THERMO-CATALYTIC POLYMERISATION IN WOOD

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Scope and Contents:

An experimental investigation of polymerisation of several monomers in wood was performed using free radical initiators such as benzoyl peroxide and 2-azo-bis-isobutyronitrile. The most promising comonomer system appeared to be styrene and acrylonitrile. As a result of copolymerisation of styrene and acrylonitrile in the cell cavities of wood, many improvements in physical properties of wood resulted. The improvement in physical properties of wood containing thermo-catalytically copolymerised styrene and acrylonitrile was found to be better than those of radiation initiated graft copolymerised wood. Thermo-catalytically produced wood polymer combinations showed as much improvement in physical properties as shown by those produced by radiation initiation without the use of swelling agents.

Preface

The objective of modifying the physical properties of wood is to improve some characteristic or to correct some deficiencies. Many of the wood polymer combinations have the potential to achieve both for certain applications. In this investigation, thermo-catalytic process to produce wood polymer combinations has been investigated as an alternative to production of wood polymer combinations by radiation initiation.

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GLAVICIC

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A.N.	Acrylonitrile
Azo-Catalyst	2-Azo-bis-isobutyronitrile
DID	Division of Isotopes Development
ESR	Electron Spin Resonance
MA	Methyl Acrylate
MMA	Methyl Methacrylate
OD	Oven Dried
PEG	Poly Ethylene Glycol
PVC	Poly Vinyl Chloride
R.H.	Relative Humidity
U.S.A.E.C.	United States Atomic Energy Commission
WPC	Wood Polymer Combinations (Composites)

Chapter I

Introduction.

The world makes use of billions of board feet of lumber annually. The versatility of wood is attributed to its ease of fabrication and finishing, pleasing appearance and high strength to weight ratio in addition to many other characteristics. There have been many attempts to further improve its inherent properties. Most of the developments in the wood technology have been directed towards improvements in the characteristics such as:

1. Resistance to weather and abrasion,
2. Dimensional stability,
3. Resistance to decay and insects,
4. Mechanical properties.

Forest products industries have shown considerable interest in work directed towards increasing the utility of this versatile material and are receptive to any new developments that would further improve its characteristics at an acceptable price.

During the past few years a considerable amount of work has been done aimed at improving the properties of wood. Various monomers (1,2,3, 4) have been injected into wood and subsequently polymerised in situ using γ-radiation. Many of these projects have been sponsored by the U.S.A.E.C. at the University of West Virginia. (5,6,7). Recently two companies (8) have started the production of these materials on a pilot plant scale. At McMaster University (9,10) a study of γ-radiation initiated "graft"* copolymerisation of styrene with the cellulose in wood was started in 1960.

Most of these developments were aimed at improving the mechanical characteristics of wood. These attempts fall into two categories:

(a) Wood Filling Treatments:

As the name implies this process consists of filling the "cell cavities"**in wood by suitable monomers and subsequently initiating polymerisation by γ-radiation or other free radical initiators. For example, in 1960, Karpov and his co-workers (11) reported an improvement of physical properties of wood when the cellular spaces were filled with methylmethacrylate,methyl acrylate, styrene or acrylonitrile followed by radiation induced polymerisation. Improvements in dimensional stability, static bending strength, and rate of water sorption were reported. Kent, Winston and Boyle (5,6,7) also carried out a similar type of work with white pine, sugar maple and yellow birch species of wood. Each type of wood was impregnated with monomers or monomer solutions such as methylmethacrylate, vinyl acetate, styrene, styrene and acrylonitrile solution, vinyl chloride and vinyl chloride containing dissolved plasticiser followed by irradiation. The resulting wood polymer combinations were carefully tested for mechanical properties and other characteristics related to dimensional stability. These studies indicated that, when the cellular spaces in wood are filled with "homo-polymer"+, an improvement in properties over untreated wood results. These results were observed even though the cell wall structure of wood was not affected to any

* Please refer to page 21
** Please refer to page 12
\+ Please refer to page 21

significant extent. The following are conclusions drawn from this work as reported by Ross and Hodgins (10):

1. Strength properties are enhanced more in lower strength wood.
2. Hardness improves by a maximum factor of 3.
3. Compression parallel to grain is enhanced by about 50%.
4. Toughness values can be doubled.
5. Abrasion resistance can be more than trebled.
6. The rate of polymerisation was greater when the monomer was rigorously purified and air was excluded.
7. The rates at which the WPC absorb water, and therefore the rates at which the dimensions are altered, were much lower than for untreated wood.

(b) Chemical Modification of Cell Walls:

In this second process the cell wall structure of wood itself is modified. Two different ways of achieving this are:

A. Swelling-Impregnation-Irradiation Technique:

In this technique in addition to monomers, "swelling agents"* are also injected into wood before irradiation. Swelling agents enable the infiltration of monomers into the "secondary wall"** of wood cells, thereby making graft sites available to monomer free radicals. For example, Kenaga, Fennesy and Stannett (12) used a variety of monomers and swelling agents to prepare wood polymer combinations with this technique. In this work two methods were used for monomer and swelling agent impregnation. In the first method, the wood sample was subjected to a low

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* Please refer to page 18

** Please refer to page 12

or high degree of evacuation before introducing the impregnating solution. In the second method, the solvent displacement method, wafers of wood are swelled first by water and in a sequence of time-consuming operations, the water is displaced by a solution of the monomer, using intermediary solvents of increasing solubility with respect to the monomer. The final solvent is eventually evaporated off and the monomer polymerised.

The following are conclusions (10) drawn from the work of Kenaga et al (12):

1. The efficiency of initiation decreases with increasing dose rate.
2. Polymer retention increases with increased dose.
3. The amount of time for wafers to reach ultimate swelling in water increases by a factor of about 35.
4. The amount of styrene required for a given degree of stabilisation was high relative to the loading used in other methods.

Hodgins et al (13,14,15) carried out a comparative study of the two methods and report the following conclusions (10) on the Swelling-Impregnation-Irradiation technique:

1. A swelling agent was necessary for grafting to occur.
2. The bending load (not modulus of rupture) was increased by about 50% based on the equilibrated control samples.
3. The penetration rates of water vapour and liquid were drastically reduced, with corresponding stabilisation of dimensions.
4. The physical properties of wood in which the cell cavities were filled with homopolymerized styrene were at least as good as those of wood containing graft copolymer.
5. The bending behaviour of WPC was independent of the method of

initiation (radiation, heat or catalyses).

6. Free radicals arose in the wood on irradiation, with some transient species persisting for days.

Apparently most free radicals generated by irradiation are not utilized in the grafting process. In an attempt to use the graft sites more efficiently, irradiations of the impregnated wood can be performed at elevated temperatures. The higher mobility of the monomer would be expected to increase its diffusion rate to radical sites to such an extent that it would outweigh the higher rate of radical destruction at elevated temperatures. In order to study this, Ross and Hodgins (15) impregnated wood with styrene and with styrene-methanol-water solution followed by irradiation over a temperature range of 39 to 77.5°C. In the wood cell cavities the kinetics of polymerisation and the molecular weight of the polymer products were found to be influenced by temperature, as is to be expected.

However, the transfer of monomers into the cell walls was found to be independent of temperature during irradiation, which means that an increase in temperature did not increase the extent of the diffusion of styrene into the cell wall. The predominant factor in the grafting process was therefore the swelling of the cell wall achieved before-hand.

B. Formation of Cellulose Derivatives in Wood:

Water adsorption and swelling of cellulosic materials can be considerably reduced by making them less hygroscopic (16). This could be accomplished if the hydroxyl groups of both cellulose and lignin could be changed to hydrogen groups by such a procedure as hydrogenation (17). However, all present methods of hydrogenation of wood result in decomposition products of both lignin and cellulose (17). The hygroscopicity of both wood and paper can be reduced permanently to about half of its normal value by acetylation (18,19,20). This depends upon the fundamental knowledge that acetyl groups are less hygroscopic than hydroxyl groups. But the accompanying reduction in swelling and shrinking of wood, frequently referred to as the "antishrink efficiency"* (19), is almost invariably greater than the reduction in hygroscopicity. Also, acetyl groups in addition to their being less hygroscopic, act as bulking agents (16). Acetylation is usually carried out through treatment with liquid acetic anhydride or gaseous acetic anhydride. A similar effect can be obtained by the use of phenylisocyanate (21) vapour which alters the portion of the cell wall responsible for its hygroscopicity.

Methods of improving dimensional and strength properties of wood have been briefly reviewed in the previous section. A critical study indicates that to begin with none of these heretofore discussed processes achieve graft copolymerisation with the cellulosic macromolecules to a high degree. Secondly, and probably with greater significance, there is also a lack of evidence (10) that graft copolymerisation with the cellulose in wood really results in a greater degree of improvement than that which can be obtained by filling the cell cavities with homopolymer. But a recent study (22) of wood filling by pure methyl methacrylate compared to a methyl methacrylate-water-dioxane solution shows that with the latter swelling - impregnation - irradiation technique, at low polymer loadings, a material is produced which has a negative antishrink efficiency. That is, we obtain a material which swells in water vapor to an extent greater

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* Please refer to Experimental Part, Chapter III.

than that of the untreated wood. This result (12,22) is probably because during treatment with swelling impregnants, the more ordered areas of the cellulosic structure become disorderly. Unless sufficient polymer is added to counteract this effect, an increased swelling of the sample results. On the other hand, where no swelling solvent is used, and consequently no appreciable breakdown of the cell walls occurs, much higher antishrink efficiencies were obtained at comparable low polymer loadings. It has also been reported (12) that products prepared by this method with relatively high loadings (50 - 60%) of poly methyl methacrylate give only very small values of antishrink efficiency. Therefore it has been concluded (10) that no advantage is gained by using swelling agents. It would seem that the possible benefits of effecting graft copolymerisation are offset by the disruptive action of the solvent.

Wood homopolymer combinations can be obtained either by irradiation polymerisation or by free radical initiated polymerisation. An example of the latter is impregnation of wood with a mixture of initiator such as benzoyl peroxide and monomer (10,23,24) followed by heating. No significant differences in the physical properties of the wood-homopolymer combinations produced by either of the two methods have been reported (10,23, 24).

The use of irradiation to initiate polymerisation in wood would certainly be justified if a better polymerised or graft co-polymerised product results, radiation is especially applicable for this type of reaction. Further it has also been observed that weakening of the wood due to the use of swelling agents (10) more than outweighs the gain in strength obtained due to graft copolymerisation. For example (15), on the oven dry basis, the modulus of rupture for a sample treated with a styrene:methanol:water solution (ratio 54:42:41) is 23.8±8.1% less than that of untreated wood. Moreover, in order to achieve dimensional stability equivalent to that obtained by wood filling technique, one has to use, on a weight by weight basis, a higher polymer to wood ratio (22).

On the other hand, the filling of the cell cavities with homopolymer has the advantage that it can be accomplished either catalytically or by γ-radiation initiation. Further the two processes yield products, at least on a laboratory scale, of similar strength properties and dimensional stability (10,23). For this reason the employment of γ-radiation merely as a homo-polymerisation catalyst needs additional justification. In addition large scale irradiation units cannot easily be distributed widely. Shipping cost of lumber to and from a central irradiation facility will also be significant. However at the present time the simplicity of plant installation and actual processing costs favor a thermo-catalytic method. The objective of the present study therefore is to investigate thermo-catalytic processes to produce WPC.

Chapter II

Fundamentals.

a) "Structure of Wood"

Wood is made up predominantly of "lignocellulosic"* structures. It can be divided into two broad classifications, namely, coniferous, or evergreen species (softwoods) and deciduous species (hardwoods). These differ not only in structure but also in chemical composition.

Wood is a highly porous but not very permeable material. The porosity follows from the fact that most dry commercial woods with "dry volume specific gravities"** of 0.3 and 0.8 have void volumes ranging from about 80 to 45 percent(16). The lack of permeability is due to the fact that the voids are largely discrete in nature, with little communication between them. The size, nature, and number of intercommunicating structures in wood have a major effect upon movement of water and other materials through wood (25,26). In the following section therefore the void and communicating capillary structure, as well as cell wall structure, will be considered briefly. A detailed study of the structure, organic and analytical chemical aspects of wood and cellulose are covered quite extensively in a number of books. (27,28,29,30,31).

b) "Gross Structure of Soft Woods"

These are made up of long, hollow, tubular fibers tapered and sealed off at the ends. These fibers, which extend in the length direction of the tree and serve for the conduction of sap, are known as tracheids.

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* Please refer to page 14

** Please refer to Appendix I

Their length usually ranges from about 2.5 to 7 mm, averaging about 3.5 mm. The tracheids are on the average about 100 times longer than their diameter. The fiber cross-sections are somewhere between rectangular and circular in shape. The width of fiber cavities, or lumens, varies considerably, both with variations in specific gravity and as between fibers laid down in the early and late parts of the growth season. Softwoods with an average "swollen-volume specific gravity"* of 0.4 will have an average lumen width of 26.1 microns.

The fibers, or tracheids, of softwoods are arranged in quite uniform rows in the radial direction, from the pith of the tree to the periphery, whereas the arrangement is rather random in the tangential direction, tangent to the annual rings and the periphery of the tree.

Communication between fibers takes place through bordered pits. These pits are circular openings in adjacent cell walls; they are spanned by a thin membrane which is a continuation of the compound middle lamella, the cementing structure between fibers.

Most softwoods contain some resin ducts, which are continuous tubes extending in the fiber direction and randomly interspersed among the tracheid fibers. Resin ducts are, in general, ineffective for movement of liquids and gases over any appreciable distance in softwoods, despite the fact that they are continuous. This is because they are always clogged with resin.

Besides the chief structural units of softwoods that extend in the longitudinal direction of the tree, there are some tubular structures that are oriented horizontally in the tree and extend from pith to the

* Please refer to Appendix I.

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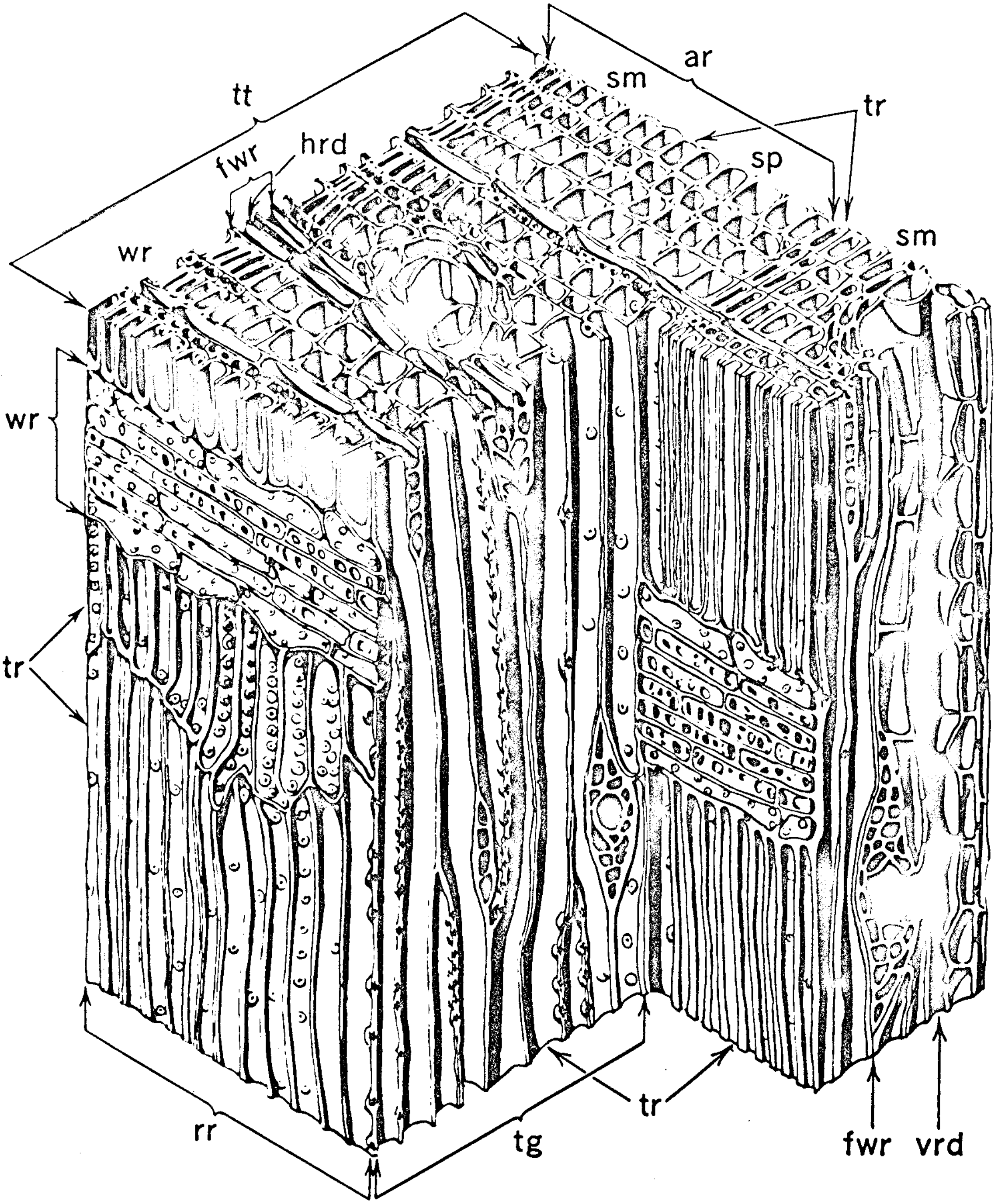


Fig. 1. Magnified three-dimensional diagrammatic sketch of a softwood.
tt: end-grain surface; tg: tangential surface; rr: radial surface;
tr: tracheid; wr: wood ray; fwr: fusiform wood ray; vrd: vertical resin duct;
hrd: horizontal resin duct; sp: springwood; sm: summerwood; ar: annual ring.

periphery. Their combined void volume usually ranges from a few percent up to 6 to 8 percent of the total void volume (16). These cell groups are known as wood rays. Communication between the wood rays and the tracheids occurs through either half-bordered pits, having the typical tapering pit chamber on the tracheid side and a straight bore chamber on the ray cell side, or simple pits with straight bores on both sides.(Fig. 1).

There are two important zones in a tree. The outer zone, known as sapwood, is active in the life process. The sapwood is usually lighter in colour than the inner non-active heartwood. This colour change is due largely to infiltration into the heartwood of various extractable extraneous materials. The deposition of these materials in the pits greatly decreases the permeability through the wood. The permeability through sapwood may be as high as one hundred times greater than through heartwood (16).

c) Structure of Cell Walls

In a tissue each cell consists of a thin primary wall which surrounds a secondary wall which in turn acts as an envelope for the lumen or cell cavity (Fig. 2). Between the cells, the layer of intercellular substance is known as the "middle lamella". It is primarily composed of "lignin"* The primary and secondary walls of the individual cells are also lignified. The primary wall along with the intercellular material is conventionally grouped together as the "compound middle lamella" since it is so heavily lignified that in reactions it behaves much like middle lamella.

The main constituent of the secondary wall is cellulose although

* Please refer to page 14

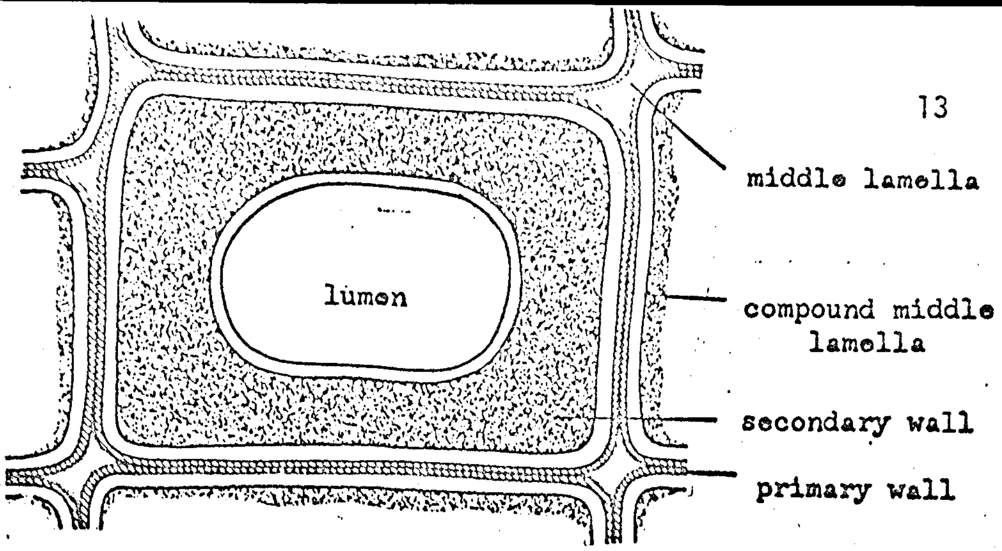


FIGURE 2 Wood Cell
(Textbook of Wood Technology)

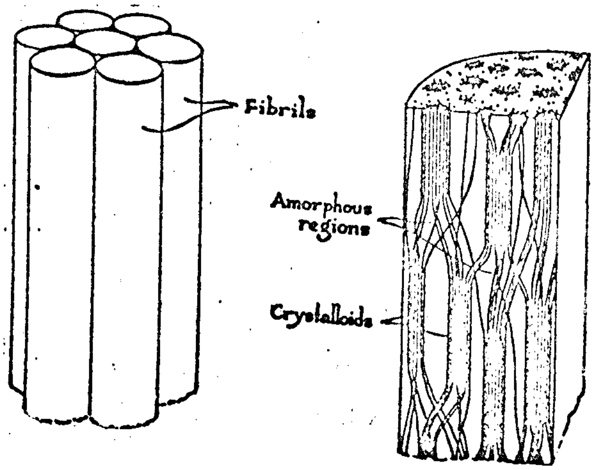


FIGURE 4 Alignment of Cellulose in Fibrils

(Textbook of Wood Technology)

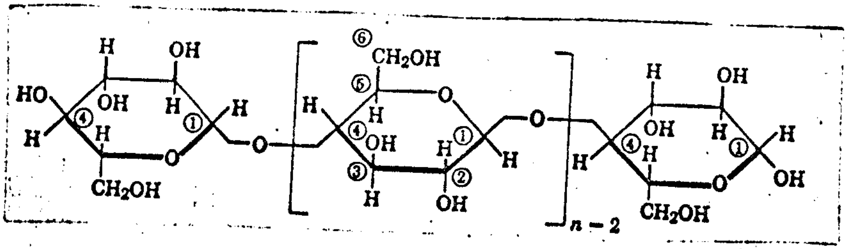


FIGURE 3 Cellulose Macromolecule

(Browning: The Chemistry of Wood)

Reproduced from reference 15

some lignin is also present. Fine, thread-like structures known as fibrils make up the cellulose lattice structure in the secondary wall. The diameter of the fibrils range from about one micron to beyond the range of human vision.

At the molecular level the fibrils of the cell walls are made up of cellulose. Its chemical structure consists of a stereo-regular chain of anhydroglucose monomer units joined together in the 1-4 configuration by primary valences (Fig. 3). Crystallographic methods (32,33,34,35,36,37) establish the length of one pair of the monomer unit to be 10.3A° and the entire chain length is estimated to be from 4000 - 10,000A°. Each fibril consists of one hundred or more of these long chain molecules. The cellulose pattern in the fibrils is discontinuous. (Fig. 4). According to the Micellar Network (38,39) theory, the long chain molecules are parallel to each other lengthwise only at intervals (crystalline or non-accessible regions). The zones of parallelism (known as micelles or crystallites) alternate with the less ordered regions (amorphous or accessible regions).

The length of crystallites are in the range 400-600A° and the width, approximately 50°A. The width of the spaces between the crystallites vary from 10-100A°. There is no sharp distinction between zones of parallelism and amorphous regions. Also there is no connection between the length of the crystalline regions and the molecular chain length, therefore, it is believed that the chain ends do not correspond to the ends of crystallites but rather usually terminate within a crystalline zone (40). The parallel portions of chain molecules are believed to be held together by strong hydrogen bonds and somewhat weaker Vander Waals' forces (41).

Lignin differs very much from glucose both chemically and structurally. Compared to cellulose which is made up of chains of repeating anhydroglucose units with relatively low and definite basic repeating molecular weight units of 162, lignin is made up of larger basic repeating units involving a not too well-understood combination of C_6-C_3 units (42,43). There is a wide agreement on the C_6 unit which is a benzene ring with attached methoxyl and possibly hydroxyl and other groups (16). The nature of the C_3 ring is still uncertain whether it is in the form of an attached straight chain or in the form of a pyranose ring in which two of the carbon atoms are shared with benzene (42,42,44,45). According to some authors (42,46) the smallest possible repeating unit appears to be $C_6H_9O_3.OCH_3$. This has a molecular weight of 196 on the basis of different reactants combining with various forms of lignin, minimum molecular weights ranging from 400 to 960 have been obtained (42). Therefore it follows that there must be between two and five of the smallest possible repeating units in an actual repeating unit, owing to slight differences in the smallest repeating unit. This broad spread in values is probably due to the fairly well-established fact that lignin is not a single compound but a mixture of related compounds that vary somewhat from species to species and are modified to different degrees by the different isolation methods and reactants. (42,43,44). This is in accord with the finding that lignin is virtually noncrystalline, although a few workers have obtained diffuse X-ray diffraction rings that indicate the existance of an imperfect repeating structure (47).

d) Shrinking and Swelling of Wood

All natural hygroscopic gels such as wood and various forms of cellulose, that are originally formed in a water saturated state, shrink on loss of moisture. This shrinkage and its accompanying effects of warping, cupping, checking, and splitting constitute wood's most troublesome physical property. Therefore a brief discussion of shrinking and swelling of wood will be given here. For a thorough discussion one should refer to a number of excellent books and articles on this subject (48,49,16,50).

Shrinking and swelling may be defined as the decrease or increase in the dimensions of a gel material per unit dimensions of the starting material accompanying desorption or adsorption of an adsorbate held in naturally formed solid solution within the gel. It is only in cases where the adsorbate is taken up spontaneously as a solid solution that dimension changes occur.

When an adsorbate is held only on pre-existing surfaces of a powder or within permanently existing rigid pores of a solid, no shrinkage accompanies, desorption (16). When water in the cell walls of a cellulosic material is replaced by a non-polar, non-wetting liquid, such as pentane, with a small surface tension, only a relatively small shrinkage accompanies evaporation of the pentane leaving the cellulose in the form of an aerogel (16). It thus appears that it is necessary for the adsorbate to have a real affinity for the adsorbent, as well as being intimately dispersed within the adsorbent for significant shrinkage to accompany desorption (16). Any adsorbate that has sufficient affinity for a cellulosic material to spontaneously form a solid solution with the cellulosic material accompanied by the evolution of heat will upon desorption also be accompanied by shrinkage (16).

