PREPARATION AND PROPERTIES OF WHITE-PINE - PMMA COMPOSITES

by

Günseli Ayşe İnhan

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ABSTRACT

Wood-polymer composites from Turkish White pine (pinea siber)-Polymethylmethacrylate (PMMA), are prepared by heat catalysis method. Monomer loss during polymerization is prevented by impregnation of wood in PMMA + MMA solution and subsequent polymerization. Volatility of MMA is decreased in a significant degree. % conversion values greater than 85% are obtained.

A.S.E. values are determined. It is observed that A.S.E. values for PMMA-MMA impregnated, polymerized samples are higher than pure MMA impregnated,polymerized ones, probably due to MMA shrinkage during polymerization which occurs less in the first case. A.S.E. values greater than 70% are observed for 70% polymer load for PMMA-MMA impregnated samples.

Different results are obtained for hardness parallel to grain and for hardness perpendicular to grain. An increase of about 2 fold is observed in case of hardness perpendicular to grain whereas in case of hardness parallel to grain a 3 fold increase is obtained.

Staining wood samples with Rhodamine B-dye and subsequent examination under U.V. showed that PMMA had penetrated inside the wood and polymer distribution was mainly along the grain.

ÖZET

Isı kataliz yoluyla Polimetilmetakrilat (PMMA), Türkiye'de yetişen beyaz çam (Pinea siber) kompozitleri hazırlandı. Polimerizasyon sırasındaki monomer kaybı tahtaya başlangıçta PMMA + MMA solusyonu emprenye edilmesiyle büyük ölçüde engellendi. Bu şekilde MMA"ın volatilitesinin azaldığı görüldü ve %85'in üzerinde bir verim elde edildi.

PMMA-beyaz çam kompozitlerinin su emmeye direnci ölçüldü. Aynı polimer oranı için polimer ve monomer emdirilmiş tahtanın su emmeye direncinin monomer emdirilmiş tahtanın katsayısından daha büyük olduğu görüldü. Başka bir deyişle polimer-monomer emdirilmiş tahta aynı polimer oranında çok daha az su emdi. %70 polimer yüklü tahtanın su emmeye direncinin %70 olduğu görüldü.

Polimer tahta kompozitlerinin elyafa paralel ve elyafa dik sertlik ölçümlerinden değişik sonuçlar elde edildi. Elyafa dik sertlik, muamele görmemiş tahtaya oranla 2 misli, elyafa paralel sertlik ise 3 misli oranında arttı.

Tahtadan alınan ince kesitlerin önce Rhodamine B ile boyanıp, ultraviole ışını altında incelenmesi PMMA'ın yüzeyde kalmayıp tahtaya girdiğini ve polimer dağılımının elyaf boyunca olduğunu gösterdi.

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I. INTRODUCTION

1.1 HISTORY

Wood is the most ancient structural and in a way industrial material used by mankind. Wood as a renewable resource has provided man with tools weapons and shelter. Although now days it has been succeeded by light metals and plastics it has not been superseded. It is still used in industry in a wide variety of ways.

Apart from its well known advantages of usage (durability, strength, advantage in price, ease of workability) there are some drawbacks from technical point of view. One of the most important of these is the dimensional instability resulting from changes in moisture content which causes warping and assymetrical distortion. Other serious drawbacks of wood are its relatively low resistance to abrasion, to the effects of wheater and to bacteria microbes and insects.

As man increased his knowledge he tried to improve the properties of wood. Over the years, tars, pitches, creasole, resins and salts have been used to coat wood or fill its porous structure [2].

With the advent of plastic age scientists found another group of chemicals to coat and treat wood. This group of chemicals are polymers which resemble the chief chemical constituent of wood, cellulose in many respects. Polymers are macromolecules which have crystalline and amorphous parts and are strong and resistant below softening point just like cellulose [1].

The similarity of these substances and also the defference in their properties promised favorable combinations. During World War II phenol formaldehyde based on the research of the Forest Products Laboratory was used to treat wood veneer (named as "compreg"). During these years some of the monomers used were of condensation type and reacted with the hydroxyl groups in wood. Another group of compounds simply bulked the wood by replacing the moisture content in the cell walls [2].

During the early 1960's vinyl type monomers that could be polymerized into the solid polymer by means of free radicals begun to be used. The monomer was first impregnated and then polymerized among the fibers of wood. This vinyl polymerization was an improvement over the condensation polymerization reaction because the free radical catalyst was neither acidic nor basic and the reaction did not leave behind a side product that must be removed from the final composite.

In general the free radicals used for the polymerization reaction came from two sources; temperature sensitive catalysis and cobalt 60 gamma radiation. In each case a free radical is generated by the process but from that point the vinyl polymerization mechanism is the same. Each process for generation free radicals has its own problems. However since the vinyl polymerization mechanism is the same, little if any difference in the physical properties of catalyst heat initiated or gamma radiation initiated in situ polymerization of vinyl monomers in wood is observed.

1.2 STRUCTURE AND CHEMICAL COMPOSITION OF WOOD

1.2.1 Structure of Wood

Commercial timbers fall into two main groups: Softwoods and Hardwoods. The former are known as Gymnosperms that is conifers or cone bearin plants with needle shaped leaves and seeds which are not enclosed in a see case. The latter belong to a group known as angiosperms that is dicotyledo or broad-leaved plants with seeds enclosed in a seed case [3]. The terms hardwood and softwood do not imply a direct klationship with the actual har ness of the wood..

A mature tree of either softwood or hardwood type generally consist of a single stem which is covered with a layer of bark. This central trunk is the principal source of woody material for the manufacture of various products [4]. The bark protects the wood from extremes of temperature, drought and mechanical injury.

The inner layers of the bark conduct the food manufactured in the leaves to regions of active growth (like the root) and to places where it can be stored. So it is rich in chemical substances such as tannins and dyes. Between the bark and the wood is a layer of thin walled living cells invisible without a microscope called the cambium. Only cambium is responsible for the enlargement in width of the trunk. New wood cells are formed on the inside and new bark cells on the outside of the cambium. As the diameter of the woody trunk increases the bark is pushed outward and the outer bark layers become stretched and crack in patterns characteristic of a specie [5]. When viewed cross-sectionally the wood consists of a series of concentric layers of tissues called growth rings. These rings are the wood produced by the cambium in a single growing season [3]. Food storage and sap conduction is performed by the outer or youngest growth rings which are usually light colored and are called as sapwood. In many trees the conducting channels of the inner core called the heartwood are blocked because remains of stored food material become changed to tannins and other substances. Hearthwood contains no living cells except the ray cells which are responsible for food storage and are mostly dark colored. These changes cause durability and strength in heartwood relative to sapwood [4,3] (Fig. 1.2.1).

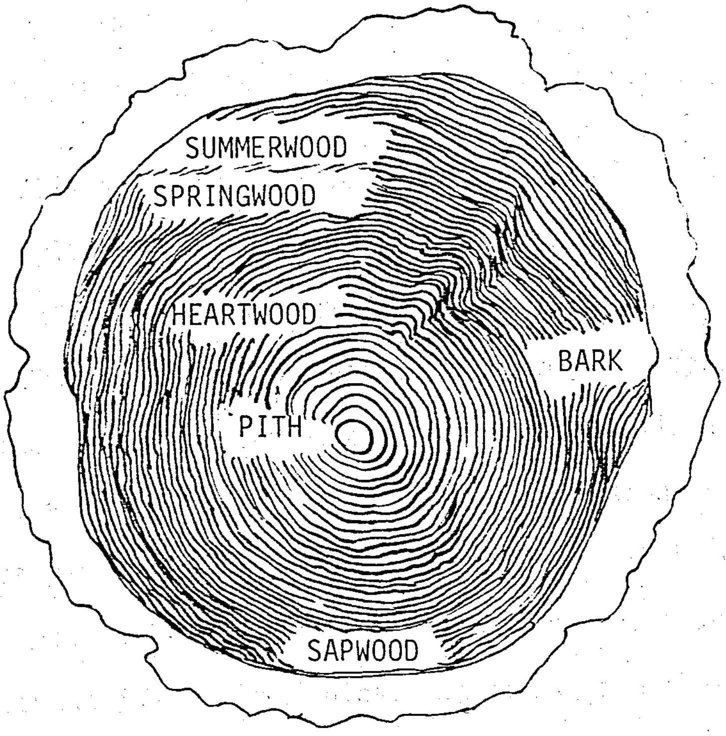


Fig. 1.2.1 - Cross section of softwood log showing bark, wood, and pith [3].

Cellular structure of wood can be analysed in two ways.

a) Arrangement of cells in the tree

b) Type of cells generated from the cambium.

Cells in the tree are arranged mainly in two ways.

Longitudinal cells: These are long cells that make up the bulk of the wood and provide grain to the material [4].

Wood rays: These are perpendicular to the longitudinal cells and are specialized for food storage and conduction. Rays extend-radially from pith at the center of the stem to the cambium and continue into the bark.

Cambium generates two main cells in the stem.

a) The phloem cells which form the inner part of the bark and conduct food.

b) The xylem cells which form the woody part.

Some xylem cells are food storage cells and remain alive for a long period while other xylem cells are found in wood rays.

The main difference between softwood and hardwood is their cellular structure. Softwood anatomy consists of mainly two types of cells. These are parenchyma cells and tracheids. Parenchyma cells are oriented perpendicular to the longitudinal tracheids and are responsible for food storage. In softwoods parenchyma cells form less than 5% of the total volume whereas in hard wood it is 20% by volume. In softwoods tracheids are responsible for conducting and mechanical functions, and these make about 95% of total wood volume [3]. At the beginning of the growing season when water requirement of leaves care at maximum thin walled tracheids with

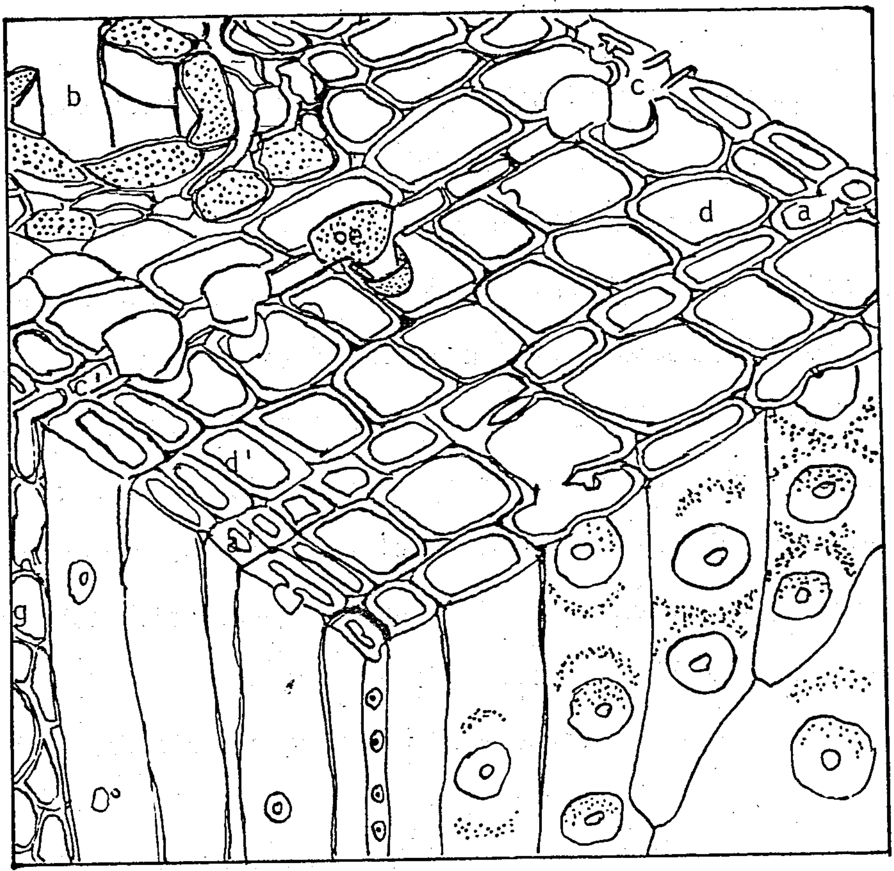


Fig. 1.2.2 - Schematic three-plane drawing of the softwood

a-a': portion of an annual ring
b : resin canal
c-c': wood ray
d-d': longitudinal tracheids
e : window-like pit pairs between longitudinal tracheids and ray parenchyma
g : cells of ray parenchyma

large cavities are formed and these are primarily concerned with the conduction of sap. Thick walled ones which are formed later are responsible for maintaining mechanical rigidity. The quality of softwood depends largely on the proportions of thin to thick walled tracheids which form alternating zones according to the time they are formed [3] (Fig. 1.2.2).

In hardwood conducting and mechanical functions are performed by two different kind of cells. Vessels or pores which are longitudinal and have no end walls are responsible for conduction. The vessels of heartwood are often blocked by tyloses. Tyloses are known to prevent the growth of fungi [3]. Narrow spindle shaped cells called wood fibers are responsible for mechanical support in hardwoods.

1.2.2 Chemical Composition of Wood

The walls of wood cells are composed of three principal chemical materials; cellulose, hemicellulose and lignin all of which are polymeric. Cellulose contributes to the wood's high tensile strength. Lignin provides rigidity thus making upright growth possible, and it also add toxicity making wood durable. Hemicelluloses are thought to be a temporary matrix before lignification.

Cellulose is 1-4 linked β-D-glucoglycan. It consists of β-D-gluco pyranose units linked together into straight chains by 1-4 glycosidic bonds [7]. These straight chains take the form of microfibrils in each cell wall layer. These are held together by strong hydrogen bonds and also by Van der Waal's forces and by covalent bonds. Therefore they make a chain lattice and a layer lattice[8].

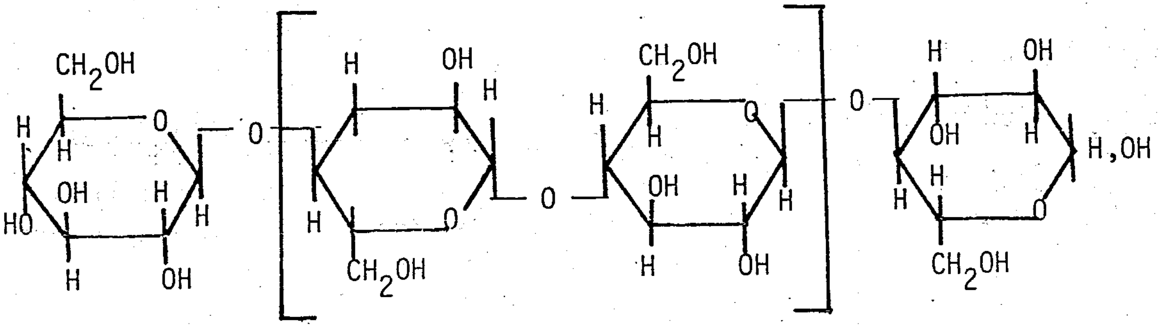


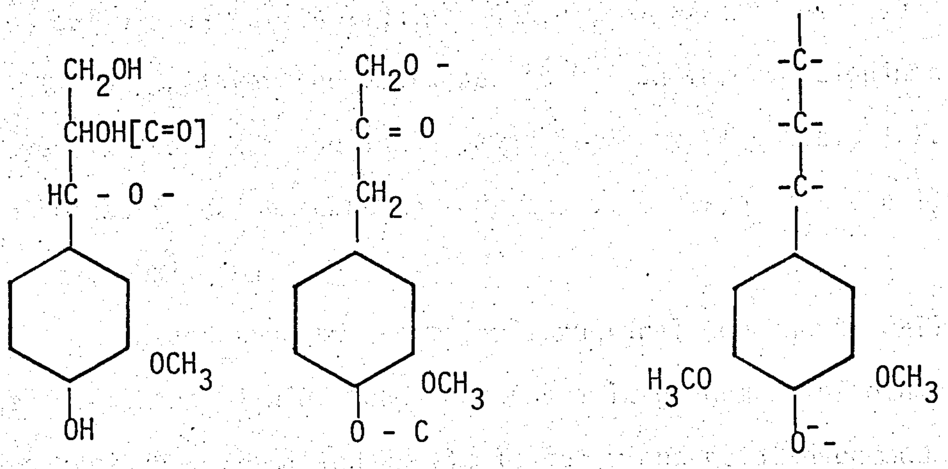
Fig. 1.2.3 - Structural formula of cellulose

Cellulose is not soluble in water due to its regularity and hydrogen bonding [4]. Aqueous alkali though can swell cellulose, does not dissolve it, however strong alkali will degrade cellulose.

