ENHANCEMENT OF PROPERTIES OF WOOD BY

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GAMMA-INDUCED GRAFT POLYMERIZATION

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ENHANCEMENT OF PROPERTIES OF WOOD BY GAMMA-INDUCED GRAFT POLYMERIZATION

By

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TITLE: Enhancement of Properties of Wood by Gamma-induced Graft Polymerization

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SCOPE AND CONTENTS:

1. Conditions have been established which favour graft copolymerization with cellulose, when styrene-impregnated red pine wood is exposed to gamma radiation from the nuclear reactor.

2. The formation of the graft co-polymer within the wood structure effects significant improvement in bending strength, dimensional stability and moisture and water absorption. The homopolymerized styrene was distinguished from the graft copolymer with cellulose, by means of prolonged extraction of the homopolymer with benzene.

3. The transient species responsible for the grafting reaction were revealed by electron spin resonance studies to be long-lived free radicals, ostensibly from the cellulose.

h. Preliminary examination of the monomeric acrylonitrile and methyl methacrylate indicate them to be less effective than styrene in the enhancement of physical properties by this process.

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This thesis consists of two parts. Part I is concerned with the optimization of conditions for the treatment of wood with styrene to obtain graft co-polymerization with cellulose and the assessment of the physical and chemical properties of the treated material. Part II deals with the work undertaken with a view to establish the transient species responsible for graft co-polymerization.

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PART I

INTRODUCTION

1. Dimensional Instability of Wood

One of the serious difficulties encountered in the structural use of wood is its considerable affinity for moisture. This causes shrinkage and swelling when the atmospheric conditions surrounding the wood fluctuate. This dimensional instability can be related to its cellular structure. Cellulose along with hemicelluloses form the cell-wall substance with lignin acting as a cementing medium for the individual cells. The model of wood cellulose consists of long chains of cellulose, the individual chain being built up of cello-These chains are parallel only at intervals and constibiose units. tute the crystalline regions. Between zones of parallelism the chains are disordered and result in the so-called amorphous regions. There is no sharp demarcation between these two regions. A long chain molecule can successively pass through several amorphous and crystalline regions but it usually terminates in the latter. The amorphous regions between crystallites act as transient capillaries in which liquids can penetrate (1). In green wood the amorphous regions are completely saturated with water and the cell cavities are filled with As the green wood dries, water is first lost from the cell water. cavities till the fibre saturation point is reached. At this point the coll walls are saturated to their fullest capacity but no free water exists in the cell cavities. It is assumed that the fibre

saturation point for wood is around 30 percent moisture content. As the wood dries further, the moisture in the cell walls evaporates and this causes a contraction of cell walls in proportion to the moisture that is lost. This shrinking of the cell leads to changes in dimensions and volume. Similarly when dry wood absorbs moisture it swells due to expansion of cell walls caused by the entrance of water into the minute capillaries formed by the amorphous regions. This swelling continues till the fibre saturation point is reached, after which the entering water merely fills the cell cavities. Thus it is only the adsorbed water held within the structure of cell walls which is responsible for the dimensional instability of wood. The dimensional changes are contingent on the water content of the cell walls below the fibre saturation point.

2. Dimensional Stabilization of Wood

Control of these dimensional changes of wood with changes in moisture content has occupied the attention of several people during the last few decades. As a result of intensive studies various impregnation treatments have been perfected (2). One method has been to locate thin films of water-repellent materials in the internal surfaces of the fibres which act as barriers to the entering of water inside the cell structure; various coating treatments belong to this category. A second method consists in depositing within the cell walls bulking agents that are capable of holding the cellulose chains together in a rigid matrix. A typical example that is commercially successful is the treatment with phenol-formaldehyde resin precondensates.

A third process consists in replacing by chemical means the hydrophilic hydroxyl groups of cellulose with less hydrophilic groups. A well exploited technique in this category is the acetylation process. Lastly, formation of chemical bridges or cross-links between structural units in cellulose has been found to impart considerable dimensional stability to wood. Formaldehyde has been found to be a very efficient cross-linking agent. Because the formaldehyde cross-linking reaction takes place only in the presence of an acid catalyst and heat, the wood becomes seriously embrittled.