For free shrinking and swelling to occur in an adsorbent, the following conditions must be fulfilled (16) :

1. The adsorbent must be a plastic solid.
2. The adsorbate must have sufficient affinity for the adsorbent to

spontaneously form intimate solid solutions with the adsorbent, accompanied by heat. The wood-water and cellulose-water systems meet both of these criteria (16).

Cellulosic materials adsorb water (16) only in the amorphous regions between the imperfectly long, threadlike cellulose chains and on the surface of crystallites. Evaporation of water on desorption causes surface tension forces to set up over the areas of contact of water with cellulose chains which leads to drawing together of the cellulose chains. (51). This drawing together of the cellulose chains in the imperfectly oriented amorphous regions tends to better orient these chains, and on the average to occur at right angles to the length direction of the crystallites. Shrinking and swelling thus take place chiefly at right angles to the direction of orientation of the fibril structure which is virtually the same as the direction of orientation of the crystallites (52,53,54,55).

Cellulose chains range from about 500 to more than 2000 times as long as their diameter (16). Thus the desorption or adsorption forces drawing together or separating the ends of chains could be at most, only 0.05 to 0.2 percent of the corresponding movement at right angles to the chains. It is for this reason that shrinking and swelling of all natural cellulosic materials, with large amount of preferred orientation, are only a small fraction as much in the fiber direction as across the fiber direction. For example, the longitudinal shrinkage of normal wood ranges from about 0.1 to 0.3 percent in contrast to transverse shrinkages of 3.0 to 10.0 percent (56). In a few cases where shrinking and swelling in the fiber direction are significant, as in the case of "compression wood", the dimension changes can be accounted for on the fibril orientation being at a sufficient angle to the fiber direction, for an across-the-fibril component of dimension change to be significant. In such cases longitudinal shrinkage may amount to several percent (56,57).

As swelling proceeds, liquids, which normally are incapable of entering the structure, can penetrate into the cellulose due to the destruction of the hydrogen bonding and the consequent loosening up of the cellulose structure.

Two variables are significant in the sorption of a solvent on cellulose (16):

1. Ability to form hydrogen bonds.
2. Molecular volume of the solvent.

For example water produces a swelling of up to 10% depending upon the specific gravity of wood. Methanol, since it is less polar compared to water has about 95% the swelling capacity of water (15).

Swelling of cellulosic materials is governed by the simple relationship (16,58,59)

$$S = f.g.$$

where S = total volumetric swelling from dry to green condition on a percentage basis, g = specific gravity based on oven-dry condition, f = fibre saturation point on a percentage volume-per-weight basis, which means that, on drying, wood and other cellulosic materials exhibit considerable change in properties as soon as capillary absorbed water is completely removed and water bound as solid solution within the cell walls starts to be removed. As mentioned previously, no shrinkage occurs until some bound water is lost. Most strength properties of wood begin to increase with the first loss of bound water (16). Evolution of heat takes place over the whole bound-water adsorption range, but becomes negligible for the absorption of water in the coarse capillary structure (16). This critical moisture content of wood, at which all capillary absorbed water has been removed but no water has been lost from the cell walls, was given the name fiber-saturation-point by Tiemann (60).

As previously mentioned, wood's most troublesome property from the standpoint of structural uses is that it swells and shrinks. Non-uniformity of these dimensional changes accounts for warping, cupping, honey-combing, face-checking and grain raising. Considerable research (10,61) has therefore been undertaken to find ways to impart additional dimensional stability to wood. These efforts have met with only partial success. No cure-alls for swelling and shrinking of wood have been found. Methods suitable for speciality items, made up of readily treatable component parts, are available for products that can bear the increased cost. All methods for attaining improved dimensional stability of wood fall into one or more of five different types. These are:

1. Laminating of anisotropic sheets so as to restrain the dimensional changes of one sheet in the direction in which swelling is the greatest by cross-sheets that swell less in this direction, as in plywood.
2. Applying water-resistant surface and internal coatings to retard moisture adsorption or loss.
3. Reducing the hygroscopicity of the cellulose materials, thus reducing water adsorption and swelling.
4. Bulking the fiber so as to reduce the amount of water that the component fibers can hold.

5. Cross-linking the cellulose chains of the component fibers so that their separation by water adsorption is minimized.

e) Polymer

A Polymer is a large molecule built up by the repetition of simple chemical units. In some cases the repetition is linear, just as a chain is built up from its links. In other cases the chains are branched or interconnected to form three-dimensional networks. The repeat unit of the polymer is usually equivalent or nearly equivalent to the monomer, or starting material from which the polymer is formed. Thus the repeat unit of the poly vinyl chloride is $-CH_2-CH-Cl$, its monomer is vinyl chloride, $CH_2 = CHCl$. The length of the polymer chain is specified by the number of repeat units in the chain. This is called the degree of polymerisation. Most high polymers useful for plastics, rubbers or fibers have molecular weights between 10,000 and 1,000,000. Unlike many products whose structure and reactions were well known before their industrial application, some polymers were produced on an industrial scale long before their chemistry or physics were studied. Impricism in recipes, processes, and control tests was usual. The recent explorations in the complex domain of polymer technology have reached a stage where one can produce materials for specific requirements rather than having to adapt existing materials.

f) Copolymer

The term copolymer as will be used here refers to a polymer having two different monomers incorporated into the same polymer chain. In most cases, these are random copolymers in which the units of one monomer and the units of the other have no definite order or arrangement along any given chain, and generally one chain may have a slightly different composition or ratio of one monomer to the other. If A and B are two monomers, a random copolymer should be like

-A-A-B-B-B-B-A-A-A-A-B-B-B-A-etc, etc.,

Block copolymers on the other hand have a long segment or block, one monomer followed by a block of a second monomer. The effect is that of joining end to end the same chains of two different homo-polymers, e.g.,

-A-A-B-B-B-A-A-B-B-B-A-A-

Stereo block copolymers are those which have blocks of the same monomer with different stereo-chemical configurations. The term graft co-polymer refers to a type of block copolymer in which one monomer has been grafted onto the main chain of the other, e.g.,

```
-A-A-A-A-A-A-A-
 l   l   l   l
 B   B   B   B
 l   l   l   l
 B   B   B   B
 l   l   l   l
 B   B   B   B
```

Copolymers are often important industrial products since the properties of a copolymer are those unobtainable by a homo-polymer of either of the monomers making up the copolymer.

g) Polymerisation Processes

According to W.H. Carothers (62), polymers are classified into two groups: These are:

1. <u>Condensation polymers</u>

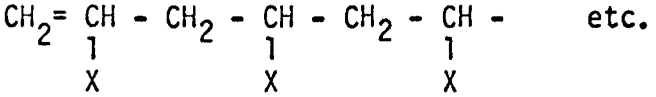
Condensation polymers are those in which the molecular formula of the repeat unit of the polymer chain lacks certain atoms present in the monomer from which it is formed (or to which it can be degraded).

For example, a polyester is formed by a typical condensation reaction between bifunctional monomers with the elimination of water, i.e.,

$$XHO - R - OH + XHOOC{-}R'{-}COOH \rightarrow HO\left[-R-OCO-R^1-COO\right]_{X} + (2X-1)H_2O.$$

2. Addition Polymers

Addition polymers are those in which unlike the condensation polymers, the loss of a small molecule does not take place. The most important group of addition polymers includes those derived from unsaturated vinyl monomers, i.e.,



$$CH_2{=}\underset{\substack{|\\X}}{CH} - CH_2 - \underset{\substack{|\\X}}{CH} - CH_2 - \underset{\substack{|\\X}}{CH} - \quad \text{etc.}$$

The two processes are kinetically very different (63). In the following sections a brief outline of nature and kinetics of only the addition polymerisation will be discussed since the condensation polymerisation is beyond the scope of this work.

The vinyl monomers may be regarded as monosubstituted derivatives of ethylene, of the structure $CH_2{=}CH\,X$. One must, however, include in any discussion of vinyl polymerisation, monomers of the following structures (where X and Y are substituents other than hydrogen):

1)	$CH_2 = CHX$	Vinyl monomers
2)	$CH_2 = CXY$	1,1 Disubstituted ethylenes and vinylidene monomers
3)	$CHX = CHY$	1,2 Disubstituted ethylenes
4)	$CF_2 = CXY$	Tetra-fluoro-ethylene derivatives
5)	$CH_2 = CH{-}CH{=}CH_2$	Butadiene and its derivatives.

These substances shall be referred to as vinyl type monomers, or more simply and less accurately, as vinyl monomers (64) and their conversion to high polymers will be referred to as vinyl polymerisation (65).

Not all compounds which have structures (66) corresponding to those written above have been polymerised, at least to the present date. However, it is quite striking, how very high a proportion have been converted into high polymers (66). It is also quite notable that a very high proportion of these polymers have proved to be of commercial importance.

The phenomenon of copolymerisation, in which mixtures of any of the above-mentioned substances are allowed to coreact to produce chain molecules with residues of each monomer incorporated in the chain, enhances enormously the synthetic possibilities (67).

In many cases, monomers such as the 1,2 disubstituted ethylenes which polymerise with difficulty by themselves will enter into copolymerisation reactions with great ease (67). Vinyl type polymerisations (64) may be propagated by a free radical chain mechanism or an ionic chain mechanism, depending upon the type of catalyst employed. This also enhances the synthetic possibilities since monomers such as isobutylene and propylene, for example, which cannot be polymerised by free radical producing catalysts, will polymerise readily in the presence of cationic catalysts (64). However, vinyl polymerisations initiated by radical producing catalysts and therefore propagated by growing free radical chains are the most widely used and most important from the mechanistic point of view. Highly purified styrene and methyl methacrylate can be polymerised by heat alone or by ultra violet radiation (65). These polymerisations are referred to as thermal and photo-polymerisations respectively. Small amounts of substances which decompose thermally into active free radicals markedly accelerate the polymerisation of these and other vinyl monomers (66). Similarly, substances which are decomposed into active free radicals by ultraviolet light or even visible light will markedly accelerate the photo-polymerisation of vinyl monomers via a radical mechanism are first and foremost peroxides, also azo compounds, persulphates and disulphides.

h) The Elementary Steps in Vinyl Polymerisation

The simplest kinetic (66) situation for vinyl-type polymerisation is obtained when a pure vinyl monomer such as styrene or methyl methacrylate is polymerised under constant temperature conditions through the agency of a radical producing catalyst such as benzoyl peroxide. For a homogeneous reaction the polymer and the catalyst should both be soluble in the monomer. Analysis of the reaction mechanism has, to this date, been restricted to systems where conversion to polymer amounted to about 15% of the monomer present. The discussion can also be extended to the case where the polymerisation is carried out in an "ideal solvent". The definition of an ideal solvent will be clarified in further discussion.

The reaction steps for polymerisation under these conditions (66) are:

1. Decomposition of Catalyst:

$$\text{catalyst} \longrightarrow 2R^{o} \qquad \text{(h-1)}$$

The rate of spontaneous homolytic decomposition of the catalyst is K_d [Cat]. The rate of formation of primary radicals from the catalyst is:

$2Kd$ [Cat].

2. Initiation of Polymer Chains:

$$R\cdot + M \rightarrow RM_1\cdot \qquad \text{(h-2)}$$

The rate of initiation of polymer chains will be denoted by Ri.

3. Propagation of Polymer Chains:

$$RM_n^\circ + M \xrightarrow{Kp} RM\overset{\circ}{n+1} \qquad (h\text{-}3)$$

It is assumed that Kp is the same for the growth of polymeric species of all kinds. The rate of disappearance of monomer by reaction (h-3) is Kp (RMn°)[M].

Let $[C^\pm]$ represent the total concentration of polymeric radicals of all types

$$[C^\pm] = \sum_{n=1}^{\alpha} [RMn^\circ] \qquad (h\text{-}4)$$

Monomer disappears by reaction (h-2) and (h-3). The total rate of disappearance of monomer is denoted by R_p (the rate of polymerisation) and is given by

$$Rp = Ri + Kp\,[C^\pm]\,[M] \qquad (h\text{-}5)$$

Under almost all circumstances the second term on the right hand side is enormously larger than the first term. Hence in nearly all cases where high polymers are formed:

$$Rp = Kp\,[C^\pm]\,[M] \qquad (h\text{-}6)$$

4. Termination of Growing Polymer Chains:

$$RMn^\circ + RMp^\circ \xrightarrow{Ktc} RMn{+}p\ R \qquad (h\text{-}7)$$

$$RMn^\circ + RMp^\circ \xrightarrow{Ktd} RMn{+}RMp \qquad (h\text{-}8)$$

Two types of termination are possible, although it now appears that one of these predominates under usual conditions. The first is combination (h-7); the second one is called disproportionation. The notation RMn and RMp refers to polymeric chains which no longer have their radical reactivity. The mechanism of combination and disproportionation are illustrated below in the case of vinyl monomers, i.e.,

$CH_2 = CHX.$

$$R(CH_2CHX)_{n-1}\ CH_2CHX^{\circ} + {}^{\circ}CHXCH_2(CHXCH_2)_{p-1}R \xrightarrow{Ktc} R(CH_2CHX)_{n+p}\ R.$$

$$R(CH_2CHX)n-1\ CH_2CHX^{\circ} + {}^{\circ}CHXCH_2(CHXCH_2)p-1\ R \xrightarrow{Ktd} R(CH_2CHX)n-1\ CH_2- CH_2X + CHX = CH\ (CHXCH_2)p-1\ \ R$$

The rate of disappearance of pairs of radicals by combination and disproportionation respectively is $Ktc[C^{\pm}]^2$ and $Ktd[C\pm]^2$. The rates of disappearance of radicals (moles per litre per second) by these processes are $2Ktc[C^{\pm}]^2$ and $2Ktd[C^{\pm}]^2$. It is assumed that Ktc and Ktd are independent of the size of the polymeric radicals.

5. Transfer Reactions:

The growing polymer radicals can interact with solvent, initiator, or polymer in the following ways:

$$RMn^{\circ} + S \xrightarrow{Ktr,S} RMn+S^{\circ} \quad \text{(h-9)}$$

$$RMn^{\circ} + M \xrightarrow{Ktr,m} RMn+M^{\circ} \quad \text{(h-10)}$$

$$RMn^{\circ} + Cat \xrightarrow{Ktr,Cat} RMn+Cat^{\circ} \quad \text{(h-11)}$$

$$RMn^{\circ} + P \xrightarrow{Ktr,P} RMn+P^{\circ} \quad \text{(h-12)}$$

In the above equations S,M,Cat and P refer to molecules of solvent, monomer, initiator and polymer respectively. These reactions are illustrated for the monomer CH_2=CHX for the cases in which toluene and carbon tetrachloride act as the solvents and t-butyl hydroperoxide is the initiator (66).

$$\mathrm{RMn}^{\circ} + \mathrm{C_6H_5\ CH_3} \longrightarrow \mathrm{RMnH} + \mathrm{C_6H_5CH_2}^{\circ} \qquad \text{(h-13)}$$

$$\mathrm{RMn}^{\circ} + \mathrm{CCl_4} \longrightarrow \mathrm{RMnCl} + \mathrm{CCl_3}^{\circ} \qquad \text{(h-14)}$$

$$\mathrm{RMn}^{\circ} + \mathrm{CH_2 = CHX} \longrightarrow \mathrm{RMnH} + \mathrm{CH_2 = CX}^{\circ} \qquad \text{(h-15)}$$

$$\mathrm{RMn}^{\circ} + \mathrm{(CH_3)_3\ COOH} \longrightarrow \mathrm{RMnH} + \mathrm{(CH_3)_3\ COO}^{\circ}$$

or (h-16)

$$\mathrm{RMn}^{\circ} + \mathrm{(CH_3)_3\ COOH} \longrightarrow \mathrm{RMnOH} + \mathrm{(CH_3)_3\ CO}^{\circ}$$

$$\mathrm{RMn}^{\circ} + \mathrm{RM_p\ CH_2CHXMnR} \longrightarrow \mathrm{RMnH} + \mathrm{RMpCH_2\overset{\circ}{C}\ XMnR} \qquad \text{(h-17)}$$

If the solvent radicals produced by the interaction of the solvent with the growing chain (e.g. $C_6H_5CH_2^{\circ}$ and CCl_3° in the cases illustrated above) react very rapidly with a monomer molecule to start a new growing polymer chain, the solvent may be termed an ideal solvent. When a polymerisation is carried out in the presence of such a solvent, the molecular weight of the polymer is markedly affected by the nature of the particular solvent, but the rate of polymerisation is affected only by the change of monomer concentration, and is therefore independent of the solvent used at a fixed molar concentration of monomer. If, on the other hand, the radicals produced by the interaction of growing polymer chains with the solvent do not react rapidly with monomer to start new polymer chains, but instead undergo wasteful reactions, such as recombination, e.g.:

$$2\ \mathrm{C_6H_5\ CH_2}^{\circ} \longrightarrow \mathrm{C_6H_5\ CH_2CH_2\ C_6H_5}$$

the solvent is in reality an inhibitor or retarder. A solvent which exhibits no tendency to enter into transfer reactions may be considered an "inert solvent".

Substances which are regarded as effective inhibitors or retarders must exert potent effects in very small concentrations. This means that these substances must have a very high reactivity toward growing polymer chains (or to the radicals produced by the catalyst), in addition to their property discussed above of forming radicals which do not readily start new polymer chains. Oxygen acts as an effective inhibitor (64) due to its ability to form peroxides with types of radicals present in polymerising systems. Another type of inhibitor is diphenylpicrylhydrazyl (D.P.P.H.) which leads to radical-radical recombinations.

Chain transfer to monomer may occur by the mechanism shown in eg.(h-15) or by transfer of an atom (e.g., a hydrogen atom) from the growing polymer chain to the monomer. Chain transfer to the initiator, as shown in (h-16) for the catalyst t-butylhydroperoxide, is an example of the multiple role that many reagents play in vinyl-type polymerisation.

When growing polymer radicals interact with completed polymer as shown in equation (h-17) the net effect of the reaction is to transfer radical activity from the end of a polymer chain to some other atom along the chain. This does not affect the rate of polymerisation of the polymer formed, but causes the production of branched rather than linear polymer molecules.

The rates of all the transfer reactions discussed above (h-9 through h-12) are given by:

$$\text{Rate of transfer} = K_{tr,x}[C^*][X] \qquad \text{(h-18)}$$

i. Rate of Polymerisation

For a certain set of conditions , i.e., fixed temperature and fixed catalyst and monomer concentrations, there is a definite rate of production of growing polymeric radicals in a polymerising system which is denoted by Ri (rate of initiation of polymer chains in mole liter^{-1} sec^{-1}). For a catalysed polymerisation Ri is given by the following formula:

$$Ri = 2\ fk_d\ \lfloor Cat \rfloor + Ri,th. \qquad (i\text{-}1)$$

In the above equation, kd $\lfloor Cat \rfloor$ is the rate of spontaneous first order homolytic cleavage of the catalyst. The factor 2 appears because two primary radicals are produced by every spontaneous cleavage (at least for simple catalysts such as benzoyl peroxide). The factor f is the catalyst efficiency, i.e., the fraction of primary radicals which are effective in starting polymer chains. The second term on the right hand side is the rate of purely thermal initiation.

As in other chain reactions, a steady state concentration of active intermediates is rapidly attained. In this case the active intermediates are the growing polymer radicals, where total concentration can be denoted by [C*]. The steady state condition is characterised by the fact that the rate of initiation of growing polymer radicals is equal to the rate of disappearance of the growing polymer radicals, i.e.,

$$Ri = (2\ ktc + 2\ ktd)\ [C^*]^2 \qquad (i\text{-}2)$$

The rate of polymerisation, Rp is given by the formula:

$$-d[M]/_{dt} = Rp = kp[C^*]\ [M] \qquad (i\text{-}3)$$

From equations (i-2) and(i-3) one obtains:

$$Rp^2 = ([M]^2\ /2A'')\ Ri \qquad (i\text{-}4)$$

where

$$A'' = (ktc + ktd)\ /_{kp}{}^2 \qquad (i\text{-}5)$$

Substituting equation (i-1) in (i-4), the following is derived:

$$Rp^2 = \frac{Ri,th}{2A''}[M]^2 \frac{fkd}{+ A''}[CAT]\,[M]^2 \qquad (i\text{-}6)$$

It has been found empirically that the rate, Rp, for catalysed polymerisations can be expressed as follows: (68)

$$Rp^2 = Rp^2,th + K^2[Cat]\,[M]^2 \qquad (i\text{-}7)$$

where Rp,th represents the purely thermal rate under the given conditions of temperature and monomer concentration and K is an over-all rate constant. If the initiator is effective and is present in appreciable concentration, the contribution of the thermal polymerisation is negligible and equation (i-7) becomes:

$$Rp = -d[M]\,/_{dt} \approx K[CAT]^{1/2}\,[M] \qquad (i\text{-}8)$$

It is clear from (i-8) that the polymerisation rate is first order with respect to monomer concentration and varies as the square root of catalyst concentration.

j. Catalyst Efficiencies.

The initiator azo-bis-isobutyronitrile (66) decomposes by a first order reaction at nearly the same rate in all solvents. The rate of decomposition is therefore believed to be a measure of the rate of production of monoradical pairs. The catalyst efficiency, f, of this initiator is defined as the rate of initiation divided by twice the rate of initiator decomposition:

$$f_{AZO-1} = \frac{Ri}{2kd[Cat]} = \frac{Ri/[Cat]}{2kd}$$

In the case of benzoyl peroxide, the decomposition in various solvents can be represented as the sum of a spontaneous cleavage into radicals plus a radical induced decomposition. The spontaneous decomposition is nearly the same in all solvents but the induced decomposition depends very much on the nature of the solvent. The catalyst efficiency for benzoyl peroxide is given by the following expression:

$$f_{Bz_2O_2} = \frac{Ri}{2K_d[Bz_2O_2]}$$

where kd is the specific rate of spontaneous decomposition of benzoyl peroxide. The efficiency(63) with which radicals initiate chains can be estimated by comparing the amount of initiator decomposed with the number of polymer chains formed. Most initiators (63) in typical vinyl polymerisations have efficiencies between 0.6 and 1.0 i.e., between 60 and 100% of all the radicals formed ultimately initiate polymer chains. A thorough discussion of catalyst efficiency is given in Refs. 64 and 66.

k. Heterogeneous Polymerisation.

'Heterogeneous polymerisations' may be defined (64) as those polymerisations in which the propagating free radicals pass from one phase to another. Frequently this behavior is a consequence of the separation of solid polymer from monomer which is initially present in either the gaseous or liquid phase; in the latter case the monomer may be either undiluted, or present as a solution, emulsion or suspension in another liquid, frequently water. Many such examples (64) are halogen and pseudo-halogen substituted ethylenes which give rise to high polymers are heterogeneous. Vinyl Bromide, vinyl Chloride and acrylonitrile all show the general characteristics of heterogeneous polymerisations. For such polymerisations all the relationships which govern the kinetics of homopolymerisation breakdown and are extensively covered in Ref. 64.

1. Copolymerisation:

Dostal (69) made the first attempt to elucidate the mechanism of copolymerisation by assuming that the rate of addition of monomer to a growing free radical depends only on the nature of the end group on the radical chain. Thus monomers M_1 and M_2 lead to radicals of types M_1° and M_2°. The four possible ways in which monomer can add are:

$$\begin{array}{ll}
\text{Reaction} & \text{Rate} \\
M_1^{\circ} + M_1 \longrightarrow M_1^{\circ} & k_{11}[M_1^{\circ}][M_1] \\
M_1^{\circ} + M_2 \longrightarrow M_2^{\circ} & k_{12}[M_1^{\circ}][M_2] \\
M_2^{\circ} + M_1 \longrightarrow M_1^{\circ} & k_{21}[M_2^{\circ}][M_1] \\
M_2^{\circ} + M_2 \longrightarrow M_2^{\circ} & k_{22}[M_2^{\circ}][M_2]
\end{array} \qquad (1\text{-}1)$$

Applying the assumption (70-73) of the steady state to each radical type separately i.e., the concentrations of M_1° and M_2° must each remain constant. It follows that the rate of conversion of M_1° to M_2° must equal that of conversion of M_2° to M_1°:

$$k_{21}[M_2^{\circ}][M_1] = k_{12}[M_1^{\circ}][M_2] \qquad (1\text{-}2)$$

The rates of disappearance of the two types of monomer are given by:

$$\begin{aligned}
-d[M_1]/_{dt} &= k_{11}[M_1^{\circ}][M_1] + k_{21}[M_2^{\circ}][M_1] \\
-d[M_2]/_{dt} &= k_{12}[M_1^{\circ}][M_2] + k_{22}[M_2^{\circ}][M_2]
\end{aligned} \qquad (1\text{-}3)$$

The composition of copolymer being formed at any instant is given by:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \times \frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]} \qquad (1\text{-}4)$$

TABLE 1

RELATIVE REACTIVITIES OF SOME MONOMER PAIRS (67)

NO.	M_1	M_2	R_1	R_2	T_1°C
1.	STYRENE	ACRYLONITRILE	0.41±0.08	0.04±0.04	60
2.	VINYL CHLORIDE	ISOBUTYLENE	2.05±0.03	0.08±0.1	60
3.	VINYL CHLORIDE	VINYL ACETATE	2.1	0.3	68
4.	VINYL CHLORIDE	METHYL-METHACRYLATE	0.1	10	68

where as $r_1 = \frac{k11}{k12}$ and $r_2 = \frac{k22}{k21}$. This is known as the copolymer equation, it has been verified by many experimental investigations (64).

m. Monomer Reactivity Ratios:

The monomer reactivity (63) ratios r_1 and r_2 are the ratios of the rate constant for a given radical adding its own monomer to that for its adding the other monomer. Since the rate constants for initiation and termination do not appear in (1-4), the composition of the copolymer is independent of over-all reaction rate and initiator concentration. The reactivity (63) ratios are unaffected in most cases by the presence of inhibitors, chain transfer agents, or solvents. Even in heterogeneous (64) systems they remain unchanged unless the availability of the monomers is altered by their distribution between phases. A change (63) from a free radical to an ionic mechanism, however, changes r_1 and r_2 markedly. A few typical values of monomer reactivity ratios are listed in Table 1.

n. Types of Copolymerisation:

1. Ideal:

A copolymer system is said to be ideal (64) when the two radicals show the same tendency for adding one of the monomers over the other:

$$k11/_{k12} = k21/_{k22} \text{ or } r_1 = 1/_{r_2} \text{, or } r_1 r_2 = 1.$$

In this case the end group on the growing chain has no influence on the rate of addition, and the two types of units are arranged at random along the chain in relative amounts determined by the composition of the feed and the relative reactivities of the two monomers. The copolymer equation reduces to:

$$\frac{d[M_1]}{d[M_2]} = \frac{r_1[M_1]}{[M_2]}$$

2. Alternating:

Here each radical prefers (64) to react exclusively with the other monomer: $r_1 = r_2 = 0$. The monomers alternate regularly along the chain regardless of the composition of the monomer feed. The copolymer equation simplifies to $d[M_1]/_{d[M_2]} = 1$.

