| Molecular formula | $Ca(CH_3(CH_2)_{16}COO)_2$ |
| Mean molecular weight | 607 |
| Physical state | Fine powder |
| Color | White to yellowish white |
| Melting point [°C] | 147 |
| Total ash % | 10.6 |
| Free fatty acid % | 0.4 |
| Moisture % | 2.8 |

## 3.1.5.2 Paraffin wax (Marklube 367®)

It was supplied by Crompton Vinyl Additives GmbH, Germany. Its properties as specified by the producer are presented in Table 3.7.

**Table 3.7 Properties of Marklube 367 [40]**

| | |
|---|---|
| Appearance | Slightly yellow powder |
| Solidification point [°C] | 68-72 |
| Unmolten part DSC at 70°C [%] | <=3 |
| Penetration number at 25°C [mm] | 1.1-1.7 |
| Colour value Gardner | <=3 |
| Bulk density [g/l] | 450-520 |
| Storage time | max. 12 months |
| Density [g/cm$^3$] | 0.89-0.93 |

## 3.1.6 Heat stabilizers

### 3.1.6.1 Butyltin mercaptide/carboxylate (Mark TK 262)

It was supplied by Crompton Vinyl Additives GmbH, Germany. Its properties as specified by the producer are presented in Table 3.8.

**Table 3.8 Properties of Mark TK 262 heat stabilizer [41]**

| | |
|---|---|
| Chemical composition | Butyltin Mercaptide/Carboxylate |
| Physical appearance | Clear, yellow to orange liquid |
| Refractive index at 20°C | 1.504-1.512 |
| Element tin [Sn %] | 21.9-22.9 |
| Density at 20°C [g/ml] | 1.13-1.17 |
| Colour value Gardner | <=6 |

### 3.1.6.2 Dibutyltin dilaurate (DBTDL)

It was obtained from Sigma Aldrich-Canada Ltd, Oakville Ontario. Its chemical and physical properties are summarised in Table 3.9.

**Table 3.9 Properties of DBTDL heat stabilizer [42]**

| | |
|---|---|
| Molecular formula | $(C_4H_9)_2Sn(OOC(CH_2)_{10}CH_3)_2$ |
| CAS number | 77-58-7 |
| Relative molecular mass | 631.6 |
| Physical state | Oily liquid |
| Color | Yellow |
| Melting or freezing point [°C] | 22-24 |
| Boiling point or range [°C at 9.75 mm Hg] | 205 |
| Specific gravity | 1.1 |
| Solubility in water | None |

### 3.1.6.3 Butyltin carboxylate (Mark T 634)

The main heat stabilizer, in this study was Butylin carboxylate (BuSnO/S, liquid) which was supplied by Crompton Vinyl Additives GmbH, Germany. Its characteristics as specified by the producer are presented in Table 3.10.

**Table 3.10 Properties of Mark T 634 heat stabilizer [43]**

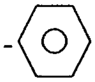
| | |
|---|---|
| Chemical composition | Butyltin Mercaptide/Carboxylate |
| Physical appearance | Clear, yellowish liquid |
| Element sulphur [%] | 2.5-2.9 |
| Refractive index at 20°C | 1.486-1.49 |
| Element tin [Sn %] | 19.7-20.7 |
| Density at 20°C [g/ml] | 1.09-1.100 |
| Colour value Gardner | <=4 |

## 3.1.7 Coupling agents

### 3.1.7.1 Dow Corning® Z-6032 silane

It contains a vinyl benzyl (R) and amine organic and a trimetoxysilyl inorganic group. Its chemical formula is:

$$(CH_3O)_3\text{-}SiCH_2\text{-}CH_2\text{-}CH_2\text{-}NR\text{-}CH_2\text{-}CH_2\text{-}NH_2$$

Where R is -  - $CH=CH_2$

It was supplied in methanol by Dow Corning–Specially Chemicals Midland MI. Its typical properties, as indicated by the producer are presented in Table 3.11.

**Table 3.11 Properties of Z-6032 silane [44]**

| | |
|---|---|
| Active ingredients [%] | 40 |
| Appearance | Greenish-yellow changing to reddish-amber with time |
| Viscosity at 25°C [cs] | 2 |
| Specific gravity at 25°C | 0.90 |
| Refractive index at 25°C | 1.395 |
| Flash point-closed cup [°C] | 13 |
| Solubility | Self emulsifying in water, soluble in alcohols |

### 3.1.7.2 Dow Corning® Z-6011 silane

It contains amino propyl organic group and a triethoxysilyl inorganic group, having the chemical formula: $H_2N\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}Si(OC_2H_5)_3$. It is designated as gamma-aminopropyltrie-toxysilane. Its typical properties as specified by the producer, Dow Corning-Specially Chemicals Midland MI, are indicated in Table 3.12.

**Table 3.12 Properties of Z-6011 silane [45]**

| | |
|---|---|
| Appearance | Colorless to very pale yellow liquid |
| Viscosity at 25°C [cs] | 1.6 |
| Specific gravity at 25°C | 0.946 |
| APHA color | <25 |
| Flash point-setaflash closed cup [°C] | 96 |
| Purity by GC [%] | >98.5 |
| Molecular weight [g/mol] | 221.37 |

#### 3.1.7.3 Chitin

It was obtained from Sigma Aldrich Canada Ltd Oakville Ontario. It is a technical powder product obtained from crab shells. Its specific gravity as determined in our laboratory is 0.185.

## 3.2 Experimental procedures

The experimental procedures are made of few steps. These steps are explained in following sections and Table 3.13 is a summery of these steps.

### 3.2.1 Formulation and processing parameters

The starting composites where different lignins i.e. AL, IN and T replaced 20 parts of PVC were formulated with Lindol as plasticizer, and three types of heat stabilizers and two types of lubricants as they were mentioned before in this chapter. The level of PVC replacement with lignin in blends, the processing parameters as well as the level of plasticizer were established in a previous work [46]. Controls containing only PVC polymer were also prepared in the same condition. The matrices were formulated with 100 parts PVC (controls) or 80-20 parts PVC-AL (blends), 35 parts per hundred parts of the resin (phr) plasticizer, 3phr heat stabilizer, 1.5phr lubricant and the WF in variable proportions.

#### 3.2.1.1 Variation of the amount of WF and assessing the lignins

After establishing the best heat stabilizer-lubricant system, the controls and blends were formulated with 20, 30 and 40phr WF (related to PVC or PVC-lignin matrices). As the blends formulated with IN presented some degree of decomposition, visible as voids on the surface of the materials, only AL and T were retained for further experiments.

Further, controls and blends with AL and T were formulated with 20, 30 and 40phr WF. The mechanical tests indicated very close results for composites formulated with AL and T and consequently only AL were retained for further experiments.

#### 3.2.1.2 Establishing optimum amount of WF and processing conditions

As the mechanical properties of both control and blend composites formulated with 30 and 40phr WF presented a visible deterioration, only composites formulated with 20phr WF were utilized for additional studies; there were done in view of improving the compatibility between the polymer matrix and WF. Accordingly, in the first step the processing temperature in melt mixing was increased from 145 to 155°C, the mixing time from 8 to 10 minutes, the compression molding temperature from 158 to 160°C and the compression molding pressure from 4.37MPa to 6.56MPa were changed.

### 3.2.1.3 Compatibilization

As the changes in processing parameters did not bring a substantial improvement in mechanical properties of controls and blends-WF composites, in order to improve the compatibility between WF and PVC or PVC-AL matrix and consequently the mechanical properties of the composites, the WF was treated with two types of silane solutions described before, further, chitin in a new set of experiments or AL in different proportions were utilized as compatibilizer.

Following are detailed descriptions of specimen preparations and testing methods utilized to evaluate the obtained composites.

**Table 3.13 Different steps of the experimental procedures**

| | |
|---|---|
| **Formulation and processing parameters** | 1. Examining 3 lignins in formulation<br>2. Determining heat stabilizer and lubricant |
| **Variation of the amount of WF and assessing the lignin** | 1. Examining different amount of WF<br>2. Determining the kind of lignin |
| **Establishing optimum amount of WF and processing conditions** | 1. Determining amount of WF and Lignin<br>2. Changing the mixing temperature, mixing time and modling pressure<br>3. Examining another plasticizer |
| **Compatibilization** | 1. Examining different kind and amount of coupling agent<br>2. Determining the kind and amount of coupling agent |

## 3.2.2 Experimental methodology

### 3.2.2.1 Specimen preparation

The preparation of PVC-lignin-WF composites involved a few steps. They were mixing in a special equipment, grinding, compression molding, specimen preparing, specimen conditioning and testing (Figure 3.3). Detailed description of each step is discussed bellow:

- WF and lignin for any composite and blend were first dried in an oven (WF 20 hrs at 80°C and lignin 2 hrs at 105°C).

- Solid ingredients of each compound were weighted and manually dry mixed for 2 minutes in a closed container.
- Liquid ingredients of each compound were weighted and manually mixed in a vessel.

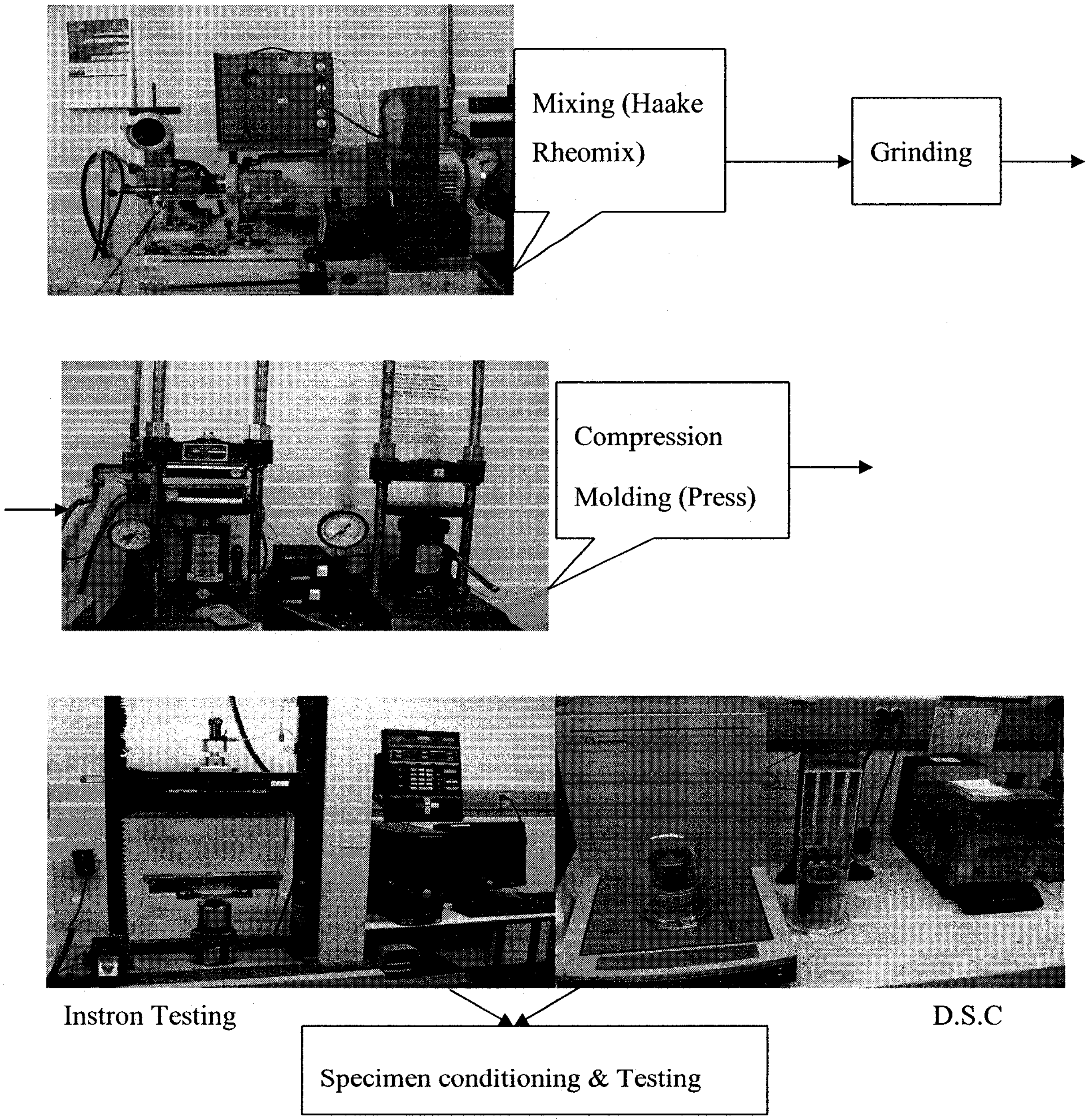


**Figure 3.3 Specimen preparations of PVC-WF control and PVC-lignin-WF composites**

- Liquid ingredients were added to powder ingredients in two steps, after each step the material was mixed manually for two minutes, and at the end the total bulk mixed manually for another 5 minuets.
- The obtained formulations were melted and mixed for 10 minutes at 145°C or 155°C at a rotor speed of 65 rpm in a Haake Rheomix equipped with roller blades and accurate temperature controllers which maintained constant temperature in each mixer zone; it was electrically heated and air-cooled. The filling volume of the mixer was always 70% of its net volume (69 $cm^3$) and therefore the charge weight of each formulation was calculated as a function of its specific gravity. The Haake Rheomix 60 is equipped with a torque rheometer, the Haake Rheocord-M 300, which continuously measures the mixing torque. The record torque showed that a plateau was reached in about 6 minutes.
- After melt mixing, the material was ground to small chips with thickness of 2-3 mm and maximum length of 10mm.
- Sheets of 1.5 mm thickness were molded by compression which was carried out on a Carver Laboratory press equipped with temperature controllers. Certain amount of material was placed in the mold heated between the platens of the press which were set at the desired temperature (158°C or 160°C). A heating period of 6 minutes with no pressure was allowed, and then the pressure of 4.37MPa or 6.56MPa applied for 2 minutes, followed by cooling with air at a rate of 10°C/min under pressure of 2.18MPa.
- Prepared sheets were cut with a cutting die into dog-bone shaped specimens for tensile testing, according to ASTM D638 [47].

- The specimens were conditioned at 23±2°C, and relative humidity (RH) of 50±5%, for at least 7 days prior to testing.

## 3.2.2.2 Treatment of WF with Silanes

### 3.2.2.2.1 Treatment of WF with silane Z-6032

50 g dried WF was treated with 350ml solution of coupling agent having the concentration of 0.03, 0.086 and 0.14% silane corresponding to a concentration of silane to WF of 0.2, 0.6 and 1%. The respective solutions of different concentration in silane were obtained by diluting 0.34, 0.68 and 1.6 g respectively of a solution of prehydrolyzated concentrate with 350 ml water. The prehydrolyzated concentrate was obtained by mixing 5 parts silane Z-6032 with 0.25 parts glacial acetic acid and 1.25 parts water. The prehydrolyzed concentrate was prepared first in order to ensure the formation of silanol groups following a procedure suggested by Dow Corning.

The mixture WF-silane solution was kept on a hot plate (55°C) and slowly stirred for 2 hrs and thereafter slowly stirred without heating for another 22 hrs. The silane treated WF was filtered under vacuum and finally dried in an oven at 80°C for more than 24 hrs until constant weight was achieved. As a hard cake was formed after filtering and after evaporation of more than 85% water, the WF was stirred in a Waring commercial blender for 30 sec to separate the aggregated particles.

#### 3.2.2.2.2 Treatment of WF with silane Z-6011

The treatment of WF with solution of Z-6011 silane was similar with that of Z-6032 solution and was performed with 0.1, 0.24 and 0.3% silane aqueous solution corresponding to a concentration of silane to WF of 0.6, 1.4 and 1.8%, in accordance to Dow Corning specification to use a dilute aqueous solution having a concentration range between 0.1 and 0.3% silane.

### 3.2.2.3 Testing

#### 3.2.2.3.1 Processability

It is known that the forces involved in mixing a highly viscous melt, which are measured as the torque acting on the rotors, can be correlated with the melt viscosity.

A torque rheometer, the Haake Rheocord-M 300 which was attached on the Haake Rheomix 600 was used for continuous measurement of mixing torque. The indicated torque values represent the equilibrium torque which was attained generally after six minutes mixing.