3. Radiation as a Reagent for Chemical Reactions

During recent years radiation has been used as a means of initiating chemical reactions. There are three different ways in which radiation has been put to use. They are

1) polymerization of monomeric materials like ethylene, vinyl chloride, styrene, acrylonitrile etc.

ii) modification of certain polymers like polyethylene by cross-linking.

iii) grafting of monomers on to polymeric chains to obtain what is called graft co-polymers.

Excellent reviews pertaining to these uses are available in recently published books (3 - 5). The last of the above techniques is recent and is stimulating much interest at the present time. A graft copolymer can be defined as a chemical combination of polymers in which there occurs branching of polymer units on the main chain at regular intervals, the branched polymer being different from the main- chain

polymer. Such a combination of two polymeric systems in a single molecule may give rise to useful materials having properties different from that of either polymer constituting the graft co-polymer. It is quite conceivable that radiation can be used as a means to induce graft co-polymerization of monomers with cellulose in wood and thus to bring about improvement in dimensional stability and other properties.

4. Effects of Radiation on Cellulose

Before such a possibility can be examined it is necessary to consider the effect of radiation itself on the properties of cellulose. Lawton and co-workers (6) found that basswood became fermentable by rumen bacteria after exposure to 6.5×10^6 rep* of 1 Mev electrons. At 100 mega rep the digestibility was comparable to that of hay. At this stage the wood became hygroscopic and friable. At 3.35 x 10^8 rep the cellulose almost became water soluble. They concluded that cellulose underwant profound degradation at these high radiation doses. Later. Saeman. Millett and Lauton (7) working with wood pulp and cotton linters demonstrated the degradation of cellulose by estimating the molecular weight of cellulose exposed to cathode rays. Holecular weight estimates were carried out by viscosity measurements using cupri-ethylenediamine as A dosage of 10⁵ equivalent roentgens* had a small effect the solvent.

> * Rep: roentgen equivalent physical: one rep is the quantity of ionization produced when 83.8 ergs are dissipated by radiation per gram of the tissue.

* <u>Roentgen</u>: one roentgen corresponds to absorption of 83.8 ergs of energy per gram of air. This applies only to x-rays and gamma-rays. For ionization caused in tissues by radiation other than x- or gamma-rays (electrons etc.) the 'rep' is used.

on the degree of polymerization of cellulose*. Large changes occurred at irradiation levels in excess of 10⁶ equivalent roentgens. At a dosage of 5 x 10⁸ equivalent roentgens cellulose was converted to watersoluble materials. It was also found that irradiation produced reduction in crystallinity of cellulose. Charlesby (8) using Saeman's data made some theoretical calculations and showed that the crystalline as well as amorphous regions of cellulose were equally susceptible to degradation unlike the case of acid hydrolysis where the susceptibilities of these two regions are different. Later Glegg and Kertesz (9) irradiated cotton and wood cellulose with gamma rays within the dosage range of 60 x 10^3 rads* to 2300 x 10^3 rads. There was progressive degradation of cellulose with increase in dosage as indicated by viscosity studies in cupri-ethylenediamine solutions. They found that the moisture content of the cellulose did not influence the results. Cotton cellulose irradiated in presence of excess moisture was degraded to the same extent as that containing 3.5 percent moisture. They also found an after-effect in cellulose-degradation at low moisture levels in which the solution viscosities of the irradiated samples progressively decreased over a storage period of up to 30 days. Paton and Hearman (10) demonstrated that sitka spruce wood did not undergo any change in hygroscopicity below 10⁷ rads, but that a slight reduction in equilibrium moisture content at all humidities took place with 108 rads dose.

* Degree of polymerization: The degree of polymerization is the average number of auhydroglucose units that go to form a cellulose chain.

* Rad: rad is the unit of absorbed dose and corresponds to an energy absorption of 100 ergs per gram of material.

Kenaga (11) has studied the effects of gamma radiation on the properties of ponderosa pine. His conclusions were that gamma radiation below 10^7 rep induced statistically significant changes in hygroscopicity and tangential swelling of wood, though the actual magnitude is small. Also small changes in decay susceptibility of wood was induced by gamma radiation below 10^7 rep.