Hemicelluloses are relatively low molecular weight polysaccharides which contain different sugar units and can be extracted by aqueous alkali. Hemicelluloses found in wood are polymers of D-xylose, D-mannose, D-glucose D-galactose, L-arabinose, 4-O-methyl-D-glucyronic acid. They usually have about 150 to 200 sugar residues and usually they have short side chains. The hemicelluloses and their content in softwood and hardwood are not the same and this causes the difference between these two woods [4]. The two principal hemicelluloses found in hardwoods are O-Acetyl-4-O-methyl-glucurono-xylan and glucomannan. Xylan is the predominant hemicellulose found in hardwoods [9]. In softwoods glucomannan is the predominant hemicellul

Apart from glucomannan, arabinoxylan and arabinogalactan are also found in softwood hemicelluloses [10].

Lignin is the major noncarbohydrate component of wood. They are three dimensional polymers formed from phenolic units linked together by C-O-C or C-C linkages. Structure of lignin in hardwood and softwoods is different. Softwood lignin contains guaiacyl units only but hardwood lignin contains guaiacyl and syringyl units in 1 to 1 ratio.[11].



guaiacyl units

syringyl unit

Fig. 1.2.4 - Basic lignin structures [11]

At the time the cell is produced by cell division it consists of a primary wall which is capable of enlarging both longitudinally and transversely. After the cell reaches full size a secondary wall is deposited internal to the primary wall adding thickness and rigidity to the cell wall. Middle lamella lies between two neighbouring cell walls.

After the primary wall there are three distinct layers which make up the secondary cell wall. These are the S_1, S_2 and S_3 layers. S_2 is the largest layer and the total cell wall thickness is largely controlled by the thickness of the S_2 layer. Microfibrils are oriented at different angles to the long axis of the cell within each layer. It is believed that the microfibrils consist of a crystalline core of cellulose by an amorphous region containing hemicelluloses [6].

The distribution of the chemical constituents across the cell wall is not uniform. Primary wall and middle lamella contains about 10% cellulose and 70% lignin. Cellulose content increases to more than 50% in the S_2 layer and decreases in the S_3 layer. Lignin content in S_2 layer is about 22% and in S_3 layer it is approximately 15%. The hemicellulose fraction tends to vary about the same as the cellulose across the cell wall [6].

In addition to its major structural components cellulose, hemicellulose and lignin, wood contains a large number of other compounds. These can be classified as (1) Terpenes and related compounds, (2) Fatty acids, (3) Aromatic compounds, (4) Volatile oils.

1.3 PROPERTIES AND STRUCTURE OF WOOD - POLYMER COMPOSITES -

1.3.1 Properties of Wood - Polymer Composites

It is now known that a wood polymer composite has greatly enhanced mechanical and physical properties than untreated wood.

Wood combined with plastics like hardwood is easily and readily machinable by traditional wood working operations. That is it can be sawn, planed, drilled, worked on a lathe chiselled and polished. Also is readily screwable and maintains the screwed connection much better untreated wood. Among these technological properties the only one tha worries the users is that it may deteriorate when nailed [1].

A careful analysis of mechanical properties of wood polymer co posite (W.P.C.) was done by Kent [12]. According to his results hardn is the property in which we see the major improvement.

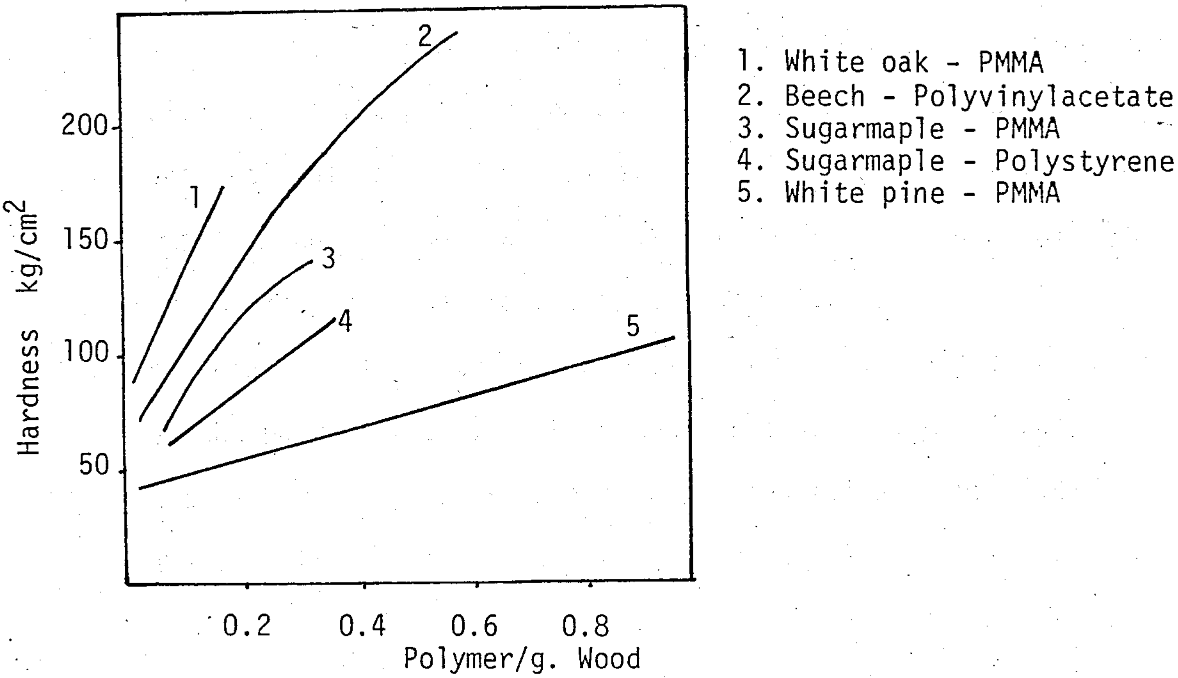


Fig. 1.3.1 - Hardness of WPC as a function of polymer content [29].

Similar results are obtained in shear strength and static bending stre measurements [1].

From the results of the mechanical tests (static bending, compression parallel to grain and toughness) done on baswood-PMMA composites it was seen that a great improvement in all the properties except modulus of elasticity was achieved [13]. Considering the significant increase in toughness tests it appeared that W.P.C. made from softwoods could challen high density hardwoods. Languig also concluded that "Comporing the coefficient of variations for the treated and untreated material it can be seen that treated material produced much more uniform data". This is mos important from industrial point of view where uniform standards are required.

Most of the mechanical properties of W.P.C. are improved proportionally to the polymer content. However any improvement is not directly proportional to polymer uptake. As can be seen from Fig. 1.3.1 [29] at small amounts of polymer retention improvements can be relatively greater or smaller according to the specie of wood. However polymer loading does not depend only on the permeability of wood species concerned but also on the part of the tree where the particular piece of wood is taken from that is from sapwood or heartwood. Theoretically void volume is approximately the same for these two regions but it is found that there is a difference in % polymer loading in pieces taken from these two regions of the wood. In most species of wood sapwood polymer loading is greater than that in heartwood probably because organic deposits, tyloses block the penetration of the monomer into the vessels [14]. After treatment sapwood shows a greater increase in compressive strength perpendicular to grain, tangential hardness, density and % polymer load than does the heartwood. However the untreated hearthwood has enhanced physical properties due to the organic deposits and the net result is an averaging of the physical properties of sapwood and heartwood [14].

A part from these improvements in physical properties, a decrease in water uptake, that is an increase in dimensional stability, improvement in abrasion resistance and a decrease in permeability is observed in W.P.C.

In technical use the increase in dimensional stability is one of the most important improvement in a W.P.C. relative to untreated wood. This property is measured as Anti-Shrink Efficiency.

$$\text{A.S.E.} = 100(S_c - S_p)/S_c \qquad [15]$$

where S_c and S_p are the volumetric swellings of the untreated control and polymer treated wood respectively. Thus high A.S.E. values indicate a sample that has very low water retention and swelling. It is claimed that A.S.E. is directly proportional to the polymer content in the cell wall [16]. A.S.E. values of 25 to 40 percent for vacuum impregnated dry samples have been reported by John and Siau [24]. The results coincide the swelling data in indicating the entry of material into the cell wall [17]. A detailed study on A.S.E. values was done by Siau and Meyer[15].

As long as the wood and the monomer used are the same the properties of a W.P.C. do not change with the method of polymerization. Heat-catalytic polymerization or polymerization by gamma radiation do not make any significant changes on the properties of the resulting W.P.C. [18,19].

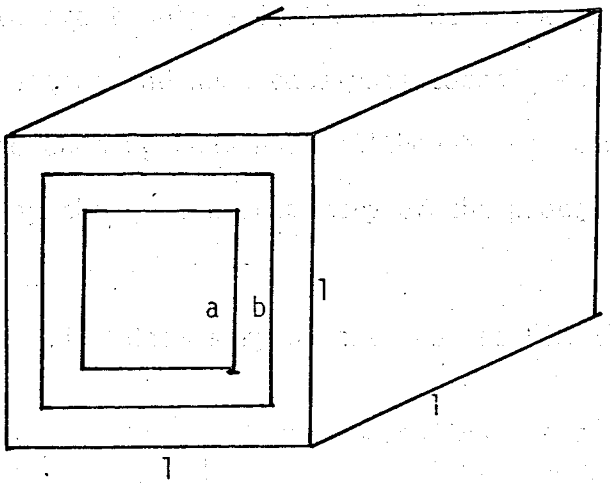
1.3.2 Structure of Wood-Polymer Composite

The wood polymer composite consists of a high strength cell wall matrix with an included low strength polymer. However the W.P.C. itself has enhanced physical properties than either single component. Improvement in physical properties depends greatly on the location of polymer in W.P.C. Polymer incorporated into the cell wall results in higher A.S.E. values and also in improved mechanical properties, compared to polymer between cell walls.

Timmons et.al used autoradiography at the light microscopic and electron microscopic level to locate the polymer in the cell wall layers. Experiments were done on three differently impregnated sets of wood, that is monomer impregnated by solvent exchange (where wood is first swelled by a polar solvent and then impregnated with monomer), in solvent dried and in ovendried wood. As expected different results were obtained. The greatest amount of monomer diffusion into the cell wall is achieved by solvent exchange method. Monomer diffusion into the ovendried and solven (pentane) dried cell wall was time dependent. After 12 hours of monomer soaking the ovendried cell wall seems to be impermeable. There is very little penetration only in the outer layers of the cell wall. This observation agrees with 2 to 4 percent void volume determined by Stamm [20] for ovendried cell walls and it shows the inability of the nonhydrogen bond forming monomer to readily swell wood. However in the ovendried pine soaked in the monomer for 100 hours there was a consistent penetration into the outer area of S_2 layer. Siau showed that after prolonged immersion in MMA nine percent volumetric swelling indicating penetration into the cell wall layer could be obtained [17].

It must be noted here that nonhydrogen bond forming monomers do swell dry wood to some extent. After 360 hours pure dry MMA swells loblolly pine volumetrically 0.3 percent [21]. Actually moisture of the wood under treatment is the determining factor in swelling or shrinkage of wood. When there is moisture in the wood, the wood is dehydrated by the monomer and volumetric shrinkage or reduced swelling is observed. At low moisture content of wood, the wood swells.

Siau et.al developed a geometrical model for a wood-polymer composite. The theoretical equations derived from this model gave results that were in good agreement with experimental values [24].



V_a = Volume fraction of air.

V_b = Volume fraction of polyme

$V_w = 1 - b^2$ = Volume fraction of cell wall material.

Fig. 1.3.2 - Model for one cell of wood-polymer composite [24].

The model consists of wood and polymer in long, parallel hollow columns. The constituents are assumed to be perfectly bonded along their lengths. Cell morphology is neglected. It is also assumed that cell wall thickness and polymer wall thickness are equal in the radial and tangential direction.

The good agreement between theoretical and experimental results indicated that "the model may be a useful tool for the prediction of properties of a composite from those of the constituent material".

1.4 OUTLINE OF THE IMPREGNATION - POLYMERIZATION PROCESS

Formation of a W.P.C. essentially consists of two main steps: Impregnation and polymerization. The method of impregnation (solvent exchange, solvent dry, over dry) and technique of impregnation (vacuum or soak) varies and different loadings are obtained according to the method and technique chosen. There are three main methods for polymerizing the impregnated material all of which produce free radicals to start polymerization. These are gamma radiation, Radio frequency heating and heat catalysis techniques. These will be discussed in the forecoming headings. Although the method of producing a free radical may change the chemistry of the process is essentially the same.

1.4.1 Chemistry of the Process [18,2]

Wood polymer composites are produced by free radical polymerization. When gamma radiation passes through a material its energy is absorbed by photoelectric, compton and pair production collisions. As a result excited and ionized molecules are formed.

$M \xrightarrow{\gamma\text{-ray}} M^* + e^- + M^+$ M-molecule (1.4.1)

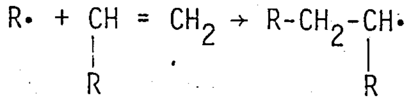
$M^+ + e^- \rightarrow M^*$ M^*-excited molecule (1.4.2)
e^--free e^-
M^+-molecular ion.

During these excitation and ionization reactions the weaker bonds in the excited molecule like the covalent bonds are broken. Usually the excited molecule breaks a covalent bond homolytically to produce free radicals.

$$(R\text{-}R)^* \rightarrow R\cdot + R \qquad (R\text{-}R)^*\text{- excited molecule} \tag{1.4.3}$$

$R\cdot$ - free radicals

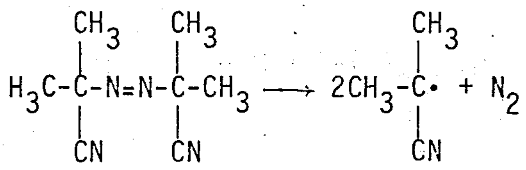
These free radicals act as initiators for the polymerization reaction.



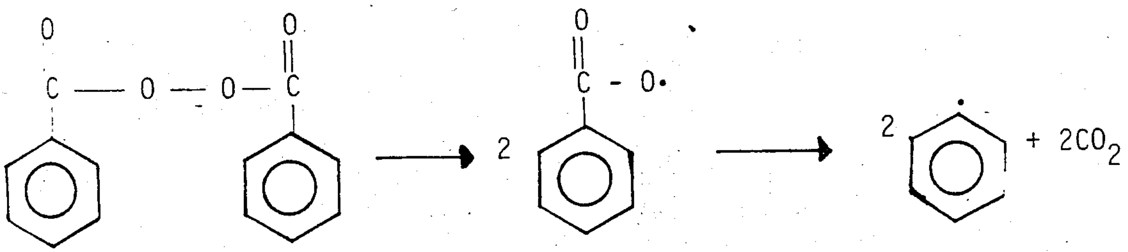
$$R\cdot + \underset{\displaystyle R}{\underset{|}{CH}} = CH_2 \rightarrow R\text{-}CH_2\text{-}\underset{\displaystyle R}{\underset{|}{CH}}\cdot \tag{1.4.4}$$

When gamma-radiation passes through wood, free radicals ara generated on cellulose and lignin molecules which initiate polymerization, when an unsaturated vinyl monomer is present. However free radicals produced by γ-radiation can and do degrade wood by breaking the cellulose or lignin chains after a critical dose is exceeded (10^6 rad. [1]). Below this dose degradation of fibrous cellulose is negligible and cellulose forms a certain amount of cross-linking which increases its strength. After the free radical is formed the polymerization reaction proceeds as usual.