#### 3.2.2.3.2 Mechanical properties

The tensile strength tests were carried out according to ASTM D638 [47], using an Instron Universal Testing Machine model 1125. The machine is of the cross-head movement type which is composed of a fixed member and a movable member; one grip is connected to each member to hold the specimen between the fixed and moveable members. These self-aligning grips avoid alignment problems during tensile tests. A controlled velocity drive mechanism and a load-indicating mechanism capable of indicating total tensile load are employed. An extensometer is used to determine the distance between two points located within the gauge length of the test specimen as the specimen is stretched.

The speed of testing that produces rupture of the specimen in 5 min was selected for each type of formulation.

The tensile strength at break was calculated by dividing the recorded load at break by the cross sectional area of the specimen. Percent elongation at break was calculated by dividing the recorded extension at break (change in the gage length) by the original gage length and multiplying by 100. The Young modulus and toughness were automatically calculated by the Instron software-series IX.

For each formulation, five samples were tested. All of the indicated values are an average of the determinations where the coefficients of variation were inferior to 10%.

## 3.2.2.3.3 Thermal properties

The thermal properties of samples respectively glass transition temperature (Tg) were measured by differential scanning calorimetry (DSC). It is a thermo-analytical technique which is basically used to distinguish a range of materials like polymers, metals, ceramics, composites, and organic materials. DSC calculation is based on differential heat flow with temperature for a reference and a sample when they are placed in individual cells and heated over a predetermined time-temperature program. The amount of heating flow to the sample and reference, at any time, keeps them at the same temperature, so there is a differential heat flow which is directly related to the thermal resistances of the sample and reference. This differential heat flow is constant until the sample exhibits thermal transitions like melting, crystallization, and the glass transition (Tg). At these transition temperatures the unit heat capacity of the sample is changed and the sample needs more or less heat to be at the same temperature as the reference, depending on whether the change is endothermic or exothermic [48].

The Tg measurements were done with a TA instrument 2010 DSC controlled by Advantage Software (TA Instruments). The DSC data were analyzed with TA Instruments Universal Analysis 2000 program.

At least two specimens of about 16 mg for each control, blend and composite formulations were examined at a heating rate of 20°C/min., under nitrogen atmosphere, between -40°C and 160°C according to ASTM D638-99 [49].

# *Chapter 4 Results and Discussions*

## 4.1 Establishing the formulations' additives

As it was outlined in introduction, PVC is subjected to degradation during processing and consequently the proper selection of heat stabilizer is of great importance in PVC processing.

In addition, as the plasticized lignin is a quite sticky material the selection of a good lubricant would reduce the adhesion between the metallic surface of the processing equipment and the melted polymer.

In order to select the proper heat stabilizer-lubricant pair PVC controls and blends were formulated with following heat stabilizer-lubricant pairs:

- DBTDL-CaSt
- Mark TK 262- Marklube 367
- Mark T 634-CaSt

As it was already mentioned, three kinds of lignin were used for blend formulations: AL, IN, and T. The used formulations are indicated in Table 4.1.

**Table 4.1 Formulations for controls and blends for establishing the proper additives**

| Ingredient | Composition | |
|---|---|---|
| | PVC-control (phr) | PVC-lignin blend (phr) |
| Resin: PVC homopolymer | 100 | 80 |
| Lignin: | | |
| Alcell or | 0 | 20 |
| Tomlinit or | 0 | 20 |
| Indulin | 0 | 20 |
| Plasticizer : Lindol | 35 | 35 |
| Heat stabilizer: | | |
| DBTDL or | 3 | 3 |
| Marklube 367 | 3 | 3 |
| Mark T 634 | 3 | 3 |
| Lubricant | | |
| Calcium Stearate or | 1.5 | 1.5 |
| Mark TK 262 | 1.5 | 1.5 |

Tensile properties for controls and blends as function of different additives and lignins, as well as the equilibrium torque of each formulation are shown in Table 4.2. Tensile properties were obtained at test speeds of 15 mm/min. From the three lignins tested, only the results obtained with AL and T are indicated in Table 4.2. All the sheets of blends formulated with IN presented some degree of decomposition, visible as voids on their surfaces and consequently were not taken into consideration.

### Table 4.2 Properties of controls and blends with AL or T as function of heat stabilizer-lubricant pairs

| Sample Identification | Torque [m.g] | Modulus [MPa] | Break Strength [MPa] | Elongation [MPa] | Toughness [MPa] |
|---|---|---|---|---|---|
| **Controls** | | | | | |
| DBTDL-CaSt | 1125 | 107.55 | 19.45 | 414 | 62.93 |
| Mark T 634-CaSt | 1125 | 78.93 | 20.21 | 433 | 63.34 |
| Mark TK 262-Marklube | 1150 | 75.40 | 18.75 | 399 | 59.30 |
| **Blends with AL, or T** | | | | | |
| AL-DBTDL-CaSt | 700 | 46.12 | 12.9 | 347 | 31.95 |
| AL-Mark T 634-CaSt | 700 | 57.9 | 12.12 | 338 | 33.9 |
| AL-Mark TK 262-Marklube | 825 | 68.96 | 11.30 | 315 | 29.78 |
| T-DBTDL-CaSt | 750 | 34.59 | 12.05 | 312 | 33.73 |
| T-Mark T 634-CaSt | 825 | 47.80 | 12.44 | 335 | 35.53 |
| T-Mark TK 262-Marklube | 900 | 56.44 | 12.79 | 308 | 34.81 |

From the data presented in Table 4.2, it can be seen that for the control specimens break strength and elongation are quite similar when DBTDL-CaSt and Mark T634-CaSt were used as additives. They decreased slightly for Mark TK 262-Marklube. The modulus values were highest for DBTDL-CaSt and lowest for Mark TK 262-Marklube and the viscosity was almost the same for all the pairs of additives.

For AL or T blends (PVC-lignin) the values of break strength and elongation present the same trends as in the case of respective controls. However, the modulus values of both blends are slightly higher when Mark TK 262-Marklube were utilized as additives. Furthermore, for AL and T blends with different pairs of heat stabilizer-lubricants, the values of modulus are lower than that of their respective controls.

All the controls and blends with different additives had a single Tg (quite short and narrow glass transition range) which indicates a relative homogeneous system as it can be seen from the data presented in Table 4.3 and Fig.4.1 (a-c). Replacing part of PVC with lignin decreased Tg. The interesting observation that all the blends have a lower Tg than the respective controls suggests that in blends, lignin acts in a manner similar to that of a plasticizer by further breaking PVC polymer attachments and interactions, thus generating additional free volume with consequent increased freedom of molecular movement. Also, this is the reason why both blends with all pairs of additives had lower torque values than their respective controls, which indicated AL and T blends were less viscose than their respective controls and required less energy for processing.

A comparison of the mechanical properties of controls and respective blends led to the same conclusion, that the modulus, break strength, toughness and viscosity values of the blends are being lower than the respective values of the controls.

**Table 4.3 Tg's of controls and blends as function of heat stabilizer-lubricant pairs**

| **Sample Identification** | **Tg (°C)** |
|---|---|
| Control DBTDL-CaSt | 28.9 |
| Control Mark TK 262-Marklube | 27.2 |
| Control Mark T 634-CaSt | 27.2 |
| Blend-AL,DBTDL-CaSt | 24.1 |
| Blend-AL, Mark TK 262-Marklube | 25.4 |
| Blend-AL, Mark T 634-CaSt | 25.5 |
| Blend-T, DBTDL-CaSt | 22 |
| Blend-T, Mark TK 262-Marklube | 23.5 |
| Blend-T, Mark T 634-CaSt | 22.5 |

From the data represented in Table 4.2 it can be seen that formulations (controls and blends) with Mark T 634 as heat stabilizer, and Calcium Stearate as lubricant presented higher toughness and higher elongation which means better compatibility, so this system was used in further experiments.

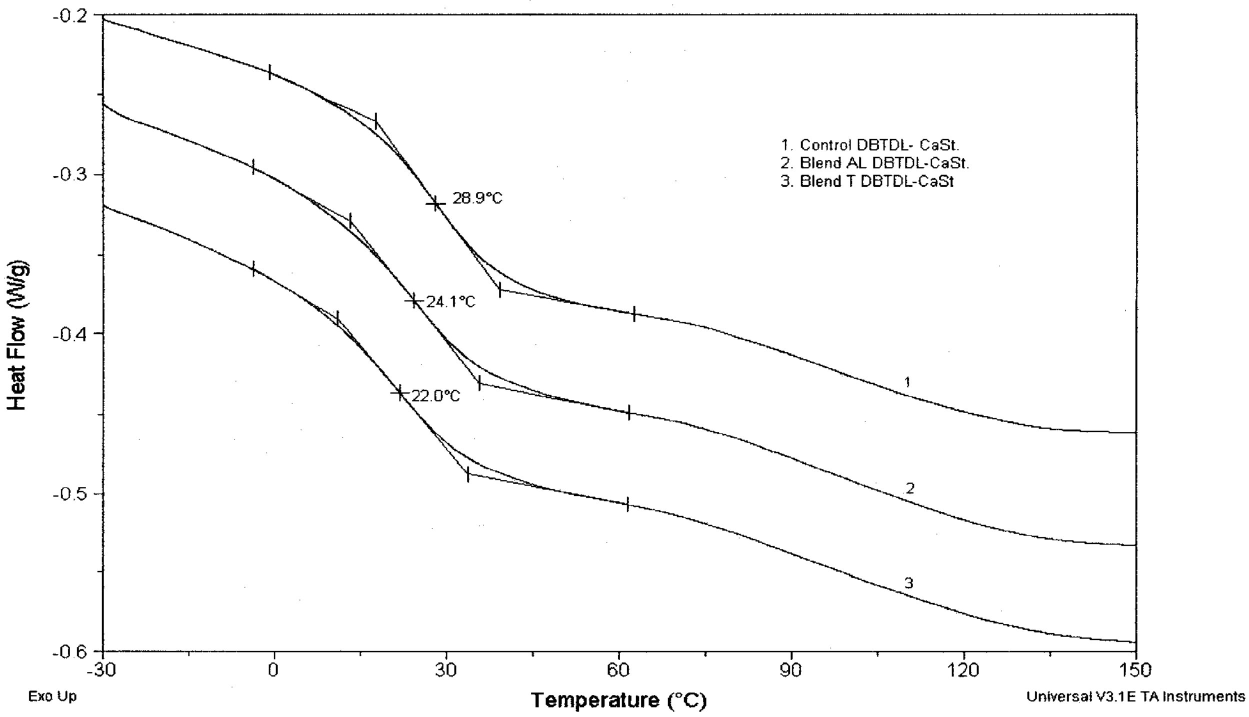


**Figure 4.1 (a) Control and blends DSC curves as the effect of DBTDL-CaSt (heat stabilizer-lubricant) pair additives**

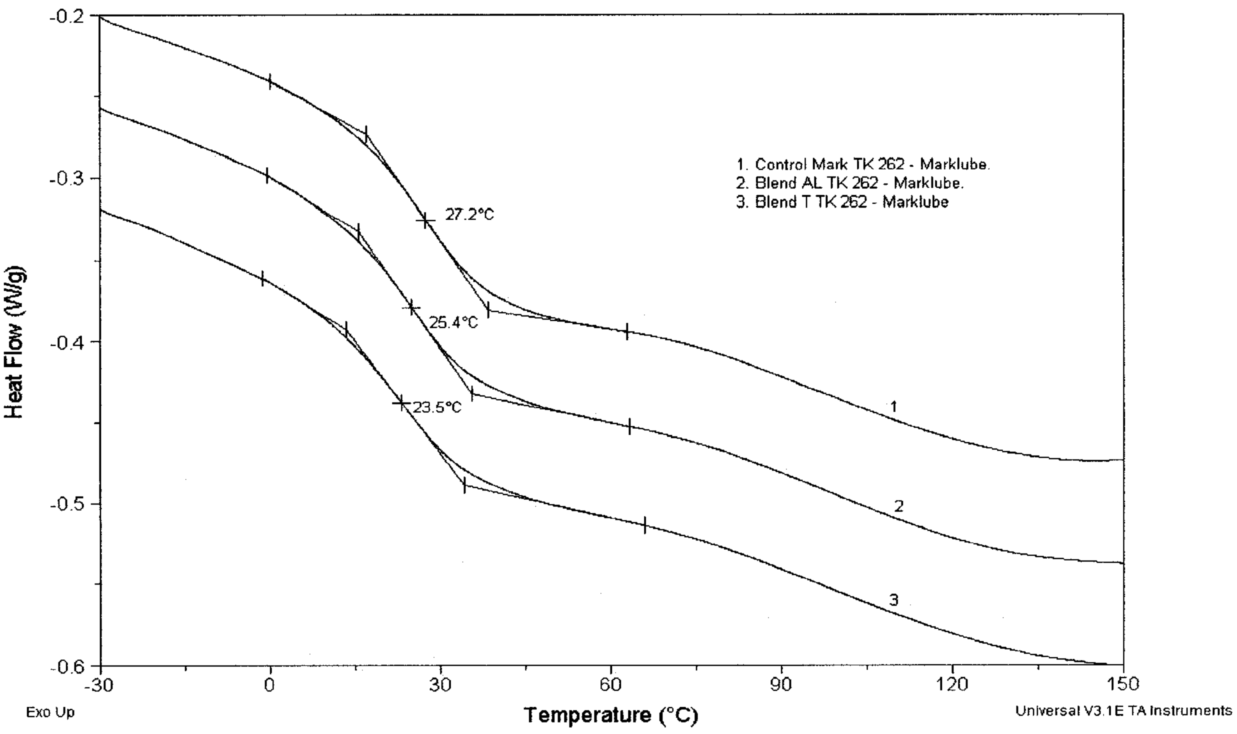


**Figure 4.1 (b) Control and blends DSC curves as the effect of Mark TK 262-Marklube (heat stabilizer-lubricant) pair additives**

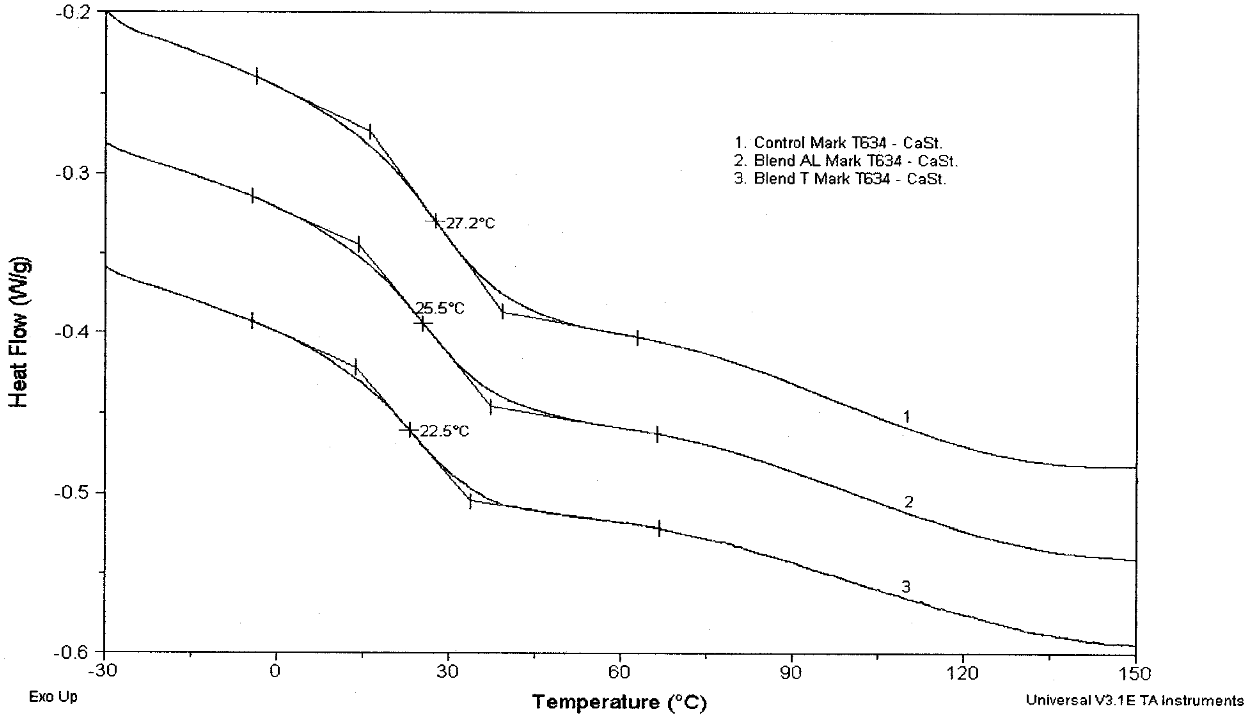


**Figure 4.1 (c) Control and blends DSC curves as effect of Mark T 634-CaSt (heat stabilizer-lubricant) pair additives**

## 4.2 Effect of different WF loading

Once the additives were established, controls and blends with 20, 30, and 40phr WF were prepared and tested. Their compositions are indicated in Table 4.4.