The chemical changes brought about by irradiation of pure cellulose influence the mechanical properties of the fibre also. For example Arthur and Blou in (12) have shown that high energy gamma-irradiation brings about a decrease in the tensile strength of fibres. In another case (13) cotton, rayon and cellulose acetate samples were subjected to a series of neutron bombardments as well as gamma radiation. The radiation damage was evaluated with respect to changes in tenacity, elongation and stiffness, modulus of elasticity and viscosity. All these materials were found to be damaged by radiation. In all cases there were losses in mechanical properties. Most of the damage resulting from radiation occurred at the early stages of irradiation.

In view of the fact that cellulose is degraded by radiation, one may expect that the strength properties of wood may be affected by irradiation, because cellulose in wood influences such characteristics as resistance to splitting and bending. But it has been shown that only high doses lead to significant strength losses. A dose of 10⁷ rads reduces the bending strength of wood only by about 3 percent (14). This difference between the behaviour of wood and that of pure cellulose is due to its heterogeneity. Wood substance, in addition to cellulose and hemicelluloses, contains about 30 percent lignin and it has been

shown (15) that lignin affords a protective action and reduces the number of scissions of cellulose chains caused by radiation. Lignin itself is fairly resistant to damage by moderate levels of radiation because of It is assumed that a major part of lignin is its aromatic nature. chemically combined with the cellulosic component and only a small amount It has been demonstrated (16) that in a is present in the free state. co-polymer of styrene and isobutylene the aromatic portion (styrene) "protects" the aliphatic isobutylene portion from degradation by radiation. The action of lignin in wood resembles that of styrene in the styrene-isobutylene co-polymer. It is, therefore, possible under certain conditions to modify the cellulose in wood by radiation grafting with a resultant enhancement of mechanical and chemical properties.

5. Graft Co-polymers of Cellulose

Graft co-polymers have been prepared from pure cellulose using a variety of monomeric materials including styrene, acrylonitrile, methyl-Arthur and co-workers (17) have grafted acrylomethacrylate etc. nitrile on to cotton yarn using an aqueous zinc chloride solution of By exposure to 10^6 roentgens they were able to graft acrylonitrile. 25 - 30 percent on to the cotton yarn. Okamura and others (18) have grafted styrene on to cellulosic fibres by first swelling the fibre in a methanol solution of formamide and then irradiating with gamma-rays in a They claim that internal grafting can be styrene-methanol solution. obtained only when the styrene is able to diffuse into the interstitial regions of the fibre. Huang, Immergut and Rapson (19) claim to have grafted a considerable amount of styrene on to cellulose by using what

is called the "inclusion technique" to impregnate the fibre. The technique consisted in using a series of replacement steps in which the liquid to be removed was completely miscible with the one replacing it. They have employed a three-stage inclusion procedure. Cotton linter sample was first saturated with distilled water. After sucking-off the excess water, the sample was immersed in methanol so as to exchange the water in the swollen cellulose. After this the methanol was replaced by styrene by immersion of the sample in pure styrene. Chapiro and Stannett (20) have accomplished the radiation-grafting of styrene on to cellulose by using styrene-methanol solution in conjunction with water; they claim water is essential for grafting.

Because of high susceptibility of cellulose to degradation, a close control of radiation is necessary to bring about grafting and at the same time minimize depolymerisation of cellulose. The main effect of depolymerization is, as already stated, depreciation of strength properties. Perhaps this is the reason why relatively little information is available as to the practical usefulness of cellulose graft co-polymers compared to those prepared from synthetic polymers like polyethylene where it has been shown that grafting invariably improves mechanical properties (h).

6. Radiation-induced Reactions in cellulosic Materials

Radiation-induced polymerization of monomers inside cellulosic materials with a view to improve mechanical and other properties was first investigated by Karpov, Melinsky and others (114). Their substrate was pine wood and working with styrene as the monomer they reported a considerable improvement in bending strength and a reduction

in the absorption of water, both liquid and vapour. Little information was, however, given about the nature of the reaction or about the conditions of impregnation. In another example (21) internal polymerization of acrylonitrile in filter paper was accomplished by using radiation. A 100 percent increase in dry tensile strength of the paper resulted with 50 percent wet strength retention. The author claimed that the treatment resulted in an intimate mixture of polyacrylonitrile and cellulose or that a graft co-polymer was formed.