In the heat-catalysis method the free radical source is a catalyst which dissociates upon heat. 2,2'-azobisisobutyronitrile (Eq. 1.4.5) and benzoyl peroxide (Eq. 1.4.6) are the most commonly used ones.

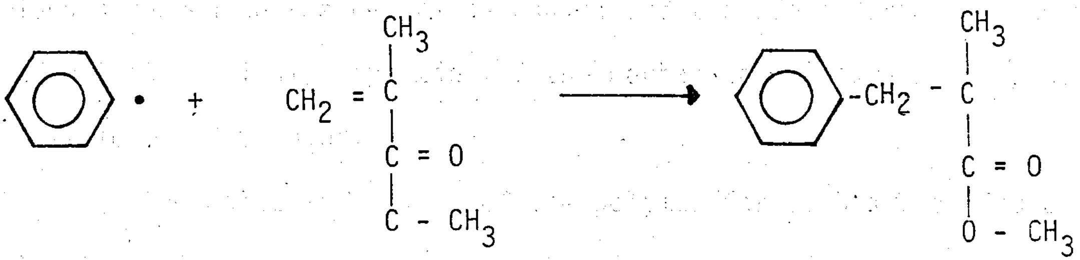


$$H_3C\text{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CN}{C}}\text{-}N{=}N\text{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CN}{C}}\text{-}CH_3 \longrightarrow 2CH_3\text{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CN}{C}}\cdot + N_2 \tag{1.4.5}$$



(1.4

The dissociation energy required to break benzoyl peroxide bond is 35 kcal/mol. The phenyl radical thus formed initiates the polymerization of vinyl monomers (Eq. 1.4.7).



(1.4.7)

or $I\cdot + M \rightarrow I\text{-}M\cdot$ (initiation step)

The propogation step can be shown as

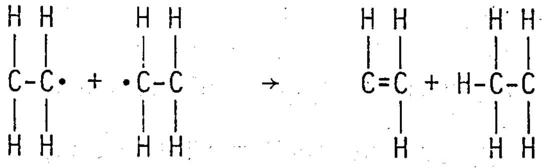
$$I\text{-}(M)_n\text{-}M\cdot + M \rightarrow I\text{-}(M)_{n+1}\text{-}M\cdot \qquad (1.4.8)$$

Normally a polymerization reaction can terminate in three ways.

1) *Recombination of radicals*

$$\mathrm{I{-}(M)_n{-}M\cdot + I{-}(M)_n{-}M\cdot \rightarrow I{-}(M)_n{-}M{-}M{-}(M)_n{-}I} \tag{1.4.9}$$

2) *Disproportionation reaction*



$$\underset{\mathrm{H\ H}}{\overset{\mathrm{H\ H}}{\mathrm{C{-}C\cdot}}} + \underset{\mathrm{H\ H}}{\overset{\mathrm{H\ H}}{\mathrm{\cdot C{-}C}}} \rightarrow \underset{\mathrm{\quad H}}{\overset{\mathrm{H\ H}}{\mathrm{C{=}C}}} + \mathrm{H{-}}\underset{\mathrm{H\ H}}{\overset{\mathrm{H\ H}}{\mathrm{C{-}C}}} \tag{1.4.10}$$

3) *By chain transfer reaction*

$$\mathrm{R{-}(M)_n{-}M\cdot + H{-}S \rightarrow R(M)_n{-}M{-}H + S\cdot} \tag{1.4.11}$$

At this point when polymerization is taking place in wood a hydrogen can be extracted from cellulose or lignin thus forming a polymer branch growing on wood. However Stannet [25] found that the copolymer branch is not very long compared to the cellulose chain; and therefore "branching has little effect on physical properties of the mechanical mixture of homopolymer, cellulose and lignin".

The molecular weight of the polymer formed has been found to be 1.5 to 2 times greater than that obtained under similar conditions in bulk polymerization. This is because of the limitation, on the mobility of growing polymer chains. This immobility inhibits the termination of chains and forms high molecular weight polymers in wood-polymer composites [22].

1.4.2 Impregnation Methods

Impregnation is the first step in the formation of a W.P.C. A wood polymer composite can be made by impregnating wood in three different ways.

1. W.P.C. prepared from Polymer Impregnated Systems
2. W.P.C. prepared from Monomer Impregnated Systems
3. W.P.C. prepared from Polymer and Monomer Impregnated Systems.

1. <u>W.P.C. prepared from polymer impregnated systems:</u>

In this method the polymer is dissolved in a suitable solvent and then impregnated in wood. Polymers used for this purpose are polyesters, polyethers, polyvinylalcohol, polyethylene glycol, phenolic resin, amino resins and aromatic poly isocyanates. The disadvantages of this method are:

i. It is difficult to impregnate high molecular weight polymers into wood.

ii. Large amounts of solvent is needed to dissolve the polymer.

Its advantage is that there is no problem of volatility of the monomer and it does not involve the difficulties of in situ polymerization.

2. <u>W.P.C. prepared from monomer impregnated systems:</u>

Monomers are small molecules that can be impregnated more readily and more uniformly in wood. Impregnation and and subsequent polymerization with monomer increases the mechanical properties and dimensional stability of wood.

The main disadvantage of this method is that monomers used are very volatile and a lot of monomer loss during impregnation and polymerization occurs.

3. W.P.C. prepared from polymer and monomer impregnated systems:

In this method polymer (oligomer)-monomer solutions are prepared. These solutions are dilute enough to impregnate the wood satisfactorily. Then they are completely polymerized. The polymer can be the monomers own oligomer or a foreign one. A foreign polymer creates a new combination but perhaps the most important aspect of this method is the possibility of creating a cross-linking structure. The most significant polymers in this respect are polyesters, polyisocyanate resins and the epoxy resin [1].

Technically impregnation into wood can be achieved by vacuum impregnation or simple immersion (soaking). Apart from these there is the solvent displacement technique in which a swelling agent is required.

Vacuum impregnation although more costly than simple immersion has several advantages; wider irregularly shaped pieces can be handled easily and the depth of penetration can be controlled by regulating immersion time and pressure [1].

In vacuum impregnation method a half hour pumping at 1 mm. pressure in sufficient to remove the air from wood vessels [2]. After evacuation the catalyzed monomer (which may contain cross-linkers, dyes, fungicides, bacteriostatic agents [1]) is introduced into the evacuated chamber through a reservoir. After the wood is covered with the monomer solution atmospheric air or nitrogen is admitted into the container. A surge tank is included in the system to allow the air dissolved in the monomer to expand without greatly changing the pressure in the system before wood is covered with monomer [2,18]. However with this procedure much monomer is lost due to high vapor pressure of monomer (40 mm at 100 m temperature for MMA).

Loos et.al determined the parameters (pressure, time) that control the impregnation of wood. It was found that to fill the void volume of wood completely a good vacuum (less than 1% atm pressure) and a sufficient liquid pressure (greater than 100 pounds/square inch gage) was necessary. They also obtained controlled uniform partial loadings by applying partial vacuum followed by monomer soak under atmospheric pressure after which excess monomer was removed. Uniform distribution of monomer was obtained by applying high pressures [31].

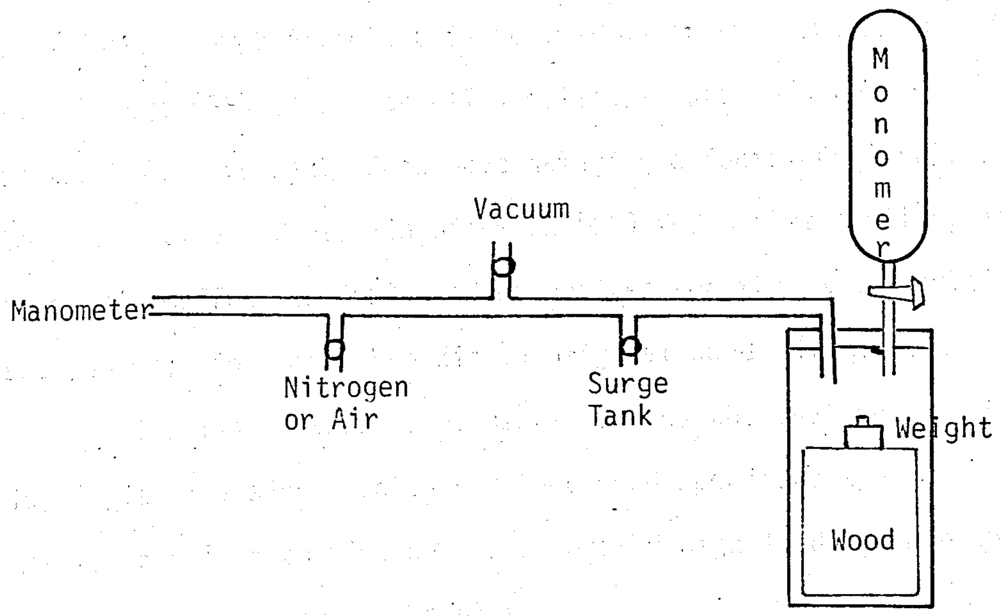


Fig. 1.4.1 - Vacuum-pressure apparatus [2]

The best results for forming a W.P.C. are obtained when the monomer is incorporated into the cell wall layers. Swelling of wood enables the penetration of monomer into the cell wall layers more easily due to the fact that it loosens the amorphous parts of cellulose. This is achieved by solvent displacement technique.

In solvent displacement technique wood is first impregnated with water (or some other solvent like ethanol which proved to be an excellent swelling agent [1]) and then immersed in an intermediate solvent which also dissolves the monomer in concern. (A mixture of swelling agent and monomer can be impregnated at the same time.) The water is replaced by the intermediate solvent and allowed to exchange for 24 hours. After equilibrium is reached this solvent is gradually replaced by the monomer and solvent is then evaporated from the wood. Siau et.al found that at least four to six exchangers of solvents were necessary to insure a complete displacement. They obtained very high A.S.E. values (up to 84%) which showed efficient incorporation of the monomer into the cell wall layers [15]. However all swelling agents do not have positive effects on the W.P.C. formed. Some have damaging effects and A.S.E. values turn to be negative. Gibson in his work [23] found that swelling agents had a negative effect on PMMA wood composites and that the resulting W.P.C. swelled more in water than did in original wood. (Fig. 1.4.2)

The last method to be mentioned and the one used in this work is simple immersion. In this method wood specimens are immersed in monomer for a prolonged time and considerably high loadings are obtained as will be discussed in the results.

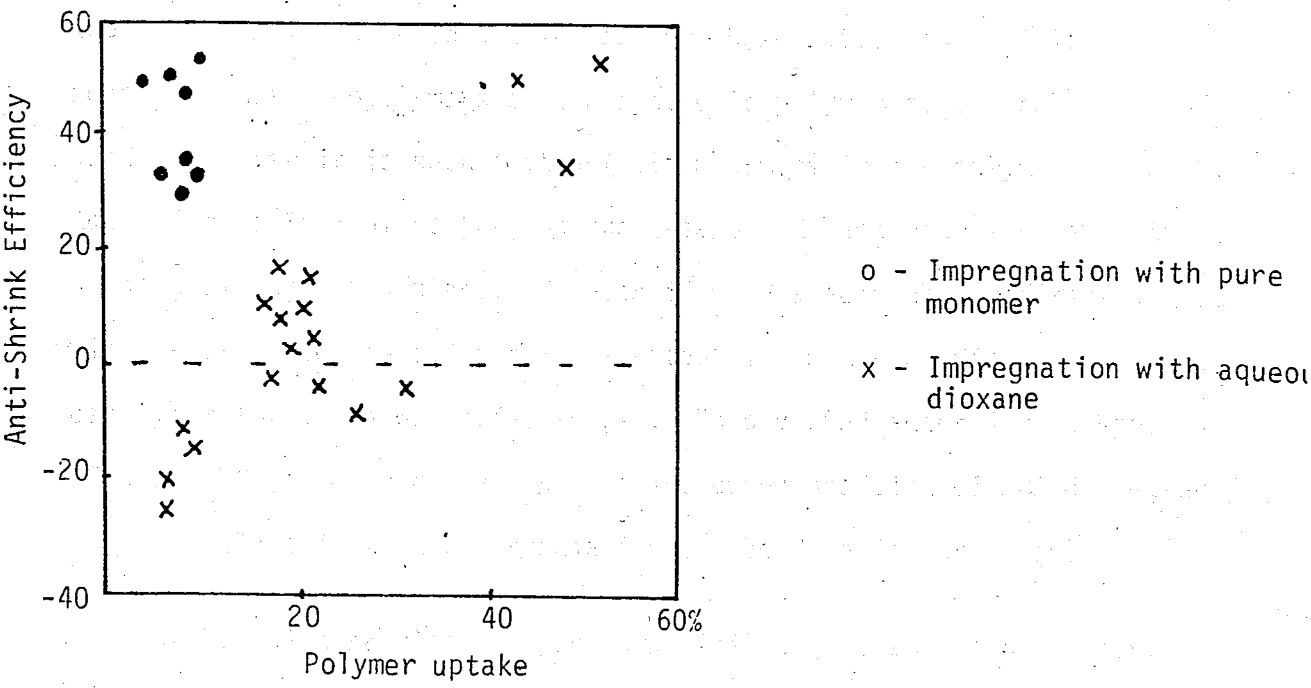


Fig. 1.4.2 - Effect of PMMA content on A.S.E. in birch [23]

1.4.3 Polymerization Method

Polymerization is achieved by mainly two methods.

A) Radiation Polymerization

B) Heat Catalysis Process.

A) Radiation Polymerization

A dose of 10^5 to 10^6 rad. is necessary for the polymerization of monomers in wood. This radiation dose causes very minor decreases in the strength of wood which is compensated by the formation of W.P.C.

Radiation causes free radical sites on cellular structure of wood.

When wood is impregnated with a monomer these sites can be initiation points of graft copolymers of the synthetic polymer to the cell wall of wood. However it is seen that not all monomers form copolymers in wood. According to Ballantine [22] in the case of MMA and vinyl acetate little or no grafting takes place. However if wood specimens are first swelled with water, dried in air and impregnated with MMA significant amounts of copolymer formation was detected [1]. This varied according to species of wood. Gibson found that as dose increased grafting of MMA decreased [23].

Polymerization by irradiation can be done in three ways.

1. With samples wrapped in Al foil to prevent monomer loss.
2. Samples immersed in monomer solution.
3. By combination of 1 and 2.

The third method generally gave much greater polymer loading. Radiation polymerization is usually done with a Cobalt 60 source and usually 8 to 10 hours are required for completion of polymerization [12]. When polymerization is to be done by irradiation an inhibitor is used in the monomer solution. Radiation polymerization has important advantages:

1. Since no catalyst is used storage of monomer can be prolonged.
2. The rate of polymerization can be controlled. Since the method adds no excess heat to the heat of polymerization, there is no overheating which can cause faster polymerization and thus shorter chains.
3. The process is carried out at ordinary pressure and temperature which eliminates the problem of monomer evaporation to a great extent.

4. The product will contain no residual catalyst that would later on lead to againg and disintegration [1].

However, radiation polymerization has serious disadvantages in its technical use. Meyer [2] states that radiation implies government regulations and environmental pollution is another problem. Cost considerations imply that a significant investment must be made before production can begin.