**Table 4.4 Formulations of controls and blends with WF**

| Ingredients | PVC-control (phr) | PVC-lignin blend (phr) |
|---|---|---|
| Resin: PVC homopolymer | 100 | 80 |
| Lignin: AL or<br>T | 0<br>0 | 20<br>20 |
| Plasticizer : Lindol | 35 | 35 |
| Heat stabilizer: Mark T 634 | 3 | 3 |
| Lubricant: Calcium Stearate | 1.5 | 1.5 |
| Wood flour | 20,30, or 40 | 20,30, or 40 |

The tensile properties for controls and blends as function of WF loads are indicated in Table 4.5 and Figures 4.2-4.5. They were obtained at a 15mm/min testing speed.

**Table 4.5 Mechanical properties variations as function of WF loads**

(Testing speed 15 mm/min)

| Tensile Properties | 0 Part WF | 20 parts WF | | 30 parts WF | | 40 parts WF | |
|---|---|---|---|---|---|---|---|
| | | value | %change | value | %change | value | %change |
| **Controls** | | | | | | | |
| Modulus [MPa] | 78.93 | 164.3 | +108.3 | 206.7 | +162.0 | 239.2 | +203.2 |
| Break St. [MPa] | 20.21 | 11.9 | -41.1 | 10.7 | -47.1 | 10.6 | -47.6 |
| Elongation [%] | 432 | 146 | -66.2 | 42 | -90.3 | 14 | -96.8 |
| Toughness (MPa] | 63.3 | 17.7 | -72.0 | 6.43 | -89.8 | 3.82 | -94.0 |
| **80-20 AL Blend** | | | | | | | |
| Modulus [MPa] | 57.9 | 119.1 | +105.7 | 151.3 | +161.3 | 203.4 | +251.3 |
| Break St. [MPa] | 12.12 | 7.83 | -35.4 | 7.4 | -38.9 | 7.25 | -40.2 |
| Elongation [%] | 338 | 145 | -57.1 | 80 | -76.3 | 13 | -96.1 |
| Toughness (MPa] | 33.9 | 11.47 | -66.2 | 6.82 | -68.1 | 4.14 | -87.8 |
| **80-20 T Blend** | | | | | | | |
| Modulus [MPa] | 47 | 129.4 | +175.31 | 142.1 | +202.3 | 190.1 | +304.5 |
| Break St.[MPa] | 12.44 | 9.7 | -22.0 | 8.97 | -27.9 | 9.5 | -25.2 |
| Elongation [%] | 335 | 97 | -71.0 | 53 | -84.1 | 20 | -94.0 |
| Toughness (MPa] | 35.5 | 9.42 | -73.5 | 6.39 | -82 | 2.89 | -91.9 |

% change is related to control or blend values without WF

The data presented in Table 4.5 indicated clearly the poor compatibility between the hydrophilic nature of wood and hydrophobic PVC controls or PVC blends matrix where the synthetic polymer is predominant. This incompatibility leads to a poor interfacial adhesion between the wood fibers and plastic matrix which results in reducing the mechanical strength and ductility. Control specimens at WF loadings of 20, 30 and 40phr the modulus values increase by 108, 162 and 203% and the elongation values decrease by 66, 90 and 97% respectively.

However, at the same WF loading the modulus values increase by 106, 161 and 251% for AL blends and the elongation values decrease by 57, 76 and 96%.

The same trend is noticeable for strength at break values. They decrease by 41, 47 and 48% for controls loaded with 20, 30 and 40phr WF and by only 35, 39 and 40% for respective blends.

Data represented in Table 4.5 also indicated that the mechanical strength and ductility of WF composites formulated with AL or T decreased almost in the same way, respective values of composites formulated with AL being slightly superior to those formulated with T.

DSC data (not included) indicated, as it was supposed, that WF presence both in controls and blends did not influence substantially their Tg.

Although the mechanical strength and ductility of PVC-lignin blends WF composites decreased less than that of PVC-WF composites, lignin presence does not improve substantially the adhesion between polymer matrix and WF. In addition, the small lignin macromolecules (MW 800-900) have a small contribution to the breaking strength of blends (PVC-lignin) and blend composites (PVC-lignin-WF).

Consequently in a new set of experiments, other blends were formulated where the 10, 15 and 20 parts of PVC were replaced by lignin.

Due to the almost similar properties of AL and T blends-WF composites, the further composites were formulated only with AL. In addition the time in melt mixing process was increased from 8 to 10 minutes in order to permit a longer contact between polymer matrix and WF. The pressure of compression molding was increased from 4.37MPa to 6.56MPa based on the higher stiffness of WF composites. Also, due to the low ductility of WF composites, the tensile tests were performed at a speed of 5 mm/min in order to produce the rupture of the specimens in about 5 min. The effect of these changes on the mechanical properties of controls, blends and on their WF composites will be discussed.

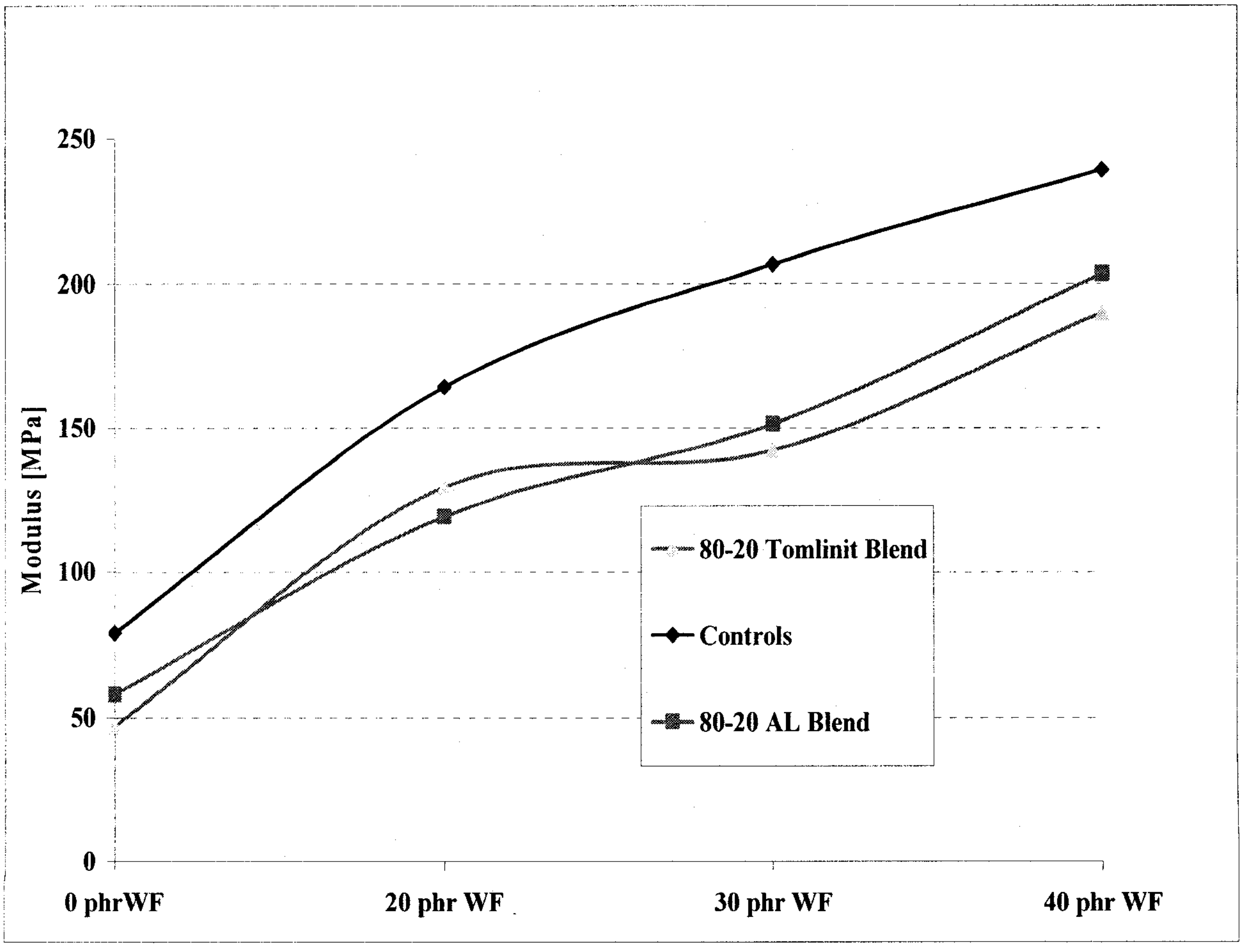


**Figure 4.2 Modulus variations of controls and blends as function of WF loads**

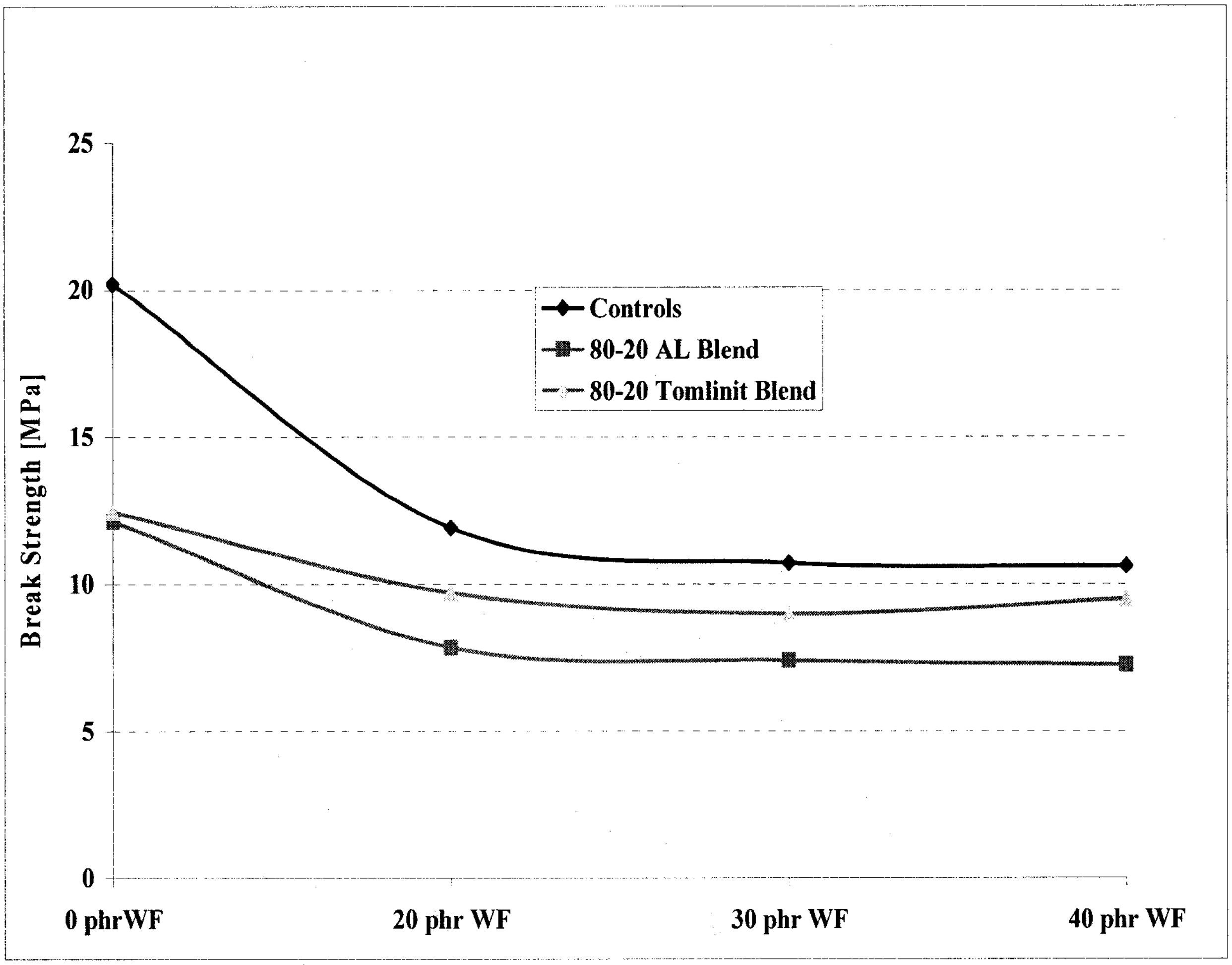


Figure 4.3 Break strength variations of controls and blends as function of WF loads