✓ Most actual cases lie between the ideal and the alternating systems; $0<r_1r_2<_1$. A third possibility, with both r_1 and r_2 greater than unity, would exist if each radical preferred to add its own monomer: in the extreme, the two monomers would simultaneously homopolymerise . No such case is known, (64) indeed there is no established instance of free radical polymerisation in which the product r_1r_2 is significantly greater than unity.

0. Instantaneous Composition of feed and polymer:

Let F_1 and F_2 be the mole fractions of monomers 1 and 2 in the polymer being formed at any instant

$$F_1 = 1-F_2 = d[M_1]/_{d([M_1] + [M_2])} \qquad (0\text{-}1)$$

If f_1 and f_2 similarly represent mole fractions in the monomer feed,

$$f_1 = 1-f_2 = [M_1] /_{([M_1] + [M_2])} \qquad (0\text{-}2)$$

the copolymer equation can be written: (63)

$$F_1 = \frac{(r_1f_1^2 + f_1f_2)}{(r_1f_1^2 + 2f_1f_2 + r_2 f_2^2)} \qquad (0\text{-}3)$$

It is apparent that in general F_1 does not equal f_1, and both f_1 and F_1 change as the polymerisation proceeds. The polymer obtained (63) over a finite range of conversion consists of many increments, each differing in composition.

It follows from equation (ℓ-4) that, except for the special case when both reactivity ratios are unity, the ratios of the rates of consumption of monomers, i.e., $\frac{d(M_1)}{d(M_2)}$ is not equal to the ratio $\frac{(M_1)}{(M_2)}$ except for a unique value of the later.

For this value (63)

$$\frac{r_1(M_1) + (M_2)}{r_2(M_2) + (M_1)} = 1,$$

i.e.,

$$\frac{(M_1)}{(M_2)} = \frac{1-r_2}{1-r_1}$$

or from eq. (0-2)

$$(f_1)c = \frac{(1-r_2)}{(2-r_1-r_2)}$$

By analogy with binary distillation this is commonly referred to as the azeotropic composition (64). At all other values of $\frac{[M_1]}{[M_2]}$ the reaction mixture will progressively become richer in one or the other of the monomers as the polymerisation proceeds, with a corresponding drift of the composition of the copolymer.

Chapter III

"Literature Survey".

There have been two types of development in the treatment of wood. These are:

a) Conventional chemical treatments in which nuclear radiation is not utilised.

b) Methods involving the use of nuclear radiation to initiate polymerisation.

The following is a summary of developments in the abovementioned fields:

a) The year 1909 saw the development of Bakelite (74) which was compounded of wood flour, carbon black and phenol-formaldehyde resin and is perhaps the first wood plastic alloy which was used in the manufacture of telephones. Wood flour in Bakelite acts as a filler and is present in minor proportion compared to phenol formaldehyde resins. Its utility in the manufacture of laminates for electrical insulation parts (75,76) was mainly due to its dielectric characteristics, dimensional stability and strength properties. The development of Bakelite followed the technique for manufacturing phenol-formaldehyde condensation products by Leo-Bakelite (74).

By 1940 the use of phenolic resins to impregnate wood became quite extensive on a commercial scale with the development of Impreg and Compreg by the U.S. Forest products laboratory (77). The process to make Impreg consists of impregnation of wood with a low molecular weight, water dispersed phenolic resin which is allowed to diffuse into the cell walls and results in swelling of the wood. Following diffusion, water is removed by drying the wood at low temperature, and the resin is cured by heating the impregnated wood at the suitable temperature. There are some inherent difficulties in treating larger sized pieces of wood with resin forming chemicals; therefore, both Impreg and Compreg are generally produced from thin veneers. Compreg differs from Impreg in that the impregnated, dry wood is compressed in a hot press. Compreg found applications (61) in airplane propellers and was also used for making machinery parts that required the combined properties of electrical insulation, hardness and dimensional stability. It is still in use in North America where it is utilized in the manufacture of cutlery handles (75). Impreg is frequently used for making automobile die models.

When furfuryl alcohol (78) monomer containing a dissolved catalyst is used to impregnate wood followed by heating, the product obtained has a better alkali resistance than wood impregnated with phenolic resin, therefore it found application (61) in certain tanks, filter press components, and other parts where resistance to alkali was important. Good antishrink efficiencies and a marked increase in hardness also resulted.

Wood impregnated with dimethoyl urea (D.M.U.) provided an alternative to the phenolic based impregnation process (61) and was reported to be very plastic in the swollen state, and also resulted in increased hardness and compression strength after the completion of the condensation reaction following drying and curing. It was trade-named Arboneeld (79). Pilot plant studies resulted in the production of test flooring and other applications requiring hardness and improved stability. Investigations carried out by the U.S. forest products labs. proved that urea-formaldehyde resins were not as effective in producing high antishrink efficiencies as were commercially available phenolic resins (80). Phenolics were more resistant to high heat and humidity than the urea resins.

A product was developed in 1954 (61) which combined the features of both Impreg and Compreg and provides dimensional stability and water resistance. The phenolic impregnated product is still being made on a commercial scale in limited quantities and finds application as a meat cutting board. The trade name for this product is Chem-Board*. Details about the manufacture of this product are not available due to its proprietary nature.

Flapreg (81), a member of the family of phenolic modified woods appeared in 1957 and is made by a combination of operations such as resin spraying, diffusion, and drying the product (77). Flapreg has the following advantages:

1. Very high specific gravity,
2. remarkable dimensional stability in all directions, and
3. improved strength in several mechanical properties.

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* Chem-Board is manufactured by Chem-Wood Products, Inc., 1115 S.W. Florida St., Seattle, Wash.

Attempts to commercialize this product failed because of its high cost of production (61).

More recently poly ethylene glycols (P.E.G.) (82) have been used to dimensionally stabilize wood through bulking of the cell walls. P.E.G. is water soluble up to a certain molecular weight, but have low vapour pressure. It remains as a waxy substance in the cell walls and keeps wood permanently in the swollen state after the water has been removed. The degree of dimensional stabilization obtained is 80%. Cost of treatment in this process can be tolerated only in very high value articles such as art forms, archeological relics, and valuable gunstocks where the price of raw materials is much less than the fabrication cost. (83).

By chemically converting the reactive hydroxyl groups on cellulose in wood to acetate groups (21) through treatment with liquid or gaseous acetic anhydride, antishrink efficiencies of more than 75% are obtained, commercialisation of this process is however limited by its relatively higher cost (84).

A similar process (21) involves the use of phenyl iso-cyanate vapour to alter that portion of the cell wall that accounts for its hygroscopicity. No chemical analysis of the product is available but presumably this compound reacts with accessible hydroxyl groups to provide the urethane derivative. Other isocyanates have also been tried (61). Phenyl isocyanate (85) might result in some practical use for the process in the near future.

Ethylene oxide (86) in vapour form has been polymerised in situ in wood and its antishrink efficiency depends upon the formation of ethylene and polyethylene glycols within the cell wall as well as from the chemical attachment to the cellulosic materials.

Ethylenimine polymerises (87) to give a straight chain macromolecule similar to polyethylene glycol. Ethylene amine derivatives have been found to be much effective in modifying paper, presumably by direct reaction with cellulose (87).

Vogel (76) reported on work done at Alabama Polytechnic Institute to impregnate wood with metal alloys. Small blocks of wood, 1 1/2 inches in cube, were immersed under pressure in molten metal alloys, which filled the cell cavities. Dimensional stability of the metal-treated wood was reported as significantly increased, but no data were presented to support the statement. Vogel found that metal-impregnated wood could be given subsequent treatment with other impregnants, such as oil, to produce self-lubricating bearing blocks. In fact, he reported some metalized wood bearings were used in Europe prior to World War II.

No cell cavity filling technique can result in complete dimensional stability of wood (16) due to the simple reason that any impregnation of wood that results in a solid being formed in the lumina of the cells can only retard the normal movement of water vapour from cell to cell through the cell cavities. The effectiveness of such treatment will depend on the completeness of the cavity-filling operation. The thickness of the untreated cell wall will ultimately change in response to changes in humidity; although this change may be resisted in well-filled cavities, it will eventually result in a dimensional change in the wood.

b) Numerous instances have appeared in chemical literature which make use of high energy radiation to trigger chemical reactions (2). In many of these instances the potential use of radiation is contemplated in commercial and near commercial processes. At present commercially produced materials (2,88,91) include ethyl bromide, shrinkable tubing, plastic film, polyethylene wire insulation and poly vinyl acetate resin.

There are several reasons (92) why radiation polymerisation is one of the important practical applications of high energy radiation.

1. Due to the high molecular weight of the products, polymerisation results in a high energy yield.
2. The reaction takes place more smoothly than other free-radical polymerisations and can therefore be more readily and accurately controlled, while using catalysts, the reaction can be very violent.
3. The resultant products are as pure as the monomer, whereas in conventional mehtods, additives contaminate the product.
4. Free radicals are equally distributed throughout the material as a result of the high penetrating power of the γ-rays and especially with solid materials like wood, γ-radiation has definite advantages due to its penetrating power.
5. Grafting over homo-polymerisation can be the preferred reaction in cases where the number of radicals formed on the backbone polymer is greater than the number of free radicals produced in the monomer.

It is not surprising therefore that much work has been done on the preparation of WPC by using nuclear radiation as a polymerisation catalyst. All such processes as lead to the production of WPC fall neatly into two categories. These are:

1. Impregnation - Irradiation Technique

In this technique, wood is impregnated with a monomer followed by exposure to nuclear radiation, which results in the polymerisation of monomer in the cell cavities of wood. This is essentially a wood filling technique and does not result in the alteration of cell wall structure of wood.

Early work in this field was described by Karpov (11) and co-workers, who reported the improvement of physical properties of wood such as dimensional stability, static bending strength and rate of water sorption by filling the cellular spaces in wood with γ-radiation polymerised M.M.A., M.A., styrene and acrylonitrile. Some of the Russian workers (93) in 1960 reported the application of WPC in the metal-casting process, predicted commercial polymerisation of monomers with textiles, paper and mentioned the possibility of preserving fibrous museum items and archaelogical treasures by the WPC method.

Most of the research work on the production of WPC by the irradiation-impregnation technique has been sponsored by the Division of Isotopes Development (DID) of USAEC at West Virginia University (5,6,7). This work has been directed by Prof. J.A. Kent.

Kent et al reported on work with many different monomers and wood species using samples 2 x 2 x 6 inches, impregnation was done under low pressure, and the samples were then soaked under atmospheric pressure followed by wrapping in foil to prevent monomer evaporation and irradiation. The pure monomers as such and/or in combination with other

TABLE 2

ABRASION RESISTANCE OF WPC OF SUGAR MAPLE (7)

POLYMER	POLYMER LOADING g POLYMER/ 100 g WOOD	RELATIVE ABRASION RESISTANCE
Poly Vinyl Acetate	0	1.00
	14	2.73
	26	1.99
	27	3.84
	53	2.49
	59	3.06
	62	5.39
Poly Methyl Methacrylate	80	3.31
	80	3.64
	82	7.30

TABLE 3 TOUGHNESS DATA FOR WPC (7)

SPECIES	POLYMER	AVERAGE POLYMER LOADING: g POLYMER/100 g WOOD	AVERAGE RELATIVE TOUGHNESS	LEVEL OF SIGNIFICANCE
WHITE PINE	PMMA	36	1.20	*
		68	1.36	+
		100	1.69	+
		144	1.99	#
	PVA	31	1.22	*
		50	1.46	#
		83	1.18	*
		109	0.99	N.S.
YELLOW BIRCH	PMMA	20	1.09	N.S.
		41	0.99	N.S.
		67	1.29	#
		75	1.56	#
	PVA	14	0.98	N.S.
		37	1.01	N.S.
		55	1.06	N.S.
		73	1.32	+

* Significant at the 5% level

\+ Significant at the 1% level

\# Significant at the 0.1% level

N.S. Not Significant

monomers or plasticizers tested were methyl methacrylate, vinyl acetate ethyl acrylate, styrene and ethylene glycol, dimethyl acrylate acrylonitrile and vinyl chloride. The species of wood employed in this work were white pine, sugar maple, white oak and birch. Irradiations were performed with two CO^{60} sources of 350 curies and 10,000 curies. The latter provided a dose rate of 55,000 rads per hour.

Following is a brief summary of the results of this work.

1. All the properties studied i.e., dimensional stability, water absorption, hardness, compressive strength, static bending strength, and sheer strength were improved by impregnation with resin. The degree of improvement depended on the nature of wood and the resin used. (Tables 2 and 3 list some of the properties of WPC as reported in this work).
2. The compressive strength of all WPC tested increased with the introduction of increasing amounts of polymer up to 0.6 pound of polymer per pound of wood. With further increase in the amount of polymer, the compressive strength appeared generally to approach a limiting value as might be expected.
3. The wood plastic materials are readily machinable, the grain is accentuated, and the finish is satiny.
4. In an effort to decrease the radiation dose required for polymerisation, the effect of various sensitizing, cross linking, inhibiting, and transfer agents was studied. Although the performance of additives could be quite different in the in situ polymerisation from that in bulk because of different diffusion rates, solubilities and also due to naturally occurring substances in the wood, the results of various

experiments showed that in such polymerisation the reaction rates and the degree of polymerisation can be controlled to a high degree. Inhibiting effect of air was also noticed.

5. With styrene and M.M.A., carbon tetrachloride produced a significant increase in the polymerisation rate and also behaved as a chain transfer agent.

6. Little or no grafting of the polymers to the wood occurred, as shown by extraction with appropriate solvents of various woods that had been impregnated with M.M.A and vinyl acetate

7. The molecular weights of the polymers were found to be higher in wood than in bulk polymerisation.

8. It was reported that vinyl chloride, one of the cheapest commercially available monomers can be readily polymerised by exposure to nuclear radiation. However, it presents many problems due to its low boiling point (-14°C). Also the polymer of vinyl chloride is insoluble in the monomer and precipitates out during polymerisation to yield a fine, powdery, nonhomogeneous polymer with no mechanical strength. This problem was easily overcome by the use of plasticizers and copolymerizing it with various monomers in the cell cavities of wood. Copolymerisation studies suggested that 10 vol.% acrylates impart plasticity to vinyl chloride copolymers. Polymerisation of vinyl chloride with 20 vol.% dioctyl phthalate and Santicizer 141* gave, in general, softer polymers than the acrylate copolymers. Wood-plastic combinations with vinyl chloride contained fairly large but varying amounts of polymer, and the distribution of polymer throughout a given sample was very non-uniform

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* Trade name for one of the plasticizers, manufactured by Monsanto Chemical Company.

TABLE 4 HARDNESS DATA (23)

TREATMENT	SAMPLE NUMBER	% POLYMER IN WOOD	AVERAGE DEFORMATION (INCHES)
UNTREATED	12	0	0.192
	13	0	0.208
	14	0	0.191
AVERAGE		0	0.199
DIRECT HEATING	15	67.5	0.048
	16	63.9	0.051
	17	68.0	0.044
AVERAGE		66.5	0.048
R-F HEATING	18	71.5	0.041
	19	73.2	0.038
	20	69.0	0.042
AVERAGE		71.2	0.040
GAMMA IRRADIATION	21	63.9	0.037
	22	69.5	0.041
	23	64.2	0.039
AVERAGE		65.9	0.039

MAXIMUM LOAD = 1,200 lbs CROSS HEAD SPEED = 0.08 IN/MIN as can be expected from very low boiling monomers. Radiation copolymerization of styrene-acrylonitrile in wood appeared to be feasible.

9. A number of polymer dyes could be added to accentuate the wood grain and impart attractive colours to the wood. Although the dyes have inhibitory effects on the polymerization reaction, at dye concentrations that are potentially useful for WPC, the inhibition is not serious.

Meyer (23) carried out a comparative study of impregnation-irradiation technique and thermo-catalytic method for the production of WPC. He impregnated samples of straight-grained yellow-birch sapwood and subjected them to one of these three treatments;

(1) Irradiation with a 1000-curie source (5 M rads), (2) Addition of 0.2% benzoyl peroxide and direct heat, or (3) Addition of 0.2% benzoyl peroxide and radio-frequency heat.

Physical properties of the treated and untreated samples differed, but no significant difference was seen in the hardness or compression of WPC produced by any one of the three polymerization methods. (Table 4) Preliminary examination showed that the polymer was located in the vessels, rays, and cell lumens of the wood.

2. Since the internal area of contact within the secondary wall is more than 1000 times greater than that of the lumen, (16) in order that monomer free radicals may come in contact with cellulose free radicals, i.e. the graft sites, it is absolutely essential that monomer should be present in this area, the only way it could be achieved is through the use of a swelling agent which permits infiltration of the monomer into the secondary wall. The earlier experiments in this field have beem reported by Kenaga (94), in the form of four patents. The patents

claim the use of a variety of monomers, i.e. styrene, acrylonitrile, vinyl aromatics, acrylics and epoxides..

It was observed by Kenaga (8) in 1956 that, with doses below 10 M rads, little grafting or polymerization of styrene in wood took place in relatively dry systems of styrene in solvent solutions capable of swelling the substrate.

At the same time when this work was being carried out, Rapson and Huang (95,96) reported grafting of styrene to cellulosic materials by "solvent displacement technique." Other reports on grafting vinyl monomers on cellulose have been made by Schwab and his co-workers. (97) Systems of grafting vinyl monomers on hydrophilic polymers initiated by radiation have been described by Chaprio and Stannett. (98) They demonstrated that water plays an important role in the rate of grafting of vinyl monomers from a neutral solvent. At dry conditions, little or no grafting occurs; whereas as little as 1.5 % water in solution increases the rate many-fold.

Sakurada and co-authors also reported similar results. (99) As early as 1956, workers at Brookhaven National Laboratories investigated the use of water-soluble monomers, which were capable of penetrating the cellulose cell structure, and irradiation to improve the ageing characteristics of wood. (100)

Kenaga (12) made use of low and high vacuums, as well as solvent displacement variations, with the swelling agent concept. Dry, immersion, and freeze-dry processes were added to high vacuum techniques (10^{-4} mm Hg, 3 hrs) as additional treatments.

In the vacuum methods the wood was evacuated and the monomer introduced before irradiation. A water saturated 1,4 dioxane solution was mixed with styrene in the ratio 3:1 at toom temperature for most of the work.

In the solvent displacement method, wood wafers were first impregnated with water by low vacuum (5 to 6 mm Hg, 30 min) and then placed in a large volume of acetone so that at equilibrium the solution would be about 1% water after the acetone had evaporated.

Following are the experimental results of Kenaga's work:

1. Effect of Polymer Retention on Dimensional Stabilisation

The amount of styrene required for a given order of stabilization was relatively high compared to such methods as acetylation. It was determined that the homopolymerisation within the cell lumen was not the dominating cause of this inefficiency; the main reason was the opening up of the more ordered cellulose areas by means of impregnation and irradiation. In this manner water enters and swells regions which under ordinary circumstances are inaccessible.

The displacement or "inclusion technique" was used in order to eliminate the nonproductive use of polystyrene in the cell cavities. This method gave an increase in the antishrink efficiency because there was a reduction of material deposited in the lumen and there was less opening up or swelling of the cellulose structure.

2. Water pick up of Styrene Stabilized Wood

To test the effect of styrene stabilisation on the rate of water pickup, wafers which had 37%, 24% and 0% retention of styrene were oven-dried followed by immersion in water. At intervals the wafers were removed from the water and their volumes were measured. It was found that

TABLE 5

TENSILE STRENGTH OF DIMENSIONALLY STABILIZED WOOD (12)

SOLUTION	DOSE M RAD	PERCENT RETENTION	MODULUS OF ELASTICITY (1000 PSI)	MOISTURE CONTENT %	MAXIMUM LOAD PSI
A.	0.75	11.22	1207	7.01	12470
	1.20	27.56	1407	6.07	11340
	1.65	39.33	1347	5.37	10320
	0.75	16.22	1307	6.93	12460
B.	1.20	27.60	1440	6.38	11360
	1.65	42.39	1292	5.59	10020
	0.75	3.15	1302	6.68	12730
C.	1.20	2.49	1148	7.01	11170
	1.65	2.94	1150	7.46	11000
UN-IRRADIATED CONTROL		0.00	1309	10.04	11430

the amount of time required for the treated wafers to reach their maximum swell was about 12 hours in all cases. Untreated wafers were completely swollen in 21 minutes.

(3) Dimensional stabilization of wood (61) often results in a decrease in strength; for example, treatment with phenol formaldehyde resin results in shock resistance, and stabilisation with formaldehyde causes a decrease in both shock and abrasion resistance. Table 5 gives the results for three impregnating solutions.

(A) 25% styrene, 75% dioxane and 5.75% water

(B) 2.5% styrene, 12.5% ethyl acrylate, 75% dioxane and 5.75% water

(C) 25% toluene, 75% dioxane and 5.75% water; all by volume.

At McMaster University,(13,14,15) the gamma-initiated grafting of styrene to wood was studied, with the primary objective of improving the physical properties, notably bending strength. This work was performed by Ramalingam in 1960, Werezak in 1963 and Ross in 1965, under the direction of Professor J.W. Hodgins.

The experimental method consisted of the following basic steps;

1. Evacuating samples of wood (16" x 3/4" x 3/4") to the micron level for a number of hours.
2. Impregnating this sample with a styrene solution under a pressure of nitrogen gas for a pre-determined period.
3. Irradiating the sample in the McMaster Swimming Pool Reactor or CO^{60} irradiation facility in the reactor building.
4. Heating the treated sample for a number of hours.
5. Grinding the final dry treated sample to 40 mesh in a Wiley Mill. Extracting the wood flour to constant weight in a Soxhlet extractor using benzene as a solvent.

Experiments were carried out with pure styrene, solutions of styrene and methanol, and solutions of styrene, methanol and water with a small amount of chemical initiator, with or without the addition of benzoyl peroxide.

Ramalingam (13) carried out preliminary investigations concerning;

1. Study of conditions for the treatment of wood with styrene to obtain graft copolymerisation and the assessment of the physical properties of the treated wood,
2. Study of the nature of the transient species responsible for graft copolymerisation using the E.S.R. technique.

Following is a brief summary of Ramalingam's (13) experimental results;

1. When pure styrene was used as an impregnant, no significant grafting had occured, suggesting that the styrene was not penetrating into the secondary wall of the wood but was merely filling the cell cavaties.
2. When styrene, methanol and water solution was used as an impregnant, there was a considerable decrease in the amount of polymer extracted compared to the pure styrene treatment, thereby suggesting that grafting of polystyrene with cellulose took place when the styrene was able to diffuse into the secondary wall of the wood.
3. When polymerisation was thermo-catalytically initiated, it resulted in homo-polymerisation as could be expected.
4. The E.S.R. results indicated that free radicals were formed in the irradiated wood. The number of free radicals present one hour after an irradiation of approximately 10^8mr was around 10^8 per gram of treated material. Continual radical measurements after irradiating the wood

TABLE 6

EFFECT OF POLYSTYRENE ON THE BENDING STRENGTH OF WOOD (13)

IMPREGNANT	INITIATION	WT. OF POLYSTYRENE IN SAMPLE / WT. OF WOOD BEFORE TREATMENT X100	B.S. OF TREATED WOOD (LBS) / B.S. OF CONTROLS (LBS) X10
PURE STYRENE	THERMALLY AT 105°	100	156.0
PURE STYRENE	4.5Mr	100	156.8
76% STYRENE 22.5% Methanol 1.5% Water	4.5Mr	90	146.5
76% Styrene 22.5% Methanol 1.5% Water	THERMALLY AT 105°	42	127.4
76% styrene 22.5% Methanol 1.5% Water	THERMALLY AT 105°	80	141.3
76% Styrene 22.5% Methanol 1.5% Water	0.2% by vol. Benzoyl peroxide	46	127.0
76% Styrene 22.5% Methanol 1.5% Water	0.2% by vol. Benzoyl peroxide	74	141.7

sample in air showed that the concentration dropped off rapidly in the first three hours and then decreased more slowly for several days. It was also reported that by heating the irradiated wood at 105°C, a more rapid decrease in radical concentration occurred.

5. On testing the humidified samples, the percent change in bending strength in pounds varied from -5.5 to 56.8%. The results indicated that the bending strength of the samples is strongly dependent upon the polystyrene in the sample and is independent of the method of initiation. For example, consider the results shown in Table 6. It is evident that the bending strength, measured in pounds of load of treated samples is substantially higher than that of the controls.

6. The percent decrease in moisture absorption (measured by placing the samples in a 76% relative humidity environment) also appears to be a strong function of the amount of polymer in wood and independent of the type of initiation. For samples impregnated with pure styrene and irradiated with a dose varying from 0 to 18.9 m.rad, the percent decrease in moisture absorption was relatively constant at 65%. Most other treatments yielded about the same value. The decrease in water absorption (measured by immersing the samples in distilled water) for the treated samples varied from 43 to 85%. Again the results indicate that the water absorption is a strong function of the amount of polymer in the sample. This result is expected since the polystyrene (grafted and homo-) is occupying volume which the incoming water would normally fill. Generally speaking, the dimensional stability of the wood was improved by the treatment. For the "optimum" treatment of 76% styrene, 22.5% methanol and 1.5% water at a dose of 4.5 M.rad, the volumetric shrinkage was reduced by about

80%. Also the swelling of wood was reduced by about 85%.

Werezak (14) continued the work initiated by Ramalingam and carried out the following investigations:

1. In order to establish optimum conditions for radiation and thermal treatment with respect to six variables, i.e., time of evacuation, composition of impregnant, uptake of impregnant, total gamma dosage, duration and temperature of the heating treatment, a two factorial experimental design was set up using bending strength as the dependent variable.
2. A qualitative and quantitative analysis of free radicals using E.S.R. spectrometry was carried out with the following materials:

1. Wood irradiated in air.
2. Air dried cellulose, spruce-periodate lignin, dioxane lignin and Braun's native lignin irradiated in air.
3. Wood irradiated in vacuo.
4. Impregnated wood and α-cellulose irradiated in vacuo.

Werezak (14) set up an equation for the relationship of variables as:

$$Y=bo+b_1X_1+b_2X_2+b_3X_3 \dots b_nX_n.$$

where Y = the product yield, in this particular case, it is bending strength increase,

$bo, b_1 \dots b_n$ = constant coefficients

$X_1, X_2 \dots X_n$ = the value of each dependent variable such as time of evacuation, total gamma dose, etc. The coefficients or slopes represent the change in Y per unit change in X. From a knowledge of the coefficients for a given factorial design, a second design can be set up from the trend indicated by the slopes.