B) Heat-Catalyst Process

In this process, the monomer contains a catalyst which upon heating decomposes generating free radicals that initiate polymerization reaction. The samples are kept at a certain temperature (according to the catalyst) for 6-24 hours. For Vazo catalyst about $60^{0}C$ is used to initiate polymerization [2] and for benzoyl peroxide about 80 are needed [18].

A W.P.C. by heat-catalyst process was first prepared in 1964, six years after the patent for the radiation method by Ericsson et.al who polymerized styrene in wood [26]. The first thorough study on the subject was made by Meyer [18]. Meyer tried to develop the heat-catalyst process because radiation polymerization arised many technical handicaps.

It was seen that for approximately the same amount of polymer uptake modulus of elasticity, compression strength, or hardness results did not depend on the method of polymerization [18]. The major drawback in heat-catalyst polymerization is the evaporation of monomer from wood surface which leads both to monomer wastage and non-uniformly impregnated products.

Table 1.4.1 - Comparison of Mechanical Test Data [18]

Method	Polymer Uptake	Modulus of Elasticity lb/inx10^{-5}	Compressive Strength lb/in^2	Polymer Uptake	Hardness Average Deformation (ball pres.)(in)
Untreated	0	14.27	6.39	0	0.199
Direct heating	66.8	17.26	8.51	66.5	0.048
Gamma Irradiation	62.8	16.72	8.43	65.9	0.039
R.F. Heating (Radio frequency)	69.7	17.33	8.49	71.2	0.040

1.5 MONOMER LOSS

1.5.1 Monomer Loss During Polymerization

Polymerization reactions are exothermic and considerable amounts of heat is evolved depending on the monomer in concern. In case of heat catalysis process heat is needed to start polymerization reaction. Once the exothermic reaction begins heat is generated.

In both heat catalysis and gamma radiation processes the heat generated during polymerization is same for a given amount of monomer [2]. The rate at which the heat is released is controlled by the free radical initiator decomposition rate and the chain's propagation rate. So if in polymerization reaction rate of initiation and propagation is high as in heat catalysis process, all the catalytic heat of polymerization of a given monomer mass will be released in a shorter period causing an increase in temperature.

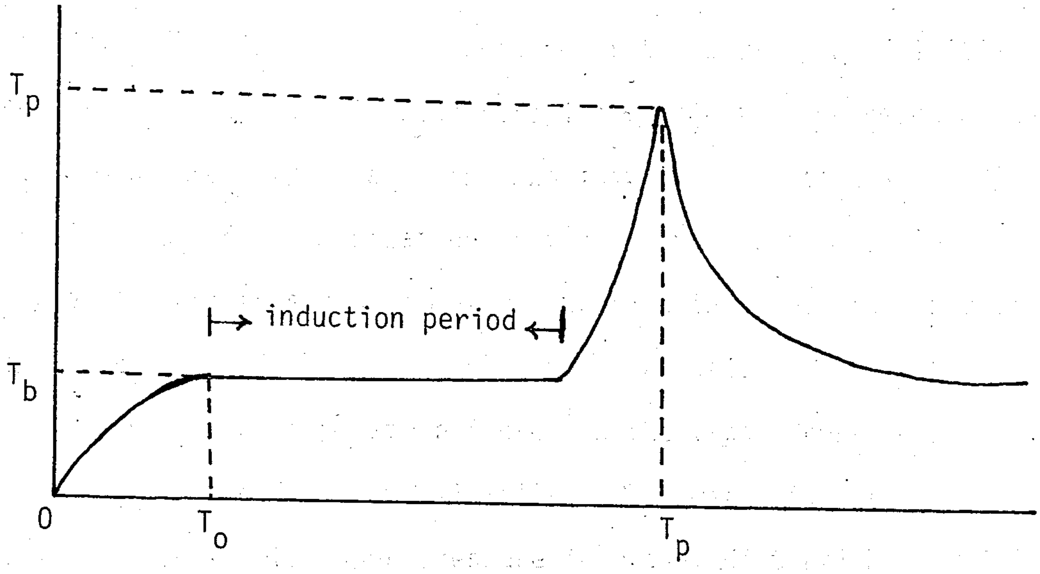


Fig. 1.5.1 - Idealized temperature-time exothermic curve [2]

Wood is a poor heat conductor. So when heat is released due to exothermic reaction the temperature inside the wood can very easily rise to damaging levels. An increase in temperature causes faster polymerization which in turn results in an increased heat generation. This self acceleration is harmful in three respects; First of all in such a reaction polymer chains with innate tensile and conformational strains are obtained. Secondly the rise in temperature which can exceed 100°C can cause damage to the wood structure and therefore to the W.P.C. formed [1]. Last but not least is the monomer loss due to temperature increase and volatility of the monomer.

The advantage of radiation polymerization was that polymerization rate could be controlled. Complete radiation curing of wood-monomer composite requires 8 to 10 hours. The exothermic heat is still released but temperature is much lower because of the slow rate of initiation. However in catalysis initiated reaction the initiation reaction terminates much more faster (e.g. in Vazo initiated reaction it is 30 to 40 min [2]) heat of polymerization of a certain monomer is released in a shorter period; thus causing a greater rise in temperature additional to that required for initiation of polymerization.

This high temperature increases the vapor pressure of the water and of the monomer in the cell walls. When water is driven out of the cell wall due to its vapor pressure increase, distortion of original shape and shrinkage is observed [2]. Siau and Meyer observed considerable shrinkages which occurred after heat polymerization. This is contrary to radiation polymerization in which swelling was observed [15]. They concluded that heat had driven out monomer out of the cell wall. An evidence to this was the lower A.S.E. values obtained by heat polymerization.

Also studies on hardness, tangential mechanical strength and density showed that loss of monomer occurred in a considerable amount from the surfaces during the polymerization reaction. A slight increase in composite density was observed after the machining operation. The decrease in surface hardness confirmed it [19,13]. Meyer stated that W.P.C. cured by heat catalysis process had to be machined to the final shape after treatment [2].

1.5.2 Previous Works Done to Prevent Monomer Loss

Most monomers used in W.P.C. formation are more or less volatile. Several attempts were made to prevent monomer loss during heat polymerizatio

Wrapping to Aluminium foil did not give satisfactory results [19]. High pressures can be used to limit the volatility of the monomer but this is not an efficient way from technical and economical points of view. Addition of a cross-linker (1-5% by weight) is an efficient way to decrease monomer loss. A considerable amount of monomer loss thus a decrease in polymer loading occurs due to the initial heat of the curing oven and heat released at the beginning of the exothermic polymerization reaction. A cross-linker such as a divinyl monomer [e.g. ethylene glycol dimethacrylate (EGDMA)] which contains two double bonds forms a gel initially and prevents the escape of the monomer. Cross-linker also increases the molecular weight and a thermosetting polymer is formed which will decompose before melting. The nonmelting characteristic is important in the machining and sending of the final product [2].

Another way to prevent monomer loss during heat catalysis process is to make highly viscous constant temperature bath. Lawniczak Maciej polymerized wood impregnated in styrene and/or vinylacetate which contained a catalyst in molten wax. He claimed that wax hindered the evaporation of monomer and gave greater than 90% conversion to polymer [27]. However we think that paraffin diffusion into wood has not been allowed for our own experiments on wax bath heating will be discussed in Results and Discussion Section.

Moragne tried to develop a method for producing a plastic impregnated article by heat catalysis process [28]. The porous material is vacuum impregnated with a treated methyl or ethyl monomer and the impregnated material is thereafter heated by an external heat source to the temperature required to initiate. The external heat source is then removed and the heat generated by the initial polymerization is used to complete the polymerization of the remaining monomer. Moragne treated the monomer with some additives (methacrylic acid and methanol). It was found out that the quantity and type of chemical added to the monomer controlled the polymerization temperature of the monomer, the rate of polymerization, the amount of polymerized monomer remaining in the final product and the time required to effect a complete cure of the remaining polymer. It was discovered that reaction temperature determined as one would expect the amount of monomer remaining in the finished product. These data are given for % monomer loss at certain temperatures.

Table 1.5.1 - % Monomer Loss at Certain Temperatures [28]

Temperature	% Monomer Loss
121°C	90%
93.3°C	75%
65.5°C	50%
37.7°C	20%

1.6 POLYMER SYSTEMS USED FOR WOOD-POLYMER COMPOSITES

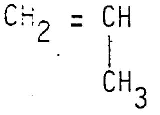
The properties of wood are improved when a W.P.C. is formed. The improvement in the physical and dimensional properties of the wood depends on the polymer with which it is combined. Wood polymer composites made thus far can be mainly classified into two groups. Those made by irradiation polymerization and those formed by heat catalysis polymerization. However some are formed by direct impregnation of wood samples with the polymer without any need of polymerization.

When a W.P.C. is to be made it must be kept in mind that for a certain polymer improvement in physical properties can not be obtained for all species of wood. While some species give very satisfactory results with one kind of polymer, for the same polymer combination with other kind of species is unsuccessful.

Given below are the vinyl monomers used in W.P.C. formation and the properties of some W.P.C. formed with these monomers.

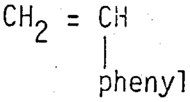
$CH_2 = CH_2$

ethylene



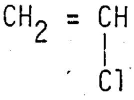
$CH_2 = CH(CH_3)$

propylene



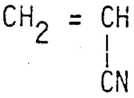
$CH_2 = CH(\text{phenyl})$

styrene



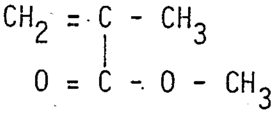
$CH_2 = CH(Cl)$

vinyl chloride



$CH_2 = CH(CN)$

acrylonitrile



$CH_2 = C(-CH_3)(-C(=O)-O-CH_3)$

methyl methacrylate

Table 1.6.1 - Types and Properties of W.P.C.

	Type of W.P.C.	Improved Properties	Technical Advantage/Disadvantage
Radiation initiated polymerization	Wood-polystyrene	Great reduction in water uptake i.e. increase in dimensional stability	- Can impregnate most species of wood satisfactorily. - High radiation doses required, which is harmful to wood.
	Wood-PMMA	Enhanced mechanical properties Increase in dimensional stability	- Appropriate doses required for polymerization - High cost.
	Wood-polyvinyl acetate	- Enhanced mechanical properties	- Polymerized easily by radiation - Polymerization inhibited by the natural resin of some wood species.
	Wood-polyvinyl chloride	- Increase in abrasion resistance - Increase in dimensional stability - Reduction in combustibility	- Gaseous at room temperature therefore difficulty in impregnation.
	Wood-polyolefins (ethylene)	- Improved dimensional stability	- High pressure required for impregnation
	Wood-unsaturated polyester+vinyl monomers	- Improved mechanical properties increase impact strength, bending strength and bulk density	- Polyester impregnation without irradiation also shows considerable improvement. - Difficulty in impregnation.
Chemically initiated polymerization	Wood-PMMA	Same improvements obtained by radiation polymerization	- Less costly than radiation polymerization - Monomer loss during polymerization.
	Wood-polyester +vinyl monomers	Same improvements obtained by radiation polymerization.	- High heat of polymerization i.e. significant rise in temperature.

II. PRESENTATION OF THE PROBLEM

Wood is used in industry in a wide variety of ways and continuous attempts are made to modify it for a specific usage.

When a polymer is incorporated with wood the mechanical and dimensional properties of wood can be greatly improved. Formation of a wood polymer composite with impregnation of vinyl monomers can be achieved in two ways. Radiation polymerization and heat catalysis polymerization. The former although has many advantages over the heat catalysis polymerization method is too costly and requires great investments due to source of radiation, pollution and safety considerations. This would increase the cost of the end product thus making the process quite improfitable.

Heat catalysis polymerization is less costly and therefore can be efficiently applied in industry. One of the serious drawbacks of this method is the monomer loss during polymerization. When large scale production is considered this loss would reach to such high values that production of a wood-polymer composite would be quite insignificant due to cost considerations since the monomer is quite expensive. Since an improvement in the properties of wood does not depend on the method of polymerization heat catalysis polymerization can be efficiently used if the monomer loss can be prevented during polymerization.

The aim of this work is to develop a method to decrease the monomer loss during heat catalysis polymerization so that a profitable large scale production can be made.

White pine, a soft, light and coarse grained softwood specie is chosen for the work. The low cost of this specie is also taken into account. When the increasing cost and shortage of hardwoods is considered hardened white pine with increased dimensional stability can challenge hardwood used in industry.

The polymer chosen for the formation of the composite is polymethylmethacrylate the polymer of methyl mechacrylate. PMMA-wood combinations have been widely investigated due to the excellent mechanical properties of this polymer. However not much work has been done to decrease the monomer loss during polymerization.

Finally the increase in dimensional stability and hardness obtained in the resulting composite is measured. This is important from commercial point of view because the properties of the composite will determine its adaption to a specific usage.

III. RESULTS AND DISCUSSION

Catalyst heat process for polymerization requires a heating medium. Simple oven heating of an impregnated sample results in unacceptably high losses of monomer due to volatilization. Therefore some sort of a heating bath containing a fluid for heat transfer is required. This fluid should have a number of properties such as ease of handling inertness, immiscibility with the monomer used and ease of removal from wood after polymerization. Water looks like a good choice and polymerization was first tried in a water bath. Monomer loss through dissolution-evaporation was still quite high which required further work on the monomer loss problem.

Methods used to decrease monomer loss involved improvements in heating medium and reduction of polymerization temperature through the use of different catalysts. The obvious method, high pressure polymerization was not tried because we believe that this may be a costly process in a large scale operation. Impregnation with polymethylmethacrylate methyl methacrylate mixtures was also tried with quite successful results.

To decrease monomer loss during polymerization by catalyst heat technique several methods were tried. Before going into the details of these solutions and analysing the results obtained, the experiments done beforehand will be mentioned.

3.1 EFFICIENCY OF IMPREGNATION

Temperature and time dependence of monomer loading in wood was determined. Three sets of monomer solutions were prepared each containing 4 samples and at different temperatures. In each set two of the samples were hornbeech and two were of softwood (white pine) species. These three sets were maintained at $0^{o}C$ 5ice bath) room temperature and $40^{o}C$ respectively. The samples were first treated in an oven at $60^{o}C$ until they reached constant weight then these were immersed in the three different temperature monomer solutions. The plot is made by taking the average of softwood and hardwood samples at each temperature.

The impregnation rate is highest in the first 24 hours (Fig. 3.1.1). A constancy is observed after the eighth day and then an increase after the tenth day. This may be due to the high resistance of the lamella where monomers enter the cell wall. As penetration proceeds the structure will relax gradually resulting in an increased diffusion rate [17].

At $40^{o}C$ very high loadings are observed. At high temperatures the air trapped in the voids can be more easily replaced by the incoming monomer which has a high vapor pressure. The difference in impregnation at $0^{o}C$ and room temperature was not found to be significant. This result is promising for an industrial plant since at $0^{o}C$ monomer loss is at its minimum.