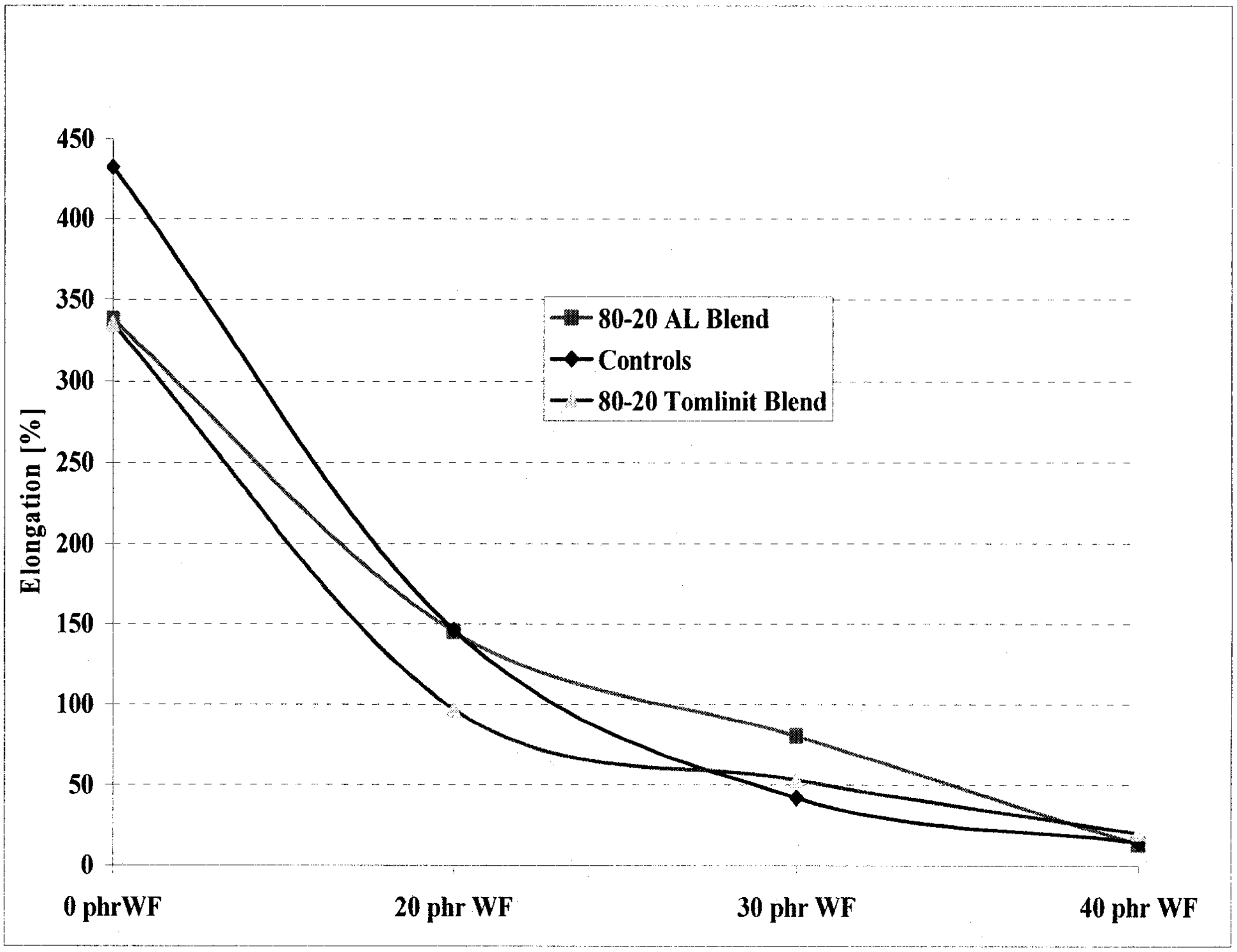


Figure 4.4 Elongation variations of controls and blends as function of WF loads

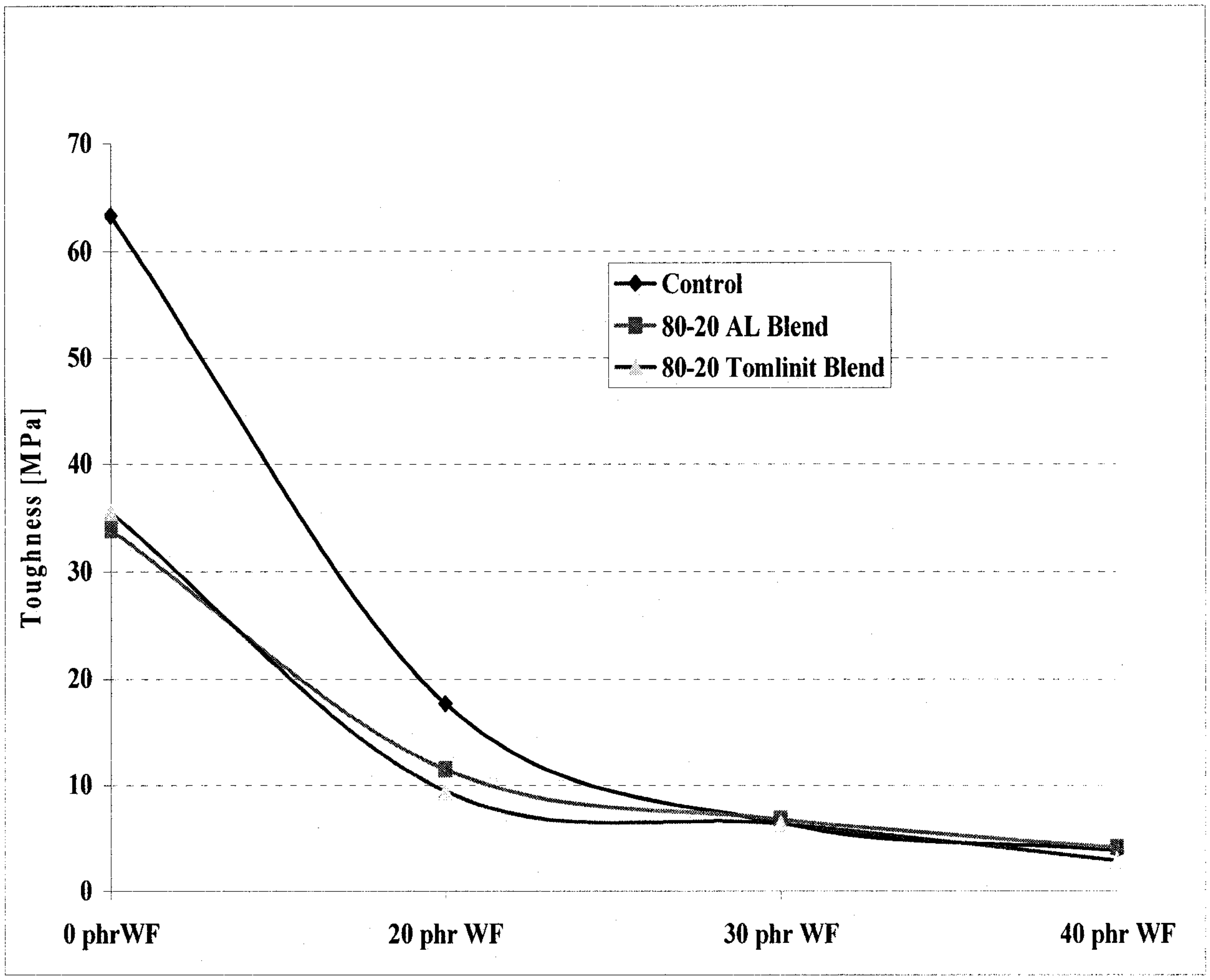


Figure 4.5 Toughness variations of controls and blends as function of WF loads

## 4.3 Effect of changing processing parameters and AL loading on the properties of controls, blends and their WF composites

As it was discussed earlier, new formulations were prepared and processed at other processing parameters with the aim of improving their performances. The melt mixing time was increased at10 minuets, and the compression molding pressure was increased at 6.56MPa. Tensile test speed for the obtained specimens was of 5 mm/min.

The composition of new formulations is indicated in Table 4.6 and their mechanical properties in Table 4.7.

**Table 4.6 New formulations of controls, blends and their WF composites**

| Ingredients | Composition | |
|---|---|---|
| Resin: PVC homopolymer | PVC-control (phr) | PVC-lignin blend (phr) |
| | 100 | 90,85, or 80 |
| Lignin: AL | 0 | 10,15, or 20 |
| Plasticizer : Lindol | 35 | 35 |
| Heat stabilizer: Mark T 634 | 3 | 3 |
| Lubricant: CaSt | 1.5 | 1.5 |
| Wood flour (WF) | 0, 10, 20, and 30 | 0, 10, 20, and 30 |

**Table 4.7 Mechanical properties variations as function of WF loads for the formulations indicated in Table 4.6**

(Testing speed 5 mm/min)

| Tensile properties | 0phr WF | | 10phr WF | | 20phr WF | | 30phr WF | |
|---|---|---|---|---|---|---|---|---|
| **Controls** | | | | | | | | |
| | Value | %change | Value | %change | Value | %change | Value | %change |
| Modulus[MPa] | 136.9 | 100 | 199.8 | +45.9 | 249.8 | +82.5 | 260.6 | +90.4 |
| Break St.[MPa] | 22.4 | 100 | 14.38 | -35.8 | 12.45 | -44.4 | 11.4 | -49.1 |
| Elongation[%] | 334 | 100 | 179 | -46.4 | 111 | -66.8 | 32 | -90.4 |
| Toughness[MPa] | 58.13 | 100 | 22.67 | -61 | 13.7 | -76.4 | 5.07 | -91.2 |
| **90-10 AL Blends** | | | | | | | | |
| Modulus[MPa] | 85.57 | 100 | 169.78 | +98.4 | 206.82 | +141.7 | 225.7 | +163.7 |
| Break St.[MPa] | 16.57 | 100 | 13.35 | -19.4 | 11.84 | -28.5 | 10.26 | -38.1 |
| Elongation[%] | 322 | 100 | 181 | -43.8 | 116 | -64 | 48 | -85.1 |
| Toughness[MPa] | 46.72 | 100 | 19.92 | -57.4 | 14.4 | -69.2 | 6.36 | -86.4 |
| **85-15 AL Blends** | | | | | | | | |
| Modulus[MPa] | 66.84 | 100 | 143.94 | +115.4 | 164.95 | +146.8 | 199.6 | +198.6 |
| Break St.[MPa] | 15.13 | 100 | 11.4 | -24.7 | 9.75 | -35.6 | 9.82 | -35.1 |
| Elongation[%] | 322 | 100 | 141 | -56.2 | 101 | -68.6 | 42 | -86 |
| Toughness[MPa] | 45.56 | 100 | 13.86 | -69.6 | 10.19 | -77.6 | 5.73 | -87.4 |
| **80-20 AL Blends** | | | | | | | | |
| Modulus[MPa] | 74.45 | 100 | 150.53 | +101.9 | 174.8 | +134.8 | 208 | +179.4 |
| Break St.[MPa] | 12.92 | 100 | 10.31 | -20.2 | 9 | -30.3 | 8.1 | -37.3 |
| Elongation[%] | 371 | 100 | 217 | -39.9 | 114 | -68.4 | 57 | -84.2 |
| Toughness[MPa] | 41.52 | 100 | 20.67 | -50.2 | 9.86 | -76.2 | 4.32 | -89.6 |

% change is related to control and blend values without WF.

From the data presented in Table 4.7 it can be seen that changing the mixing time and compresion molding presure as well as reducing the content of AL in blends did not substantially improve the properties of controls and AL blends WF composites. As seen before, the mechanical strength and ductility of blend composites decreased less than that of the respective values of controls suggesting a slightly better degree of compatibility between the WF and polymer matrix in WF-blend composites than in their respective controls.

Howeverr, as the mechanical properties of controls and blend composites were still very poor, new experiments were performed where temperature of processing was raised to 150°C, 155°C and 160°C in order to decrease the viscosity of melt in an atempt to obtain a better dispersion of WF particles in the melt. The experiments were performed with controls and blends formulated with Lindol and also with diethylene glycol dibenzoate plasticizer (2-45) which gave also good results in plasticized PVC-AL blends [5]. The results of these experiments will be discussed next.

## 4.4 Effect of changing processing temperature on the mechanical and thermal properties of controls, AL-blends and their respective WF composites

These preliminary experiments were performed with the intention to establish the maximum possible melt mixing temperature at which the blends with AL could be processed without AL's thermal decomposition. The other processing parameters were kept as they were set up during the different experimental procedures i.e mixing time 10 min, compression molding temperature 160°C, and compression molding pressure

6.56MPa. Together with Lindol, another plasticizer 2-45 was utilized for these formulations. As it was discussed earlier 2-45 is also a very good plasticizer for AL without having the flame retardant properties of Lindol.

The mechanical and thermal properties of the formulations obtained at different processing temperatures are presented in Table 4.8.

**Table 4.8 Mechanical and thermal properties variations of controls and blends formulated with Lindol or 2-45 plasticizer as function of processing temperature**

(Testing speed 5 mm/min)

| Properties | Control 145°C | Control 150°C | Control 155°C | Control 160°C | Blend 145°C | Blend 150°C | Blend 155°C | Blend 160°C |
|---|---|---|---|---|---|---|---|---|
| | **Lindol Plasticizer (35phr)** | | | | | | | |
| Torque [m.g] | 1100 | 1075 | 925 | 825 | 825 | 800 | 750 | 500 |
| Tg [°C] | 28.1 | 29.2 | 29.1 | 28.3 | 25.6 | 22.9 | 22.9 | 24.7 |
| Modulus[MPa] | 136.9 | 133.6 | 133.5 | 104.1 | 74.45 | 51.68 | 43.37 | 68.82 |
| Break St. [MPa] | 22.4 | 20.84 | 21.88 | 22.16 | 12.92 | 12.91 | 12.75 | 13.51 |
| Elongation [%] | 334 | 456 | 456 | 465 | 371 | 416 | 450 | 378 |
| Toughness[MPa] | 58.13 | 74.07 | 76.29 | 77.74 | 41.52 | 43.46 | 45.59 | 40.71 |
| **2-45 Plasticizer (35phr)** | | | | | | | | |
| Torque [m.g] | - | 975 | 850 | 725 | - | 650.0 | 550.0 | - |
| Tg [°C] | - | 20 | 21.1 | 18.9 | - | 16.3 | 17.0 | - |
| Modulus[MPa] | - | 8.31 | 8.71 | 9.04 | - | 10.32 | 9.93 | - |
| Break St. [MPa] | - | 17.71 | 17.44 | 17.44 | - | 11.04 | 10.62 | - |
| Elongation [%] | - | 466 | 479 | 486 | - | 484 | 529 | - |
| Toughness[MPa] | - | 56.37 | 56.27 | 56.76 | - | 43.73 | 45.27 | - |

Data from Table 4.8 clearly indicate that increasing processing temperature slightly modifies the tensile breaks and visibly increases elongation and toughness of controls and blends formulated with both plasticizers. PVC is a predominantly amorphous, commercial homopolymer which has about 10% crystalinity. The crystallites are small and imperfect, having a broad range of melting from 110°C to 200°C. The properties of plasticized PVC are associated with a network structure which is believed to be physically cross-linked by crystallites and variation in tensile strength and elongation are related to the degree of fusion of these crystals. Increased fusion state leads to increased strength properties [50].

Based on these results it was concluded that the melt mixing temperature can be raised without problems of decomposition from 145°C to 155°C. WF composites formulated with these two plasticizers and processed at 155°C were prepared and tested. 20 parts of PVC were replaced with AL in blends and the WF loading in composites was of 20phr.The mechanical properties of these composites are presented in Table 4.9.

**Table 4.9 Mechanical properties of controls, blends and their WF composites (20phr) processed at 155°C melt mixing temperature**

(Testing speed 5 mm/min)

| Sample Identification | Torque [m.g] | Modulus [MPa] | Break St. [MPa] | Elongation [%] | Toughness [MPa] |
|---|---|---|---|---|---|
| **Plasticizer 2-45** | | | | | |
| Control no WF | 850 | 8.71 | 17.44 | 479 | 56.27 |
| Control WF | 850 | 47.95 | 10.07 | 220 | 18.15 |
| Blend no WF | 550 | 10.32 | 11.04 | 484 | 43.13 |
| Blend WF | 600 | 49.71 | 7.21 | 211 | 13.9 |
| **Plasticizer Lindol** | | | | | |
| Control no WF | 925 | 133.5 | 21.88 | 456 | 76.29 |
| Control WF | 900 | 209.1 | 12.32 | 135 | 15.64 |
| Blend no WF | 750 | 43.37 | 12.75 | 450 | 45.59 |
| Blend WF | 650 | 147.5 | 8.02 | 152 | 30.40 |

As it is presented in Table 4.9, in case of 2-45 plasticizer modulus and elongation of the blends with WF are very close to those of the controls with WF. With Lindol plasticiser only the modulus and toughness are better.

From the data shown in Table 4.9, it appears that the increase in melt mixing temperature has little effect in improving the strength and elongation of the composites, data obtained in these conditions (for Lindol as plasticizer) being quite close with those obtained at 145°C melt mixing temperature and slightly different processing parameters. As all the changes in processing parameters did not influence the mechanical properties of composites, addition of coupling agents and/or the treatment of WF with compatibilizer agents was next undertaken. As 2-45 plasticizer provided more elastic composites than Lindol, it was used for the further experiments.

## 4.5 Effect of compatibilizers on the properties of WF composites formulated with controls and AL blends

The results obtained so far clearly indicated the incompatibility between PVC and WF. Lignin was employed in composites to serve as a bridging agent between hydrophilic WF and hydrophobic PVC, but with little success. The mechanical strength and elasticity of blend composites decreased less than that of respective values of control composites, suggesting a slightly better degree of compatibility between the WF and polymer blend matrix. However, lignin presence did not substantially improve the adhesion between polymer matrix and WF. In addition lignin macromolecules have a small contribution to the breaking strength of blends and blend composites.

For better performances, in the next experiments, some coupling agents were used. Their selection was done based on literature information outlined in section 2.2.

The formulations for those experiments were those established previously and are indicated in Table 4.10. The processing parameters were also those previously established i.e.

- Melt mixing temperature and time: 155°C and 10 min.
- Compression molding temperature and pressure: 160°C and 6.56MPa.

The testing speed in tensile testing was of 5 mm/min.

**Table 4.10 Formulations of controls and blends**

| Ingredients (phr) | Without WF | | With WF | |
|---|---|---|---|---|
| | Control | Blend | Control | Blend |
| PVC | 100 | 80 | 100 | 80 |
| AL | 0 | 20 | 0 | 20 |
| Plasticizer: 2-45 | 35 | 35 | 35 | 34 |
| Heat stabilizer: Mark T 634 | 3 | 3 | 3 | 3 |
| Lubricant: CaSt | 1.5 | 1.5 | 1.5 | 1.5 |
| WF | 0 | 0 | 20 | 20 |

As it was mentioned earlier two types of silane were utilized for WF treatment: DuPont Z-6032 and DuPont Z-6011 silanes. Solutions of different concentarions were prepared from their prehydrolized concentrates as it was indicated in section 3.4.2.2..

Concentration of silane to WF was of 0.2, 0.6, and 1% for silane Z-6032 and of 0.6, 1.4 and 1.8% for silane Z-6011 based on manufacture specifications (for mineral fillers not for WF). The mechanical properties of controls, blends and control and blends WF composites are presented in Table 4.11 and Figures 4.6-4.9.

From the data presented in Table 4.11 and Figures 4.6-4.9, it looks likely that the treatment of WF with silane did not improve the adhesion between WF and the polymer matrix. A slight improvement is noticeable only in the case of AL blend WF composite where WF was treated with 0.6% silane Z-6011.

At section 3.4.2.2, it was pointed out that after WF treatment with diluted silanes water solutions a hard cake was formed after filtering. Altough the WF aggregated particles were mechanicaly separated, it is probable that some agregates still persisted leading to a poor dispersion of WF particles in polymer matrix.