Ross (15) pointed out that the main objection to Werezaks' calculations was that he calculated these slopes without calculating their standard deviation. It can be shown from his factorial design No. 1 that values (15) of b vary from -4.1 to 6.8 with a standard deviation of ±10.09 and for the second design these values range from -5.5 to -2.8 with a standard deviation of ±7.37 (15). In other words, these coefficients are not significantly different from zero. This (15) does not necessarily indicate that the variables as such, do not affect the percent change in bending strength; but it does show that either:

1. the range of variables is so narrow that no correlation between them and the "percent change in bending strength" may be obtained. For example, it is improbable that an evacuation time of 11 hours would lead to a significantly different bending strength than a time of 13.5 hours.

and/or

2. some highly influential variable was omitted from the design. This exclusion might have obscured the effect of other variables.

It is quite likely that both of the above factors are important. Ross (15) has shown that three of the variables selected (total gamma dose, duration of heating treatment, and temperature of heating treatment) had ranges so small that their effect on the kinetics of the system was not discernible. This should also hold for the mechanical behavior of wood.

It is known (16) that the strength properties of wood are strongly dependent upon the specific gravity or density of the specimen. The large variation in bending strength as reported by Werezak (14) could have clouded the effect of the other important variables such as impregnant uptake which actually may have been due to the variation in density since Werezak did not account for the effect of density.

The choice of indicator, (Y), was also not suitable. This term was the bending strength increase based on the loads, in pounds, required to fracture the samples. The wood samples that were treated swelled on the average 13-17%, depending on the impregnating solution. This indicator, unlike the modulus of rupture, does not take the increase in volume into consideration. Actually the true measure of the specimen's strength is the modulus of rupture which is simply the fracture load divided by the stressed area. Therefore it is quite evident that the fracture load itself is not a meaningful index of strength unless the dimensions of the treated and control specimens are identical which in this particular case are not.

In general, Werezak obtained results very similar to those of Ramalingam in regards to strength properties of the treated sample and dimensional stability improvements. In addition, one other physical characteristic was examined: resistance to microbiological attack. The weight loss by decay (using a culture of Lenzites Trabea) averaged about 14% compared to a mean loss of 71% by the untreated controls.

Continuing the previous work, Ross concentrated (15) in the following aspects of Swelling-Irradiation-Impregnation technique:

1. There were many free radical sites which were not utilized in the grafting process, and the diffusion of monomer towards these sites could be enhanced by increasing the temperature of the impregnated wood during irradiation.
2. It was believed that there was a direct correlation between the

amount of graft copolymer formed and the bending strength.

In order to utilize the graft sites more efficiently, the irradiations of the impregnated wood were performed at elevated temperatures. It was expected that the higher mobility of the monomer at elevated temperature would increase the diffusion rate of monomer to the radical sites to an extent that would outweigh the higher rate of radical destruction at the higher temperature. Therefore irradiations of wood impregnated with styrene and with the styrene-methanol-water solution were carried out at a temperature range of 39 to 77.5°C in a specially designed apparatus (101) and following studies were carried out:

1. A study of the effect of homo- and grafted polystyrene on the wood,
2. A study of the effect of wood on the polymerisation of styrene.

Following are the conclusions of this experimental work as reported by Ross (15):

1. It was observed that grafting or associating (measured by the amount of polystyrene that was unextractable) is a function of the transfer of monomer from the cell lumen into the cell wall where actual grafting (initiated by cellulose free radicals) and entangling or cross-linking occur. This transfer is found to be dependent upon such factors as the method of impregnation, the specific gravity of the wood, and moreover the amount of swelling agents, particularly water, that is present in the impregnating solution. It was theorized that the mechanism whereby styrene entered the cell wall was "preferential extraction". This process consists of an initial selective adsorption of water from the solution by the cellulose in the walls followed by a slow diffusion of styrene into the sufficiently swollen structure.

2. The transfer of monomer into the walls was found to be independent of the temperature during irradiation; i.e., an increase in temperature did not increase the diffusion of styrene into the cell walls. It is thought that this transfer can only be accomplished by swelling the wall beforehand, hence the assumption that heating the wood-styrene system increases the amount of grafting (or associating) must be rejected.

3. The belief that grafting per se would increase the bending strength of wood is still not confirmed. This is due to the fact that the grafting technique introduces other effects which weaken the wood. Two such effects are permanent swelling of the wood and degradation of cellulose by irradiation. Unfortunately Ramalingam and Werezak used bending load as the index of strength rather than the modulus of rupture because the increase in swell was not taken into account and moreover measurements were made of the humidified wood rather than the oven dried wood. As a result, increases in bending strength of 50% were reported. In fact, as shown in this work, the bending strength (as measured by modulus of rupture) of the wood treated by Werezak shows no significant improvement when compared to the humidified untreated wood. Indeed, when moisture and density are taken into consideration, it is found that the solution treated wood is about 24% weaker in bending. In addition, the modulus of elasticity, the work to maximum load and the ultimate tensile strength are weaker for the treated wood (Tables 7 to 10). The very fact of having to use swelling agents (water and methanol) to accomplish grafting has attenuated the hydrogen bonding between cellulose macromolecules and the result is a lower strength uncompensated by the grafted polystyrene.

TABLE 7

HARDNESS, COMPRESSION, STATIC BENDING AND SHEAR STRENGTH OF WPC OF SUGAR-MAPLE (10)

TEST	PROPERTY	AVERAGE POLYMER LOADING g POLYMER/ 100 g WOOD	AVERAGE RELATIVE VALUE
Hardness Side	hardness	26	1.42
		30	1.76
		47	2.92
		56	2.88
End		26	1.52
		30	1.77
		45	2.35
		55	2.55
Compression parallel to grain	Proportional Limit	20	1.32
		31	1.34
		46	1.40
	Maximum crushing strength	20	1.15
		31	1.32
		46	1.48
Static Bending	Proportional Limit	28	1.21
		49	1.18
		56	1.36
	Modulus of Rupture	28	1.13
		49	1.23
		56	1.20
	Modulus of Elasticity	28	1.05
		49	1.02
		56	1.09
Shear Parallel to Grain	Ultimate Shear	27	1.47
		29	1.24
		43	1.18
		50	1.51

TABLE 8

STRENGTH PROPERTIES OF OVENDRIED, HUMIDIFIED IRRADIATED, AND IMPREGNATED WOOD (BASIS: HUMIDIFIED WOOD)*

STRENGTH PROPERTY	ALTERED WOOD TREATMENT	CHANGE IN PROPERTY
MODULUS OF RUPTURE	OVENDRIED	38.4±3.9
	Irradiated (3.5 M.rads) humidified	-3.7±2.9
	Irradiated (4.5 M.rads) humidified	-9.9±3.7
	Impregnated (54 &65% styrene solutions) irradiated & humidified	nil
	Impregnated (76% styrene solutions) irradiated and humidified	nil
	Impregnated (pure styrene) irradiated (4.5 M rads) and humidified	56.8
	Impregnated (pure styrene) heated (105°C,24 hours) and humidified	56.0
STRESS AT PROPORTIONAL LIMIT	OVENDRIED	35.9±6.2
	Impregnated (54 &65% styrene) irradiated & humidified	25.1±6.2

Table 8 cont'd on next page

TABLE 8 (cont'd)

STRENGTH PROPERTIES OF OVENDRIED, HUMIDIFIED IRRADIATED, AND IMPREGNATED WOOD (BASIS: HUMIDIFIED WOOD)*

STRENGTH PROPERTY	ALTERED WOOD TREATMENT	CHANGE IN PROPERTY
MODULUS OF ELASTICITY	OVENDRIED	nil
	Impregnated (54 & 65% styrene solutions) irradiated , and humidified	-16.3±4.5
WORK TO PROPORTIONAL LIMIT	OVENDRIED	77.8±10.9
	Impregnated (54 & 65% styrene solutions) irradiated & humidified	78.2±12.2
WORK TO MAXIMUM LOAD	OVENDRIED	37.3±18.7
	Impregnated (54 & 65% styrene solutions) irradiated & humidified	17.9±15.5

* Data presented with 95% confidence limits;
Except where noted, the dose was 4 M rads

TABLE 9

STRENGTH - PROPERTY DATA OF OVENDRIED (10)
IMPREGNATED WOOD (BASIS: HUMIDIFIED WOOD)

STRENGTH PROPERTY	ALTERED WOOD TREATMENT*	CHANGE %
MAXIMUM TENSILE STRENGTH	Impregnated (54% styrene solution) irradiated, ovendried	-31±7.3
	Impregnated (pure styrene) irradiated, ovendried	nil
MAXIMUM CRUSHING STRENGTH	Ovendried	57.4±3.4
	Impregnated (54% styrene solution) irradiated, ovendried	17.3±5.3
	Impregnated (pure styrene) irradiated, ovendried	47.1±10.3

*DOSE WAS 4 Mrads

TABLE 10

STRENGTH PROPERTIES OF OVENDRIED, IRRADIATED WOOD (BASIS: OVENDRIED WOOD)*

STRENGTH PROPERTY	WOOD TREATMENT+	CHANGE IN PROPERTY %
MODULUS OF RUPTURE	A	-23.8±8.1
	B	-6.4±6.2
STRESS AT PROPORTIONAL LIMIT	A	0
	B	38.3±6.3
MODULUS OF ELASTICITY	A	-1309±4.7
	B	0
WORK TO PROPORTIONAL LIMIT	A	70.4±34.2
	B	63.8±24.9
WORK TO MAXIMUM LOAD	A	-33.2±16.2
	B	-40.0±14.4

* Data presented with 95% confidence limits

\+ A Impregnated with styrene, methanol, water (54:42:4 by volume), irradiated (4 Mrads) and ovendried.

B Impregnated with pure styrene, irradiated, (4 Mrads), and ovendried

4. The E.S.R. work done by Werezak indicated a grafting frequency of about one site out of two available sites on the cellulose chain.

5. The maximum crushing strength and the strength properties associated with compression such as the stress at the proportional limit and the work to the proportional limit (Table 8) are equal or higher for the treated wood than for the untreated wood is attributed to bulking. Therefore, it can be seen that wood treated with a solution of styrene, methanol and water, although being weaker in some properties, displays improvements in others. However the enhancement, in contrast to that reported by the previous workers, is not striking.

6. The situation for the wood treated with pure styrene is different, and it is observed that the strength properties of wood treated with pure styrene are better or at the least as good as the untreated wood. It is also noted from Ramalingams' results that wood in which pure styrene was allowed to polymerize thermally with a catalyst yields modulus of rupture values which are identical with the radiation-initiated treated wood.

Recently Gibson et al impregnated (22) wood with methyl methacrylate, either with pure monomer or in aqueous dioxane solution. Polymerisation was effected with γ-radiation. Even at low loadings, composite materials with satisfactory strength properties were produced in each case. Both types of treatment effectively slows down the rate of access of water or water vapour to the treated blocks.

Both procedures confer some measure of dimensional stability to the products. At low loadings, better antishrink efficiency was obtained with methyl methacrylate alone than when it was dissolved in aqueous dioxane.

This may be due to cell wall disruption in the latter process.

Infra-red measurements indicated that in experiments with aqueous dioxane solutions, no evidence could be obtained for graft copolymerisation of the poly (methyl methacrylate) with the cell wall polysaccharides. The results suggest that, if grafting is obtained at all, it may be to the wood lignin.

Chapter IV - Experimental Details

a) Materials.

1. Wood

Red pine sapwood was employed in this work because of its high porosity and good uniformity of its samples. A detailed description of this wood concerning its structural features is given in Ref. 48. Clear and knot-free planks of red pine sapwood were selected from an assortment of planks. These were planed to a dimension of approximately 0.625" x 0.625" x 0.625" and measured to 0.001 inches after heating in an electric oven at 100° - 105°C to constnat weight. Only those samples were employed in this work which had a density in the range (0.435 - 0.475 gms./c.c.) in the oven dried state.

2. Styrene

Styrene monomer (supplied by Polymer Corporation) was purified by removing the inhibitor (tert. butyl catechol) with 10% by volume sodium hydroxide solution, washing with distilled water and then drying over anhydrous calcium sulphate followed by distillation under reduced pressure.

3. Acrylonitrile

Acrylonitrile (Eastman Organic Company, Practical) was purified by distilling over silica gels.

4. Trichloroethylene.

Trichloroethylene (Allied Chemical Company, reagent grade) was used without further treatment.

5. Vinyl Acetate

Vinyl acetate (Fisher reagent) was used as supplied.

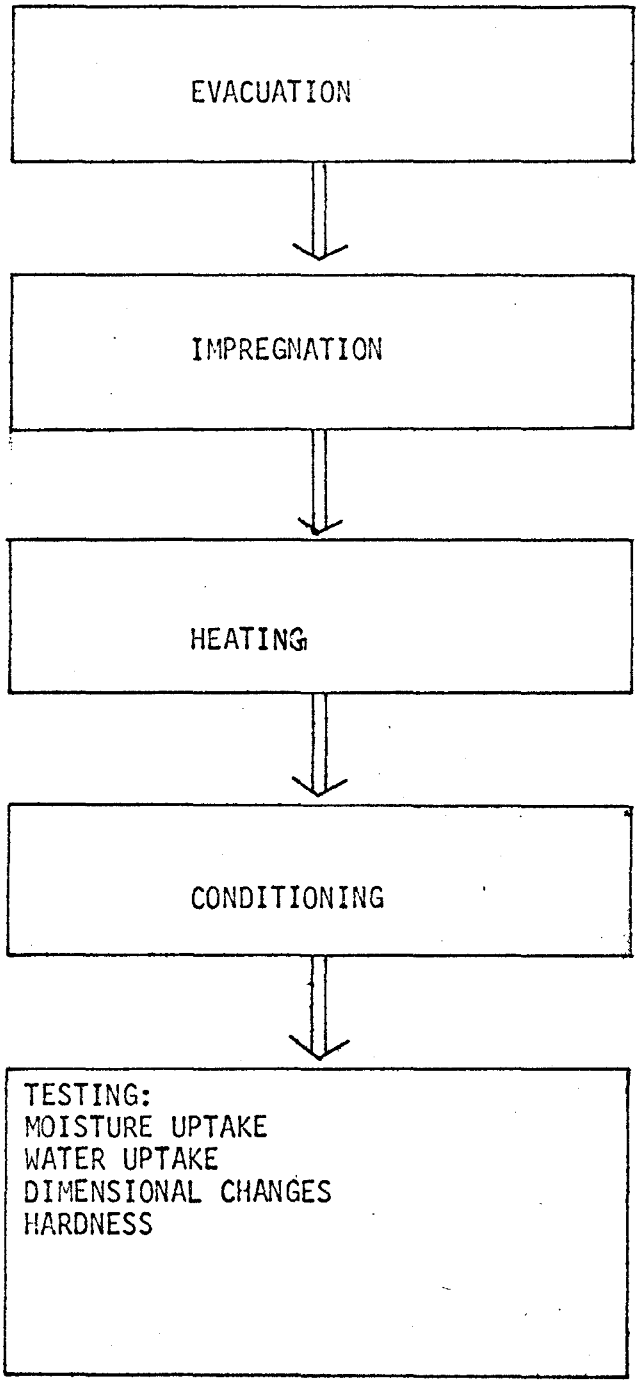


Fig. 5. Experimental Method.

6. Vinyl Chloride

Vinyl chloride monomer (Matheson & Co. Polymerisation grade) was used as supplied without further purification.

7. Cyclohexane

Cyclo-Hexane was used as supplied (Fisher Certified Reagent).

8. Isobutylene

Was used as supplied (Matheson & Co.).

9. Benzoyl Peroxide

Benzoyl peroxide initiator was used as such without further purification (Fisher Reagent).

10. 2-Azo-bis-isobutyronitrile

2-Azo-bis-isobutyronitrile (Eastman Kodak, reagent) was purified by reprecipitating it from Methanol.

b) Method.

The experimental method which was employed in this process involved four separate operations (Fig. 5). The wood samples were fixed in a wire frame which was then placed in a thick walled glass reactor (Fig. 6). There was a constriction at the top of the reactor. The wire frame was designed so as to keep the wood samples fixed in the upper half portion of the reactor, to prevent them from floating and to keep them separated from each other. The feed was introduced into the reactor and its volume was adjusted so that its surface was about 1 1/2" below the lowest wood sample. Before starting evacuation, the lower portion of the reactor was frozen in a suitable freezing mixture (Fig. 6b) depending upon the nature of the feed. This was followed by the four operations. These are:

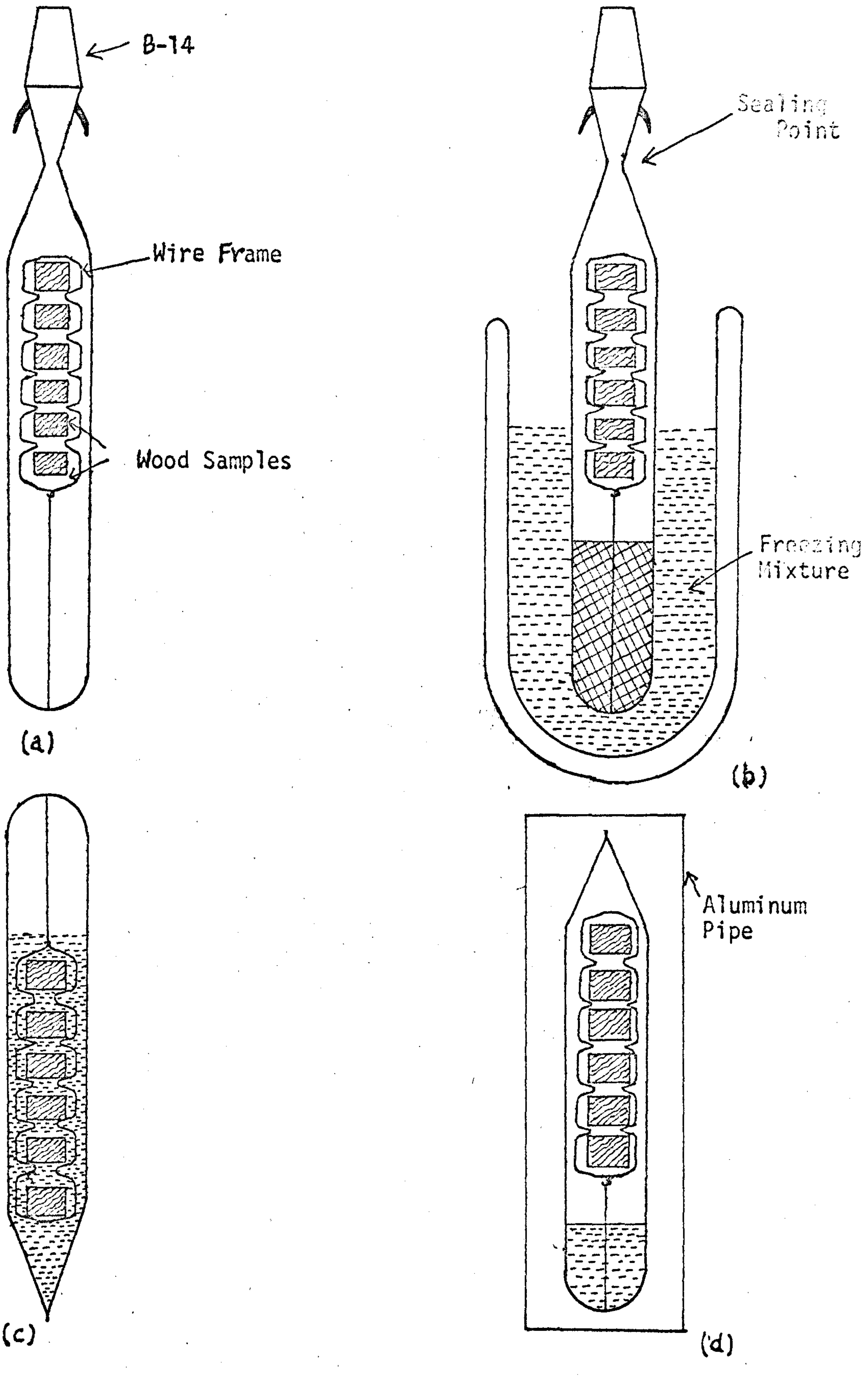


Fig. 6 Impregnation Procedure

1. Evacuation:

The evacuating system consisted of a vacuum line (Fig. 7) with a Duo-Seal high capacity oil pump for coarse vacuum (10^{-2} mm of Hg) and a mercury diffusion pump (10^{-3} mm of Hg)for fine vacuum. There was a series of liquid nitrogen traps, a "gas blow off", a vapour condenser and an Edwards' vacuostat, (range 1 m.m. - 10^{-3} m.m. of Hg.) served to measure low pressure obtained. Evacuation was carried out for periods up to 8 hours at a pressure of one micron of mercury.

The purpose of evacuation was to remove both air and free water from the wood. This degassing has two advantages. Firstly it permits larger monomer uptake, secondly it removes oxygen which inhibits the polymerisation reaction.

2. Impregnation:

When the desired evacuation had been obtained, the reactor was removed from the vacuum line by sealing the reactors under vacuum at the constriction. The reactor was removed from the freezing mixture and the feed solution allowed to liquify. Then the reactor was inverted (Fig. 6C) thereby completely immersing the wood samples. The wood samples were kept in this state for specific lengths of time and at suitable higher temperatures determined by the nature of the impregnant. The reason for employing the higher temperature was to generate sufficient impregnation pressure.

The various impregnants employed in this work included benzoyl peroxide or 2-azo-bis-isobutyronitrile as the polymerisation initiator dissolved in one of the following:

1. Vinyl Chloride

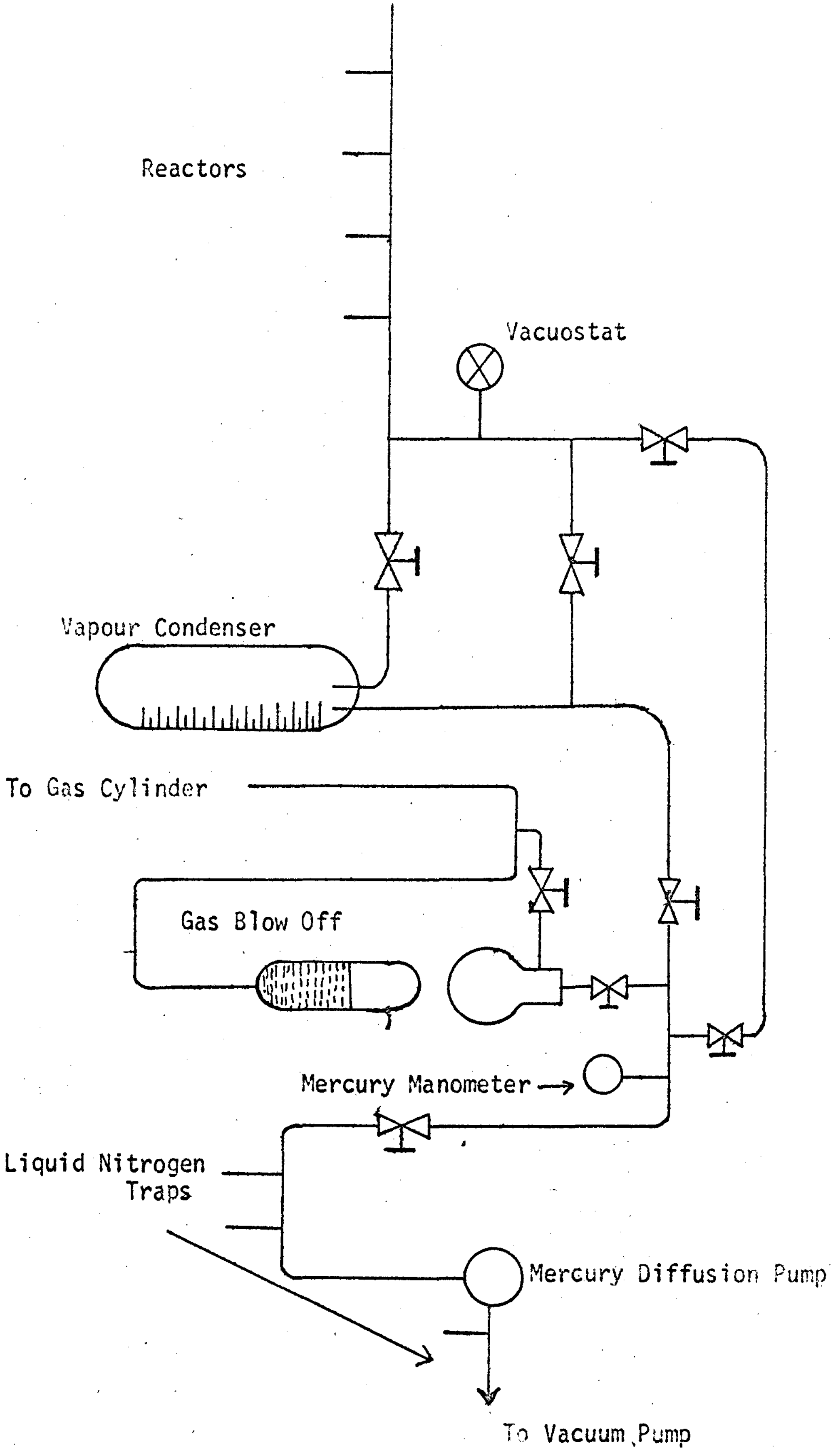


Fig. 7. Vacuum Line

2. Vinyl chloride and Trichloroethylene
3. Vinyl chloride and Cyclohexane.
4. Vinyl chloride and Isobutylene.
5. Vinyl chloride and Vinyl acetate.
6. Styrene and Acrylonitrile.

3. Heating:

After impregnation the reactor was reinverted. Now, in this normal position of the reactor, the left-over impregnant collected at the bottom of the reactor. The reactor was then introduced into an aluminum pipe (Fig. 6d), and transferred to a constant temperature bath. The pipe is useful in confining any possible explosion of the reactor due to sudden development of high pressures within its limits. The reaction was allowed to proceed for a specific period of time in the constant temperature water bath maintained at a suitable temperature.

4. Conditioning:

At the end of the reaction period, the reactor was removed from the constant temperature bath and cooled. The wood samples were then removed by carefully breaking the reactor. Each sample was heated to drive off the unreacted monomer. Normally an electric oven is sufficient to achieve this but for thermally unstable polymers, a vacuum oven operating at about 50°C was necessary. A specific example is poly vinyl chloride which is unstable at higher temperatures. The samples were heated to constant weight.

c) Testing.

1. Hardness:

The standard (102) hardness test had to be modified because the steel hemisphere of 1.13 cms. in diameter, when imbedded in the treated samples to a depth equal to its radius, splits the wood polymer composite. Therefore the modification consisted of applying a load of 500 lbs. on the hemisphere and measuring the depth of penetration. The other modification was the size of specimens which was much smaller than the standard samples. Hardness tests were carried out on the samples in the oven dried state. This was an arbitrary modification but it did provide a means of comparison between the controls and the WPC. All hardness tests were made in the transverse direction of wood.