The experiment also showed that after prolonged immersion high monomer loadings could be obtained. After 70 days at $40^{o}C$ %154 to %164 increase in weight with respect to original weight was observed. This data is in accordance with Siau's observations [17]. As a consequence

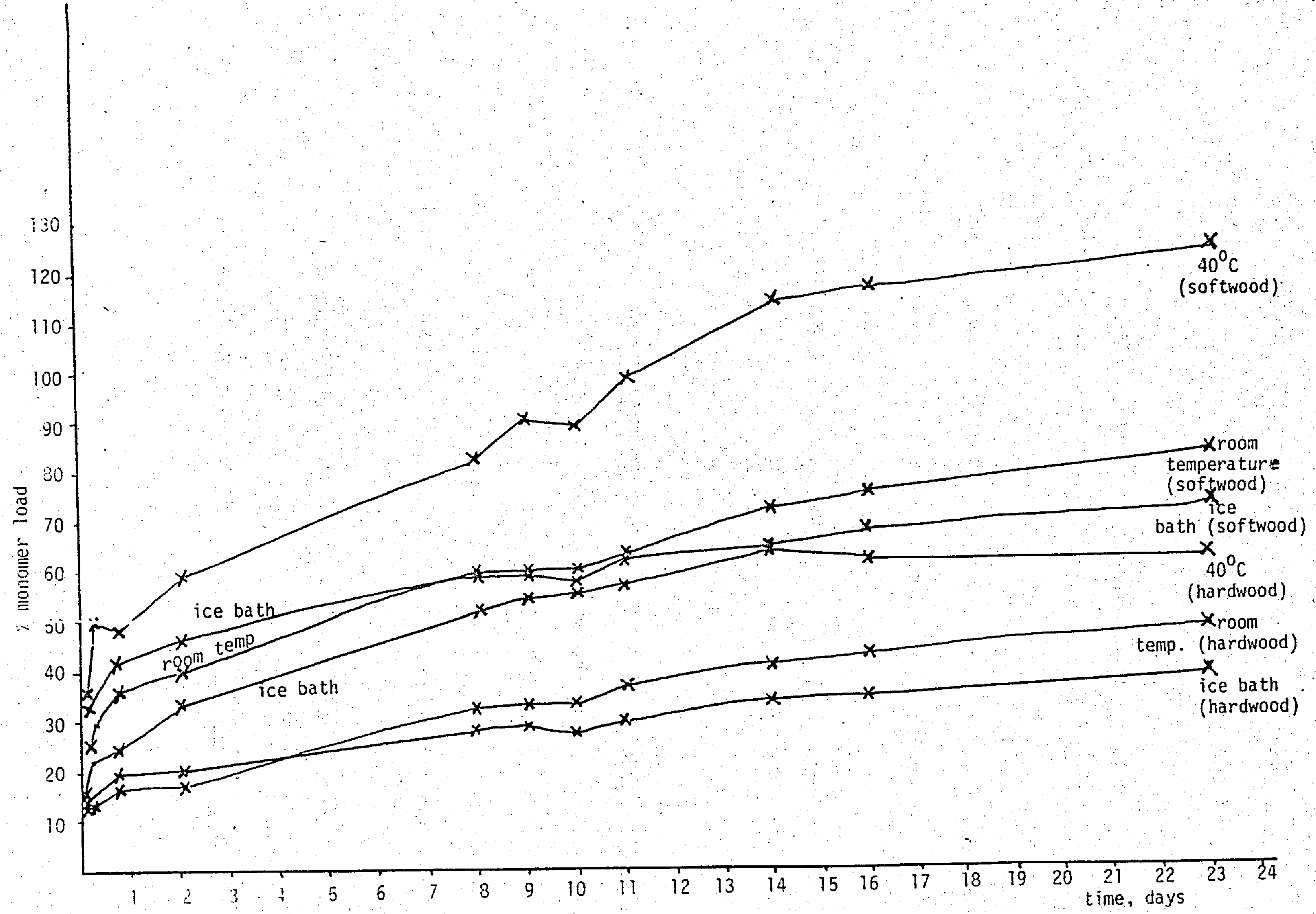


Fig. 3.1.1 - Impregnation in monomer versus time

of time dependence for monomer loading necessary time for a certain load can be adjusted to obtain the required loading. Though it must be kept in mind that loading differs greatly between different species of wood and the region of wood where the sample is taken [14].

A good method of reporting impregnation data is by means of "efficiency of impregnation". This value compares the theoretical maximum loading (TML) prossible if all the void space in the wood is filled with monomer to the actual loading.

The efficiency of impregnation can be determined by first calculating the theoretical maximum loading and dividing the actual loading to it [31,1].

The theoretical maximum loading (TML)

$$\%\text{TML} = \left[1 - \frac{D_w}{1.54}\right]\frac{D_m}{D_w} \times 100$$

where %TML = the maximum percent increase in weight of impregnated wood with respect to original wood.

D_w = Gross density (bulk density) of wood.

D_m = Density of monomer.

1.54 = Accepted density of solid material in wood [1].

$$\%\ \text{Actual Loading} = \frac{\text{Wt. of impregnated wood} - \text{Wt. of original wood}}{\text{Wt. of original wood}} \times 1$$

$$\text{Efficiency of Impregnation} = \frac{\%\ \text{Actual loading}}{\%\ \text{TML}} \times 100$$

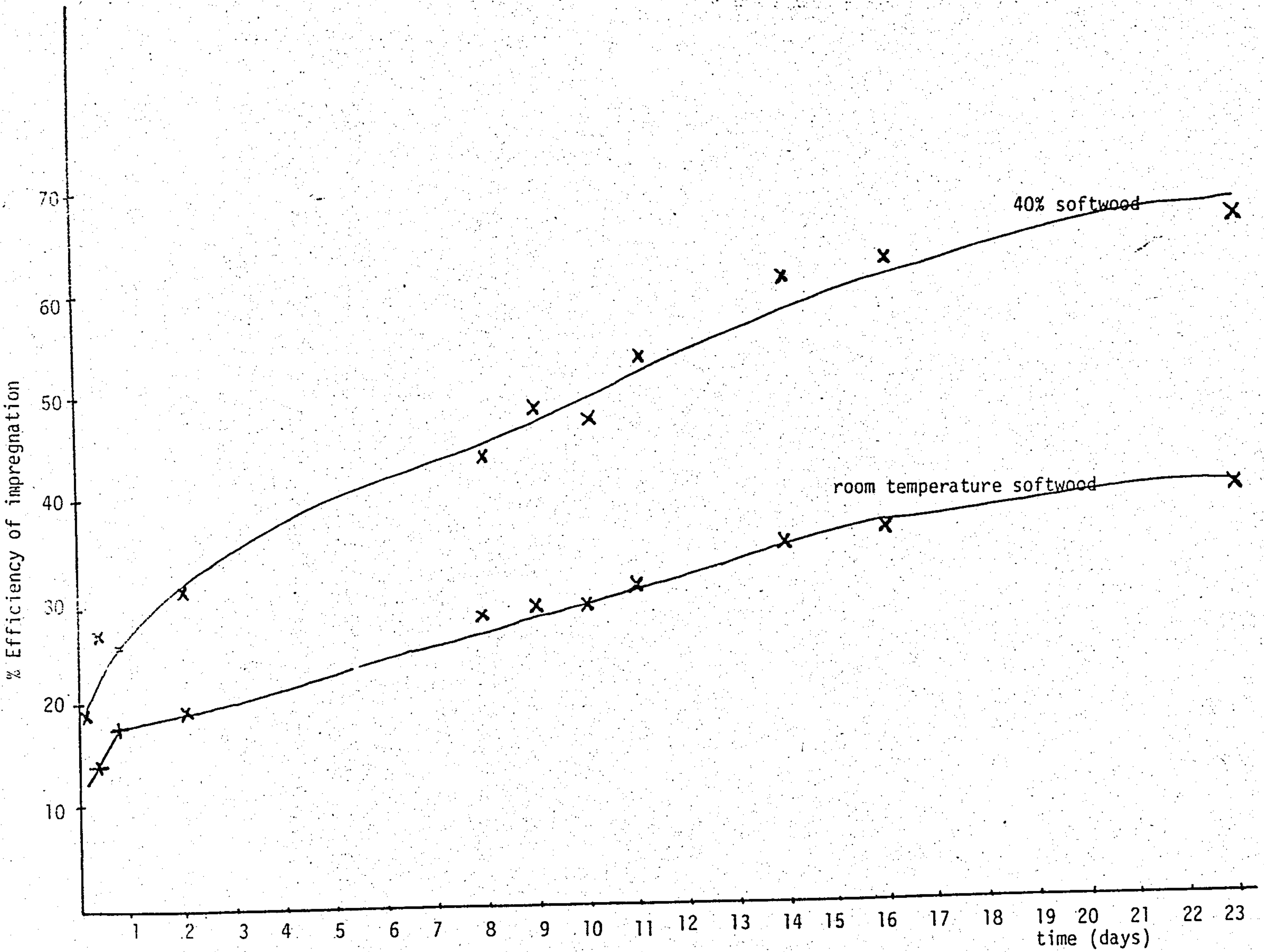


Fig. 3.1.2 - Efficiency of impregnation versus time

The approximation in these calculations is that the swelling of cell walls by the monomer is negligible and the free volume determines the maximum amount of monomer that can be impregnated [1]. This approximation is however not entirely correct when the anti-shrink efficiency (ASE is a measure of water absorbtion property of wood) data are considered, since it is claimed that A.S.E. is proportional to monomer penetration in the cell wall [16,17]. All the same efficiency of impregnation versus time gives a general view for time and temperature dependence of impregnation (Fig. 3.1.2).

To calculate D_W - gross density of wood, the volume and dry weight of the samples used were measured and a simple calculation gave an average density of 0.382.

For samples at room temperature TML% was found to be 204.5%, that is the sample could be loaded to a weight of 204.5% of its original weight. At 40°C after 70 days impregnation a 85.8% efficiency in impregnation was obtained.

3.2 THE EFFECT OF ADDITION OF CATALYST AFTER IMPREGNATION

Storage of a monomer-catalyst mixture is potentially troublesome: polymerization of the impregnation mixture would lead to a major commercial loss. Hence it would be advantageous if impregnation could be done with pure monomer and catalyst could be later added.

So it was aimed to observe the effect of the time of addition of catalyst. In one run the wood samples were placed in a monomer solution containing catalyst (1% benzoyl peroxide). In a second run the wood run the wood samples were first impregnated with pure monomer then transferred to a solution containing catalyst, and monomer. They were left for a couple of days until equilibrium was reached. These were then polymerized. The efficiency and improvement of the method used is determined by "% conversion" which is equal to:

$$\% \text{ conversion} = \frac{\% \text{ polymer load}}{\% \text{ monomer load}} \times 100$$

where

% polymer load = % increase in wt. with respect to dry weight after polymerization

% monomer load = % increase in wt. with respect to dry weight before polymerization (after impregnation).

Table 3.2.1 - Results for Addition of Catalyst During and After Impregnation

	Sample	% monomer load	% polymer load	% conversion
Impregnation with monomer catalyst mixture	16	53.7	25.68	47.8
	17	56.8	25.47	44.8
MMA impregnation followed by addition of catalyst	10	100.9	79.2	78.5
	15	114.0	75.05	65.8

As seen from Table 3.2.1 the addition of catalyst after the wood is already loaded with monomer effects % conversion in a positive way.

When the experiment done in 3.1 and this is combined we arrive at an advantageous situation from technical point of view. That is a monomer can be first impregnated at any temperature in pure monomer and then transferred to a solution containing catalyst maintained at lower temperature. The preservation of the stock solution of the monomer will be thus achieved easily.

3.3 COATING TECHNIQUE

Coating the wood samples with another polymer was one of the methods tried to prevent monomer loss during polymerization. Coating could block the pores of the wood thus preventing the diffusion of the monomer through it.

The most important thing to be considered in this method was that the solvent in which the coating polymer was dissolved had to be very volatile so that a quick and efficient coating could be obtained.

Two polymers were used for the purpose: cellulose butyrate and cellulose acetate. Three experiments were made. In the first experiment wood samples were first impregnated with MMA and 1% catalyst for 12 days. Then they were weighed coated with cellulose butyrate in butylacetate and heated to 80^{o}C in a water bath with the uncoated control samples.

Table 3.3.1 - Polymerization of Cellulose Butyrate Coated Wood

	Sample	% monomer load	% polymer load	% conversion
Control samples	1	121.9	66.2	54.3
	2	148.4	87.4	58.8
Coated samples	3	135.66	71.2	52.5
	4	105.54	56.2	53.24
	5	88.56	46.5	52.5

As seen from table no significant difference between the coated and uncoated samples was observed.

A second experiment gave the same results where the % conversion of the untreated samples was 43.1%, the average of the coated ones were 40%.

In third experiment cellulose acetate was used for coating. Cellulose acetate was thought because of its cellulosic nature, and also because the solvent acetone was very volatile. It was expected that cellulose acetate would be more efficient in preventing MMA loss during polymerization. However the opposite was observed.

Table 3.3.2 - Cellulose Acetate and Cellulose Butyrate Coated Wood

Kind of treat	Average %conversion
Cellulose butyrate coated	60.6
Cellulose acetate coated	26.8

Results obtained showed that polymer coating was not an efficient way to prevent MMA loss during polymerization. One reason may be that these polymers do not efficiently coat the pores of the wood. Also MMA is soluble in the solvents used to dissolve the coating polymers. It is probable that MMA impregnated in wood dissolved in these solvents and evaporated with it during coating. Serious MMA losses were observed during the coating operation, making this process quite useless.

3.4 POLYMERIZATION IN VISCOUS FLUID

Diffusion coefficient of a gas is proportional to its average velocity and mean free path. Since the mean free path is inversely proportional to the pressure the diffusion coefficient decreases with increase in pressure. At high pressures the molecule has to make many more collisions and its progress in any direction is slowed down.

This recalled the idea of polymerization in a viscous bath instead of water. Two different viscous fluids were tried; Polyacrylamide gel and paraffin wax. Lawniczak [27] claimed that wood impregnated with styrene and/or vinylacetate containing a catalyst when heated in molten paraffin wax hindered evaporation of the monomer and gave 90% conversion to polymer.

This experiment was repeated with wood impregnated with MMA. The first data obtained seemed to fit Lawniczak's claims. However we suspected that paraffin penetrated wood and the observed high polymer loading was actually polymer + paraffin loading.

A solvent that would dissolve paraffin but not PMMA had to be chosen to reextract the paraffin and determine the actual polymer loading. Cyclohexane was found to be fit for the purpose. Wood samples were left overnight in cyclohexane in each extraction.

The amount of paraffin extracted corresponded to the loss in weight. As can be seen from Table 3.4.1 there is a significant lowering in weight when paraffin is extracted out of the wood samples. This indicates that paraffin has penetrated into wood and the high % conversion obtained is not due to hindrence of monomer loss but due to paraffin penetration. Paraffin penetration is not desired in the end product and it gives a false impression on the improvement of % polymer loading in the end product. These conclusions show that paraffin wax usage in polymerization is not a reliable method.

Table 3.4.1 - Wood Polymerized in Paraffin and Reextracted

Sample	% monomer load	% polymer load	% conversion
Before treat	86.90	81.61	93.91
After first extraction with cyclo hexane	86.90	72.35	83.26
After second extraction with cyclo hexane	86.90	68.78	79.15

The second viscous fluid was prepared from polyacrylamide. A highly viscous polyacrylamide gel was prepared and brought to the required temperature. Wood samples impregnated with MMA were dipped in this bath. An immediate whitening of the transparent fluid was observed which indicated the formation of PMMA from the monomer evaporating from the wood samples.

When data obtained from samples polymerized in polyacrylamide gel and water bath (Table 3.4.2) were compared it was seen that polymerization in polyacrylamide gel did not prevent loss of monomer significantly.

After that these results were obtained it was decided that polymerization in a viscous fluid would not be an efficient method for a W.P.C. formation by heat-catalyst method.

Table 3.4.2 - Polymerization in Polyacrylamide Gel

	Samples	% monomer load	% polymer load	% conversion	Average % conversion
in polyacrylamide gel	11°	51.13	14.45	28.26	26.37
	8°	67.02	16.41	24.48	
in water bath	7°	64.83	13.13	20.62	21.31
	10°	57.52	12.66	22.01	

3.5 LOWERING POLYMERIZATION TEMPERATURE BY USING DIFFERENT INITIATIORS

3.5.1 Polymerization Initiated by Ceric Ions in Aqueous Solution

Santappa et.al studied the kinetics of vinyl polymerization initiated by ceric ions in aqueous solution [32,33]. The free radical nature of polymerization was indicated since polymerization was inhibited by oxygen hydroquinone and phenol. The polymerization was found to take place without an induction period and the steady state rate was attained within a short time. The following sequence of reactions were proposed.