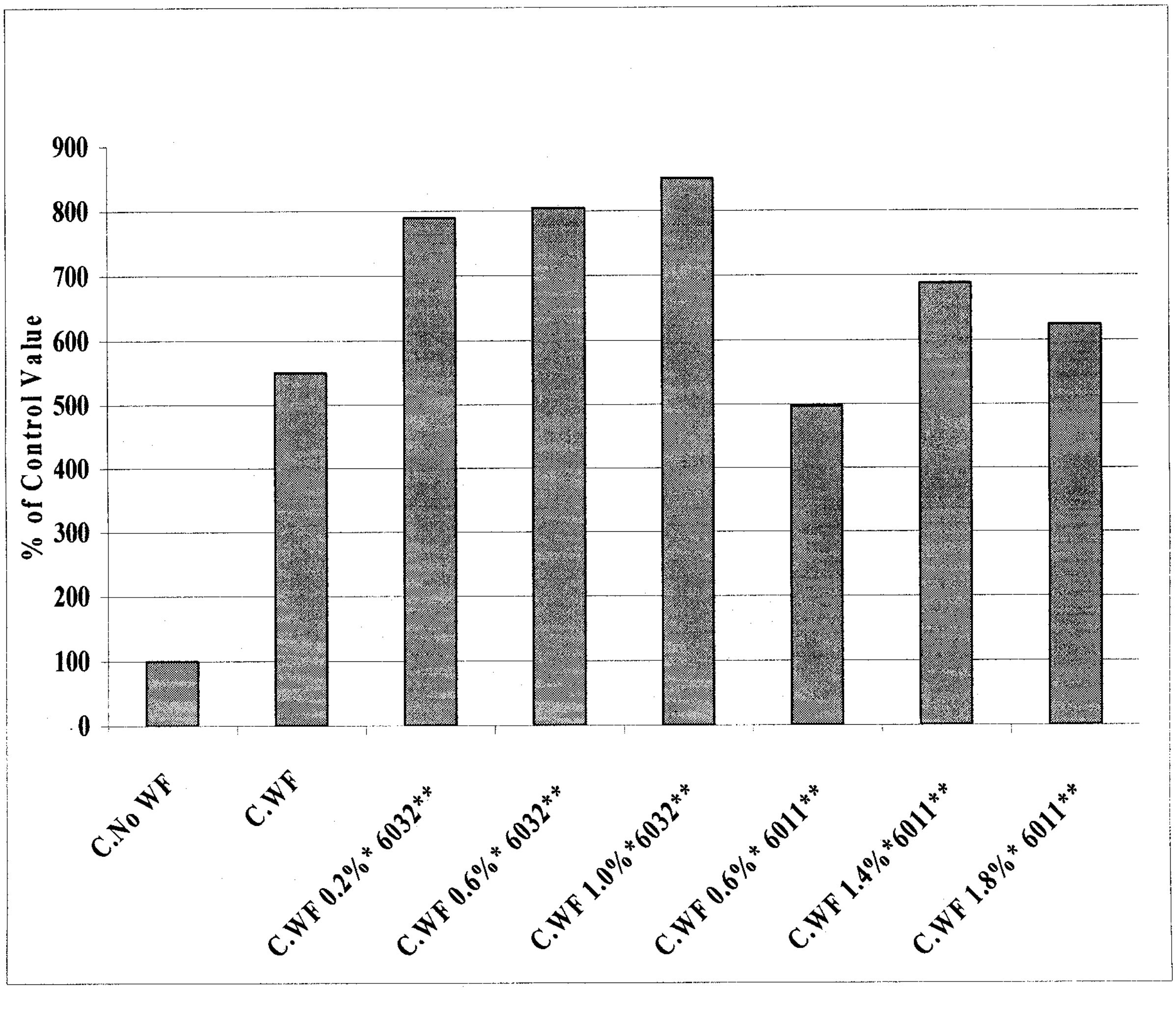
It is also possible that an evenly coating surface of WF was not achived owning to sensitivity of silanes to hydrolize and self condence [51].

Comparable results were found in literature. For a plasticized PVC–WF composite (20% WF) Kokta and al. obtained an 97.5% increase in modulus and a 61 and 54% decrease in break strength and elongation respectively. After treating the WF with 1.25% amino silane (with a chemical composition similar to Z-6011) the modulus increased with 32% and the tensile strength at break decreased by only 50%, but the elongation decreased by more than 60% [52].

Another work was done by O.S. Rodriguez- Fernandez and Colab. For a plasticized PVC-WF composite (50phr plasticizer and WF content 20-40%) the researchers found that the silane treatment of WF had little effect on mechanical properties of composites. The treatment of WF was performed also with an amino silane and the concentration of silane to WF was of 1, 2 and 3% [53].

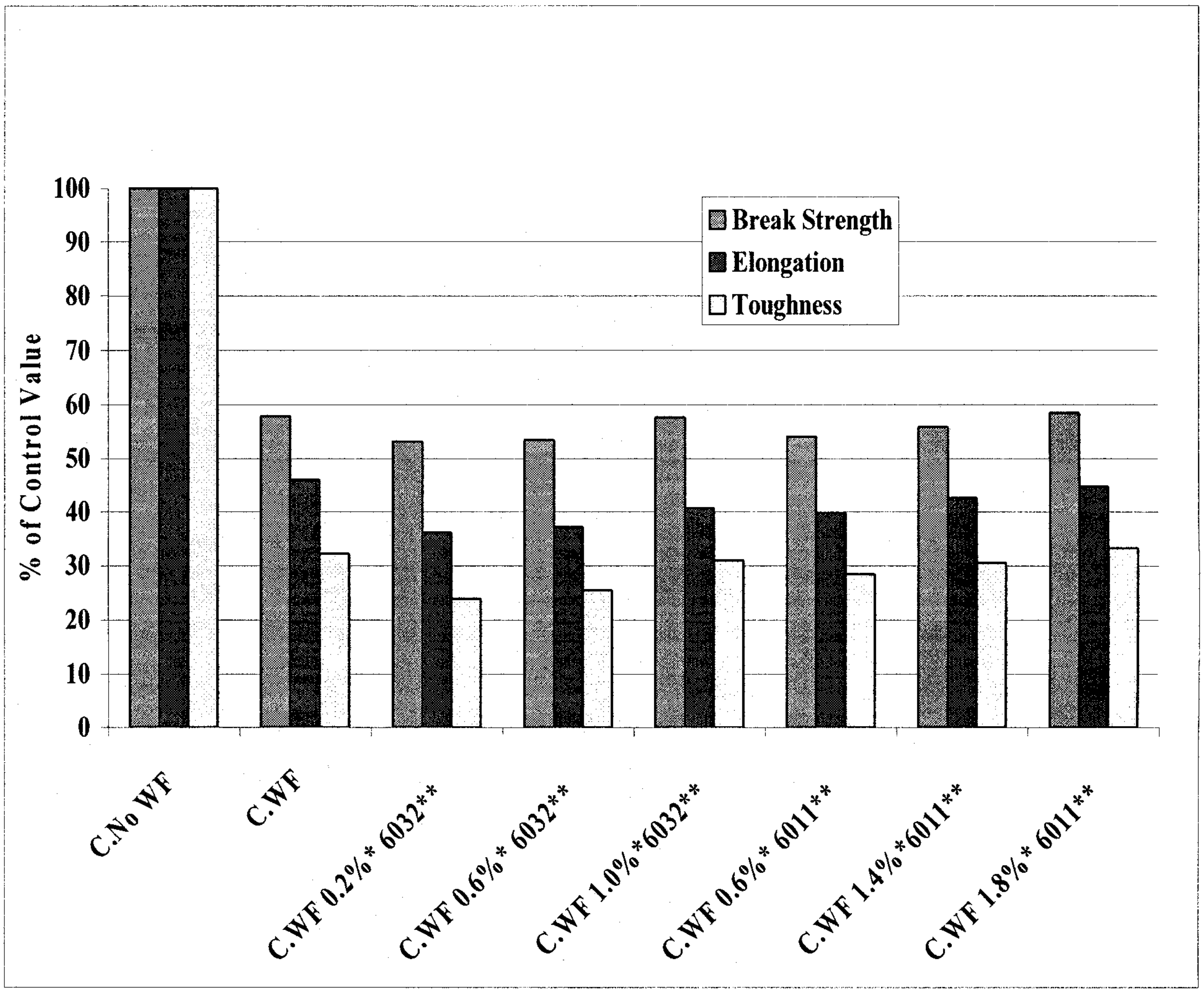
**Table 4.11 Mechanical properties of controls and blends as function of silane treatment of WF** (Testing speed 5 mm/min)

| Sample Identification | Tg [°C] | Torque [m.g] | Modulus [MPa] | Break St. [MPa] | Elongation [%] | Toughness [MPa] |
|---|---|---|---|---|---|---|
| Control No WF | 19.9 | 800 | 8.71 | 17.44 | 479 | 56.27 |
| Control WF | 19.8 | 900 | 47.95 | 10.07 | 220 | 18.15 |
| Control WF 0.2% 6032 | 18.8 | 950 | 68.75 | 9.26 | 173 | 13.46 |
| Control WF 0.6% 6032 | 20.9 | 1000 | 70.01 | 9.32 | 178 | 14.3 |
| Control WF 1% 6032 | 20.3 | 900 | 74.05 | 10.05 | 195 | 17.44 |
| Control WF 0.6% 6011 | - | 900 | 43.3 | 9.43 | 191 | 15.97 |
| Control WF 1.4% 6011 | 20.6 | 1000 | 52.18 | 9.73 | 204 | 17.2 |
| Control WF 1.8% 6011 | - | 1050 | 54.31 | 10.17 | 215 | 18.74 |
| Control WF 2.4% 6011 | 21.2 | 1100 | 91.0 | 10.35 | 191 | 16.57 |
| Blend No WF | 16.3 | 500 | 10.32 | 11.04 | 484 | 40.96 |
| Blend WF | 16.2 | 700 | 60.69 | 6.47 | 233 | 12.21 |
| Blend WF 0.2% 6032 | - | 700 | 78.3 | 6.18 | 223 | 11.41 |
| Blend WF 0.6% 6032 | 14.7 | 700 | 69.61 | 6.22 | 229 | 11.75 |
| Blend WF 1% 6032 | - | 700 | 48.7 | 6.52 | 230 | 12.24 |
| Blend WF 0.6% 6011 | - | 900 | 75.64 | 7.23 | 238 | 13.92 |
| Blend WF 1.4% 6011 | 17.3 | 750 | 81.11 | 6.41 | 168 | 12.56 |
| Blend WF 1.8% 6011 | 16.7 | 800 | 78.2 | 6.42 | 241 | 12.32 |



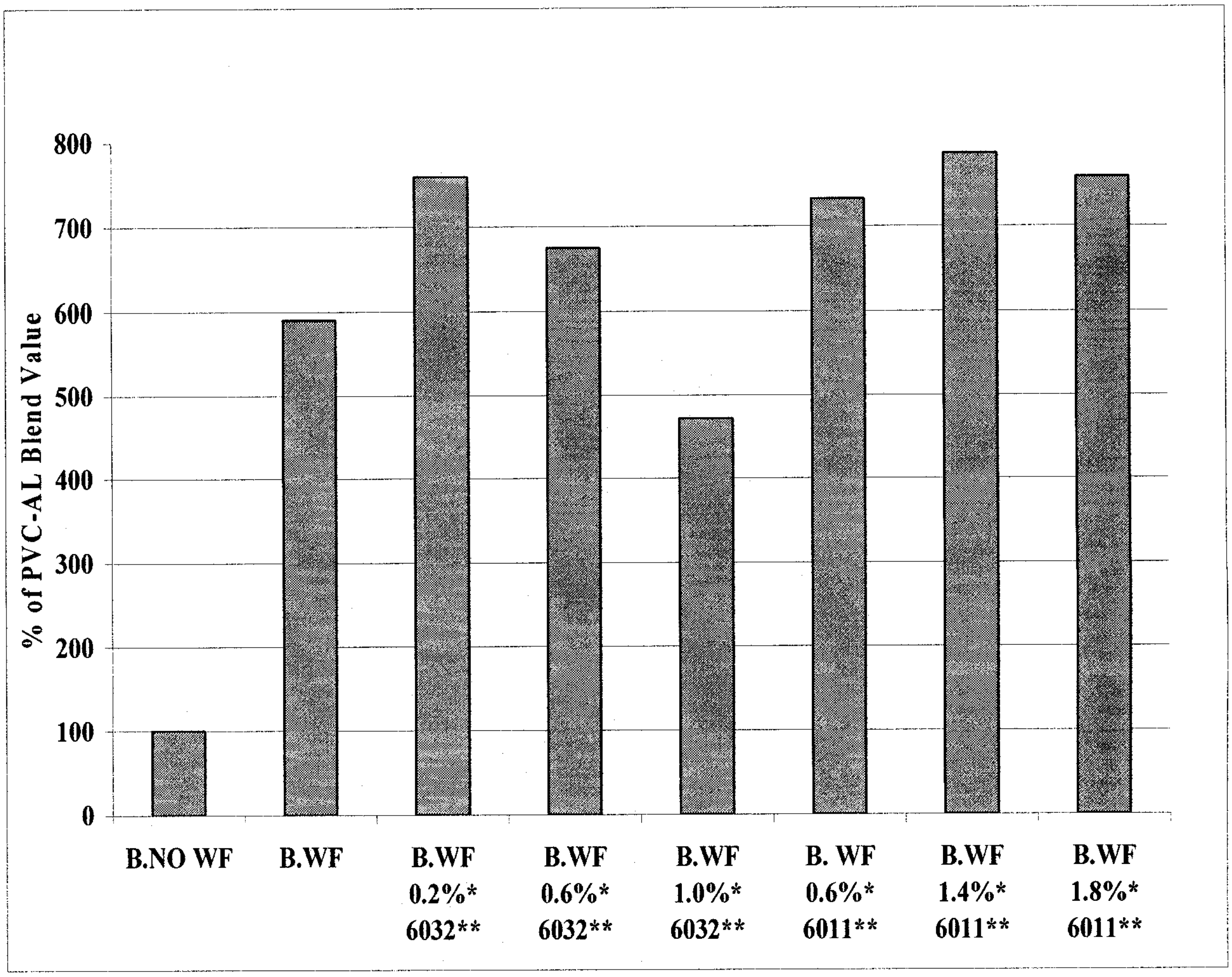
*Concentration of silane to WF, ** Type of silane

**Figure 4.6 Modulus variations of PVC-WF composites as function of Silane treatment**



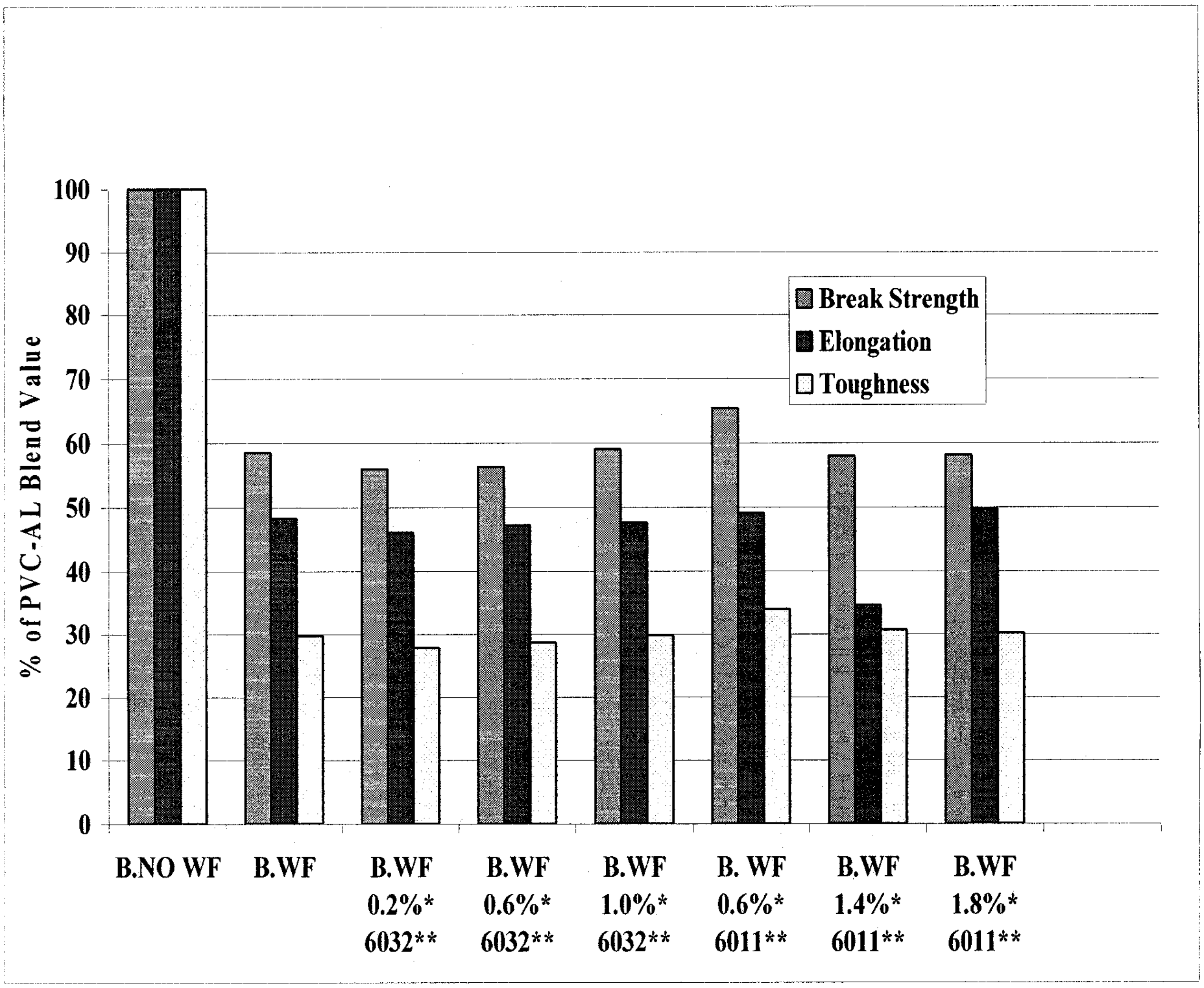
*Concentration of silane to WF, ** Type of silane