2. Dimensional Stability Tests:

The treated wood specimens were subjected to the following tests. The same tests were also run on the control samples.

A. Volumetric Change:

The dimensions of the oven dried samples were measured before and after equilibration to an atmosphere of 76% R.H. at 25°C for a period of 24 hours and the change in tangential and radial dimensions as well as the overall change in the volume was recorded. The dimensions were measured to 1/1000th of an inch.

B. Moisture Absorption:

The oven dried samples were placed in an atmosphere of 76% R.H. at 25°C for a period of 24 hours. The change in the weight of the samples as a result of this treatment indicated the amount of moisture absorbed.

C. Water Absorption:

Oven dried samples were immersed in distilled water at room temperature and atmospheric pressure for a period of 30 days. The weight increase based upon the initial oven dried weight gave the amount of water absorbed.

D. Volumetric Swelling:

Oven-dried wood samples of known volume were placed in distilled water at room temperature and atmospheric pressure for a period of 30 days. The increase in volume based upon the oven dried volume indicated the volumetric swelling of the sample. This formed a basis for calculating "antishrink efficiency".

Chapter V - Results of Experimentation

a) Definitions:

1. Percent Polymer Retention:(gms. polymer/100 c.c. of wood)

This term represents the weight of the polymer remaining in the wood after treatment, divided by the original volume of wood and expressed on percentage basis. The weight of polymer was deduced from the difference of the weight of the final treated sample from the original weight of the oven dried wood.

2. Percent Loading:(gms. of polymer/100 gms. of wood)

The percent loading is the weight of the polymer remaining in the wood after treatment, expressed as a percentage of the original weight of wood in the oven dried state.

3. Percent Moisture Uptake:(M)

This term means the amount of water vapour absorbed by wood, when placed in an atmosphere of 76% relative humidity at 25°C for a period of 24 hours and expressed on percentage basis.

4. Percent Volumetric Change:

This is defined as the change in the volume of a wood sample (oven dried), when it is placed in an atmosphere of 76% R.H. at 25°C for a period of 24 hours and expressed on a percentage basis.

6. Antishrink Efficiency:

Antishrink efficiency = $100 \times \frac{SCW-STW}{SCW}$ whereas SCW is the percent swell in the control sample and STW is the percent swell in the treated SAMPLE. ~~wafer.~~ Percent swell means the over-all change in the volume of the sample when immersed in water for a period of 30 days.

7. Hardness:

It has been defined in terms (Chapter IV) of the depth of penetration made by a steel sphere (dia. 1.13 cms) when impressed upon the sample with a weight of 500 lbs.

b) Experiments With Wood-Poly Vinyl Chloride System:

The results of polymerisation of vinyl chloride in wood cavities using benzoyl peroxide as a free radical initiator are presented in Table 11. The conditions under which these experiments were carried out are listed on the table.

These results reveal that, although wood polymer combinations with relatively high polymer loading can be prepared, there is little improvement in mechanical properties compared to untreated wood. These results are not beyond expectation, since poly vinyl chloride starts precipitating out during polymerisation in the form of a fine, powdery non-homogeneous polymer with no mechanical strength. These results are analogous to those reported by Kent et al. (7). In some experiments it is observed that the polymer, is in the form of a mixture of glass like and powdery phases (numbers 2 and 5). In those experiments (numbers 3 and 4) in which higher temperatures and catalyst concentration are used, the samples are badly split up and blackened.

In order to avoid the precipitation of P.V.C. during polymerisation, it was logical to prepare wood polymer combinations by homogeneous polymerisation of vinyl chloride, therefore polymerisation was catalytically initiated in wood impregnated with a solution of vinyl chloride in cyclohexane (1:1) by volume. The results are listed in Table 12. An analysis of these results indicate that the extent of

TABLE 11

DATA ILLUSTRATING THE COMPATIBILITY OF WOOD - PVC[a] COMBINATIONS

EVACUATION LEVEL = 1 MICRON
EVACUATION TIME = 8 HOURS
IMPREGNATION TEMP = 0°C

EXPERIMENT NUMBER	% LOADING G POLYMER/ 100G WOOD	TEMP. OF HEATING °C	CATALYST CONC. GMS/100GMS V.C.	TIME HOURS	REMARKS
1[+]	101	50	2	24	WHITE, POWDERY NON-HOMOGENEOUS POLYMER, NO IMPROVEMENT IN HARDNESS.
2	95	60	2	18	PARTIALLY GLASS LIKE. NON-HOMOGENEOUS, SLIGHTLY DARKENED POLYMER.
3	87	50	4	18	BLACK, PARTIALLY PLASTICIZED POLYMER
4	76	60	4	16	WOOD SAMPLES BADLY SPLIT UP. BLACK PARTIALLY PLASTICIZED POLYMER.
5[±]	96	60	2	16	MIXED WHITE POWDERY AND GLASS LIKE POLYMER.

(a) BULK POLYMERISATION.

(+) EVERY OBSERVATION REPRESENTS AN AVERAGE OF SIX MEASUREMENTS MADE ON ALL THE SIX SAMPLES WHICH WERE TREATED SIMULTANEOUSLY IN THE SAME REACTOR.

(±) 2% TRI-CHLORO ETHYLENE USED AS A CHAIN TRANSFER AGENT.

TABLE 12

DATA ILLUSTRATING THE COMPATIBILITY OF WOOD PVC COMBINATIONS

EVACUATION LEVEL = 1 MICRON
EVACUATION TIME = 8 HOURS
IMPREGNATION TIME = 15 MINUTES

FEED COMPOSITION = VINYL CHLORIDE: CYCLOHEXANE (1:1) BY VOLUME

EXPERIMENT NUMBER (a)	%LOADING G POLYMER/ 100G WOOD	TEMP. OF REACTION °C	CATALYST CONC. GMS.CAT/ 100 GMS SOLUTION (b)	TIME HOURS	REMARKS
1	42	50	1.5	24	WHITE POWDERY SOLID. NO IMPROVEMENT IN HARDNESS.
2	46	70	1.5	20	" " " "
3	41	50	3.0	18	" " " "
4	39	70	3.0	16	" " " "

(a) EVERY OBSERVATION REPRESENTS AN AVERAGE OF SIX MEASUREMENTS MADE ON ALL THE SIX SAMPLES WHICH WERE TREATED SIMULTANEOUSLY IN THE SAME REACTOR.

(b) CATALYST USED WAS 2-AZO-BIS-ISOBUTYRONITRILE

TABLE 13

DATA ILLUSTRATING THE COMPATIBILITY OF WOOD - VINYL CHLORIDE COPOLYMER COMBINATIONS

CATALYST: BENZOYL PEROXIDE
EVACUATION LEVEL...1 MICRON
EVACUATION TIME....8 HOURS
IMPREGNATION TIME..15 MINUTES

NO. (a)	COMONOMER		% POLYMER LOADING G POLYMER /100G WOOD	CATALYST CONC. G/100G COMONOMER SOLUTION	TEMP °C	REACTION TIME HOURS	REMARKS
	NAME	VOLUME %					
1	ISOBUTYLENE	35	60	2.0	60	100	SOFT, RUBBERY HOMOGENEOUS POLYMER
2	VINYL ACETATE	15	70	2.5	60	16	WHITE, POWDERY NON-HOMOGENEOUS POLYMER
3	VINYL ACETATE	15	80	2.5	50	24	" " "

(a) EVERY OBSERVATION REPRESENTS AN AVERAGE OF SIX MEASUREMENTS MADE ON ALL THE SIX SAMPLES, TREATED SIMULTANEOUSLY IN THE SAME REACTOR.

polymer loading appears to be lesser than the heterogeneous polymerisation (Table 11). Again the results suggest that no upswing in property improvement could be noticed due to the nature of the polymer formed.

In an attempt to produce homogeneous, thermally stable and mechanically strong W.P.C. using vinyl chloride, one of the cheapest monomers, the samples were impregnated with a solution of vinyl chloride and comonomers and subsequently copolymerised in situ in wood. Results of such experimentation are presented in Table 13. These results indicate that although homogeneous plasticised copolymers could be prepared but the major drawback is that the process appears to be very tedious and time consuming. (Tables 11 - 13).

c) Wood-Poly (Styrene-Acrylonitrile) System:

From a consideration of the results of polymerisation of vinyl chloride in bulk, in solution and copolymerisation with monomers such as vinyl acetate and isobutylene (Tables 11-13), it appears that, although WPC could be prepared with fairly large polymer loadings, they have the following disadvantages:

1. Non-uniform distribution of polymer throughout a given sample (indicated by cutting the treated samples into thin slices and observing them under a microscope)
2. Thermally unstable.
3. Little improvement in mechanical properties.
4. A very time-consuming process.

Therefore an attempt was made to investigate the effect of initiating copolymerisation in wood impregnated with a solution of styrene and acrylonitrile, since styrene/acrylonitrile copolymers offer the possibility of several distinct advantages. These are:

1. Tougher and stronger copolymers,
2. Heat and light stability
3. A simple and short process.

In this section, the results of experimentation on the laboratory evaluation of styrene/acrylonitrile system for use in the wood plastic combinations are reported. The method adopted for experimentation was a statistical design based upon the factorial concept.(104) The advantage of this approach lies in the fact that if any interaction effect exists, that is, if property improvement is dependent upon a particular combination of two variables, the use of a factorial design will give the effect of each variable independent of the interaction effects. If interaction effects are negligible, then the pattern of a factorial design still holds the advantage of permitting easy determination of the main effects.

In this work, a factorial scheme was employed which permitted the results to be analysed by ANOVA (114) (Analysis of Variance). A computer program was developed to carry out ANOVA on an I.B.M. 7040 computer.

Following are the variables which are likely to have an effect on the properties of WPC.

1. Evacuation:

The objective of evacuation is to remove both air and water from the wood. This degassing has two advantages. Firstly it permits larger monomer uptake, secondly it removes oxygen which inhibits the polymerisation reaction. Previous experience (7,13) showed that eight hours of evacuation time at a pressure of 10^{-3} m.m. of mercury is sufficient to achieve the desired objective.

2. Impregnant Composition:

At "azeotropic feed" composition of 76 weight percent of styrene, the composition of the copolymer (7) is the same as that of the feed up to high conversions. At other feed compositions, varying degrees of drift of copolymer composition occurs. In order to avoid a widely varying mixture of copolymers of different compositions, the feed should be approximately the azeotropic composition. Incompatibility of the various copolymers in WPC would result in a nonhomogeneous plastic and hence a lack of good physical properties.

A second requirement for copolymerising styrene and acrylonitrile is to achieve a rate of copolymerisation great enough to make this system satisfactory in the thermo-catalytic process. The presence of acrylonitrile monomer determines (7) the high rate of copolymerisation of styrene/acrylonitrile system , therefore the feed composition should be adjusted so that during the entire course of copolymerisation, acrylonitrile is in excess. This can be attained by using an initial feed containing slightly less than the azeotropic composition of 76% styrene. At these compositions (7) styrene enters the copolymer at a faster rate than the acrylonitrile, thereby causing an accumulation of acrylonitrile monomer in the feed and further acceleration of the rate. Towards the end of the process, styrene should be taken up almost completely to result in a product free of styrene monomer. Therefore a feed composition of (60:40) by weight of styrene and acrylonitrile was chosen. This is based upon the work reported by Kent et. al. (7). Being closer to the azeotropic composition, it would produce a copolymer which, having a narrower range of copolymer compositions would have greater internal compatibility and thus greater strength (7) in addition to having a higher rate of copolymerisation.

3. Nature of Initiator:

As previously pointed out in Chapter II, every polymerisation initiator has a characteristic "catalyst efficiency", therefore it was desirable to examine this variable. Two different types of initiators were chosen, i.e., benzoyl peroxide and 2-azo-bis-isobutyronitrile.

4. Concentration of Initiator: (C)

The molecular weight distribution and rate of reaction depend upon this variable, therefore it was decided to study the effect of this variable on the properties of the final product.

5. Temperature of Heating:(T)

The rate of reaction, molecular weight distribution and the copolymer composition depends upon the temperature at which the reaction is carried out, therefore the heating temperature becomes an important independent variable.

6. Time of Reaction: (R)

The yield of polymer in the reaction depends upon the time of reaction; therefore it was desirable to treat this as an independent variable. This also serves the purpose of making available WPC with varying polymer loadings, thus enabling a correlation of the properties of wood polymer combinations with percent polymer retention in wood.

For a more thorough discussion of 3,4,5 and 6 reference is made to Chapter II.

Depending upon the kinetics (73) of the copolymerisation process, two levels of each of the following independent variables were chosen:

1) Temperature of heating.
2) Catalyst concentration.
3) Time of reaction.

Other variables, for example, evacuation time, feed composition, and impregnation time were treated as constants.

In order to investigate the effect of the nature of catalyst, two factorial schemes were designed; each of the two schemes was carried out using a different catalyst with two levels of each of the three independent variables. The catalysts studied were: benzoyl peroxide and 2-azo-bis-isobutyronitrile in the first and second factorial designs respectively.

1. Factorial Design Number one:

Eight separate experiments each consisting of seven wood samples were carried out. The reactors were designed so as to treat seven wood samples simultaneously. For the results given in Table 14, the following experimental conditions were used. The results of testing on control samples are given in Table 15.

Expt. No.	Initiator Concentration (g/100g comonomer solution)	Reaction Time (Hours)	Temp. of Heating(°C)	
	|A|	C	B	
1	0.400	8	50	B
2	0.400	4	70	C
3	0.400	4	50	A
4	0.400	8	70	D
5	1.200	4	50	E
6	1.200	8	50	F

TABLE 14

(FACTORIAL EXPERIMENT NO. 1)

EVACUATION LEVEL....1 MICRON
EVACUATION TIME.....8 HOURS
IMPREGNATION TIME...1 HOUR

EXPERIMENT NUMBER	% POLYMER RETENTION GMS/100 CC WOOD	% LOADING GMS POLYMER/ 100 GMS WOOD	% CHANGE IN TANGENTIAL DIRECTION CMS/100CMS OF O.D. WPC	% CHANGE IN RADIAL DIRECTION CMS/ 100 CMS OF O.D. WPC.	% CHANGE IN VOLUME CC/100CC OF O.D. WPC	% MOISTURE UPTAKE GMS/ 100 GMS O.D. WPC	HARDNESS DEPTH OF PENETRATION IN M.M.
1.	28.03 (1.13)	61.84 (3.14)	1.27 (0.12)	1.03 (0.14)	2.34 (0.42)	4.61 (0.27)	0.56
2.	38.72 (0.35)	85.11 (0.64)	0.42 (0.03)	0.54 (0.26)	0.94 (0.27)	2.46 (0.15)	0.41
3.	16.07 (0.20)	34.71 (0.22)	1.89 (0.03)	1.24 (0.11)	3.22 (0.0005)	6.01 (0.11)	0.84
4.	29.03 (1.17)	62.76 (2.64)	0.65 (0.04)	0.73 (0.05)	1.33 (0.08)	3.50 (0.24)	0.76
5.	31.53 (1.91)	68.58. (3.42)	0.92 (0.11)	0.79 (0.17)	1.82 (0.23)	4.25 (0.44)	0.69
6.	41.29 (0.72)	87.47 (0.92)	1.06 (0.03)	1.20 (0.19)	2.23 (0.25)	4.76 (0.29)	0.39
7.	35.71 (0.36)	76.57 (1.93)	0.68 (0.07)	0.57 (0.04)	1.26 (0.14)	2.64 (0.33)	0.41
8.	34.65 (0.72)	75.83 (1.90)	0.47 (0.25)	0.39 (0.08)	1.04 (0.27)	2.00 (0.67)	0.52

1. ALL RESULTS ARE PRESENTED AS THE AVERAGE OF NOT LESS THAN THREE SAMPLES, WHICH FELL WITHIN 99% CONFIDENCE RANGE

2. FIGURES IN BRACKETS GIVE THE STANDARD DEVIATION IN EACH EXPERIMENT.

Table 15

PROPERTIES OF UNTREATED WOOD

Percent Volume Change of Oven Dried Wood cc/100 cc of Oven Dried Wood	5.21*
Percent Moisture Uptake G./100 G of Oven Dried Wood	9.43
Percent Change in Tangential Direction (CMS/100 CMS of Oven Dried Wood)	2.87
Percent Change in Radial Direction	2.03
Hardness Depth of Indentation (m.m.)	1.74

All Results are reported as the average of 9 measurements made on 9 different samples.

* All results are significant at 99% confidence level.

7	1.200	4	70	G.
8	1.200	8	70	H.

These results were analysed by a three way analysis of variance, the dependent variables examined were:

1. Percent volume change (V) (Table 16)
2. Percent moisture uptake (M) (Table 17)
3. Hardness (H) (Table 18)

Referring to tables 16 and 17, it appears that since F0.05 (1,4) = 7.71, only the row effect is significant, therefore heating temperature has effect on the percent volume change and percent moisture uptake within the range of temperatures studied but the heating time and catalyst concentration do not have significant effect on the dependent variables within the range investigated. The interaction effects are also not significant. However hardness (Table 18) is not affected by any of the independent variables or their interactions. Comparing these results (Table 14) with those of testing on untreated controls (Table 15) the following conclusions can be drawn.

1. The change in the volume of the treated samples when exposed to an atmosphere of 76% R.H. at 25°C, relative to the control samples decreases by about 38 to 82% depending upon the polymer loading and bath temperature.
2. The decrease in the moisture uptake of the treated samples relative to the untreated controls is in the range 34 - 82.5% depending upon the polymer loading and temperature of heating.
3. Hardness of the treated samples increases by an amount of 52 to 77.5% than the untreated control samples.

TABLE 16

ANOVA OF PERCENT VOLUME CHANGE (V)

C (Column)	Effect means effect on response due to initiator Concentration.
R (Row)	Effect means effect on response due to Heating Temperature.
L (Layer)	Effect means effect on response due to Reaction Time.

	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE	TEST STAT.
C (Column)	1	0.3	0.3	1.916
R (Row)	1	3.2	3.2	22.224
L (Layer)	1	0.0	0.0	0.079
C x R	1	0.3	0.3	2.075
C x L	1	0.1	0.1	0.405
R x L	1	0.1	0.1	0.358
Error	4	0.6	0.1	- ---

TABLE 17

ANOVA OF PERCENT MONOMER UPTAKE (M)

	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE	TEST STATISTIC
C (Column)	1	1.1	1.1	2.313
R (Row)	1	10.2	10.2	21.971
L (Layer)	1	0.0	0.0	0.065
C x R	1	0.0	0.0	0.023
C x L	1	0.0	0.0	0.014
R x L	1	0.2	0.2	0.448
Error	4	1.9	0.5	- ---

TABLE 18

ANOVA OF HARDNESS (H)

	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE	TEST STATISTICS
C (Column)	1	0.0	0.0	1.035
R (Row)	1	0.0	0.0	0.477
L (Layer)	1	0.0	0.0	0.048
C x R	1	0.0	0.0	0.021
C x L	1	0.0	0.0	0.223
R x L	1	0.1	0.1	3.570
Error	4	0.2	0.0	-----

2. Factorial Experiment Number two:

Eight separate experiments each consisting of seven wood samples were carried out. For the results given in Table 19 the following experimental conditions were used.

Expt. No.	A Initiator Concentration (g./ 100 g. comonomer solution)	C Reaction Time (Hours)	B Temp. of Heating (°C)
1	0.300	3	60
2	0.300	5	60
3	0.300	5	70
4	0.300	3	70
5	0.900	3	70
6	0.900	5	70
7	0.900	3	60
8	0.900	5	60

These results were analysed by three way analysis of variance. The results of ANOVA are reported in Tables 20 - 22.

These results indicate that unlike the first factorial experiment none of the independent variables has a significant effect upon the dependent variables, nor is there any significant interaction effect within the range of independent variables examined.

Somewhat similar to the results of first factorial experiment, the following trends are established:

1. The change in the volume of the treated samples, after exposure to an atmosphere of 76% R.H. at 25°C, relative to the control samples decreases by about 52 to 82.5% and is dependent upon the polymer loading.

TABLE 19

(FACTORIAL EXPERIMENT NUMBER 2

EVACUATION LEVEL.......1 MICRON
EVACUATION TIME........8 HOURS
IMPREGNATION TIME......1 HOUR

EXPERIMENT NUMBER	% POLYMER RETENTION GMS/100 CC WOOD	% LOADING GMS POLYMER/ 100 GMS WOOD	% CHANGE IN TANGENTIAL DIRECTION CMS/100CMS OF O.D. WPC	% CHANGE IN RADIAL DIR-ECTION CMS/ 100 CMS OF O.D. WPC	% CHANGE IN VOLUME CC/100CC OF O.D. WPC	% MOISTURE UPTAKE GMS/ 100GMS O.D. WPC	HARDNESS: DEPTH OF PENETRATION IN M.M.
1.	28.22 (0.45)	63.82	1.19 (0.08)	1.02 (0.03)	2.35 (0.05)	4.74 (0.07)	0.59
2.	39.86 (0.34)	87.20 (0.32)	0.59 (0.06)	0.78 (0.02)	1.44 (0.05)	3.02 (0.09)	0.43
3.	37.88 (3.42)	83.25 (8.19)	0.71 (0.08)	0.49 (0.04)	1.21 (0.09)	2.73 (0.19)	0.29
4.	36.52 (1.76)	78.91 (4.23)	0.44 (0.004)	0.54 (0.12)	0.92 (0.40)	2.29 (0.18)	0.58
5.	37.61 (1.02)	82.42 (4.05)	1.20 (0.04)	1.06 (0.20)	2.51 (0.38)	4.12 (0.005)	0.58
6.	39.94	85.05	0.70	0.42	1.19	2.17	0.59
7.	32.90	71.61	1.10	0.62	1.83	4.20	0.71
8.	42.61	91.91	1.01	0.82	1.82	4.37	0.37

1. ALL RESULTS ARE PRESENTED AS THE AVERAGE OF NOT LESS THAN THREE SAMPLES, THE INDIVIDUAL RESULTS BEING WITHIN 99% CONFIDENCE LEVEL.

2. FIGURES IN BRACKETS GIVE THE STANDARD DEVIATION IN EACH EXPERIMENT.

2. The percent decrease in the moisture uptake of the treated samples relative to the untreated controls is in the range 49.5% to 78% depending upon the polymer loading.
3. Hardness of the treated samples increases by 53 to 83.5% compared to the untreated controls.
4. The nature of the catalyst does not appear to have a significant effect upon the dependent variables, except that in the second factorial experiment, the lower catalyst concentration and the considerably shorter reaction time is a distinct advantage.

d) Moisture Uptake:

Figure 8 presents a comparison of relationships between water vapour uptake and time in days for the WPC [poly (styrene-A.N.)]* and untreated control samples. From the two curves it appears that the treated wood absorbed less than one third as much moisture as the untreated wood.

e.) Water Uptake:

1) Figure 9 shows a comparison of the curves between liquid water uptake and time in days for the WPC [poly (styrene-A.N.)]* and untreated controls. From the two curves it appears that the liquid water uptake of the treated wood is less than 40% of that of the untreated wood.

2) Antishrink Efficiency:

Figure 10 (a) shows the effect of polymer loading on the antishrink efficiency of WPC [Poly(styrene-A.N.)]* prepared by thermocatalytic methods without the use of a swelling agent. A comparison of these results with those of Kenaga (12) or Ross (15) (Figure 10 b), who

* Azo-bis-isobutyronitrile was used to initiate polymerisation.