$Ce^{+4} + M \rightarrow Ce^{+3} + R\cdot$ (initiation)

$R\cdot + M \rightarrow R\text{-}M\cdot$ (propagation)

$(R\text{-}M)^{\cdot}_{n-1} + M \rightarrow (R\text{-}M)^{\cdot}_{n}$

$(R\text{-}M)^{\cdot}_{n} + Ce^{+4} \rightarrow P_n + Ce^{+3} + M^{+}$ (termination)

The experimental set-up in our work was as follows:
Two test tubes each containing 9 ml water, 1 ml $HClO_4$ (0.9 M) and a tip of $Ce(SO_4)_2$(1 v). In one of these test tubes pieces of wood were added.

Time elapsed	Test tube containing wood	Test tube without wood
5 min	no change	no change
10 min	no change	turbidity in MMA
15 min	no change	turbidity increased
20 min	no change	PMMA formed

In test tube containing no wood polymerization started with a very short induction period coinciding with that given in paper. The formation of no PMMA in test tube containing wood showed that the reaction $Ce^{+4} + M \xrightarrow{k_i} Ce^{+3} + R\cdot$ did not occur in presence of wood. A charge transfer reaction may have occurred between the metal ion and molecule that acted as donors in wood. It is known that many metal ions form complexes which are often stable with olefins, dienes (usually conjugated) and aromatic rings. Electron density is transferred from the orbital to the metal. It is evident that the aromatic rings, conjugated dienes found in wood have prevented the formation of an initiator radical.

3.5.2 Initiation by Cu Powder and Formic Acid

Takashi Yamanouchi used Cu powder and HCOOH (85%) + MMA in equal amounts dissolved in water for polymerization reaction. After 24 hours a polymer having a polymerization degree of about 2000 was obtained [34].

Experiment was repeated in two different test tubes containing MMA + HCOOH + Cu powder each wood pieces were added in only one of the test tubes.

PMMA was formed in test tube that did not contain wood pieces and no PMMA formation was seen in test tube containing wood most probably due to reasons stated in 3.5.2.

3.5.3 Methyl-Ethyl Ketone Peroxide Initiated Polymerization

Methyl ethyl ketone peroxide with Cobalt Naphtanate or Cobalt Octoate initiates polymerization at room temperature. The effect of MEKP and Co octoate on polymerization of MMA in wood was observed. The following sets were prepared in test tubest at room temperature.

Composition	Observation
1. 10 ml MEKP + 2% MEKP	Polymerization
2. 10 ml MEKP + 2% MEKP + wood chips	No polymerization
3. 10 ml MEKP + 2% MEKP + Co octoate	Polymerization
4. 10 ml MEKP + 2% MEKP + Co octoate + wood chips	Polymerization

Polymerization was seen except in the second case where the test tube contained MMA + MEKP + wood chips. The initiation of polymerization at room temperature with Cobalt octoate in fourth case is not adequate for W.P.C. formation since impregnation problems would arise unless impregnation is done by vacuum pressure method and at low temperatures.

Polymerization was observed when the test tube containing MEKP + MMA + wood chips was placed in a water bath at 50-55°C. This seemed to be a promising result since polymerization temperature was reduced significantly and combination of this result with polymer-monomer impregnated systems could easily lead to high % conversion values and minimum loss during polymerization. However several trials with polymer impregnated wood with MEKP did not give satisfactory results as expected. Nevertheless we think that a further study must be carried out with MEKP catalyzed systems.

3.6 IMPREGNATION WITH POLYMER-MONOMER SOLUTIONS

Raoult's law states that the vapor pressure if a solvent over a solution is equal to the vapor pressure of the pure solvent multiplied by the mole fraction of the solvent in the solution. The vapor pressure lowering is proportional to the mole fraction of the involatile solute.

$$p^o - p = x_2 p^o \qquad (3.6.1$$

where p^o = vapor pressure of pure solvent,

p = vapor pressure of solution,

x_2 = mole fraction of solute.

Solutions of high molecular substances show deviations from Raoult's law. The great difference in size of the molecules of the solute and solvent results in a number of properties specific to these solutions. A low rate of diffusion, a high viscosity the phenomenon of swelling are observed. These solutions usually show negative deviations from

Raoult's law. That is the solvent has a lower escaping tendency than in an ideal solution of the same concentration.

Oligomer-monomer impregnated systems were prepared before from polyester, polyisocyanate resins and epoxy resins [1]. In this work polymethylmethacrylate, methyl-methacrylate solution was tried. PMMA, the polymer of MMA was chosen since PMMA loading was desired in the end product. The aim of polymer-monomer impregnation was to obtain a vapor pressure lowering which would result in a decrease in monomer loss. Use of PMMA scrap material in a large scale operation was also aimed at.

The first trial was done by preparing three different solutions containing 20, 25, 30% PMMA respectively. Impregnation versus time and %conversion was determined.

It was seen that to obtain a significant loading for a polymer-monomer mixture more time was required than that for pure monomer. It was also seen that as polymer amount increased in the mixture less loading was obtained in a certain time interval on the average (Fig. 3.6.1). However individual specimens showed unexpected decrease (or increase) in intake of polymer-monomer solution in the same period of time (Fig. 3.6.2). A sample in 20% polymer-monomer solution which was expected to have a higher loading had a lower loading in the same time interval. The same thing was observed in the second trial.

To determine the improvement obtained by impregnating wood in polymer-monomer system the % total conversion and the % net conversion was evaluated. To do this the initial polymer intake was determined as follows. One of the samples from each solution was left without polymerization to evaporated until constant weight was reached. The increase

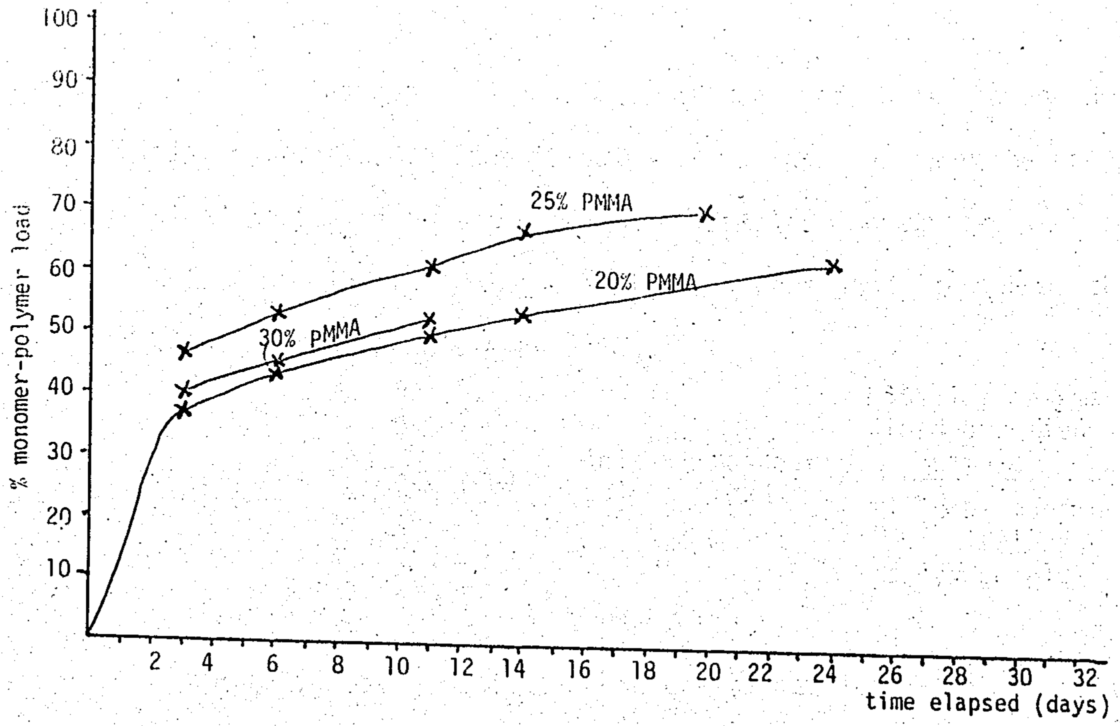


Fig. 3.6.2 - Impregnation in polymer-monomer solution versus time of some individual samples, showing the unexpectedly low intake in 20% PMMA solution.

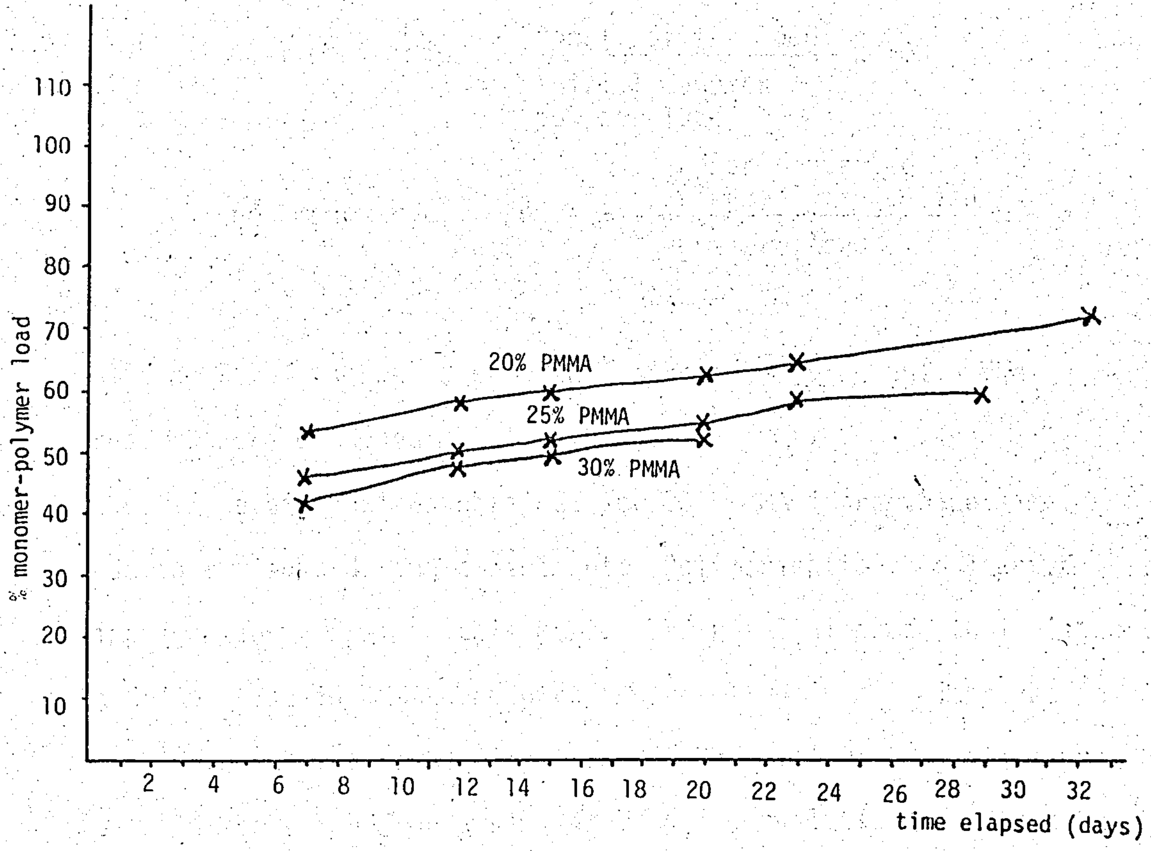


Fig. 3.6.1 - Impregnation in polymer-monomer solution versus time, Average data are taken

in weight with respect to dry weight was measured which showed the % initial poymer load. At this point it was assumed that the polymer/total load ratio was true for the other samples impregnated in the same solution. The following calculations were done throughout the experiments based on this assumption.

$$\text{\%initial polymer load} = \begin{matrix}\text{\%initial monomer}\\ \text{+polymer load}\end{matrix} \times \frac{\begin{matrix}\text{\%initial polymer}\\ \text{load of dried}\\ \text{sample}\end{matrix}}{\begin{matrix}\text{\%initial monomer +}\\ \text{polymer load of}\\ \text{dried sample}\end{matrix}} \qquad \text{(3.6.2}$$

$$\text{\%monomer load} = \text{\%initial monomer+polymer load} - \begin{matrix}\text{\%initial polymer}\\ \text{load}\end{matrix} \qquad \text{(3.6.3}$$

$$\begin{matrix}\text{\%monomer converted}\\ \text{during polymerization}\end{matrix} = \begin{matrix}\text{\%final polymer load}\\ \text{(after polymerization)}\end{matrix} - \begin{matrix}\text{\%initial}\\ \text{polymer load}\end{matrix} \qquad \text{(3.6.4}$$

$$\text{\%total conversion} = \frac{\text{\%final polymer load}}{\begin{matrix}\text{\%initial monomer +}\\ \text{polymer load}\end{matrix}} \times 100 \qquad \text{(3.6.5}$$

$$\text{\% net monomer conversion} = \frac{\begin{matrix}\text{\%monomer converted}\\ \text{during polymerization}\end{matrix}}{\text{\% monomer load}} \times 100 \qquad \text{(3.6.6}$$

All the % values are taken with respect to dry weight. The following results were obtained (Table 3.6.1).

The high values obtained for 20% PMMA impregnated samples were due to a mishap during experiment. Polymerization had started in the impregnation vessel in this case. The results seemed to indicate that a 5% increase in PMMA concentration resulted in a 5% increase in conversion on the average going from 25% PMMA to 30% PMMA solution. However in the second run a similar 1 to 1 correlation could not be observed.

Table 3.6.1 - Results of Polymerization with Polymer-Monomer Impregnated Systems

	Sample	% monomer + polymer load	% initial polymer load	% monomer load	% final polymer load	% monomer converted during polymeriz.	% total conversion	Average	% net monomer conversion	Average
% 20 PMMA	$\overline{5}$	75.11	27.96	47.15						
	$\overline{6}$	71.04	(26.44)*	(44.6)	64.94	(38.5)	91.41	(91.7)	(86.32)	86.79
	$\overline{12}$	62.5	(23.26)	(39.24)	57.5	(34.24)	92.0		(87.26)	
% 25 PMMA	$\overline{11}$	63.10	18.38	44.72						
	$\overline{10}$	58.53	(17.05)	(41.48)	46.18	(29.13)	78.9	81.97	(70.23)	74.55
	$\overline{4}$	70.77	(20.61)	(50.16)	60.18	(39.57)	85.04		(78.88)	
% 30 PMMA	$\overline{7}$	52.63	17.54	35.09						
	$\overline{8}$	52.56	(17.52)	(35.04)	45.59	(28.07)	86.74	85.7	(80.11)	78.55
	$\overline{9}$	52.30	(17.43)	(34.87)	44.28	(26.85)	84.66		(77.00)	

* *The calculated values based on the assumption and equations (3.6.2), (3.6.3), (3.6.4), (3.6.6) are shown in brackets.*

It can only be stated that as a general trend as the % PMMA concentration of the impregnating solution increases, monomer loss decreases. At this point the efficiency of high polymer concentrated solutions can be argued upon since the load with respect to dry weight is lower than the others. Neverthless quite high loadings were obtained by decreasing vapor pressure of MMA in solution.

The second run was done with 15%, 20%, 25% PMMA + 1% catalyst, to determine the most efficient concentration that would give high polymer loadings and maximum conversion. The 20% PMMA solution polymerized prematurally before the wood samples were taken out so no data could be taken. Actually in all PMMA MMA-solutions initiation of polymerization at room temperature was observed. The reason could not be understood.

From the data obtained from 15% and 25% PMMA impregnated wood samples it was seen that there was no significant difference in % conversion between these two sets of solutions (Table 3.6.3). Also there was no difference on the average in % increase in weight with respect to dry weight between them (Table 3.6.2). This was an unexpected result and it was due to the abnormal permeability or impermeability of the specific wood specimens. Considering that all samples were of the same specie these abnormalities indicated that impregnation depended very much on the region where the wood sample was from.