OBJECTIVE OF PRESENT STUDY

Although the dimensional stability of wood is important for almost all of its practical purposes, the bending strength may frequently be the decisive criterion when a structural application is contemplated. Furthermore, in the case of radiation-induced reaction in wood the main property to be evaluated must be strength, because of the undesirable effects on cellulose produced by radiation. Obviously. there is no point in improving the dimensional stability of wood at the expense of its strength. It may be assumed that any reaction performed with cellulose in wood or even insolubilization of a chemical inside wood structure improves the dimensional stability, the effect varying with the extent of reaction. The objective of the present study, therefore, has been to ascertain optimum experimental conditions for maximum enhancement of strength properties of wood by radiation polymorization of styrene in wood, and to determine how much of the polymer was grafting on to the cellulose rather than forming homopolymer.

EXPERIMENTAL

1. Materials

<u>Mood</u>: Red-pine sapwood was chosen because of its high porosity to allow a considerable range in the amount of monomeric impregnant.

Because the wood was so variable, control samples had to be used in each experiment. Accordingly, the wood was obtained in planks 54 inches long and 1 inch in thickness. Samples were examined in groups of three cut end to end from planks. One piece in the group was retained as control, one was irradiated without impregnation and the third piece was both impregnated and irradiated.

The sample size $(16" \times 3/4" \times 3/4")$ was chosen so that a standard A.S.T.M. testing procedure for bending strength could be applied (22).

<u>Styrene</u>: reagent grade styrene was shaken with 10 percent (volume) sodium hydroxide solution, washed with water and dried over anhydrous calcium sulphate. This operation removed the stabilizer (p-t-butylpyrocatechol).

2. Mathods

Apparatus for Impregnation

The apparatus consisted of a thick-walled corning glass pipe 36 inches long and 4 inches inside diameter, which was fitted on the top and bottom with brass plates screwed to flanges on the upper and lower

ends of the glass pipe. The sealing between the pipe and the plates was made by means of rubber O-rings. The top plate was provided with three connections, one each to a vacuum line, a nitrogen cylinder and an aspirator bottle which supplied the monomer. The connections were made by means of stainless steel valves fitted with Teflon diaphragms (Edwards High Vacuum Company). The pipe to the monomer supply was also In one of the early experiments copper was made of stainless steel. used as the material of construction for lines and valves and it was found that polymerization of styrene did not proceed smoothly. This was due to the fact that when styrene was brought into contact with copper or copper-bearing-alloys it picked up enough copper as to give definite inhibitor action during subsequent polymerization (23). The bottom plate was provided with an outlet valve. A glass tube was suspended inside the pipe from a hollow aluminium cylinder screwed to the top brass plate to which the glass tube was clamped by a quickrelease catch. When in position the glass tube hangs inside the pipe as shown in Fig. 1.

Procedure for Impregnation

Wood samples were placed in the glass tube and the pressure reduced to less than one micron for 12 hours in order to reduce the air content and thereby improve penetration by the monomer. Evacuation was accomplished by a high-capacity oil pump, protected by a liquid air trap. Low pressures were read on a McLeod gauge. After evacuation, the impregnant was added from the aspirator bottle without admitting air until the samples were totally immersed, and the pressure then raised by means of nitrogen to 35 pounds per square inch. Samples were left





Impregnator for wood

in the solution for periods up to 36 hours, depending upon the quantity of impregnant desired. The wood was then encased in aluminium foil in sets of three to prevent loss of styrene and sealed into polythene bags to prevent ingress of water during irradiation.

Irradiation of Samples

The bag containing the three wood pieces was attached in a vertical position to a holder in a carrier (Fig. 2) which then travelled down the face of the instrument bridge in the McMaster nuclear reactor (American Machine and Foundry Swimming Pool Reactor, Power 1 mega watt). The carrier was mounted on the north face of the instrument bridge. A ratchet arrangement at the top enabled accurate vertical location, while the horizontal travel of the bridge itself permitted horizontal positioning of the carrier. The design of the sample-holder was such that it was possible to release the sample in the pool itself after completion of irradiation. The carrier holding the samples was maintained at a predetermined position in the pool such that all the portions of the specimen were uniformly exposed to the radiation.