**Figure 4.7 Tensile strength at break, elongation and toughness variations of PVC-WF composites as function of silane treatment**



*Concentration of silane to WF, ** Type of silane

**Figure 4.8 Modulus variations of PVC-AL-WF composites as function of silane treatment**



*Concentration of silane to WF, ** Type of silane

**Figure 4.9 Tensile strength at break, elongation and toughness variations of PVC-AL-WF composites as function of silane treatment**

### 4.5.1 Chitin as coupling agent

As it was observed in previous experiments, AL presence and WF treatment with silanes could not improve the wetting and adhesion of WF to the polymer matrix. Based on data taken from literature, it was decided to examine the effect of chitin in improving the adhesion of WF to the polymer matrix and consequently in improving the mechanical properties of the composites. Formulations with 5, 6.5 and 8% of chitin based on weight of WF were prepared. Other ingredients of formulations and processing parameters were the same as those outlined in section 4.5.

B.L. Shah and Colab have utilized chitin and chitosan in rigid PVC-WF composites containing as much 75phr WF. The concentration of chitin and chitosan varied from 0-10% based on the weight of WF in the composites. Addition of both chitin and chitosan coupling agents gave composites having flexural strenght superior than that of the uncoupled composites and almost similar to that of neat PVC. The best results were obtained with o.5wt.% chitosan and 6.67 wt.% chitin.[32].

The formulations with chitin as coupling agent are shown in Table 4.12, their properties in Table 4.13, and their stress-strain curves in Figure 4.10.

**Table 4.12 Formlations used in PVC-WF composites with chitin (K) as coupling agent**

| Ingredients (phr) | % chitin to WF | | |
|---|---|---|---|
| | 5 | 6.5 | 8 |
| PVC 185 | 100 | 100 | 100 |
| 2-45 | 35 | 35 | 35 |
| WF 8010 | 20 | 20 | 20 |
| Mark T 634 | 3 | 3 | 3 |
| CaSt | 1.5 | 1.5 | 1.3 |
| Chitin | 1 | 1.3 | 1.5 |

**Table 4.13 Properties of PVC-WF composites as function of chitin (K) concentrations**

| Sample Identification | Tg [°C] | Torque [m.g] | Modulus [MPa] | Break St. [MPa] | Elongation [%] | Toughness [MPa] |
|---|---|---|---|---|---|---|
| Control WF (C) | 19.8 | 900 | 47.95 | 10.07 | 220 | 18.15 |
| C 5%K to WF | 21.5 | 1100 | 83.63 | 10.99 | 207 | 19.12 |
| C 6.5%K to WF | 21.5 | 1000 | 74.17 | 10.25 | 191 | 16.63 |
| C 8%K to WF | 21.1 | 1050 | 63.95 | 10.24 | 202 | 16.77 |

By analyzing the data presented in Table 4.13, on may discern that in contrast to silane coupling agnets the effect of chitin is superior in improving the mechanical properties of composites. A slight increase in Tg and also a slight increase in equlibrium torque are obsrved and in the mean time the modulus values are increased, the break strength values slight increased and elongation values slight decreased in comparison with the formulation of composites prepared without chitin. The best values were obtained at a concentartion of 5% chitin to WF were the modulus and break strenght values are increased by 74 and 9% respectively at a reduction of elongation values of only 6%.

At this concentration of chitin the torque values are the highest due probably to a certain degree of adhesion between WF and PVC matrix, having as a result an increased viscosity of the matrix.

The interaction of chitin and wood is probably due to its acetyl amine groups which can react with the WF's OH groups and presented data indicated that the best results are obtained at a particular concentration of chitin to WF (5% chitin (K) seems to be optimum).

Based on these observations, it appears reasonable to examine if AL too, in much lower concentration in WF composites could serve as a bridging agent between WF and PVC, due to its polar groups (hydroxyl, carbonyl, methoxy, ethoxy, etc).

Utilization of AL as a coupling agent will be further discused.

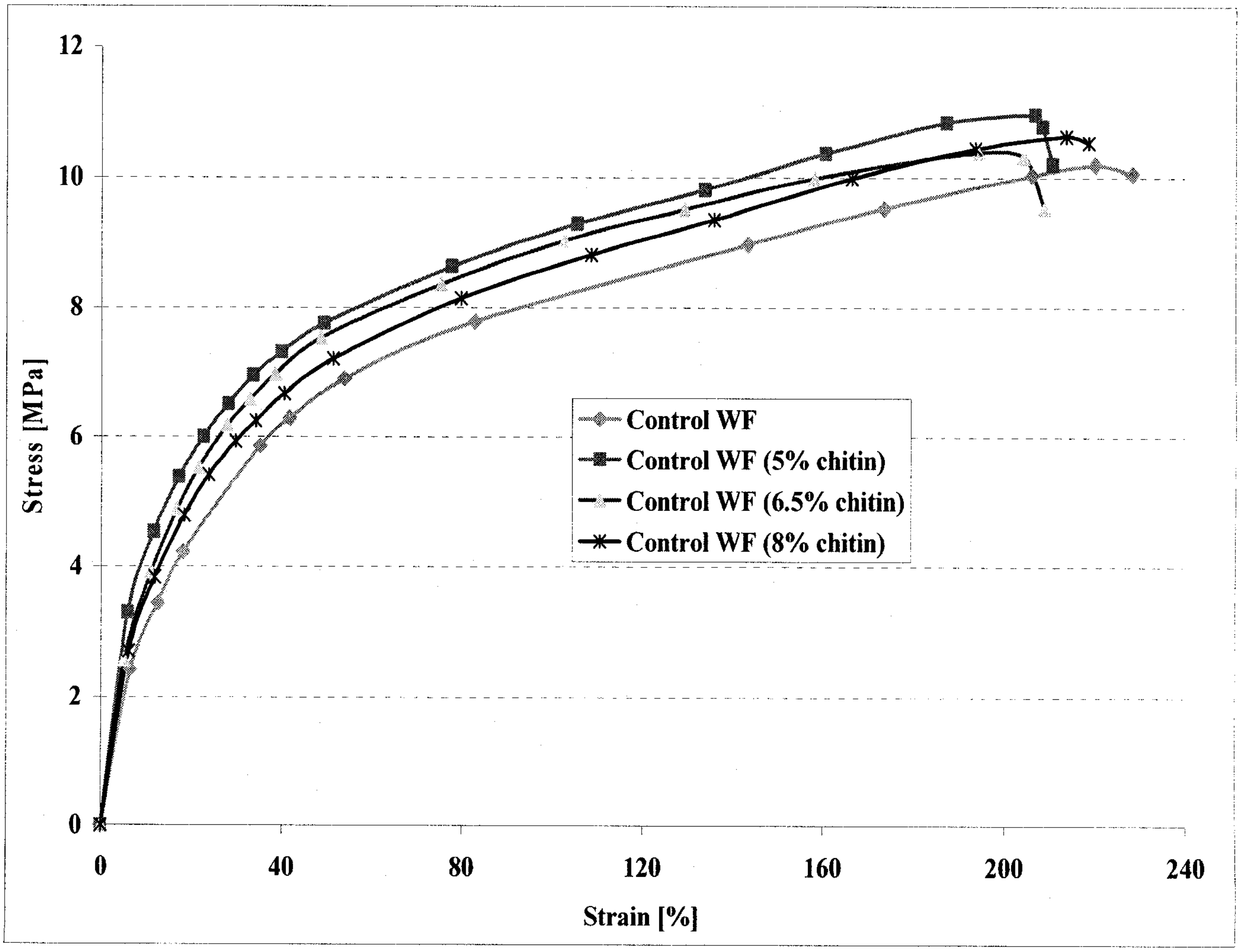


**Figure 4.10 Stress-Strain curves as function of concentration of chitin as coupling agent**

## 4.5.2 AL as coupling agent

Based on the conclusions from section 4.5.1, new formulations of PVC-WF were prepared with AL as coupling agent. The concentration of AL to WF was of 5, 10, 15 and 25wt. %. Other ingredients, as well as the processing parameters were the same as those outlined in section 4.5

The formulations of PVC-WF composites are shown in Table 4.14, their properties in Table 4.15 and their stress-strain curves in Figure 4.11. In Figure 4.12, DCS curves of formulations are presented.

**Table 4.14 Formulations used in PVC-WF composites with AL as coupling agent**

| Ingredients (phr) | % AL to WF | | | |
|---|---|---|---|---|
| | 5 | 10 | 15 | 25 |
| PVC | 100 | 100 | 100 | 100 |
| AL | 1 | 2 | 3 | 5 |
| Plasticizer : 2-45 | 35 | 35 | 35 | 35 |
| Heat stabilizer: Mark T 634 | 3 | 3 | 3 | 3 |
| Lubricant: CaSt | 1.5 | 1.5 | 1.5 | 1.5 |
| WF | 20 | 20 | 20 | 20 |

### Table 4.15 Properties of PVC-WF composites as function of AL concentrations

| Sample Identification | Tg (°C) | Torque [m.g] | Modulus [MPa] | Break St. [MPa] | Elongation [%] | Toughness [MPa] |
|---|---|---|---|---|---|---|
| Control WF (C) | 19.8 | 850 | 47.95 | 10.07 | 220 | 18.15 |
| C 5%AL to WF | 20.9 | 950 | 85.06 | 10.68 | 231 | 20.21 |
| C 10%AL to WF | 21.8 | 1000 | 86.4 | 11.29 | 244 | 22.76 |
| C 15%AL to WF | 22 | 1000 | 88.45 | 10.95 | 208 | 19.31 |
| C 25%AL to WF | 21.8 | 1050 | 76.1 | 10.88 | 204 | 18.7 |

An increase in Tg and equilibrium torque values, as compared to those of composite without coupling agent, suggests a certain degree of interaction between the components of this composite.

As far as mechanical properties are concerned, in all cases a substantially increase in Young modulus, an increase in tensile strength at break and in elongation in certain composition demonstrate the effectiveness of small amounts of AL as coupling agent.

Significant improvement in composite performance was attained when the concentration of AL in respect to WF was of 5 and 10% wt., representing an AL concentration in composite of 1 and 2phr respectively. At these concentrations the Young modulus of PVC-WF composites increased by 77 and 80% respectively, the break strength increased by 6 and 12% respectively, and elongation by 5 and 11% respectively. Also the toughness of composites was increased by 11.3% at a concentration of AL to WF of 5% and by 25.4% at a concentration of AL of 10%.

The enhanced mechanical properties of these composites and consequently the enhanced interfacial adhesion that occurs between WF and PVC matrix with the addition of AL may be explained by the potential of AL to form hydrogen bonds with both PVC and lignin between the hydroxyl groups of WF and some of their polar groups.

In Figure 4.11 stress-strain curves are illustrated as function of AL concentration, and Figures 4.12 through 4.15 show the variations of normalized mechanical properties of PVC-WF composites as function of different concentrations of experimental coupling agents, so that the data for neat PVC-WF composites represents 100%.

From these Figures too one may distinguish the effectiveness of AL as coupling agent when its concentration was of 5% and 10% in respect to WF present in composites, as well as of chitin when its concentration was of 5% in respect to WF.