The net conversion and the total conversion values for the samples impregnated in 15% PMMA and 25% PMMA were estimated as follows: (The same assumption as in the first run is valid.) Even if abnormal increases or decreases in impregnation are absorbed for specific wood samples, an approximately high average loading can be obtained in a certain period.

Table 3.6.2 - Impregnation versus Time

	Sample	% wt. incr. after 2 days	(Average) %	% wt. incr. after 7 days	(Average) %	% wt. incr. after 9 days	(Average) %
15% PMMA	1^R	40.15	(33.43)	70.27	(54.94)	73.62	(57.73)
	2^R	31.89		52.4		54.94	
	3^R	28.26		42.35		44.76	
25% PMMA	7^R	31.82	(34.76)	51.02	(55.82)	51.84	(56.11)
	8^R	45.59		74.09		77.92	
	9^R	26.88		42.36		38.59	

Accordingly the time for impregnation can be adjusted for the weight required in the end product since the approximate % conversions can be estimated with this method. This will lead to formation of wood-polymer composite of desired loading.

The net conversion of approximately 85% are the highest we or any other researcher has ever obtained. We feel that polymer + monomer impregnation has resulted in a significant improvement in heat catalyst process for preparation of wood-polymer composites.

Table 3.6.3 - Results of Polymerization with Polymer-Monomer Impregnated System

Sample	% monomer + polymer load	% initial polymer load	% initial monomer load	% final polymer load	% monomer converted during polymeriz.	% total conversion	Average	% net monomer conversion	Average
1^R	73.62	16.17							
2^R	54.94	(12.06)*	(42.87)	48.84	(36.78)	88.90	(88.84)	(85.79)	(85.78)
3^R	44.76	(9.83)	(34.87)	39.74	(29.91)	88.78		(85.77)	
9^R	38.59	13.28							
7^R	51.84	(17.83)	(34.00)	47.84	(30.01)	92.3	(90.9)	(88.26)	(86.13)
8^R	77.92	(26.81)	(51.11)	69.74	(42.93)	89.5		(83.99)	

The calculated values based on the assumption and equations (3.6.2), (3.6.3), (3.6.4), (3.6.6) are shown in brackets.

3.7 ANTI-SHRINK EFFICIENCY

Water absorbtion and the accompanying dimensional changes is one of the chief drawbacks of wood as a structural material. Surface coatings generally do not "waterproof" the wood but may decrease its water uptake. W.P.C. on the other hand generally have low water absorbtions which makes them very attractive for marine structures. Anti-Shrink Efficiency is a measure of water absorbtion properties of wood.

The mechanism of water absorbtion by dry wood proceeds in two steps. Water entering dry wood in vapor form is absorbed into the cell wall and hydrogen bonds to the cellulose. As a result the cell wall swells and the overall dimensions of the wood increase [2]. When in W.P.C. polymer is located only in the void spaces available and little is located in cell walls, this loading in capillary vessels reduces the rate of water vapor diffusion into the cell walls. However Langwig et.al found that given enough time (a factor of 10 to 20) at high humidity water will eventually reach the cell walls and cause the same swelling as untreated wood [35]. This is the case when monomer does not penetrate the cell wall. However it has been found that an improvement in A.S.E. is directly proportional to incorporation of monomer in the cell wall. Although it was first thought that penetration of the monomer into the cell wall in significant amounts could only be achieved by solvent exchange method [15] it was then found that this was not the case. Loos et.al [21] and Siau [17] showed that vinyl monomers thought to be non-swelling because of their nonpolar nature did swell cell wall to some extent. Siau et.al [24] found an A.S.E. value of 40.3% for wood-PMMA composite. They claimed that this value offered a strong evidence for the interaction of monomer (MMA) with cell wall.

Usually A.S.E. calculations are based upon volumetric swellings. In such cases

$$\text{A.S.E.} = 100(S_c - S_p)/S_c \qquad [15] \qquad (3.7.1)$$

where S_c = volumetric swelling of the untreated control

S_p = volumetric swelling of polymer treated wood.

In our work we had to modify this equation due to the possible errors that could rise from incorrect volume measurements.

Our A.S.E. calculations were based on weight considerations. The treated and untreated samples were dried at 60°C in an oven and carefully weighed before they were soaked in pure water at room temperature and left for 20 days A.S.E. was calculated as follows:

$$\text{A.S.E.} = \frac{\begin{matrix}\text{\% wt increase of} \\ \text{untreated samples}\end{matrix} - \begin{matrix}\text{\% wt increase of} \\ \text{treated samples}\end{matrix}}{\text{\% wt increase of untreated samples}} \times 100 \qquad (3.7.2)$$

$$\begin{matrix}\text{\% wt increase of} \\ \text{untreated sample}\end{matrix} = \frac{\text{wt after soak - initial dry wt}}{\text{initial dry weight}} \times 100 \qquad (3.7.3)$$

$$\begin{matrix}\text{\% wt increase of} \\ \text{treated sample}\end{matrix} = \frac{\text{wt after soak - initial wt before soak}}{\text{initial weight before soak}} \times 100 \qquad (3.7.4)$$

From the data obtained A.S.E. versus polymer loading was determined. As a general trend it can be said that as % polymer loading

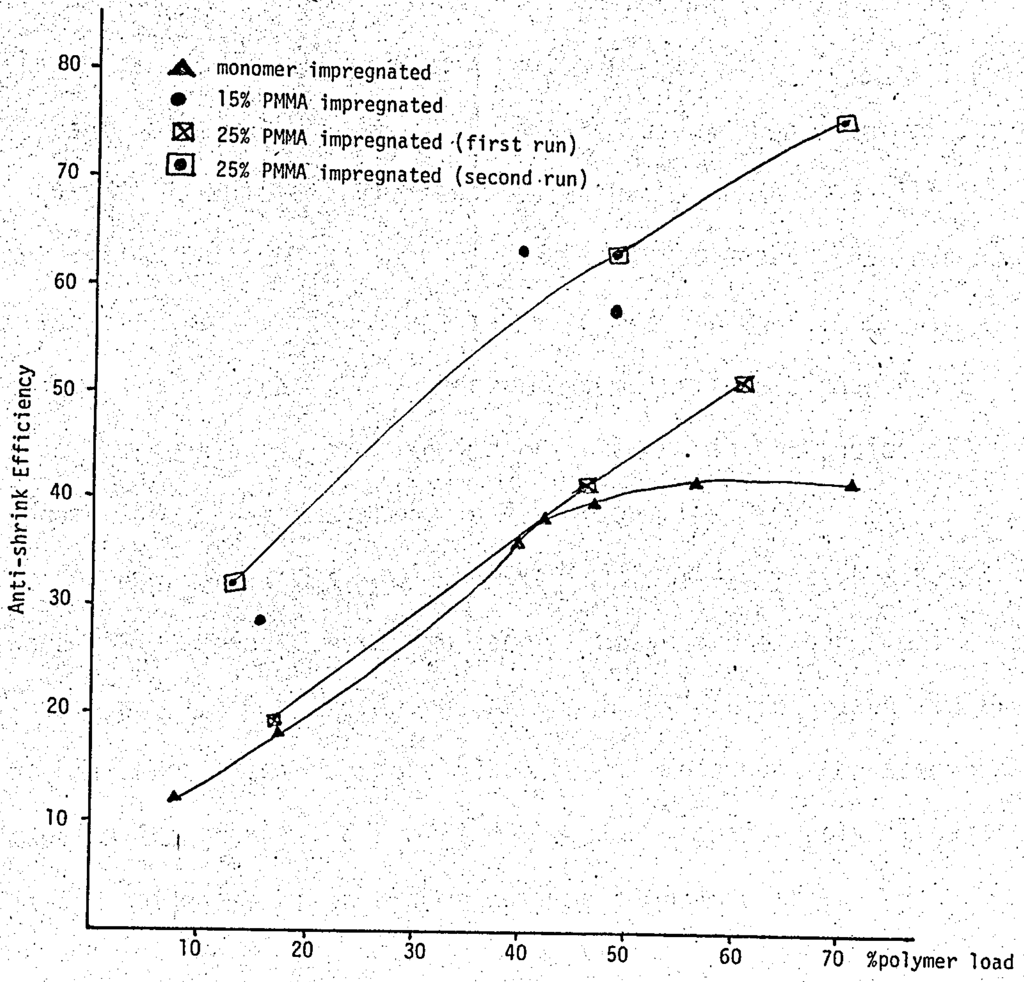


Fig. 3.7.1 - Anti-shrink efficiency versus % polymer load.

increases A.S.E. increases. However at approximately same % polymer loadings different A.S.E. values were observed. This shows the non-uniform or non equal penetration of the monomer in cell wall in different samples when it is considered that A.S.E. increases with increase of polymer content in cell wall. Another interesting observation was that the initially polymer impregnated samples had higher A.S.E. values than the purely monomer impregnated ones. This may be due to the shrinkage of MMA monomer upon polymerization. Meyer and Young estimates 25% shrinkage for MMA upon polymerization [14]. So in initially pure MMA impregnated samples voids will form in lumens upon polymerization whereas when PMMA is initially impregnated with MMA, PMMA will fill the lumens and void formation due to shrinkage will decrease. This can be the cause of lower A.S.E. values for pure MMA impregnated samples at similar loadings, when the PMMA impregnated samples have higher A.S.E. values. This observation is another important point in the choice of polymer-monomer impregnated systems in formation of W.P.C.

However it was found by previous workers that A.S.E. in case of wood-PMMA combinations as in case of polystyrene wood combinations was relative. That is the weight of specimens did not reach limit values even after periods of weeks [23,22,30]. This was the case in our work too. Although rate of swelling decreased considerably it was seen that it did not cease after prolonged immersion in water.

3.8 HARDNESS

Hardness is defined as the resistance of solid body to the entrance of another solid body by force [4]. For the anisotropic, heterogeneous, hydroscopic materials such as wood the hardness value is reliable when it is an average of many tests.

Hardness is one of the important technological property of W.P.C. and it is also the property in which we see the major improvement. The improvement of hardness in wood although proportional to the polymer content depends also on the specie of wood (See Fig. 1.3.1).

Meyer stated that the improvement in hardness in a W.P.C. was independent of the method of polymerization [18]. However Siau and Meyer later found that heat cured samples had lower tangential hardness values than radiation cured ones (the densities being the same) due to monomer evaporation from near the surfaces [19]. So a heat cured W.P.C. has to machined to its final state before usage [2].

Hardness measurements are made by forcing a hard material often a hardened steel ball into a flat surface of the material. Either the resultant degree of penetration under a known load or the load required for a certain degree of penetration is measured.

In our work the load required for a certain penetration was measured. In the initial experiment a steel ball of diameter 0.66 cm was used and the force required to immerse it in the sample up to half of its diameter was detected. No reliable results could be obtained in two different runs done to measure hardness perpendicular to grain because the steel ball of this diameter when imbedded to half of its diameter split the W.P.C. along the grain. This fact was observed by Meyer also [18]. The reason may be that PMMA is a brittle polymer.

A stell ball of greater diameter was chosen and the force required for penetration of 1/8 of its diameter was measured. An electrical contact mechanism was constructed to determine the immersion point accurately. The details of the apparatus and the preparation of the samples are given in the experimental section.

In our work hardness was determined on the surface perpendicular to grain (Figs. 3.8.1, 3.8.2) and on the surface parallel to grain (Fig. 3.8.3). The results of all of these tests for different polymer loadings showed that hardness increased as polymer loading increased. It was seen that hardness parallel to grain increased much more than the surface hardness perpendicular to grain. Increase in surface hardness perpendicular to grain at 70% polymer load is 2.2 fold in case of polymer-monomer impregnated system (it is 1.74 fold in case of monomer impregnated system) whereas increase in hardness parallel to grain at the same load for the same set is 3.15 fold. Siau and Meyer [19] explains this fact as greater amount of latewood cell material encountered when the surface is penetrated in the parallel direction.

Only a moderate increase in hardness perpendicular to grain is observed for both monomer impregnated and polymer-monomer impregnated set. Especially at lower loadings the rate of increase in hardness was found to be much slower (Figs. 3.8.1 and 3.8.2). For both of these sets a significant increase in hardness perpendicular to grain was seen only after 50% polymer load. In case of hardness parallel to grain quite high values were obtained at lower polymer loadings (Fig. 3.8.3).

The threefold increase at 70% polymer load obtained in hardness parallel to grain is still lower compared to increase in hardness of birch-PMMA composite which is 4.5 fold at the same loading [18]. However our data coincide with the results obtained by Fucillo et.al for white pine-PMMA combinations.

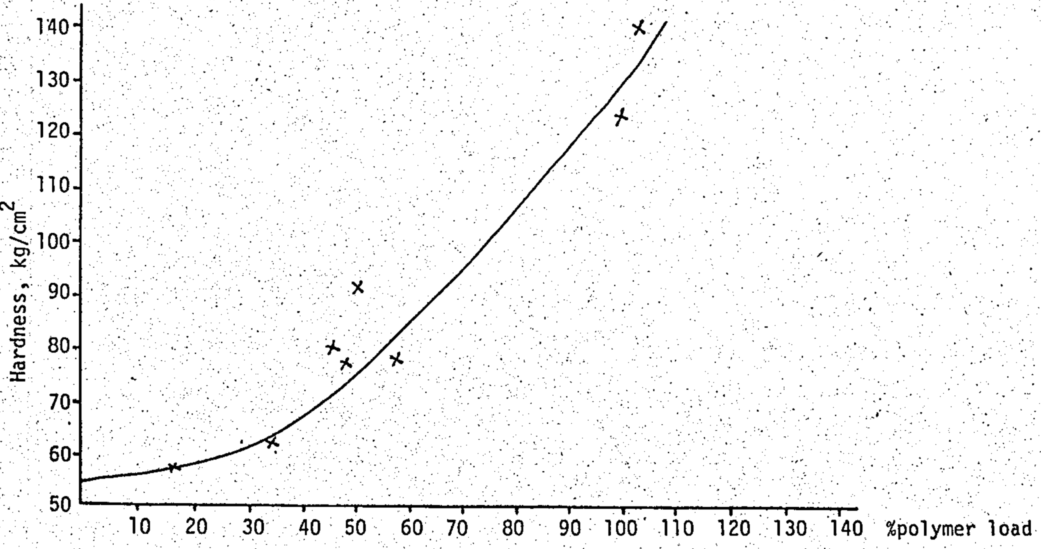


Fig. 3.8.1 - Hardness perperdicular to grain versus % polymer load for monomer impregnated system.

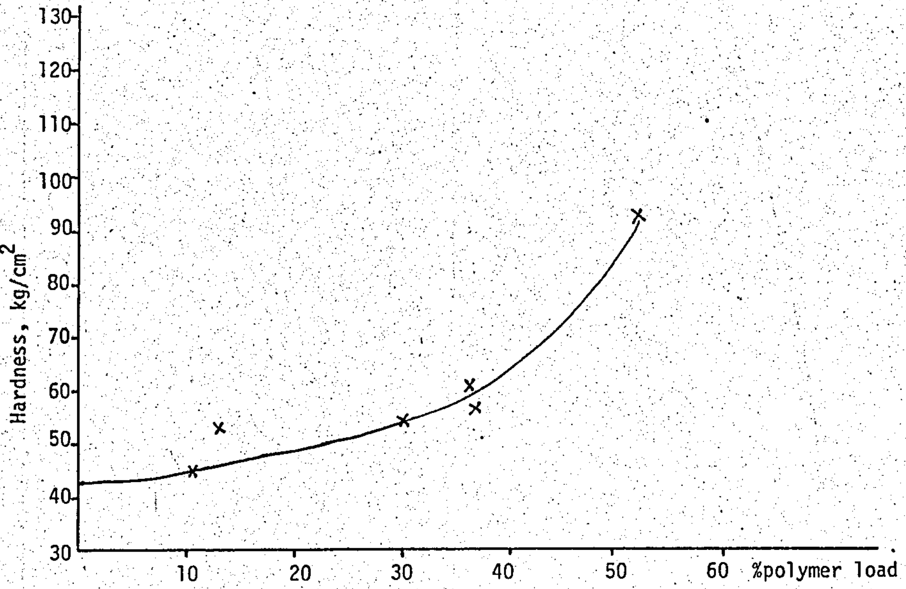


Fig. 3.8.2 - Hardness perpendicular to grain versus % polymer load for monomer-polymer impregnated system.