TABLE 20

ANOVA OF PERCENT VOLUME CHANGE (V)

	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE	TEST STATISTIC
C (Column)	1	0.3	0.3	0.770
R (Row)	1	0.4	0.4	1.101
L (Layer)	1	0.8	0.8	2.411
C x R	1	0.3	0.3	0.976
C x L	1	0.0	0.0	0.006
R x L	1	0.5	0.5	1.403
Error	4	1.3	0.3	-----

TABLE 21

ANOVA OF PERCENT MOISTURE UPTAKE (M)

	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE	TEST STATISTIC
C (Column)	1	0.5	0.5	0.620
R (Row)	1	0.0	0.0	0.030
L (Layer)	1	1.9	1.9	2.223
C x R	1	3.2	3.2	3.609
C x L	1	0.0	0.0	0.021
R x L	1	1.4	1.4	1.655
Error	4	3.5	0.9	-----

TABLE 22

ANOVA OF HARDNESS (H)

	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE	TEST STATISTIC
C (Column)	1	0.0	0.0	0.575
R (Row)	1	0.0	0.0	0.256
L (Layer)	1	0.0	0.0	0.177
C x R	1	0.0	0.0	0.016
C x L	1	0.0	0.0	0.939
R x L	1	0.0	0.0	0.044
Error	4	0.1	0.0	-----

EXPOSURE TO 76% RELATIVE HUMIDITY AT ABOUT 25°C

WOOD POLY(STYRENE-ACRYLONITRILE COMBINATIONS)

INITIATOR: Azo-bis-isobutyronitrile

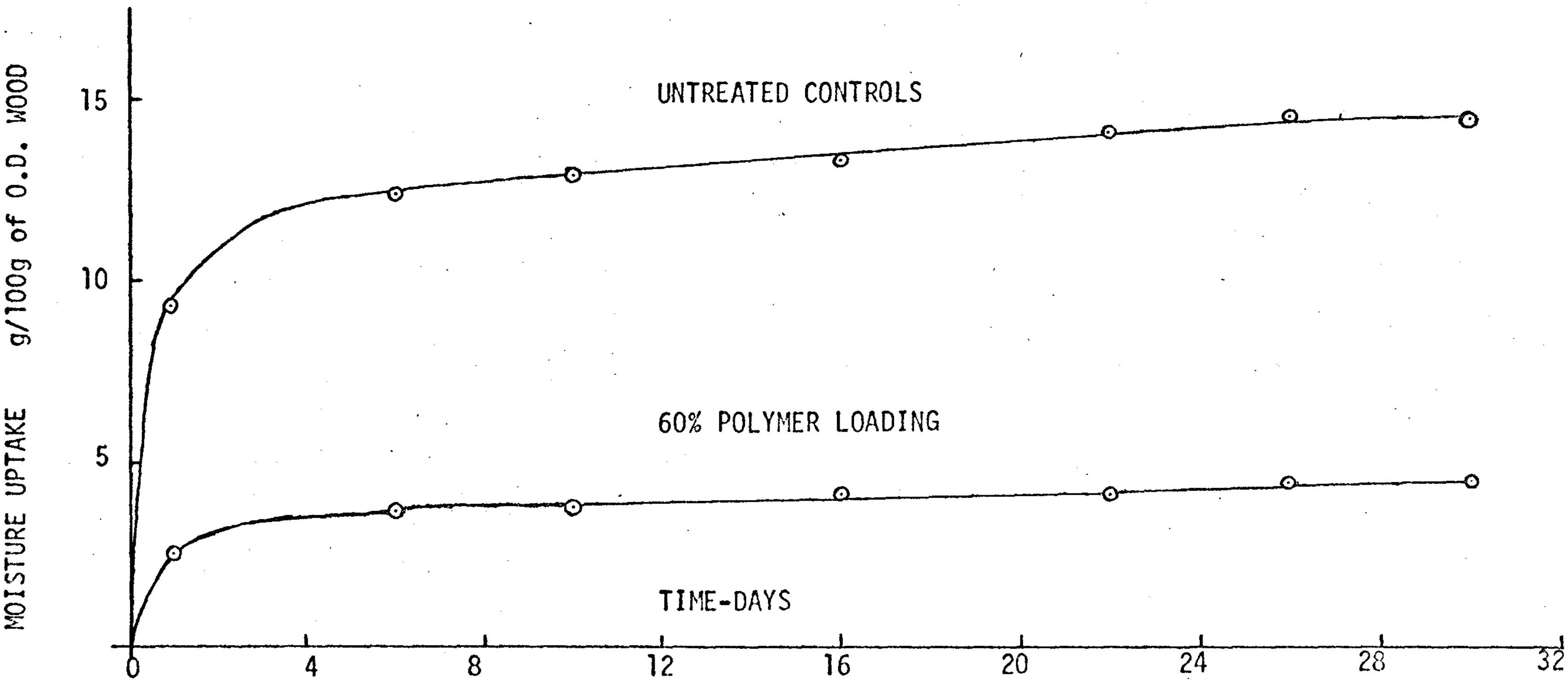


FIGURE 8 RELATIONSHIP BETWEEN MOISTURE UPTAKE AND TIME

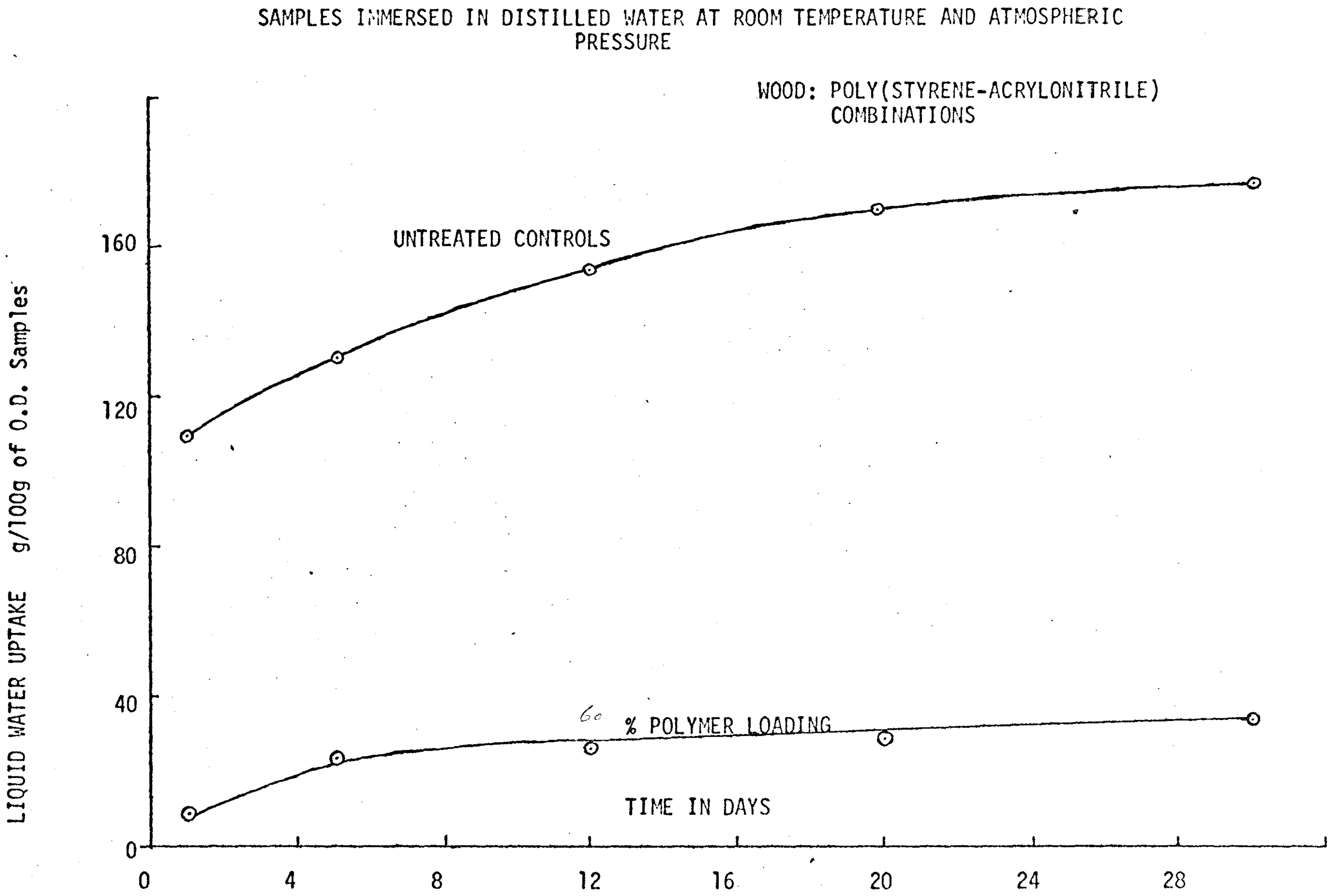


FIGURE 9 RELATIONSHIP BETWEEN LIQUID WATER UPTAKE AND TIME

Wood: Poly (styrene-acrylonitrile) composites
Initiator: Azo-bis-isobutyronitrile

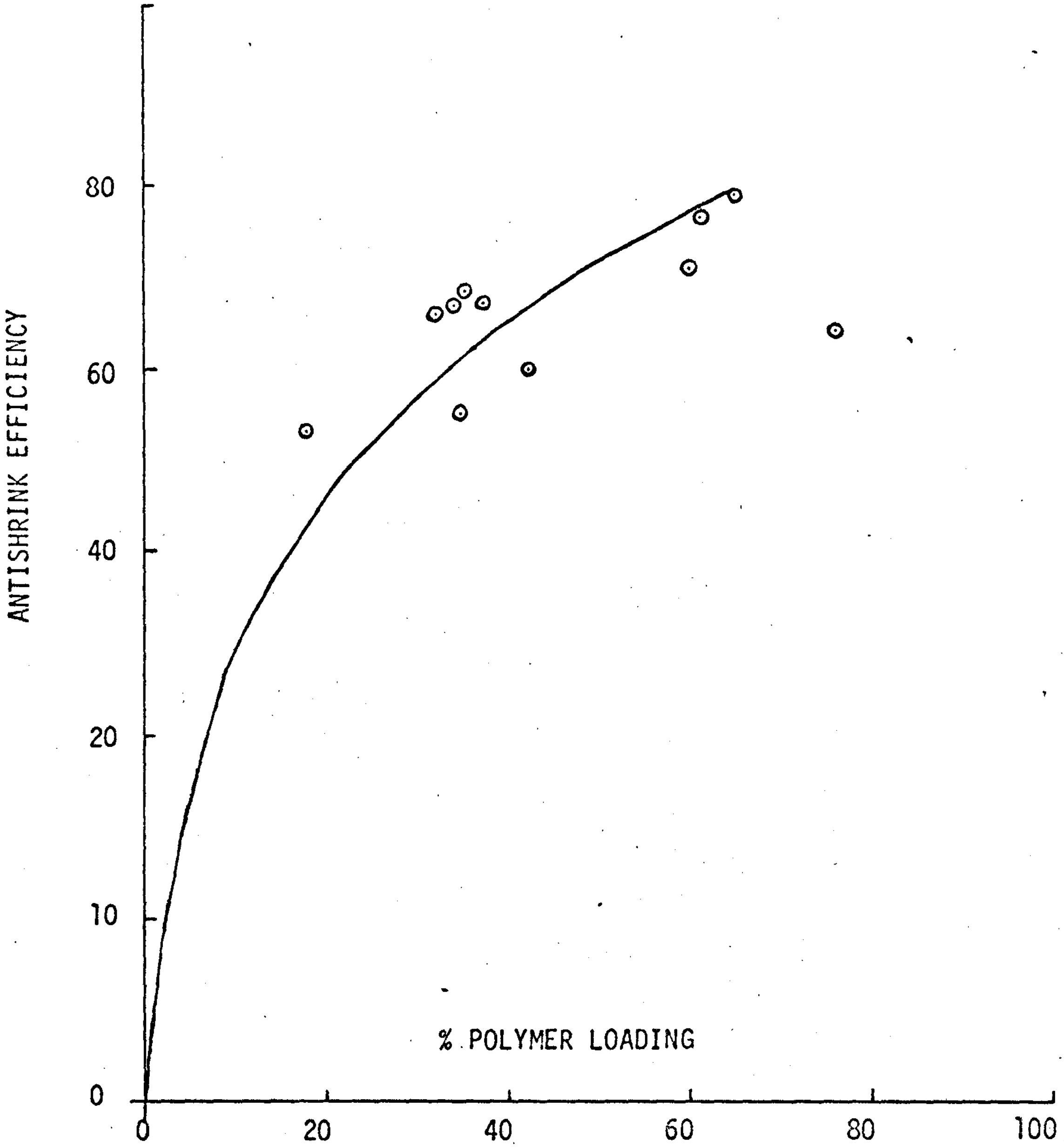


FIGURE 10A RELATIONSHIP BETWEEN % POLYMER LOADING & ANTISHRINK EFFICIENCY

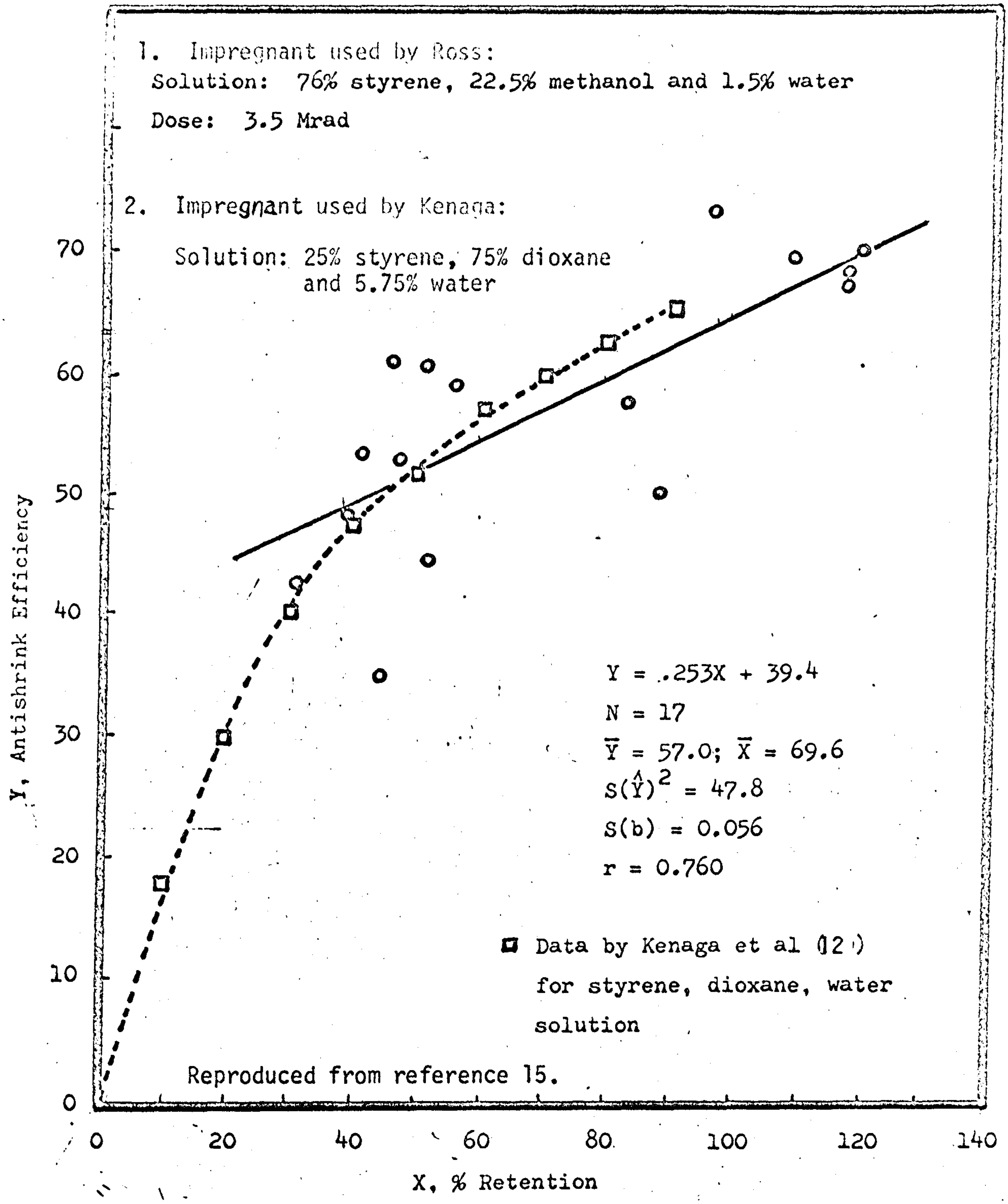


FIGURE 10b

RELATIONSHIP BETWEEN ANTISHRINK EFFICIENCY AND PERCENT RETENTION (after Werezak) used "Swelling-Impregnation-Irradiation" technique to produce WPC indicate that in the case of thermo-catalytic process one can get considerably higher antishrink efficiencies than those obtained by the "Swelling-Impregnation-Irradiation" technique, even at a lower polymer loading. In other words, the amount of polymer required for a given order of stability is lower as compared to the "Swelling-Impregnation-Irradiation technique".

Chapter VI

Discussion.

a). Characteristics of the Direct Heating Method:

The interpretation of results from the present work is greatly facilitated on the basis of Beall's (105) study of the direct heating method for the generation of wood-polymer-composites. According to Beall, there are three stages in the direct heating polymerisation process. This is illustrated in Figure 11, where the temperature attained at the centre of the wood-monomer-composite is plotted as a function of time of immersion in the water bath.

The period required for the wood-monomer composite to reach the bath temperature is known as the initial stage and it depends on the following factors for samples of identical geometry:

1. Initial temperature of the wood-monomer composite.
2. Temperature of the heating bath.
3. Density of the wood-monomer composite.
4. Thermal conductivity of the system.
5. Efficiency of heat transfer from the bath to the wood-monomer composite.

In the second stage, known as the induction period, the temperature remains fairly constant, since all free radicals generated by the thermal decomposition of the initiator react with the inhibitor instead of initiating the exothermic polymerisation reaction. The length of the induction period depends upon the following factors:

1. Inhibitor concentration.
2. Initiator concentration.

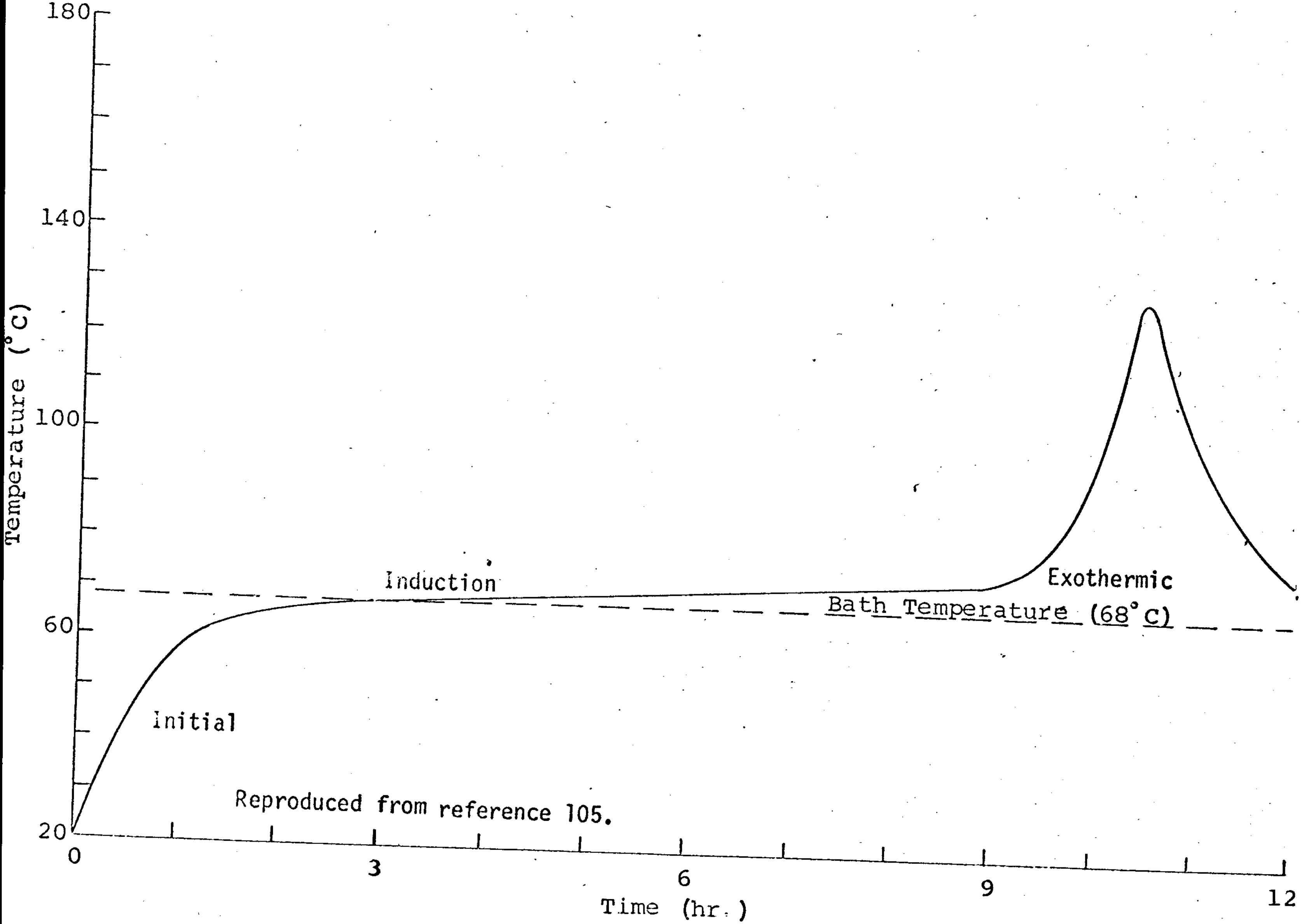


Figure 11 Preliminary test: center temperature variation of an aspen-monomer sample containing 0.2% benzoyl peroxide and 30 ppm hydroquinone with direct heating at 68°C.

3. "Half life" of the initiator.
4. Temperature of the water bath.

The final stage which is referable to as the exothermic period is characterised by an increase in temperature of the wood monomer composite to a maximum, with subsequent cooling off to the bath temperature.

The maximum temperature (105) attained and the slope of the exothermic curve are determined by:

1. Half life of the polymerisation initiator.
2. Nature of the monomer.
3. Amount of monomer in the wood.
4. The heat transfer characteristics of the system.

In the 'initial stage' of heating, transfer of heat occurs from the constant temperature bath to the wood monomer composite. During this stage, the temperature at the surface of the wood monomer composite is higher than at the centre of the wood. This difference in temperature depends upon the thickness of wood samples and the heat transfer characteristics of the wood-monomer composite. During the third exothermic stage, it is evident that the temperature will be higher at the centre of the wood compared to that at the surface.

In this stage there exists a temperature gradient in the wood monomer composite from its centre to the surface. Finally, the sample cools off to the bath temperature by the conventional heat transfer processes.

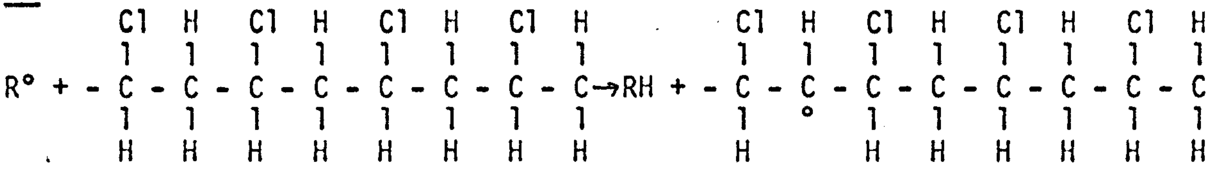
b). Study of the Wood-PVC System:

Considering the results given in Tables 11-13, it appears that although WPC with fairly good polymer loading can be prepared, they have the following drawbacks:

1.) Non-homogeneous polymers.
2.) Little improvement in mechanical properties.
3.) Lack of heat stability.
4.) Discoloring and splitting of wood samples.
5.) Time consuming process.

Because of the relatively higher heat of polymerisation, there is a local build up of heat, resulting in a higher maximum exothermic temperature, causing a thermal degradation of PVC. Degradation involves loss of HCl with the formation of conjugated double bonds along the chain leading to progressive discoloration of the polymer. Chain scission also occurs. It is likely that (106) hydrogen and chlorine atoms are successfully removed by a free radical mechanism, initiated either by oxidative attack or by photochemical reactions. Initiating radicals could come from a catalyst residue left from the polymerisation process or they could arise as a result of oxidation. A given radical attacks a methylene hydrogen atom preferentially. The labile chlorine atom thus produced in a beta position would be released to stabilize the molecule. This free chlorine atom could then abstract another methylene hydrogen atom, thus producing HCl and another labile chlorine atom. Probability favors abstraction by the free Cl atom of a hydrogen atom from one of the nearest methylene groups. Since the nearest one in the chain is also an allylic hydrogen, its abstraction is highly favored. Thus, a chain reaction is started and perpetuated which could lead to a conjugated structure with a sufficient number of double bonds to impart colour. The above reactions (106) may be written as follows:

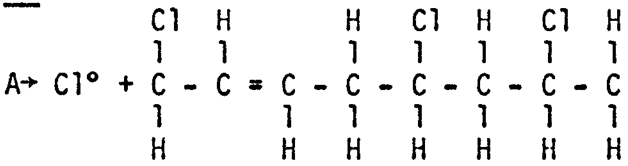
1.



$$R^\circ + -\underset{H}{\overset{\mathrm{Cl}}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{\mathrm{Cl}}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{\mathrm{Cl}}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{\mathrm{Cl}}{C}}-\underset{H}{\overset{H}{C}} \rightarrow RH + -\underset{H}{\overset{\mathrm{Cl}}{C}}-\underset{\circ}{\overset{H}{C}}-\underset{H}{\overset{\mathrm{Cl}}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{\mathrm{Cl}}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{\mathrm{Cl}}{C}}-\underset{H}{\overset{H}{C}}$$

A

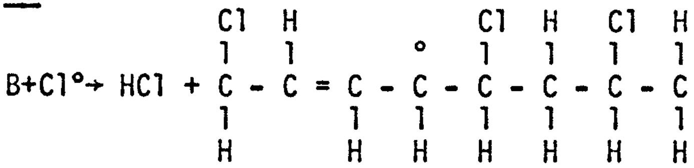
2.



$$A \rightarrow \mathrm{Cl}^\circ + \underset{H}{\overset{\mathrm{Cl}}{C}}-\overset{H}{C}=\underset{H}{C}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{\mathrm{Cl}}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{\mathrm{Cl}}{C}}-\underset{H}{\overset{H}{C}}$$

B

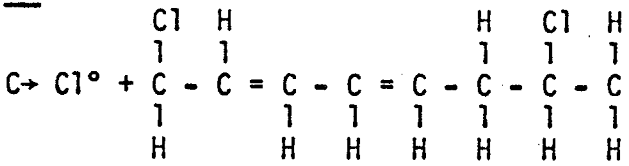
3.



$$B + \mathrm{Cl}^\circ \rightarrow \mathrm{HCl} + \underset{H}{\overset{\mathrm{Cl}}{C}}-\overset{H}{C}=\underset{H}{C}-\underset{H}{\overset{\circ}{C}}-\underset{H}{\overset{\mathrm{Cl}}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{\mathrm{Cl}}{C}}-\underset{H}{\overset{H}{C}}$$

C

4.



$$C \rightarrow \mathrm{Cl}^\circ + \underset{H}{\overset{\mathrm{Cl}}{C}}-\overset{H}{C}=\underset{H}{C}-\underset{H}{C}=\underset{H}{C}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{\mathrm{Cl}}{C}}-\underset{H}{\overset{H}{C}}$$

D

As a result of the heat evolved in the exothermic stage, the rate of decomposition of the initiator (benzoyl peroxide) increases, giving off CO_2, the vapour pressure of vinyl chloride monomer also increases, probably causing a split in the wood samples.

PVC is insoluble in its monomer and starts precipitating out in the form of a fine powder as soon as it is generated. The PVC thus generated has little mechanical strength. Therefore the WPC produced by employing such a process lacks mechanical strength.

The results for homogeneous (Table 12) polymerisation are similar to those in the heterogeneous polymerisation except that in the former case (Table 11) the WPC formed have a lower polymer loading. This can be attributed to the fact that in the former case the impregnant consists of both the solvent and the monomer rather than the pure monomer.

Copolymerisation studies of vinyl chloride (Table 13) with other monomers indicate that although homogeneous copolymers could be prepared by thermo-catalytic methods, the processing time is relatively longer. Therefore this aspect of WPC needs to be thoroughly examined.

c). Study of the Wood-Styrene -Acrylonitrile System:

1. Benzoyl Peroxide Initiator - Factorial Experiment #1.

As illustrated in chapter V, in the experiments directed at studying the effects of independent variables (T,C,R) on the response variables (M,V,H), a two level factorial experiment design was devised. Eight experiments were conducted and the observations were analysed by a three way analysis of variance (ANOVA). The results for the wood polymer composites prepared by using benzoyl peroxide as the initiator are presented in Tables 14,16 and 18. An examination of these tables indicate that within the range investigated, the hardness of the samples is not affected by any of the three independent variables or combinations of them. The other two response variables (M and V) are also not affected by the two independent variables C and R. However, these two variables seem to be significantly affected by the temperature. An attempt is made to give the most probable qualitative explanation for the results of this experimentation; it is impossible to give a quantitative discussion without a knowledge of the kinetic data, analysis of the polymer produced, "efficiency" of the polymerisation process, and heat transfer data for the system.

The reason for the temperature dependence of these variables can be explained if one considers the effect of temperature upon the polymer* composition. The properties of the WPC are significantly affected by the composition of the polymer. The composition of the copolymer produced is a function of the temperature (67) through the dependence of the reactivity ratios of the monomers on temperature (Chapter II).