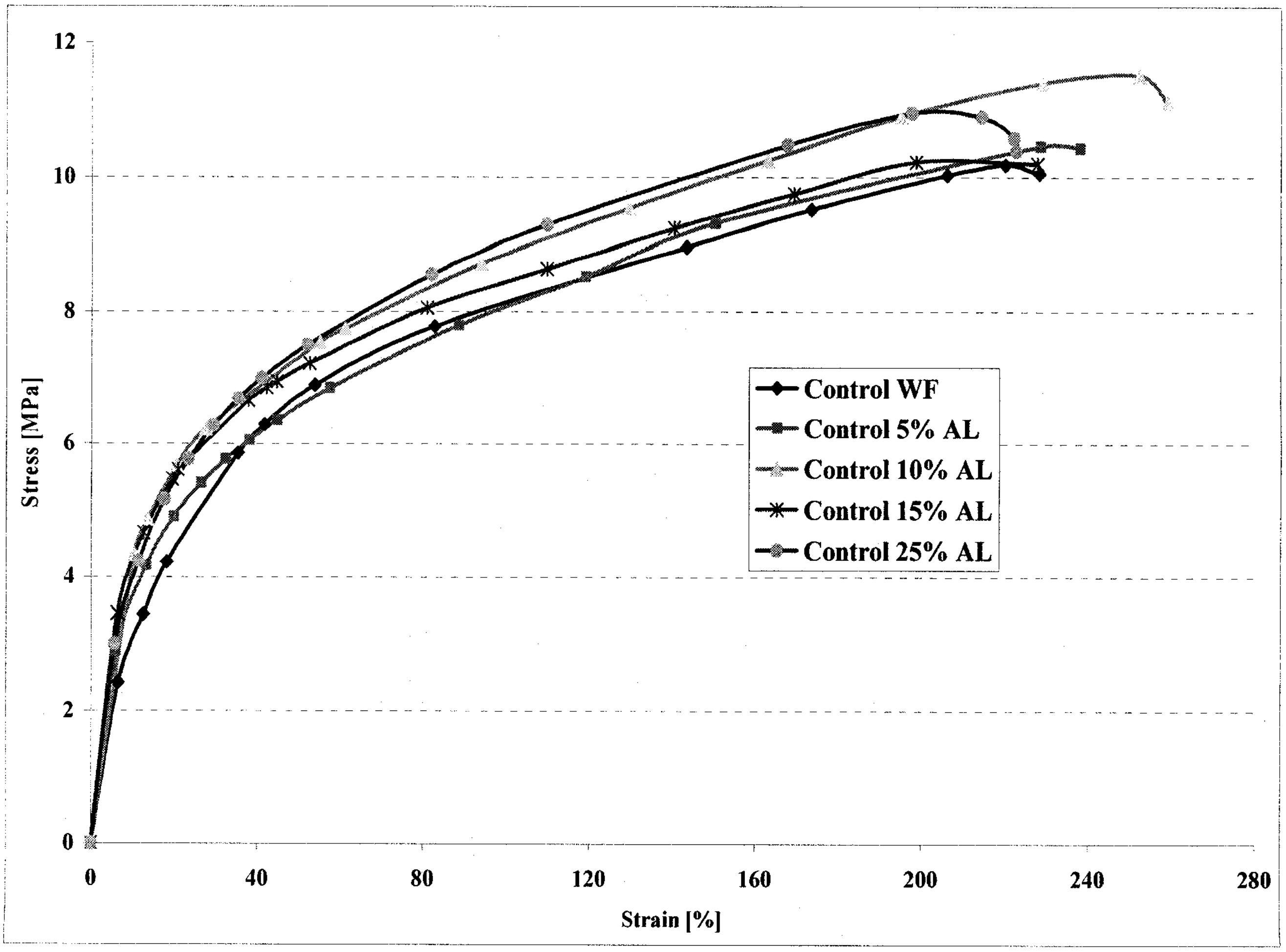


**Figure 4.11 Stress-strain curves as function of concentration of AL as coupling agent**

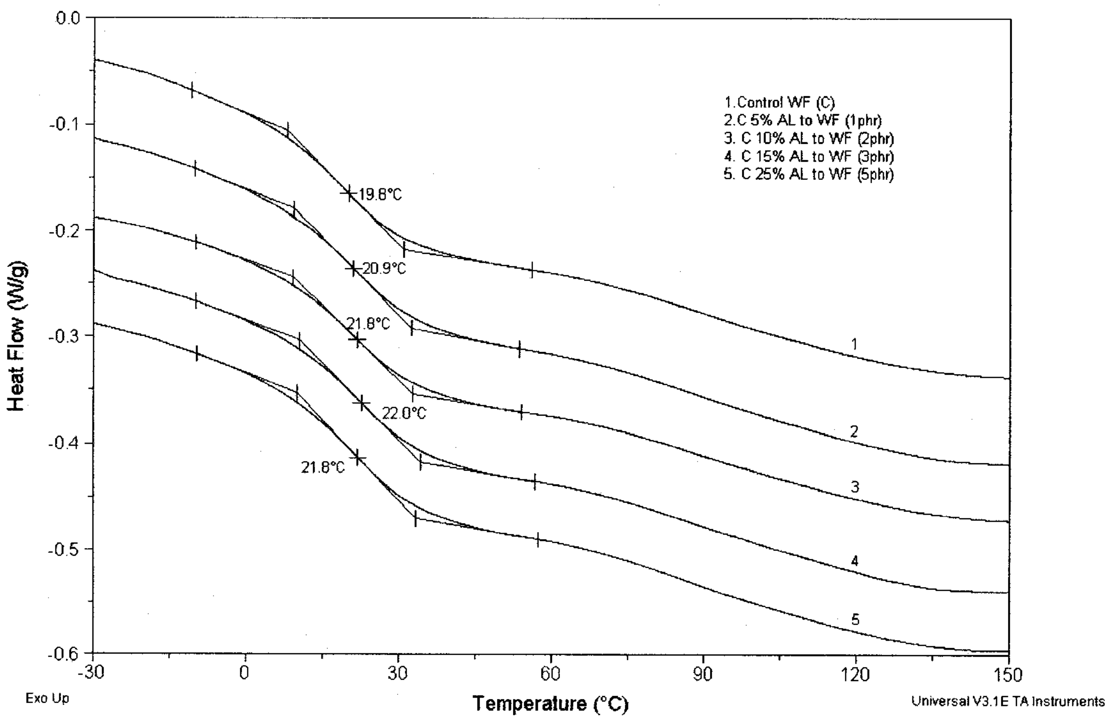


Figure 4.12 DSC curves of PVC-WF composites as function of concentration of AL as coupling agent

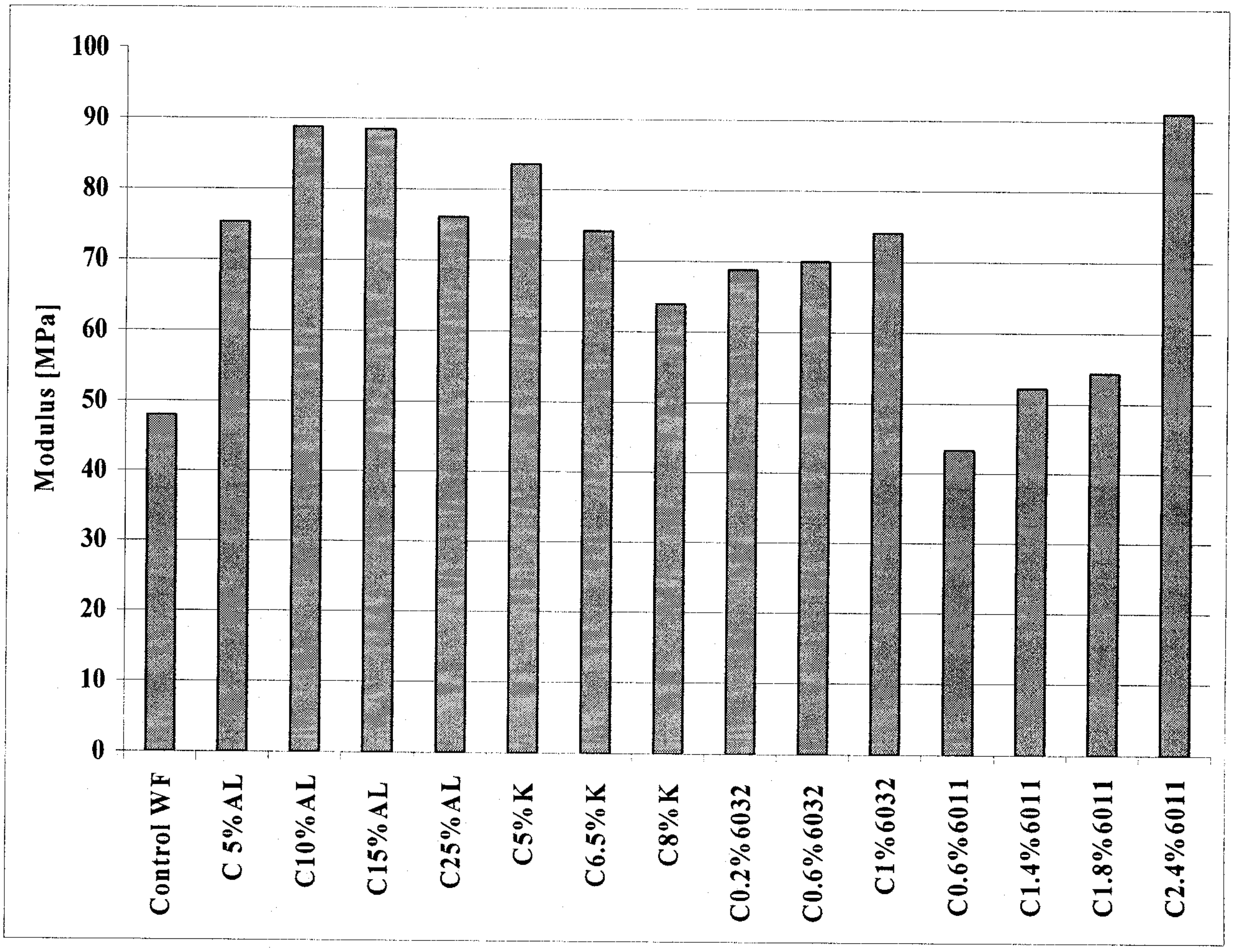


**Figure 4.13 Modulus variations as function of type and amount of coupling agents (AL (alcell), K (chitin), Z-6032 and Z-6011 (silane))**

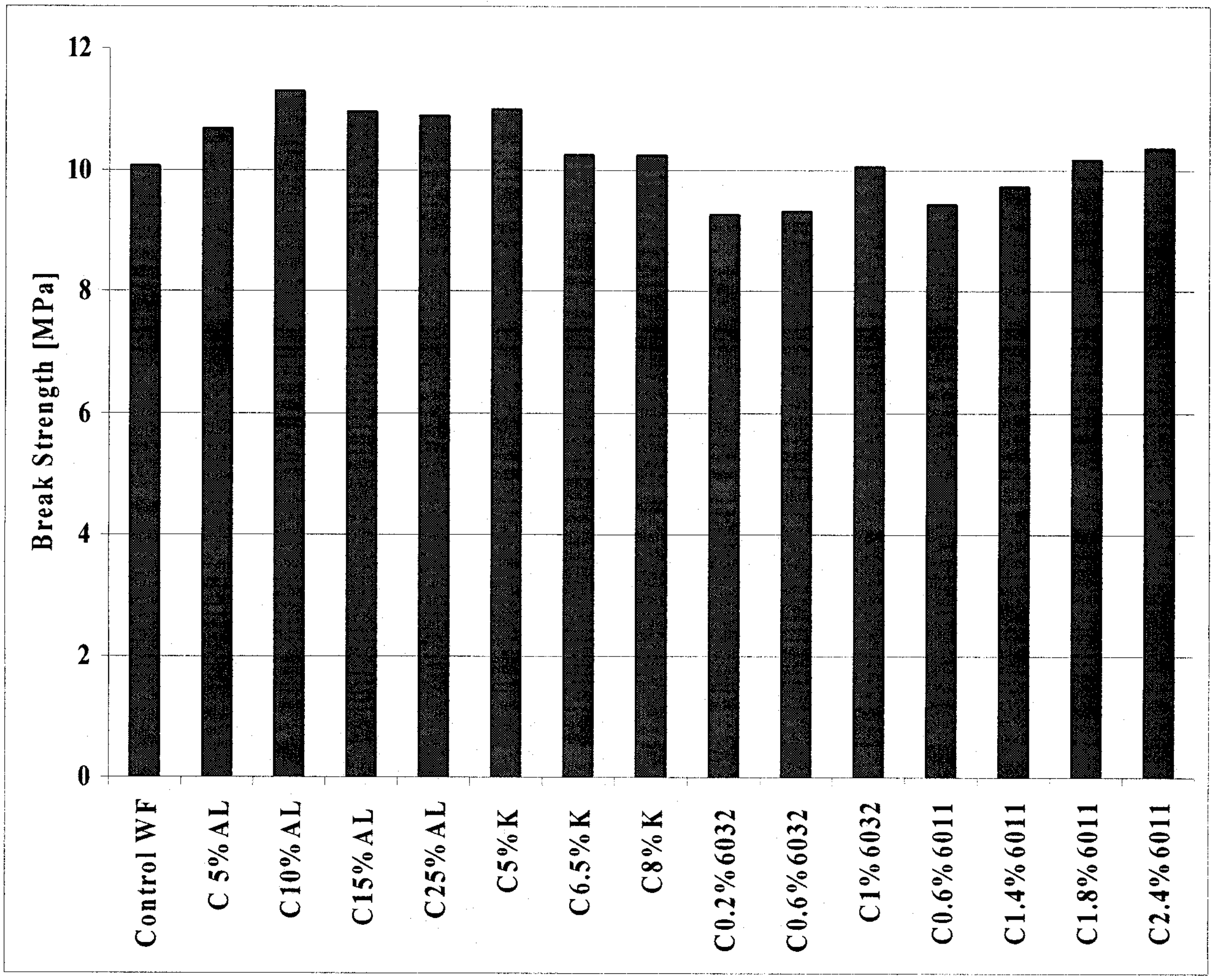


**Figure 4.14 Break strength variations as function of type and amount of coupling agents (AL (alcell), K (chitin), Z-6032 and Z-6011 (silane))**

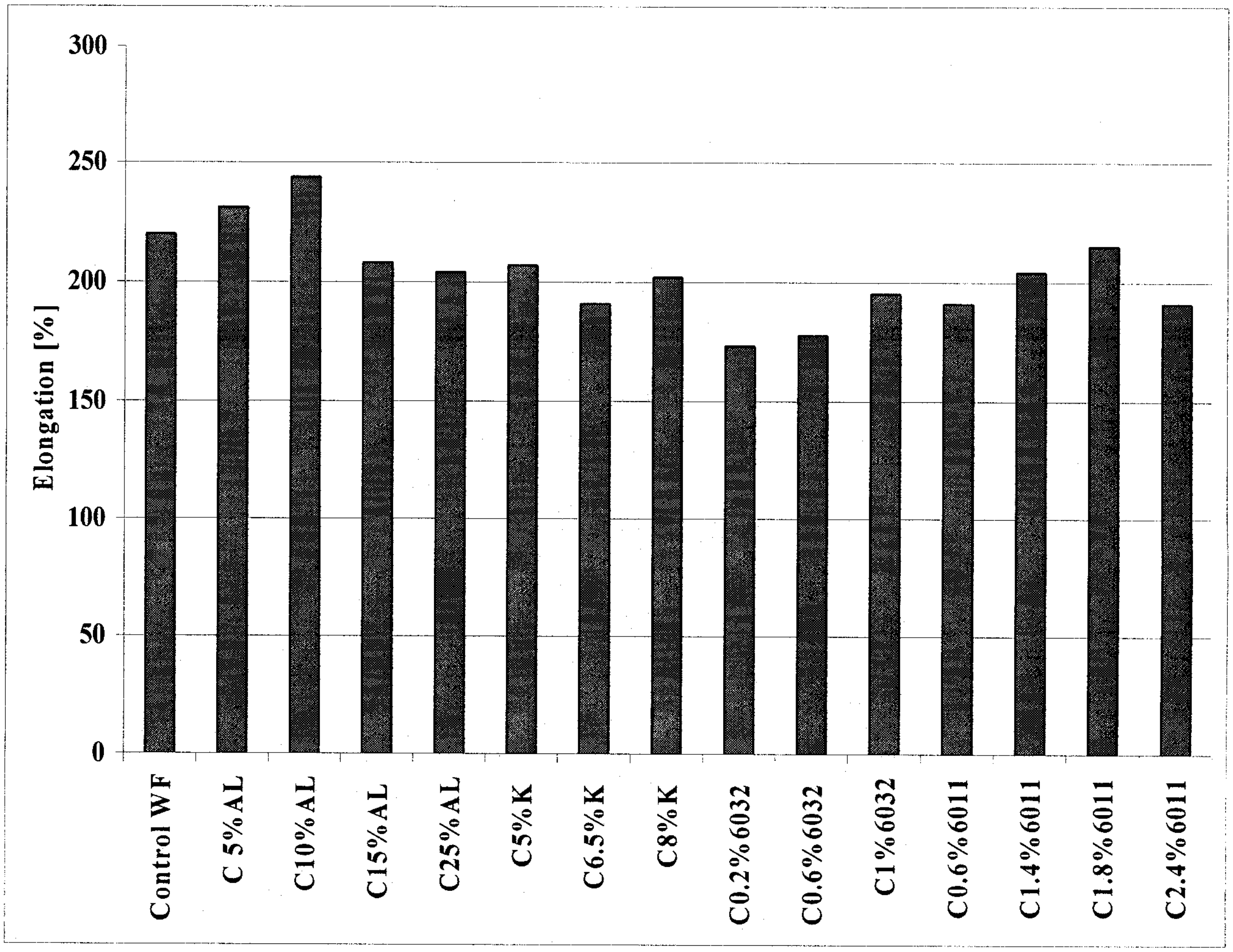


**Figure 4.15 Elongation variations as function of type and amount of coupling agents (AL (alcell), K (chitin), Z-6032, and Z-6011 (silane))**