In order to ascertain a suitable position for the wood samples with respect to the reactor core, it was first necessary to find a position where a substantially uniform gamma flux penetrated the entire length of the samples. Extensive dosimetry was therefore carried out, using the change in colour of cobalt dosimeter glass as an indication of total gamma dosage. It was found that there was a vertical zone, 17 inches in height over which the total difference in flux intensity was less than 6 percent; the samples were located in this zone for a length of time appropriate to the desired dosage. The dose rate at a position



Fig. 2 Truck for Irradiation of Wood Samples.

corresponding to 25 inches separation between the lower ends of the bridges is of the order of 9×10^5 rads per hour. All irradiations were performed at this dose rate. Fig. 3 shows the dosage profile in the reactor at various vertical distances from the surface of the grid plate.

Because the radiation in the reactor also contained a heavy neutron flux, the samples were radioactive for a period following irradiation (due to manganese in the wood) and this activity had to be allowed to decay. When the wood was safe to handle (5 - 8 hours after irradiation) its temperature was raised to 105° C for 24 hours to complete the polymerization. The physical and chemical testing could then be started.

In order for the results of the physical tests to be comparative, all the wood specimens, controls and samples alike were equilibriated in an atmosphere of 76 percent relative humidity and 25°C before any tests were made.

Extraction of Treated Samples

Although polystyrene homopolymer is soluble in benzene, grafted co-polymer with cellulose is insoluble (19). Thus to make an estimate of the extent of grafting, benzene extraction was carried out to constant weight on samples of wood flour and the decrease in sample weight determined. The air-dry wood was ground to sawdust in a wiley mill so as to pass a 40 mesh sieve and be retained on a 60 mesh sieve. Soxhlet extractors were used for extraction; six days was found to be the maximum extraction time required. Separate determinations of moisture content of the samples were made so that the results of extractions



could be calculated on the basis of moisture-free wood.

Physical Testing

The stress-strain characteristics of all samples were measured in the Tinius Olsen Universal Tester (Fig. 4) in accordance with the procedure laid down in the A.S.T.M. manual (22). The load was applied continuously throughout the test at a rate of motion of the movable crosshead of 0.10 inches per minute. The ultimate breaking strength of all samples was recorded and used as a means for evaluation of the treatment.

Moisture Content Determination

2.0 gm. samples of conditioned wood flour were weighed and then dried in an oven at 105°C to constant weight. The percent moisture content, based on the dry weight of sample, was calculated from the loss in weight on heating.

Moisture Absorption of Wood Samples

Samples of size $\mu^n \ge 3/\mu^n \ge 3/\mu^n$ were dried in an oven for 16 hours at $105^{\circ}C$ and after recording the dry weight were placed in an atmosphere of 76 percent relative humidity at $25^{\circ}C$. The increase in weight of the sample after a length of time was taken to represent the moisture absorption during the particular period. The percent moisture absorption was calculated from this.

Water Absorption of Wood Samples

Oven-dry samples as above were kept immersed in distilled water at laboratory temperature and atmospheric pressure. The percent water absorption was calculated as above.



Fig. 4 Tinius Olsen Universal Tester.

Volumetric Swelling and Shrinkage of Wood Samples

The dimensions of 4 inch samples (conditioned at 76 percent relative humidity) were measured accurately by means of Vernier calipers to the nearest 1/100th of an inch. They were then dried in an oven at 105°C for 16 hours and the dimensions again measured. From the difference in the volume of the sample before and after drying, the percent volumetric shrinkage of the conditioned sample was calculated. The oven-dry samples were next immersed in distilled water at laboratory temperature and atmospheric pressure and the dimensions were measured after the samples were completely swollen (up to 3 weeks time was allowed From the difference in volumes the percent volumetric for swelling). swelling was calculated. The swollen samples were next dried in an oven at 105°C and the dimensions again measured. From the difference in volumes the percent total volumetric shrinkage was calculated.