In this study the two levels of bath temperature employed were 50°C and 70°C. In practice the polymerisation reaction in this system does not always take place at constant temperature since it shows variation due to the heat transfer characteristics of the direct heated system. During the exothermic stage of the direct heating process, a temperature gradient is established in the wood monomer system with a higher temperature in the centre of wood and a lower temperature at the surface of the wood monomer composite, as mentioned earlier.

* It refers to a combination of copolymer, polystyrene and polyacrylonitrile.

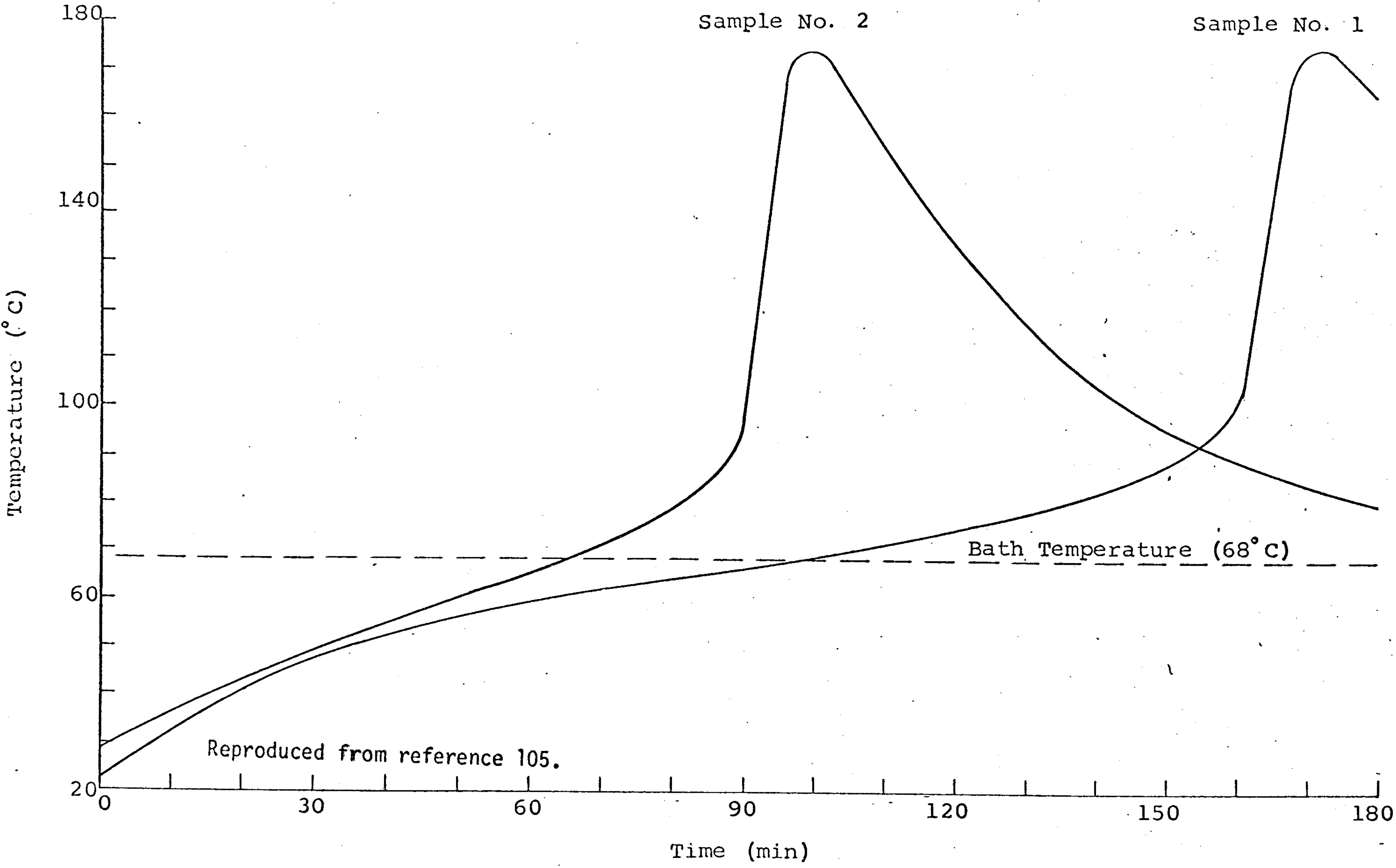


Figure 12. Center temperature variation with time for aspen-monomer samples containing 0.2 and 0.5% concentrations of benzoyl peroxide in direct heating tests at 68°C.

The maximum temperature attained as previously explained depends upon the initiator half life and the change of half life with temperature. It is independent of the initiator concentration (105), as is shown in Fig. 12 where the centre temperature variation of the methyl methacrylate -wood (ASPEN) is plotted against the heating time. Therefore corresponding to the bath temperature, a characteristic exothermic stage and maximum temperature are established. Hence it follows that the composition of the polymer generated will vary depending upon the bath temperature. Another reason for the drift in the polymer composition could be the expulsion of low boiling monomer from the wood monomer composite at higher temperatures.

The observation that the time of reaction within the range investigated does not significantly affect the response variables, could be explained on the assumption that the exothermic stage comes to an end before the lower limit of R, since it is in the exothermic region where most of the polymer is generated.

As explained in Chapter II the copolymer composition is independent of the initiator concentration, therefore it has little noticeable effect upon the nature of the polymer generated.

2. Azo-Bis-Isobutyronitrile Initiator - Factorial Experiment #2.

The experimental conditions employed in this design are listed on page 94. According to this design eight experiments were conducted and the observations were analysed by the same method as in the previous experiment. The results for the WPC prepared by using AZO catalyst as the initiator are presented in Tables 19-22. An examination of these tables indicate that within the range of variables investigated, none of the independent variables or their combinations has significant effect on any of the response variables.

These results can be explained on the basis that the properties of WPC are determined by the composition of the polymer produced. Therefore it appears that probably the polymer composition is practically the same in different wood polymer composites so as to have little significant effect upon the response variables. In order to explain that the polymer composition is practically the same, it should be assumed that the polymerisation reaction in different experiments must have taken place at similar conditions of temperature in spite of the constant bath temperature. As previously explained, the maximum temperature attained and the slope of the exothermic curve depends upon the half life of the initiator and its rate of change with temperature. Therefore this assumption can be justified if one considers that the maximum temperature attained and the slope of the exothermic curves between the range 60 to 70°C of temperature are similar. Analogous to the results of the previous experiment, initiator concentration and the time of reaction do not show significant effect upon the response variables.

3. Properties of Wood-Styrene-Acrylonitrile System:

1. Dimensional Stabilization:

When the wood structure is not swollen as in the present work, most of the polymer fills in the cell cavities and intercellular spaces, resulting in an improvement in the following characteristics:

1) Water vapour or moisture uptake (Figs. 13,14)
2) Liquid water uptake (Fig. 9)
3) Volume change due to the absorption of water vapour (Figs. 15,16)

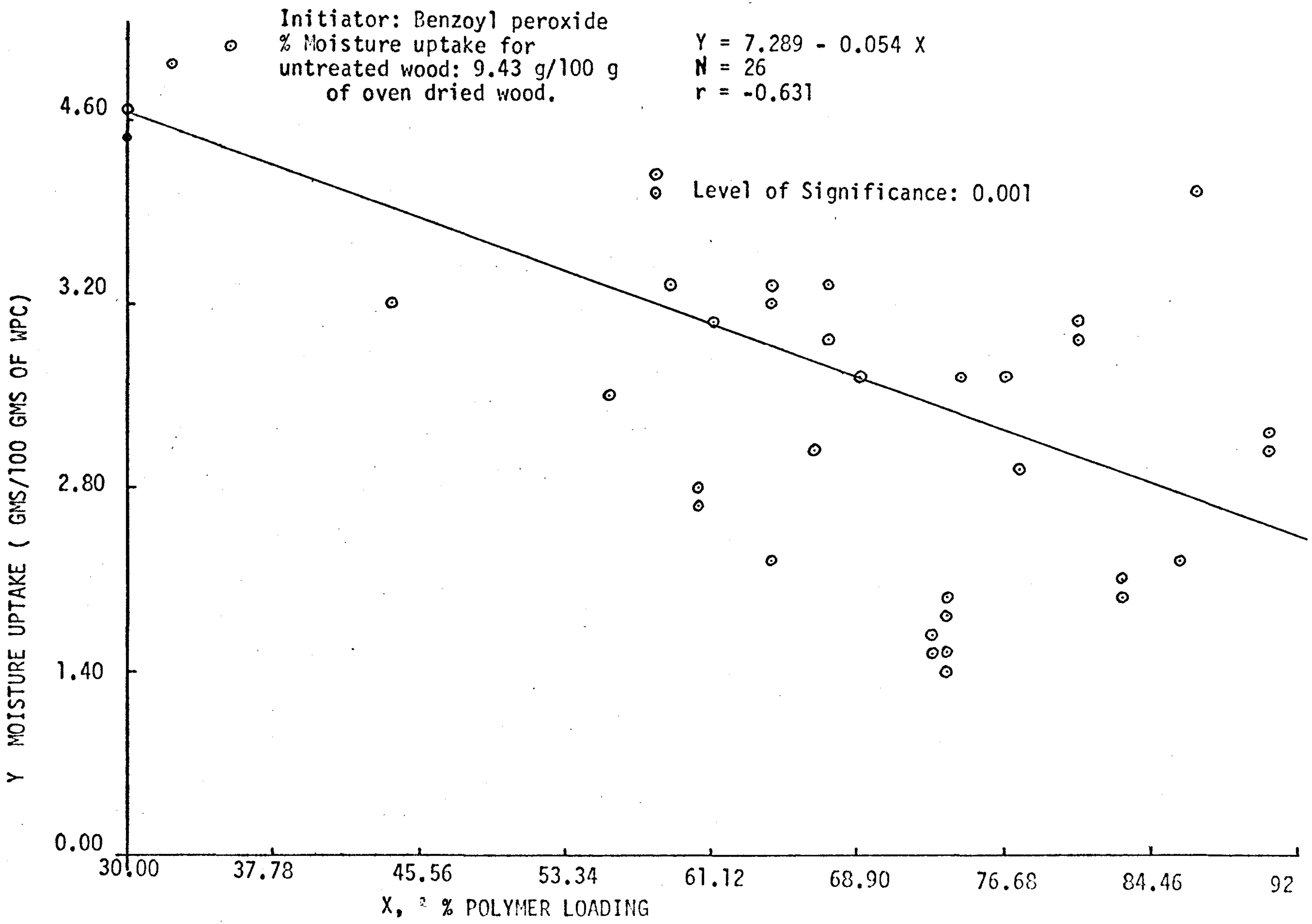


FIGURE 13 RELATIONSHIP BETWEEN MOISTURE UPTAKE & POLYMER LOADING

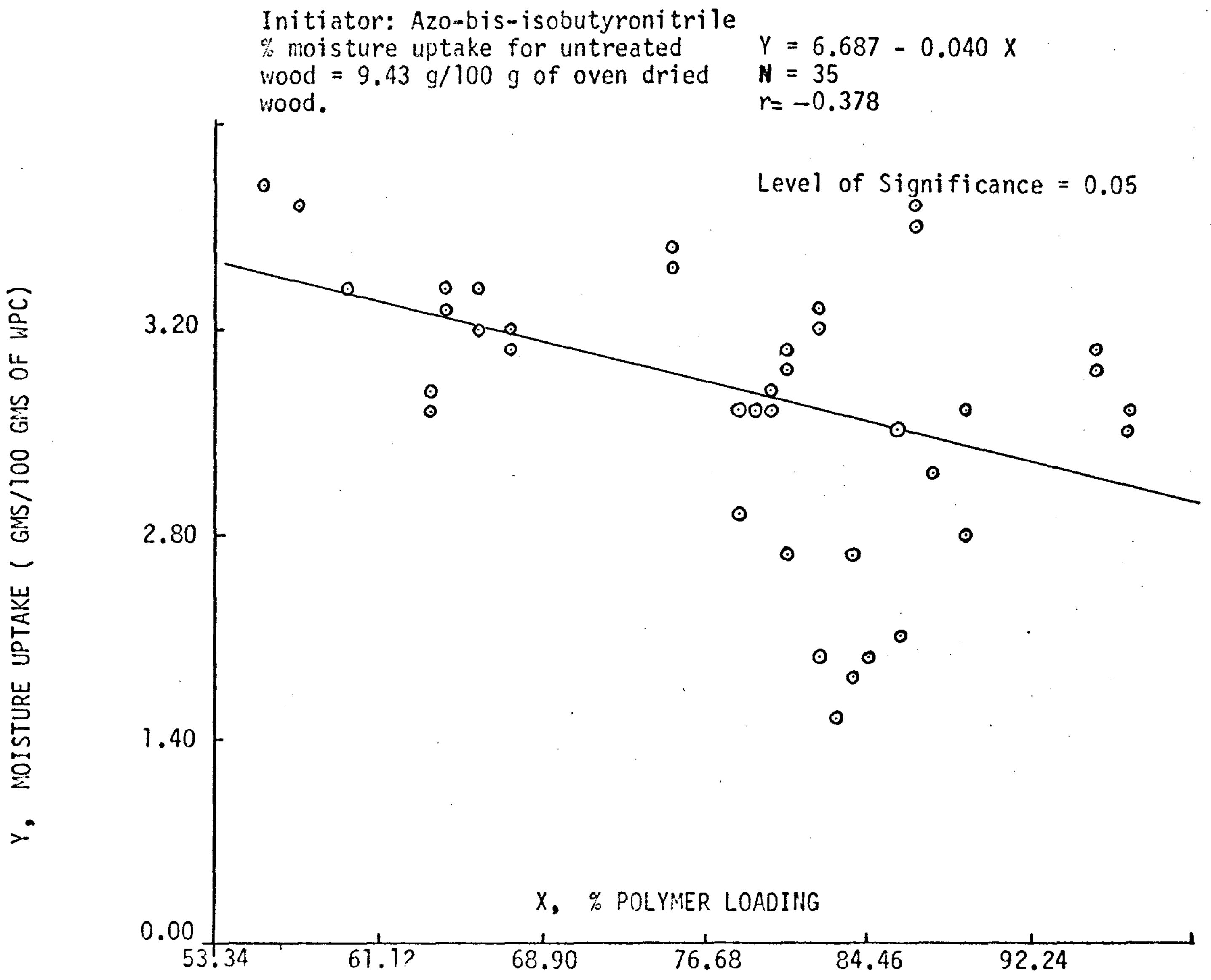


FIGURE 14 RELATIONSHIP BETWEEN MOISTURE UPTAKE AND POLYMER LOADING

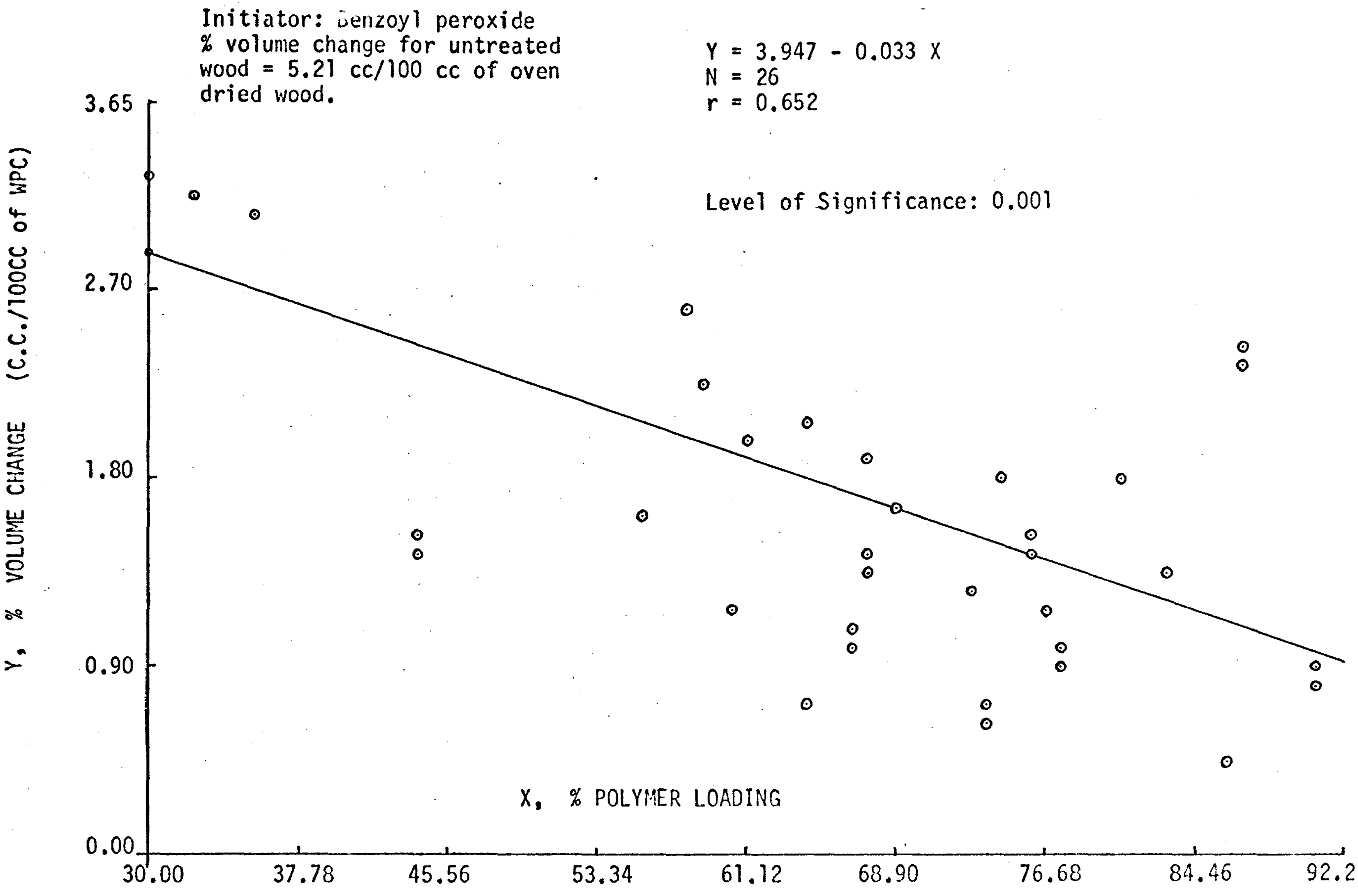


FIGURE 15 RELATIONSHIP BETWEEN VOLUME CHANGE AND POLYMER LOADING

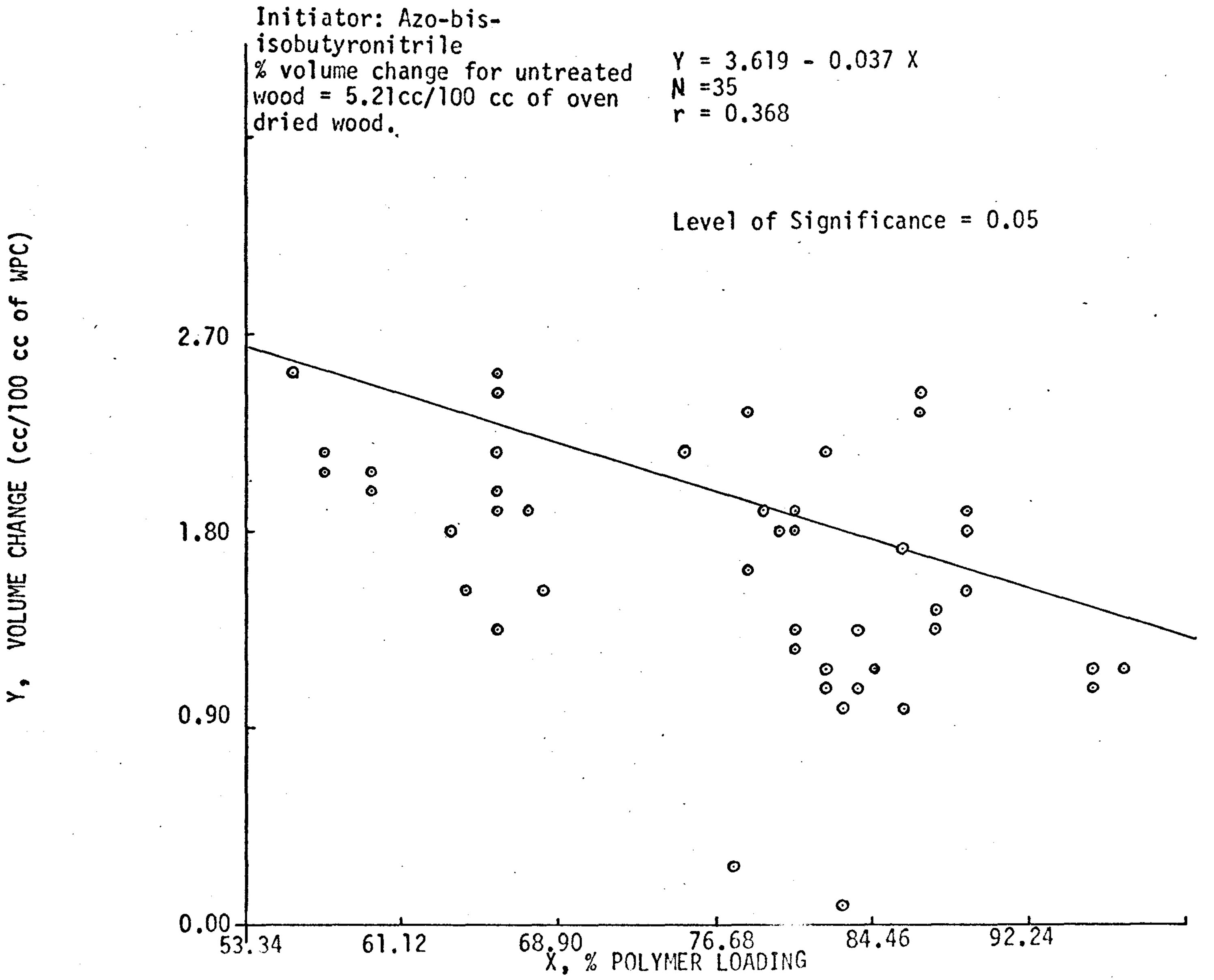


FIGURE 16 RELATIONSHIP BETWEEN MOISTURE UPTAKE AND POLYMER LOADING

The tests conducted on wood-poly (styrene-acrylonitrile) composites point out that M and V are functions of polymer loading as shown in Figures 13-16. The corresponding values for the testing on untreated oven dried wood are also reported in these figures. The correlations shown in Figures 13-16 were established by Linear Regression Analysis as explained in Ref. 107. The regression analyses were carried out on an I.B.M. 7040 digital computer. A simple computer program was developed to evaluate the statistic of the data, such as the least squares line (Appendix II).

The symbols shown on the graph are defined as follows (107):

1. $y = bx + a$ (the least squares line)
2. N = the number of data points
3. r = correlation co-efficient.

Such an impregnation of wood that results in a solid being formed in the lumina of the cells can only retard the normal movement of water from cell to cell through the cell cavities. The effectiveness of such treatment will depend on the completeness of the cavity filling operation. The thickness of the untreated cell wall will ultimately change in response to changes in humidity; although this change may be resisted by well-filled cavities, it will eventually result in a dimensional change in the wood. This explains the following observations:

1. Moisture uptake (M) and volume change (V) are dependent upon polymer loading (Figs. 13-16)
2. Complete dimensional stability of wood is not possible by filling the cell cavities of wood with polymer. (Figs. 8-10(a) & 13-16).

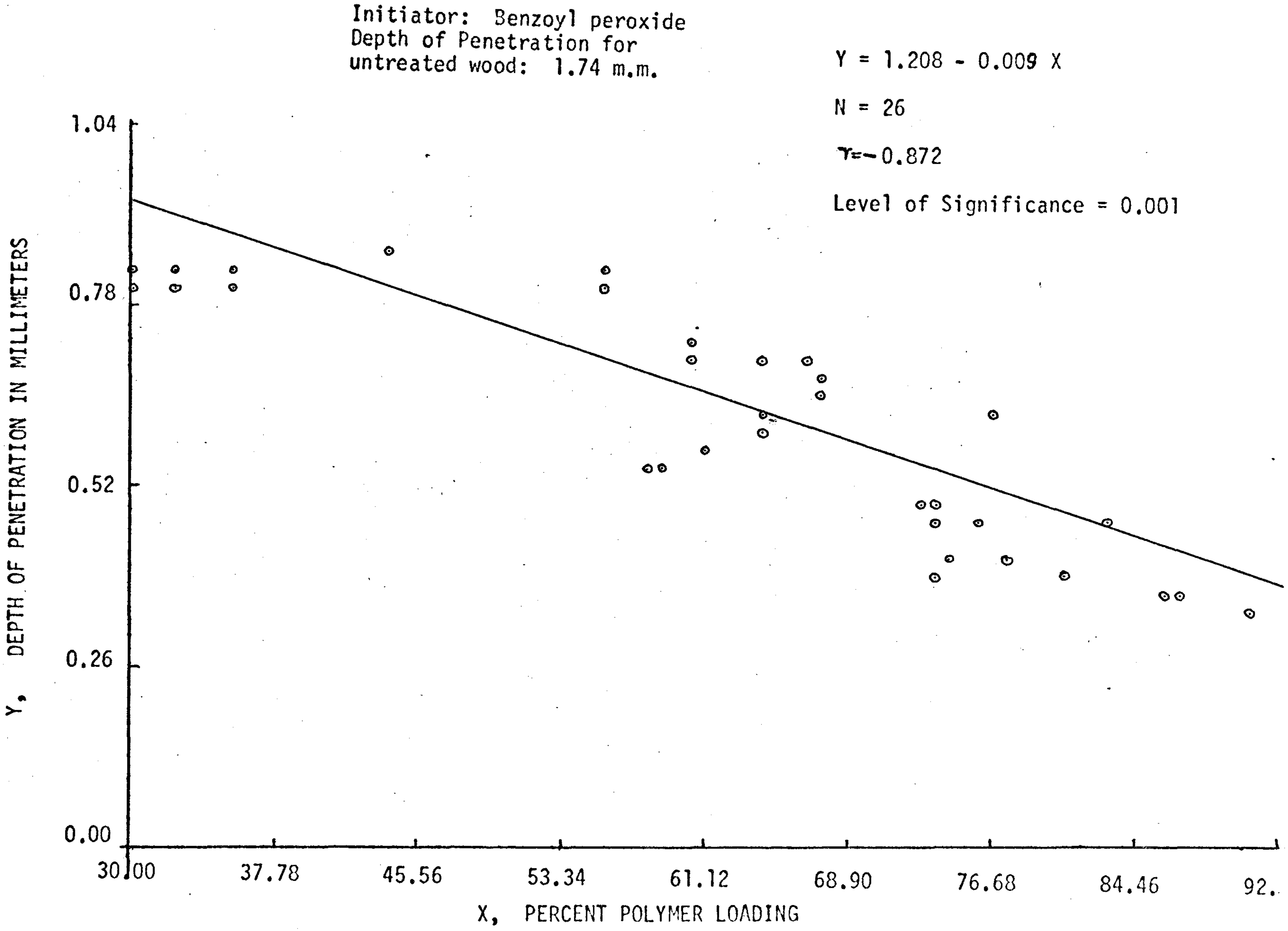
2. Antishrink Efficiency:

Figure 10(a) shows the effect of polymer loading on the antishrink efficiency of WPC (poly styrene-A.N.) prepared by thermo-catalytic methods without the use of a swelling agent. A comparison of these results with those of Kenaga (12) or Ross (15) (Figure 10(b)), who used Swelling-Impregnation-Irradiation technique to produce WPC, point out that during (12) treatment with swelling impregnants, a disruption of the more ordered areas of the cellulosic structure occurs, unless sufficient polymer is added to counteract this effect, an increased swelling of the sample results. On the other hand, where no swelling solvent is used as in the present work, and consequently no appreciable breakdown of the cell wall structure occurs, higher antishrink efficiencies are obtained at comparable, low, polymer loadings. Similar results are also reported by Gibson et.al. (22).