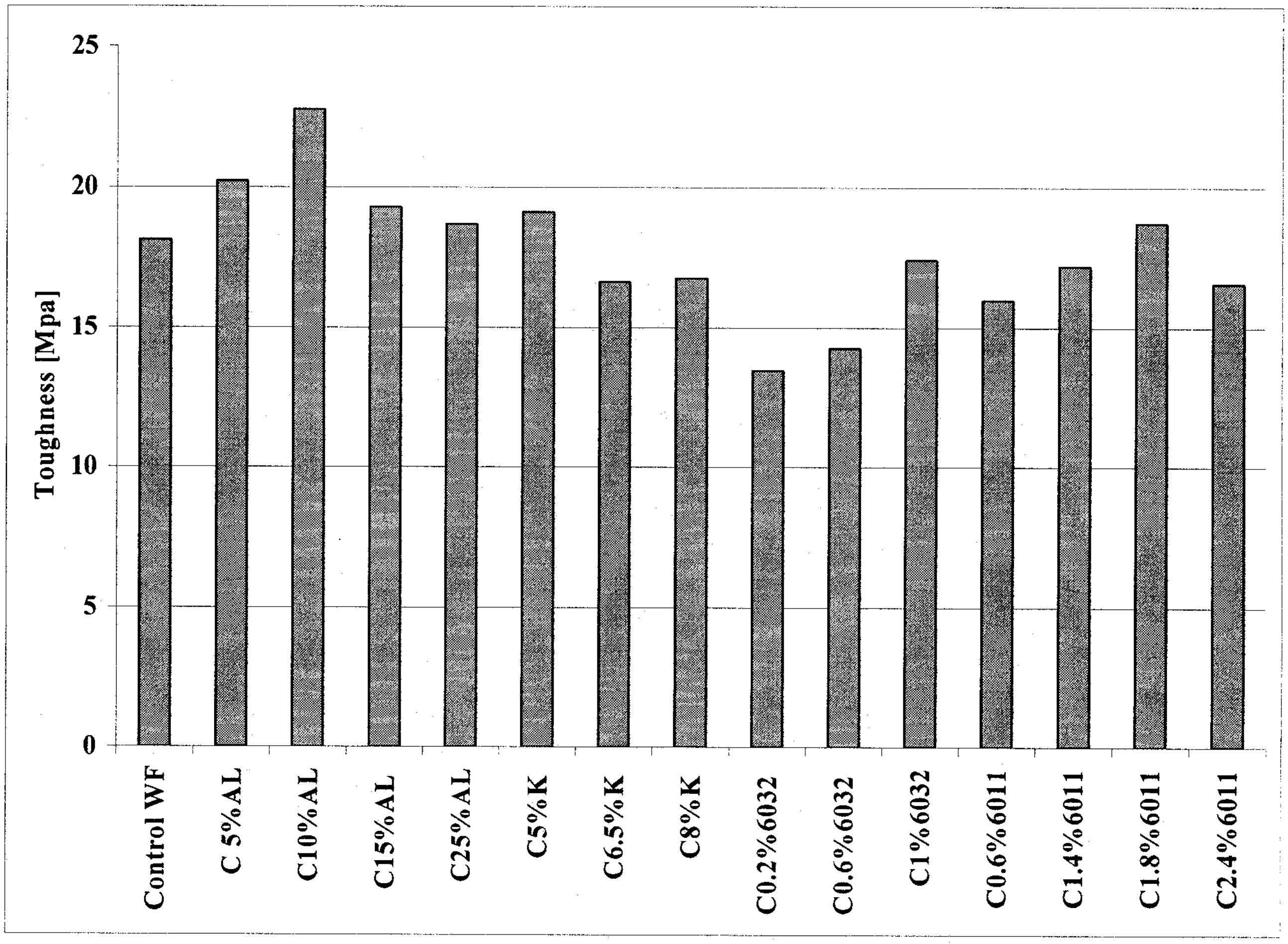


Figure 4.16 Toughness variations as function of type and amount of coupling agents (AL (alcell), K (chitin), Z-6032, and Z-6011 (silane))

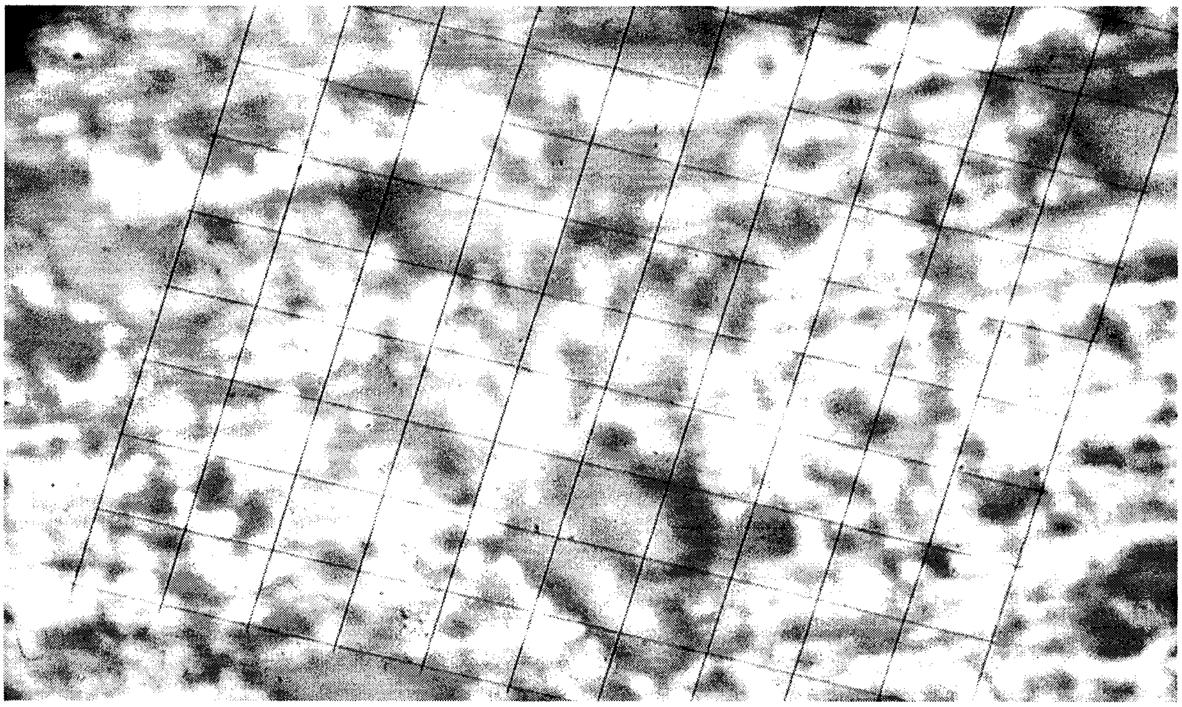


Figure 4.17 Photomicrograph of the PVC-WF, 100X magnification

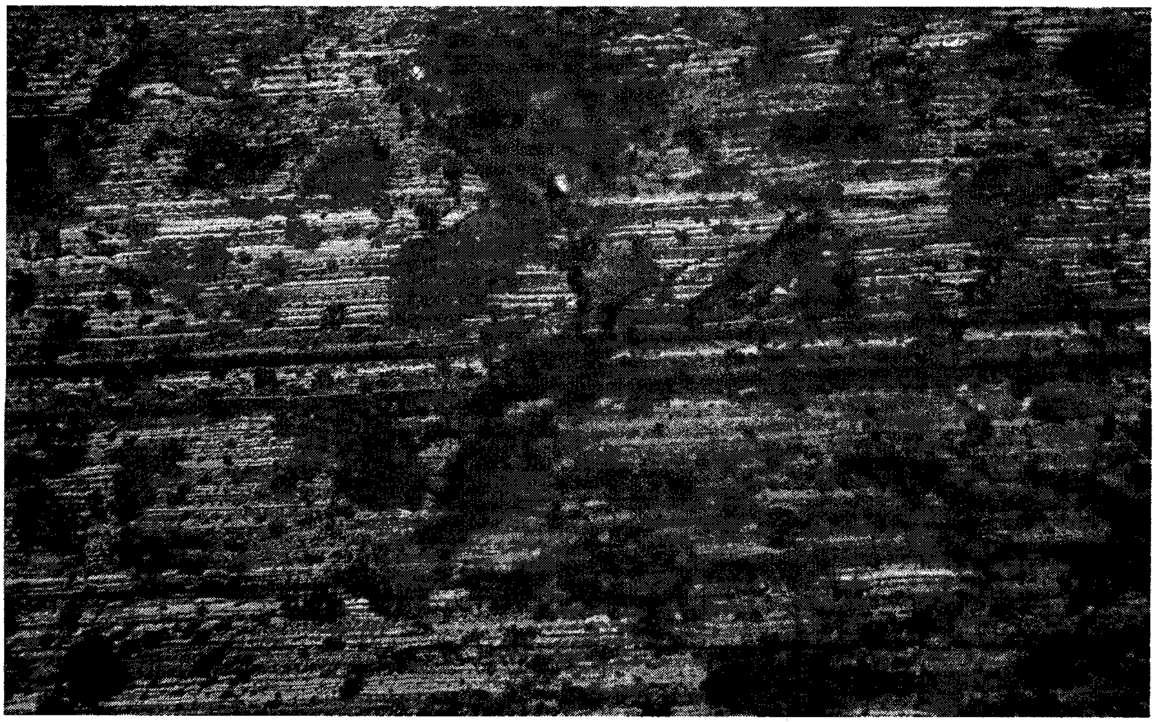


Figure 4.18 Photomicrograph of the PVC-WF with 1.6% silane Z-6011 as coupling agent, 100X magnification

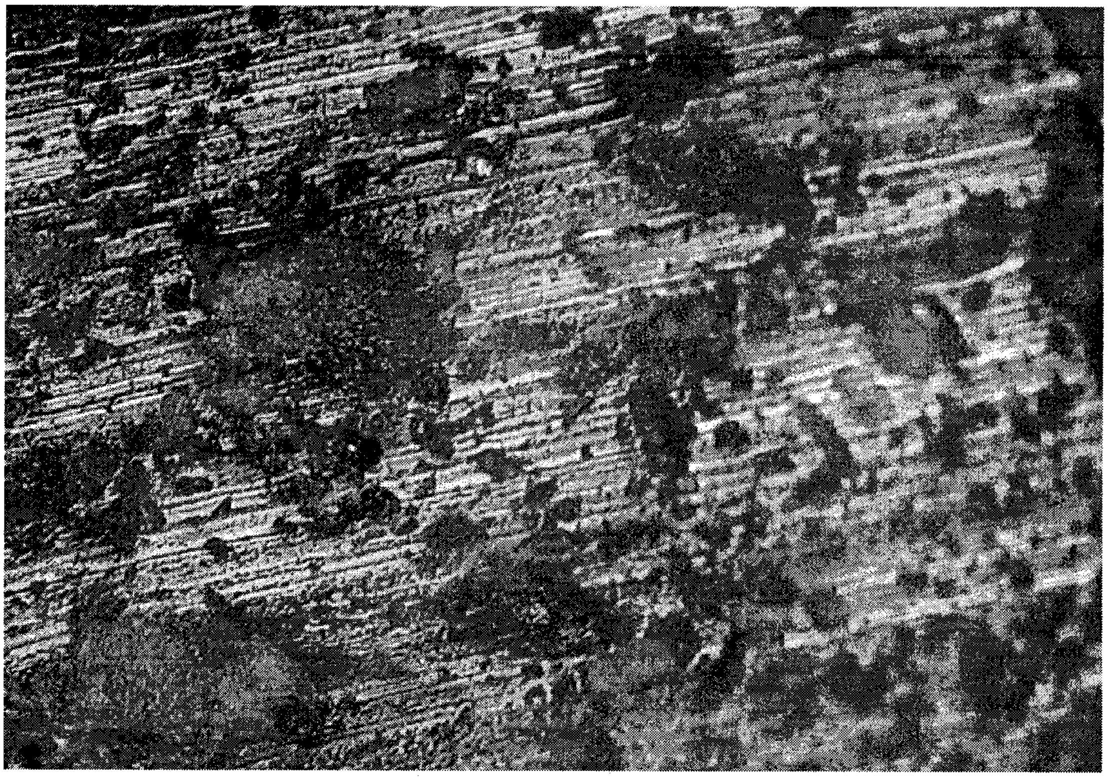


Figure 4.19 Photomicrograph of the PVC-WF with 5% chitin as coupling agent, 100X magnification

Figure 4.20 Photomicrograph of the PVC-WF with 5% AL (1 part) as coupling agent, 100X magnification

Figure 4.21 Photomicrograph of the PVC-WF with 10% AL (2parts) as coupling agent, 100X magnification

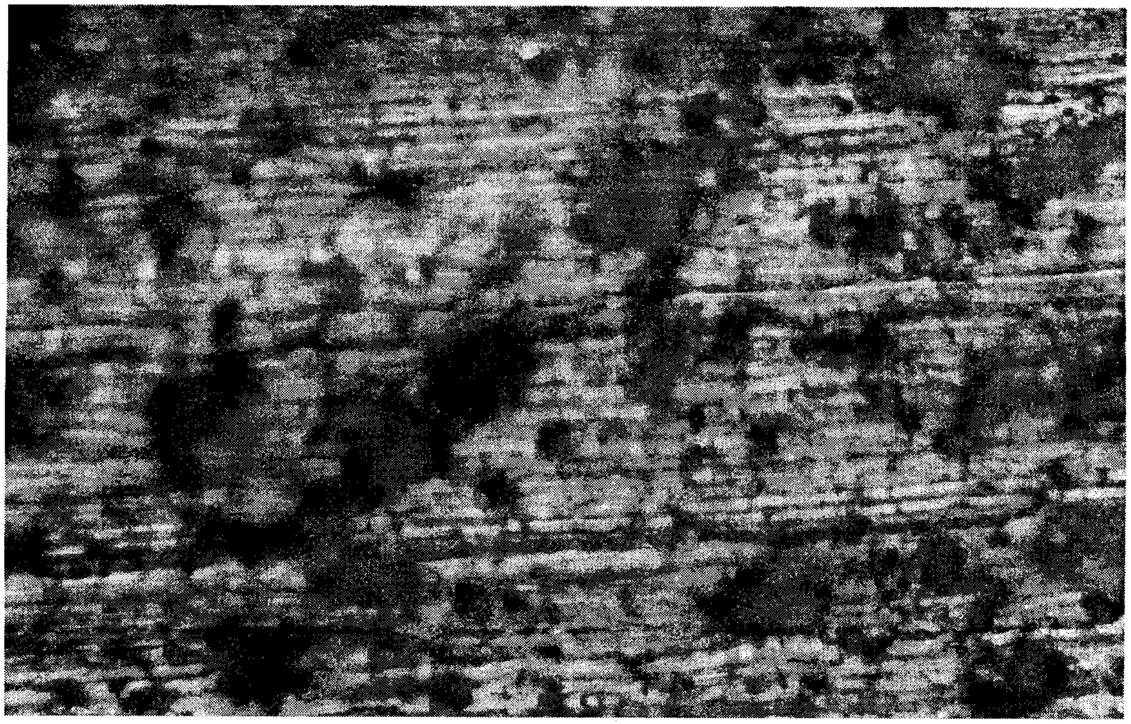


Figure 4.22 Photomicrograph of the PVC-WF with 15% AL (3parts) as coupling agent, 100X magnification

Photomicrographs at 100X magnification were obtained to examine the morphology of the PVC-WF composites as function of different coupling agents. These micrographs are shown in Figures 4.17- 4.22. The morphology of the PVC-WF composite where WF was treated with 1.6% silane Z-6011 coupling agent is seen to be quite different from that of the PVC-WF untreated composites where large WF particles are evident. The WF particles are less large in composites prepared with 5% chitin as coupling agent.

The relative smallest WF particles seem to be seen in the composites prepared with 5 and 10% AL coupling agent. There are thus differences in the dispersion quality among neat PVC-WF composites and different coupling agents. It has long been known that the toughness of a polymer composite is strongly influenced by filler size and dispersion quality [54].

The data presented in Figure 4.16 reveal that presence of 2phr AL in composite (representing 10% of WF) gives the toughest composite, also good results were obtained with 1phr AL (5% of WF) and 1phr chitin (5% of WF). The coupling agents are therefore seen to play complex roles in determining the morphology and mechanical properties of the composites and AL looks to be a promising coupling agent in polymer-WF composites.

# Chapter 5 Conclusions & Recommendations for Further Studies

## 5.1 Conclusions

The present original research was carried out in view to obtain and assess composites based on PVC-lignin matrix and WF as reinforcement.

As determining the additives for plasticized PVC-WF composite, from the three types of experimented lignins, an organosolv alcell (AL) was retained for most of the studied formulations. The best processing additives, based on the experiments done on PVC-lignin-wood flour composites, were Mark T 634 (thermal stabilizer), and CaSt (lubricant). In addition, both 2-45 and Lindol were accepted as proper plasticizers for this composite formulation.

The processing temperature of 155°C in melt mixing and 160°C for compressing molding did not affect the thermal stability of the system's components.

From different coupling agents, Silane coupling agents were not efficient for the experimented systems. On the other hand, in the formulation with chitin (5% of WF) as coupling agent, the modulus and break strength were increased by 74 and 9% respectively at a reduction of elongation of 6%. The interaction of chitin and wood is probable due to its acetyl amine groups. The best coupling agent among these experiments was organosolv lignin alcell, in concentration of 5 and 10% in respect to WF. At this concentration the Young modulus of PVC-WF composites increased by 77 and 80%, break strength by 6 and 12%, elongation by 5 and 11% and toughness by 11.3 and 25.4% respectively.

Such kinds of composites (plasticized PVC-WF) may replace PVC or VC-VAC copolymer in applications in building like flooring or others where a flexible material is requested.

## 5.2 Recommendations

The recommendations for further works are:

1. Utilization of alcell as coupling agent between matrix and WF in other kinds of polymer-WF composites is worth to study.
2. A good dispersion of alcell or other lignins would be crucial when using alcell in polymer-WF composites, so a high efficiency mixer is highly recommended for obtaining the polymer compound before melt mixing.
3. The study of new potential coupling agents from different additive families is recommended.

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