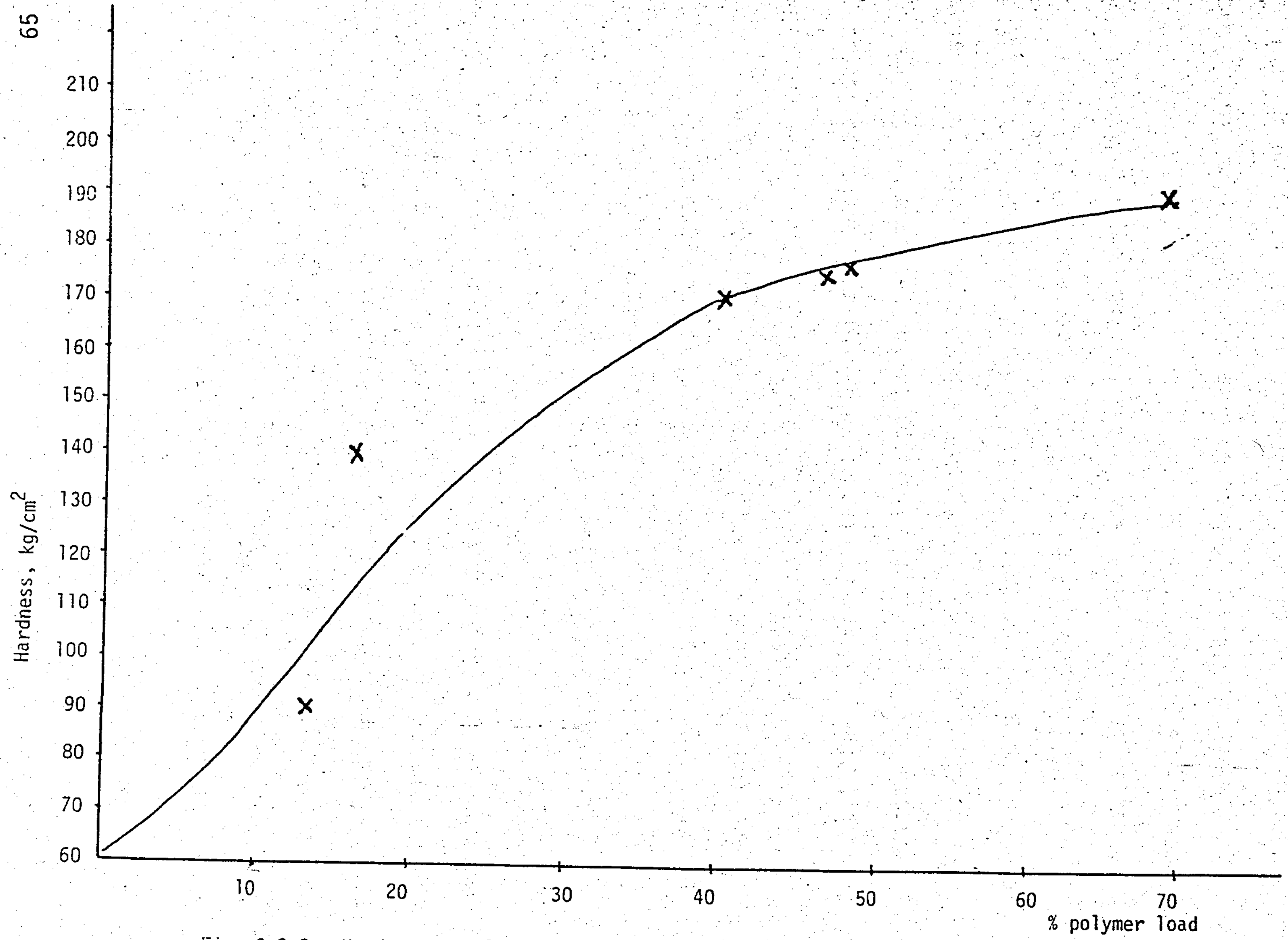


Fig. 3.8.3 - Hardness parallel to grain versus % polymer load for polymer-monomer impregnated system

3.9 DISTRIBUTION OF POLYMER IN WOOD-POLYMER COMPOSITE

It is known that monomer loss during polymerization takes place mostly at the surface regions. Whether the polymer is distributed homogeneously throughout the cross-section or is mainly concentrated in the middle region of wood is important. If it is concentrated mainly in the inner region of wood, wood has to be machined and external surface removed before a significant increase in physical properties can be achieved.

To determine the distribution of polymer in wood several reagents were applied to dye the polymethyl methacrylate and make it visible to the eye. The basic consideration was that the hygroscopic wood would absorb dyes dissolved in water while the hydrophobic polymer PMMA would not and a color gradient could be easily seen. Several reagents were tested. The name of reagents and the results of their application are summarized in Table 3.9.1. The application was done by dipping a thin section of wood in the reagent solution. Only very slight differences could be seen between untreated and treated samples. Although a distinct color gradient could not be obtained it was seen that the absorbtion of the reagent solution decreased in the treated sample indicating the presence of the polymer.

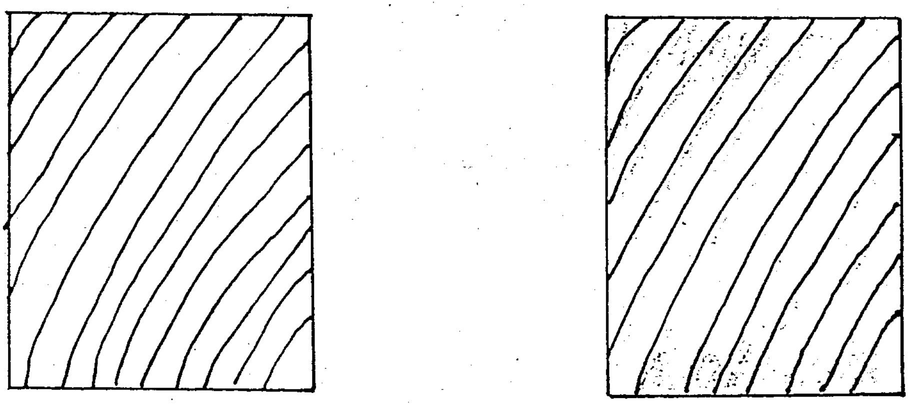
Meyer obtained a coloration with Rhodamine B-dye [18] in his work. Rhodamine B-dye colored PMMA fluoresced as dark blue and the cell wall structure as very light blue green under the microscope.

We did not use microscope in our work. Wood samples from treated and untreated wood speciments were cut in 1-2 mm thick pieces to reveal

Table 3.9.1 - Reagents Used to Stain PMMA-Wood Composite

Reagent	Observation		Remarks
	Untreated sample	Treated sample	
Iodine vapor (I_2)	Dark red	Dark red	No difference
H_2SO_4	Dark brown	Dark brown	No difference
CrO_3	Dark brown	Dark brown	No difference
Malachine green	Light green	Light green	No difference
Benzyl orange	Red	Red	No difference
Methylene blue	Blue	Blue	No difference
Methyl orange	Orange	Orange	Slight darkening along grain
Fluorescin M.V.	Yellow	Darker yellow	Slight darkening along grain. Darker than untreated control

the cross-section dipped in Rhodamine-B dye and examined under ultraviolet light. Untreated control samples fluoresced as pink, treated samples fluoresced as darker pink. The darker blue color was seen mainly along the grain. This indicated that polymer was located along the grain (late wood and partly early wood) and was distributed quite uniformly. In polymer-monomer impregnated systems dark blue color was denser near the surface of the wood (Fig. 3.9.1) which indicated that PMMA impregnation remained mostly on the surface.



Untreated sample

PMMA impregnated and polymerized sample

Fig. 3.9.1 - Cross-section of aqueous Rhodamine B- dye treated wood-PMMA composite under U.V.

VI. EXPERIMENTAL

4.1 IMPREGNATION

4.1.1 Impregnation in Pure Monomer

Methylmethacrylate was vacuum distilled before use. A vacuum of 40 to 50 mm was applied and MMA distilled at $30^{0}C$ to $35^{0}C$.

In all the experiments wood samples were first dried to constant weight in an oven at $60^{0}C$ before impregnation. Glass weights were put on wood samples to avoid floating. Beaker was covered with Aluminium foil.

4.1.2 Impregnation in Polymer-Monomer Solution

To prepare 15, 20, 25, 30% (by weight) PMMA-MMA solutions a known volume of MMA was taken. From the known density of MMA (0.994 gr/cm^3) weight of the known volume of MMA was calculated and the weight of PMMA required to obtain the desired % PMMA solution was thus determined. PMMA was dissolved in MMA with the aid of a magnetic stirrer at room temperature. The dissolution takes considerable amount of time (3 to 6 hours depending on % PMMA). Dried wood samples were placed in the solution and beaker covered with paraffin and Aluminium foil.

4.2 POLYMERIZATION

4.2.1 Polymerization in Water Bath

The impregnated wood samples were weighed and wrapped in Aluminium foil. They were then placed in a water bath at 80°C which is the temperature required for the dissociation of catalyst, (benzoyl peroxide). Curing time was 18 hours. Glass weights were used to avoid floating. Treated samples were then placed in an oven at 60°C for the evaporation of water that penetrated during the curing time. Polymerized wood samples were then weighed when they reached to constant weight to determine percent polymer load.

4.2.2 Polymerization by Coating Technique

The MMA impregnated samples were weighed and immediately dipped in the coating polymer; cellulose butyrate or cellulose acetate solution in butylacetate and acetone respectively. Then they were wiped with tissue paper; wrapped in Aluminium foil and immersed in water bath at 80°C for 18 hours. The samples were then dried to constant weight and percent polymer load determined.

4.2.3 Polymerization in Viscous Fluid

Paraffin wax was melted and temperature of melt raised to 80°C. Impregnated and weighed wood samples were placed in this melt without wrapping to Aluminium foil. Cure time was 18 hours. Wood samples were weighed to determine increase in weight. Since it was suspected that paraffin could have penetrated into wood these wood samples were placed in a weighed beaker containing cyclohexane and left for 24 hours. The wood samples were then reweighed. Cyclohexane was evaporated and the beaker reweighed to determine weight of paraffin extracted from wood. The decrease in weight of wood samples coincided with the weight of paraffin. The second extraction of paraffin was made in the same way.

In a different experiment polyacrylamide gel was prepared by dissolving polyacrylamide in water by the aid of a magnetic stirrer at room temperature. The temperature of the gel was raised to 80°C. The impregnated and weighed samples were then immersed in the gel (without wrapping in Aluminium foil). Cure time was 18 hours. Wood samples were then dried and weighed to determine polymer load.

4.2.4 Polymerization Using Different Initiators at Room Temperature

A) For the polymerization reaction initiated by Ceric ions two test tubes were taken. 1 ml of MMA, 9 ml of distilled water and 1 ml $HClO_4$ was added to each. Thus the concentration of $HClO_4$ was adjusted to 0.9 M. A spatula tip of $Ce(SO_4)_2$ (1 V) was added to each test tube. In one of the test tubes pieces of wood were added. Test tubes were left overnight at room temperature and result of the reaction was then observed.

B) Cu powder and formic acid initiated polymerization reaction was done in two different test tubes each containing 1 ml of 85% HCOOH, 1 ml of MMA, a spatula tip of Cu powder in 10 ml distilled water. In one of the test tubes wood chips were added. Test tubes were lift overnight at room temperature to observe the result of polymerization reaction.

C) Four different test tubes were prepared to observe MEKP (Methyl ketone peroxide) initiated polymerization in presence of wood. Composition of each test tube was as follows:

1. 10 ml MMA + 2% MEKP (a full droplet was added)
2. 10 ml MMA + 2% MEKP + wood chips
3. 10 ml MMA + 2% MEKP + few drops of Co octoate
4. 10 ml MMA + 2% MEKP + few drops of Co octoate + wood chips

All test tubes were left in water bath at 35°C for 18 hours. The second test tube in which no polymerization was observed was put to a water bath at 50-55°C and left for 18 hours.

4.3 ANTI-SHRINK EFFICIENCY DETERMINATION

The polymerized samples were dried to constant weight in an oven at 60°C. Then they were accurately weighed and the immersed in distilled water. Periodical weighings were taken to observe the water uptake. The last weight taken after 20 days was taken into consideration for the calculations.

4.4 HARDNESS DETERMINATION

The hardness tests were performed by determining the required load for a certain degree of penetration into wood. The ball test with a ball 13 mm in diameter was used. The load required for penetration of one eight of the diameter of the ball was measured.

A battery operated conducting circuit was fitted to the compression apparatus (Soil test - Model C-21) to indicate the penetration point accurately (Fig. 4.4.1). Different specimens with increasing polymer loading were prepared. At each specimen 4 measurements were taken for hardness perpendicular to grain. Only two measurements could be taken for hardness parallel to grain. Care was taken for the control specimen being from the same piece of wood as the treated specimens. Results were expressed as the average of these measurements.

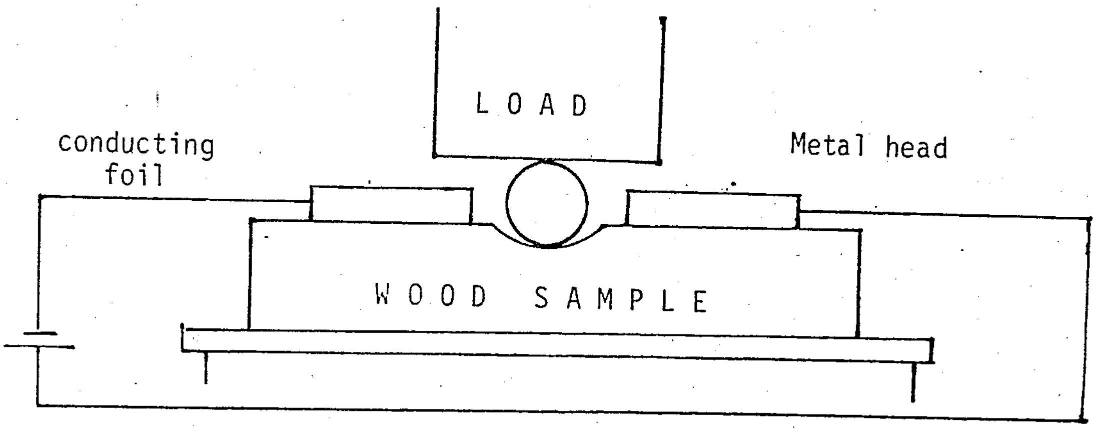


Fig. 4.4.1 - The ball hardness test apparatus

4.5 STAINING TECHNIQUE

Several indicators were used to stain wood or PMMA (Table 3.9.1). The aqueous solution of these reagents were prepared.

1-2 mm thick pieces were cut from the inner part of the polymerized wood specimens and from untreated control samples. The pieces from treated and untreated wood samples were placed in a beaker containing a small amount of reagent solution. It was expected that the reagent solution will move up along the wood dying the wood or PMMA and thus a color gradient could be observed. However a distinct color gradient could not be obtained except for pieces that were colored with Rhodamine B-dye and examined under ultraviolet light. In this case, the pieces were dipped in Rhodamine B-dye dried and examined under ultraviolet light.

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