3. Hardness:

When the cell cavities in wood are filled by polymers, the resulting product shows an improvement in mechanical properties over those of untreated wood. The hardness tests conducted on the wood-styrene-acrylonitrile combinations indicate that hardness in the transverse (Figs. 17-18) direction is a function of the polymer retention in wood. Such correlations were drawn as reported in the previous section. The value for the hardness of untreated oven dried wood is also reported on these figures so that a comparison can be made.

To understand the (61) influence of bulking treatments on hardness of wood in the transverse direction, one might think of the cross section of wood as being represented by layers of pipe squeezed together



Initiator: Benzoyl peroxide
Depth of Penetration for
untreated wood: 1.74 m.m.

$Y = 1.208 - 0.009\ X$

$N = 26$

$r = -0.872$

Level of Significance = 0.001

FIGURE 17 RELATIONSHIP BETWEEN HARDNESS (DEPTH OF PENETRATION) AND POLYMER LOADING

Initiator: Azo-Bis-isobutyronitrile
Depth of Penetration for
Untreated wood = 1.74 m.m.

Y = 0.961 - 0.005 X
N = 35
r = -0.463.

Level of Significance: 0.01

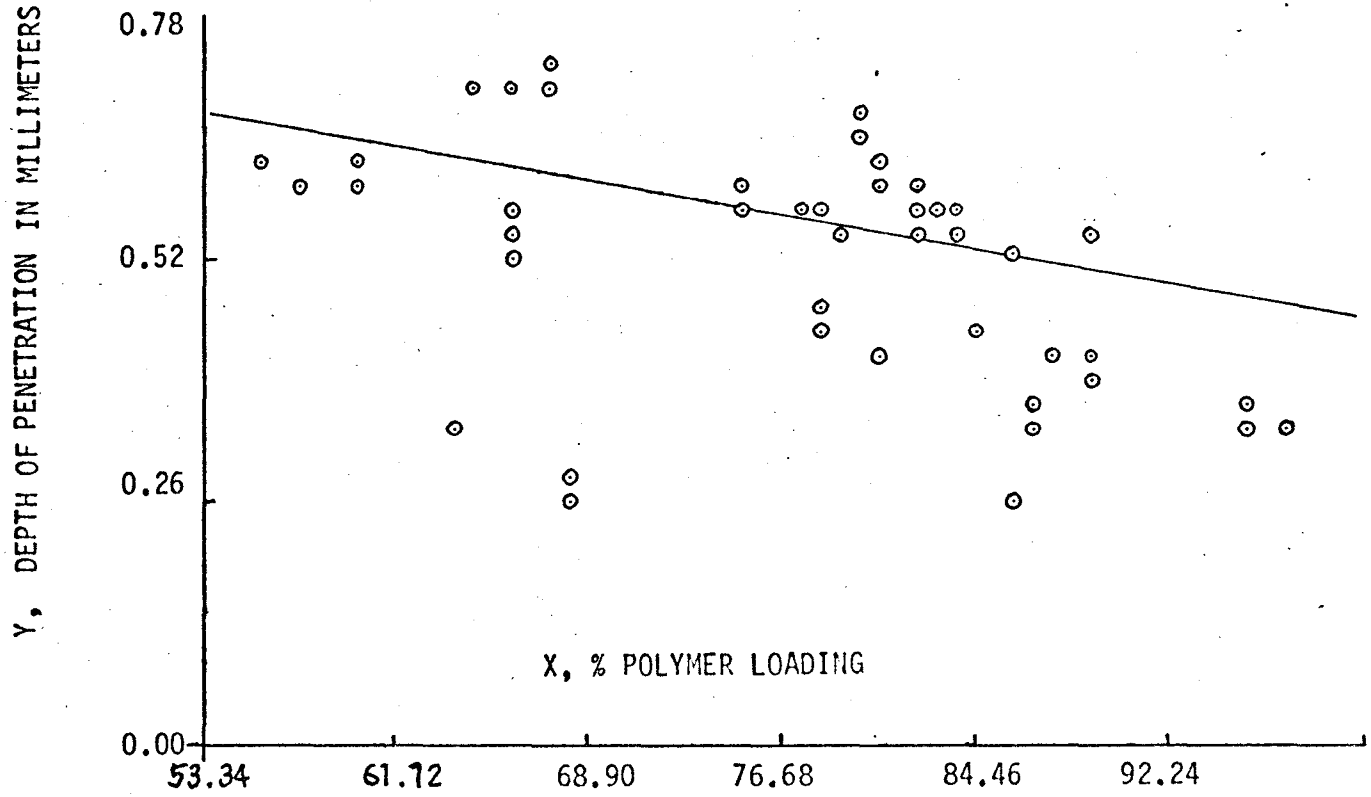


FIGURE 18 RELATIONSHIP BETWEEN HARDNESS (DEPTH OF PENETRATION) AND POLYMER LOADING

so tightly that the walls are somewhat flattened on four sides. The walls of the pipe are a limited swelling gel with the major structural elements parallel to the pipe axis. When swollen with liquids, the walls can be easily deformed by lateral forces (61). Thus, the material exhibits a high Poisson's Ratio* (108). When swollen with solids, such as a cured pehnolic resin, the hardened walls are very resistant to such deformation. But if a solid material is deposited in the cell cavities only, without even entering the cell walls, there will be an increase in hardness because it will prevent the collapse of the "pipes" from within. Based upon this explanation it is anticipated that the lumina-filled wood, without cell wall impregnation, can be expected to improve sheer resistance, by acting like elongated, microscopic sheer plates in preventing stress concentrations in the planes of weakness of wood.

* $\text{Poisson's Ratio} = \frac{\text{Lateral Stress}}{\text{Longitudinal Stress}}$

Conclusion

This work was undertaken as a final phase of a program in which the potential of radiation initiated graft copolymerisation with cellulose in wood, was under investigation. Two techniques of producing wood polymer combinations were available. The first of these involved homopolymerisation of a monomer inside the cell cavities of wood, and the second, graft copolymerisation of a monomer with the cellulose of wood. It was established that in the latter process the copolymerisation was possible only by the use of swelling agents. But these swelling agents weakened the wood structure to such an extent that any gains in physical properties of the wood due to polymerisation were lost.

The present investigation was conducted to examine the former homopolymerisation process using catalysts instead of radiation. In this work, several wood monomer systems were studied. The most promising one appeared to be the wood-styrene-acrylonitrile system. As a result of copolymerisation of styrene and acrylonitrile in the cell cavities of wood, several desirable modifications in its physical properties result. The hardness is substantially improved, penetrability of water vapour and liquid is significantly lowered, and dimensional changes with water absorption are also correspondingly reduced.

Further, as mentioned earlier, wood polymer combinations produced by this technique have physical properties superior to those produced by graft copolymerisation. In addition thermo-catalytic polymerisation seems to be at least as effective as radiation induced polymerisation in improving wood. This result could be significant in terms of the relative economics of the two processes, in that the thermo-catalytic process is cheaper and more readily available than radiation methods.

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Appendix I

Specific Gravity of Wood

A number of physical properties of wood depends upon its specific gravity, that is, the weight of wood divided by the weight of an equal volume of water. The weight is always expressed on an oven dry basis. The volume may be that of the oven dry wood, that of the completely water swollen wood, or that at any designated moisture content. When a specific gravity value is given for wood, it is customary to designate it on the volume basis: "dry volume" specific gravity, "swollen volume" specific gravity, or specific gravity "at moisture content". The specific gravity of wood on any of these basis may vary more than ten-fold between species, and may vary as much as two-fold within a species.

APPENDIX 2

COMPUTER PROGRAMS

PROGRAM NUMBER 1

LINEAR REGRESSION

```
      DIMENSION X(122),Y(61)
      READ(5,1) (X(K),K=1,61)
    1 FORMAT(8F10.3)
      READ(5,100) (X(K),K=62,122)
  100 FORMAT(8F10.3)
      DO 10 N=1,3
      READ(5,2) (Y(I),I=1,61)
    2 FORMAT(8F10.3)
      DO 10 J=1,2
      SX=0.0
      SY=0.0
      SXS=0.0
      SYS=0.0
      SXY=0.0
      DO 20 K=1,61
      IF(J.EQ.1) M=K
      IF(J.EQ.2) M=K+61
      SX=SX+X(M)
      SY=SY+Y(K)
      SXS=SXS+X(M)*X(M)
      SYS=SYS+Y(K)*Y(K)
   20 SXY=SXY+X(M)*Y(K)
      T=61.0
      XB=SX/T
      YB=SY/T
      SXV=SXS-SX*SX/T
      SYV=SYS-SY*SY/T
      SXYV=SXY-SX*SY/T
      R=(SXY-SX*SY/T)/SQRT((SXS-SX*SX/T)*(SYS-SY*SY/T))
      BETA=(SXY-SX*SY/T)/(SXS-SX*SX/T)
      ALPHA=(SY-BETA*SX)/T
      SSYT=(1.0-R*R)*(SYS-SY*SY/T)/(T-2.0)
      SSB=SSYT/(SXS-SX*SX/T)
      SB=SQRT(ABS(SSB))
      SSYB=SSYT/T
      SYB=SQRT(ABS(SSYB))
      TTEST=R*SQRT(ABS((T-2.0)/(1.0-R*R)))
      IF(N.EQ.1.AND.J.EQ.1) GO TO 11
```

```
      IF(N.EQ.1.AND.J.EQ.2) GO TO 12
      IF(N.EQ.2.AND.J.EQ.1) GO TO 21
      IF(N.EQ.2.AND.J.EQ.2) GO TO 22
      IF(N.EQ.3.AND.J.EQ.1) GO TO 31
      IF(N.EQ.3.AND.J.EQ.2) GO TO 32
   11 WRITE(6,111)
  111 FORMAT(40H1FIRST  SET OF Y'S AND FIRST  SET OF X'S)
      GO TO 10
   12 WRITE(6,112)
  112 FORMAT(40H1FIRST  SET OF Y'S AND SECOND SET OF X'S)
      GO TO 10
   21 WRITE(6,121)
  121 FORMAT(40H1SECOND SET OF Y'S AND FIRST  SET OF X'S)
      GO TO 10
   22 WRITE(6,122)
  122 FORMAT(40H1SECOND SET OF Y'S AND SECOND SET OF X'S)
      GO TO 10
   31 WRITE(6,131)
  131 FORMAT(40H1THIRD  SET OF Y'S AND FIRST  SET OF X'S)
      GO TO 10
   32 WRITE(6,132)
  132 FORMAT(40H1THIRD  SET OF Y'S AND SECOND SET OF X'S)
   10 WRITE(6,3)SX,XB,SY,YB,SXS,SXV,SYS,SYV,SXY,SXYV,BETA,ALPHA,
     1R,SSYT,SSB,SB,SSYB,SYB,TTEST
    3 FORMAT(12H-SUM OF X'S=,E12.5,6X,6HX BAR=,E12.5/
     112H-SUM OF Y'S=,E12.5,6X,6HY BAR=,E12.5/
     213H-SUM OF X2'S=,E12.5,5X,17HSUM OF (X-XBAR)2=,E12.5/
     313H-SUM OF Y2'S=,E12.5,5X,17HSUM OF (Y-YBAR)2=,E12.5/
     413H-SUM OF XY'S=,E12.5,5X,19HSUM OF (XY-XYBAR)2=,E12.5/
     56H-BETA=,E12.5,12X,6HALPHA=,E12.5/
     63H-R=,E12.5,15X,9HS2(YTOP)=,E12.5/
     77H-S2(B)=,E12.5,11X,5HS(B)=,E12.5/
     810H-S2(YBAR)=,E12.5,8X,8HS(YBAR)=,E12.5/
     97H-TTEST=,E12.5)
      STOP
      END
$ENTRY
```

PROGRAM NUMBER 2

STANDARD DEVIATIONS

```
 PAH MEANS THE PERCENT SWELL IN SIDE A DUE TO HUMIDITY
 PBH MEANS THE PERCENT SWELL IN SIDE B DUE TO HUMIDITY
 PCH MEANS THE PERCENT SWELL IN SIDE C DUE TO HUMIDITY
 PVH MEANS THE PERCENT SWELL IN VOLUME DUE TO HUMIDITY
 PAW MEANS THE PERCENT SWELL IN SIDE A DUE TO WATER
 PBW MEANS THE PERCENT SWELL IN SIDE B DUE TO WATER
 PCW MEANS THE PERCENT SWELL IN SIDE C DUE TO WATER
 PVW MEANS THE PERCENT SWELL IN VOLUME DUE TO WATER
 ASE MEANS ANTISHRINK EFFICIENCY
 UMN MEANS MONOMER UPTAKE
 PLR STANDS FOR POLYMER RETENTION
 PRE STANDS FOR POLYMER RETENTION EFFICIENCY
 PRE STANDS FOR PERCENT RETENTION
 PVU STANDS FOR PERCENT VAPOUR UPTAKE
 PWU STANDS FOR PERCENT WATER UPTAKE

      DIMENSION PAH(111),PBH(111),PCH(111),PVH(111),
     1PAW(111),PBW(111),PCW(111),PVW(111),
     2ASE(111),UMN(111),PLR(111),PRE(111),
     3PRN(111),PVU(111),PWU(111)
      WRITE(6,200)
  200 FORMAT(1H0,1X,1HN,2X,
     14HSPAH,4X,4HSPBH,4X,4HSPCH,4X,4HSPVH,4X,
     24HSPAW,4X,4HSPBW,4X,4HSPCW,4X,4HSPVW,4X,
     34HSASE,4X,4HSMNU,4X,4HSPLR,4X,4HSPRE,4X,
     44HSPRN,4X,4HSPVU,4X,4HSPWU)
      WRITE(6,5)
    5 FORMAT(5X,4HPAHB,4X,4HPBHB,4X,4HPCHB,4X,4HPVHB,
     14X,4HPAWB,4X,4HPBWB,4X,4HPCWB,4X,4HPVWB,
     24X,4HASEB,4X,4HMNUB,4X,4HPLRB,4X,4HPREB,
     34X,4HPRNB,4X,4HPVUB,4X,4HPWUB)
      DO 400 K=1,111
  400 READ(5,300)PAH(K),PBH(K),PCH(K),PVH(K),
     1PAW(K),PBW(K),PCW(K),PVW(K),ASE(K),UMN(K),PLR(K),PRE(K),
     3PRN(K),PVU(K),PWU(K)
  300 FORMAT(8F8.5/7F8.3)
      I=1
      DO 100 N=1,17
      PAHS=0.0
      PBHS=0.0
      PCHS=0.0
      PVHS=0.0
      PAWS=0.0
      PBWS=0.0
      PCWS=0.0
      PVWS=0.0
      ASES=0.0
      UMNS=0.0
```

```
      PLRS=0.0
      PRES=0.0
      PRNS=0.0
      PVUS=0.0
      PWUS=0.0
      J=0
    1 PAHS=PAHS+PAH(I)
      PBHS=PBHS+PBH(I)
      PCHS=PCHS+PCH(I)
      PVHS=PVHS+PVH(I)
      PAWS=PAWS+PAW(I)
      PBWS=PBWS+PBW(I)
      PCWS=PCWS+PCW(I)
      PVWS=PVWS+PVW(I)
      ASES=ASES+ASE(I)
      UMNS=UMNS+UMN(I)
      PLRS=PLRS+PLR(I)
      PRES=PRES+PRE(I)
      PRNS=PRNS+PRN(I)
      PVUS=PVUS+PVU(I)
      PWUS=PWUS+PWU(I)
      I=I+1
      J=J+1
      IF(I.EQ.8) GO TO 10
      IF(I.EQ.15) GO TO 10
      IF(I.EQ.22) GO TO 10
      IF(I.EQ.29) GO TO 10
      IF(I.EQ.35) GO TO 10
      IF(I.EQ.42) GO TO 10
      IF(I.EQ.49) GO TO 10
      IF(I.EQ.56) GO TO 10
      IF(I.EQ.63) GO TO 10
      IF(I.EQ.69) GO TO 10
      IF(I.EQ.76) GO TO 10
      IF(I.EQ.83) GO TO 10
      IF(I.EQ.90) GO TO 10
      IF(I.EQ.96) GO TO 10
      IF(I.EQ.103) GO TO 10
      IF(I.EQ.109) GO TO 10
      IF(I.EQ.112) GO TO 10
      GO TO 1
   10 T=J
      PAHB=PAHS/T
      PBHB=PBHS/T
      PCHB=PCHS/T
      PVHB=PVHS/T
      PAWB=PAWS/T
      PBWB=PBWS/T
      PCWB=PCWS/T
      PVWB=PVWS/T
      ASEB=ASES/T
      UMNB=UMNS/T
      PLRB=PLRS/T
      PREB=PRES/T
      PRNB=PRNS/T
      PVUB=PVUS/T
      PWUB=PWUS/T
      M=(I-J)
```

```
      PAHVS=0.0
      PBHVS=0.0
      PCHVS=0.0
      PVHVS=0.0
      PAWVS=0.0
      PBWVS=0.0
      PCWVS=0.0
      PVWVS=0.0
      ASEVS=0.0
      UMNVS=0.0
      PLRVS=0.0
      PREVS=0.0
      PRNVS=0.0
      PVUVS=0.0
      PWUVS=0.0
    2 PAHV=(PAH(M)-PAHB)*(PAH(M)-PAHB)
      PBHV=(PBH(M)-PBHB)*(PBH(M)-PBHB)
      PCHV=(PCH(M)-PCHB)*(PCH(M)-PCHB)
      PVHV=(PVH(M)-PVHB)*(PVH(M)-PVHB)
      PAWV=(PAW(M)-PAWB)*(PAW(M)-PAWB)
      PBWV=(PBW(M)-PBWB)*(PBW(M)-PBWB)
      PCWV=(PCW(M)-PCWB)*(PCW(M)-PCWB)
      PVWV=(PVW(M)-PVWB)*(PVW(M)-PVWB)
      ASEV=(ASE(M)-ASEB)*(ASE(M)-ASEB)
      UMNV=(UMN(M)-UMNB)*(UMN(M)-UMNB)
      PLRV=(PLR(M)-PLRB)*(PLR(M)-PLRB)
      PREV=(PRE(M)-PREB)*(PRE(M)-PREB)
      PRNV=(PRN(M)-PRNB)*(PRN(M)-PRNB)
      PVUV=(PVU(M)-PVUB)*(PVU(M)-PVUB)
      PWUV=(PWU(M)-PWUB)*(PWU(M)-PWUB)
      PAHVS=PAHVS+PAHV
      PBHVS=PBHVS+PBHV
      PCHVS=PCHVS+PCHV
      PVHVS=PVHVS+PVHV
      PAWVS=PAWVS+PAWV
      PBWVS=PBWVS+PBWV
      PCWVS=PCWVS+PCWV
      PVWVS=PVWVS+PVWV
      ASEVS=ASEVS+ASEV
      UMNVS=UMNVS+UMNV
      PLRVS=PLRVS+PLRV
      PREVS=PREVS+PREV
      PRNVS=PRNVS+PRNV
      PVUVS=PVUVS+PVUV
      PWUVS=PWUVS+PWUV
      M=M+1
      IF(M.GT.J) GO TO 20
      GO TO 2
   20 SPAH=SQRT(PAHVS/(T-1.0))
      SPBH=SQRT(PBHVS/(T-1.0))
      SPCH=SQRT(PCHVS/(T-1.0))
      SPVH=SQRT(PVHVS/(T-1.0))
      SPAW=SQRT(PAWVS/(T-1.0))
      SPBW=SQRT(PBWVS/(T-1.0))
      SPCW=SQRT(PCWVS/(T-1.0))
      SPVW=SQRT(PVWVS/(T-1.0))
      SASE=SQRT(ASEVS/(T-1.0))
      SUMN=SQRT(UMNVS/(T-1.0))
```

```
      SPLR=SQRT(PLRVS/(T-1.0))
      SPRE=SQRT(PREVS/(T-1.0))
      SPRN=SQRT(PRNVS/(T-1.0))
      SPVU=SQRT(PVUVS/(T-1.0))
      SPWU=SQRT(PWUVS/(T-1.0))
      WRITE(6,3)N,SPAH,SPBH,SPCH,SPVH,SPAW,SPBW,SPCW,SPVW,
     1SASE,SUMN,SPLR,SPRE,SPRN,SPVU,SPWU
    3 FORMAT(1H0,I2,15F8.4)
  100 WRITE(6,4)PAHB,PBHB,PCHB,PVHB,PAWB,PBWB,PCWB,PVWB,
     1ASEB,UMNB,PLRB,PREB,PRNB,PVUB,PWUB
    4 FORMAT(3X,15F8.4)
      STOP
      END
$ENTRY
  -----
```

PROGRAM NUMBER 3

CURVE PLOTTING

```
      DIMENSION X(122),Y(61),U(122),V(61)
    1 FORMAT(8F10.3)
      READ(5,1) (X(K),K=1,61)
      READ(5,1) (X(K),K=62,122)
      DO 10 N=1,3
      READ(5,1) (Y(I),I=1,61)
      DO 10 J=1,2
      GO TO (3,5),J
    3 DO 4 M=1,61
    4 U(M)=X(M)
      GO TO 8
    5 DO 6 M=62,122
    6 U(M-61)=X(M)
    8 DO 7 I=1,61
    7 V(I)=Y(I)
      GO TO (41,42,43),N
   41 GO TO (11,12),J
   42 GO TO (21,22),J
   43 GO TO (31,32),J
   11 CALL PLOT3(U,V,61,4.5,0.0,50.0,10.,50,90,10)
      GO TO 10
   12 CALL PLOT3(U,V,61,4.5,0.0,100.,30.,50,90,10)
      GO TO 10
   21 CALL PLOT3(U,V,61,7.0,0.0,50.0,10.,50,90,10)
      GO TO 10
   22 CALL PLOT3(U,V,61,7.0,0.0,100.,30.,50,90,10)
      GO TO 10
   31 CALL PLOT3(U,V,61,1.3,0.0,50.0,10.,50,90,10)
      GO TO 10
   32 CALL PLOT3(U,V,61,1.3,0.0,100.,30.,50,90,10)
   10 CONTINUE
      IF(N.EQ.3) CALLEXIT
      END
$ENTRY
```

PROGRAM NUMBER 4

THREE WAY ANALYSIS OF VARIANCE

THIS PROGRAM IS TAILORED TO FIT THE MODEL GIVEN IN REF104.

```
      WRITE(6,1)
    1 FORMAT(1H-,20X,30HTHREE WAY ANALYSIS OF VARIANCE)
      DO 300 N=1,18
      READ(5,100)A,B,C,D,E,F,G,H
  100 FORMAT(8F7.2)
      X1DD=A+B+C+D
      X2DD=E+F+G+H
      SSXIDD=X1DD**2+X2DD**2
      XD1D=A+E+B+F
      XD2D=C+G+D+H
      SSXDJD=XD1D**2+XD2D**2
      XDD1=A+E+C+G
      XDD2=B+F+D+H
      SSXDDK=XDD1**2+XDD2**2
      XDDDS=(A+B+C+D+E+F+G+H)**2
      SSXIJD=(A+B)**2+(C+D)**2+(E+F)**2+(G+H)**2
      SSXIDK=(A+C)**2+(B+D)**2+(E+G)**2+(F+H)**2
      SSXDJK=(A+E)**2+(B+F)**2+(C+G)**2+(D+H)**2
      SSXIJK=A**2+B**2+C**2+D**2+E**2+F**2+G**2+H**2
      SSC=SSXIDD/4.0-XDDDS/8.0
      SSR=SSXDJD/4.0-XDDDS/8.0
      SSL=SSXDDK/4.0-XDDDS/8.0
      SSCR=SSXIJD/2.0-SSXIDD/4.0-SSXDJD/4.0+XDDDS/8.0
      SSCL=SSXIDK/2.0-SSXIDD/4.0-SSXDDK/4.0+XDDDS/8.0
      SSRL=SSXDJK/2.0-SSXDJD/4.0-SSXDDK/4.0+XDDDS/8.0
      SSE=SSXIJK-SSXIJD/2.0
      EMS=SSE/4.0
      FC=SSC/EMS
      FR=SSR/EMS
      FL=SSL/EMS
      FCR=SSCR/EMS
      FCL=SSCL/EMS
      FRL=SSRL/EMS
  300 WRITE(6,200)SSC,SSC,FC,SSR,SSR,FR,SSL,SSL,FL,
     1SSCR,SSCR,FCR,SSCL,SSCL,FCL,SSRL,SSRL,FRL,SSE,EMS
  200 FORMAT(1H-,15X,18HDEGREES OF FREEDOM,5X,
     114HSUM OF SQUARES,5X,11HMEAN SQUARE,5X,14HTEST STATISTIC/
     210H-C(COLUMN),14X,1H1,16X,F6.1,12X,F6.1,11X,F7.3/
     37H-R(ROW)    ,17X,1H1,16X,F6.1,12X,F6.1,11X,F7.3/
     49H-L(LAYER)  ,15X,1H1,16X,F6.1,12X,F6.1,11X,F7.3/
     54H-CXR       ,20X,1H1,16X,F6.1,12X,F6.1,11X,F7.3/
     64H-CXL       ,20X,1H1,16X,F6.1,12X,F6.1,11X,F7.3/
     74H-RXL       ,20X,1H1,16X,F6.1,12X,F6.1,11X,F7.3/
     86H-ERROR     ,18X,1H4,16X,F6.1,12X,F6.1,12X,6H......)
      STOP
      END
```