EXPERIMENTAL RESULTS

1. Irradiation of Wood Alone

The effect of irradiation of wood on the bending strength and moisture content was first investigated. The results are given in Table 1. There was a progressive deterioration of strength with increasing dosage. However, the strength loss occurring up to a dose of about 5 mega rads was not serious so that it is possible to carry out radiation-induced reactions in wood by employing dosages below this value. Samller decreases in strength on irradiation of wood can be compensated for by the modification of wood on treatment which may be expected to alter its stress-strain characteristics.

The moisture content was not altered by irradiation up to a dose of 10 mega rads or so. Above this limit, a significant change in moisture content was observed; the magnitude of this change, however, was insufficiently large to have any appreciable effect upon the sub-microscopic structure of cellulose.

2. Polymerization of Styrene in Wood

In the first series of experiments, pure styrene was used as the impregnant and polymerization carried out by thermal and by a combination of irradiation and thermal treatment. The properties of the treated wood are given in Table 2.

1) Bending strength

At high radiation dosages the bending strength decreased, even

TABLE 1

Effect of Irradiation of Wood

Series	Irradiation (mega rads)	Equilibr <u>content</u> Non-irra	ium moisture (Percent) di-	Percent reduction in bending strength(from non-irradiated samples)
		ated	Irradiated	
l	1.35	11.90	11.90	5.2
2	2.7	11.98	11.94	7.2
3	6.3	11.95	11.92	12.5
4	9.0	11.97	11.76	19. 4
5	14.4	11.95	11.67	21.5
6	18.9	11.94	11.23	26.9
7	28.8	12.00	11.00	37.6
8	32.4	11.98	10.75	49.4

Each of the above values represents the mean of at least three separate experiments.

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The individual bending strength values differ by not more than 10 percent.

TABLE 2

Results of Polymerization of Styrene in Wood

(Properties of Treated Wood)

Series	Irradi- ation (mega rads)	Therm treat	al ment	Weight increase (%)	Percent change in bending strength (from un- treated wood)	Percent decrease in mois- ture absorption (from un- treated wood)	Percent decrease in water absorption (from un- treated wood)
1	nil	105 [°] C,	,24 h	r 100	÷ 56.0	62	78
2	4.5	11	21 23	100	* 56 . 8	66	82
3	9.0	11	ti fi	100	+ 22 . 5	67	78
4	14.4	п	11 17	100	- 4.5	69	78
5	18.9	17	17 11	110	- 11.8	72	85

though the extent of polymerization as measured by the permanent increase in weight of the treated specimen was approximately the same in all cases. This was evidently due to radiation-induced alterations in wood at higher doses.

ii) Moisture and water absorption

The moisture and water absorption of the treated wood were substantially reduced in all cases.

iii) Extraction of the treated sample

The results of benzene extraction of the polymer are shown in Table 3. Most of the resultant polymer was found to be soluble in benzene, indicating that little grafting between polystyrene and cellulose had occurred. The results suggested that styrene was not penetrating to the cellulose in wood.

3. Treatment with Styrene-Methanol-Water Solution

In order to produce swelling within the wood structure and thereby aid the diffusion of styrene to the cellulose in wood, methanol and water were added to styrene. Table 4 represents the consolidated results obtained with different proportions of the components in the impregnant. The various properties of the treated wood were improved to an extent depending on the degree of permanent increase in weight attained.

The results of benzene extraction of the polymer are shown in Table 5. Where the reaction had been accomplished by a combination of irradiation and thermal treatment, there was a considerable decrease in the amount extracted compared to the pure styrene-treatment. Thus grafting of polystyrene with cellulose took place when the styrene was able to diffuse to cellulose in wood. Thermal polymerization with this

TABLE 3

Results of Polymerization of Styrene in Wood

(Benzene Extraction of the Polymer)

Series (Same as Table 2)	Polymer extracted*
l	94.0
2	90.5
3	85.4
4	72.6
5	52.0

* Weight of polymer extracted per 100 grams of polystyrene formed, per 100 grams of dry wood.

TABLE 4

Results of Polymerization of Styrene in Methanol-Water Solution in Wood

(Properties of Treated Wood)

Series	s Impregnant (by weight)	Irradi- ation (moga rads)	The tre	rmal atmo	nt	Weight increase (%)	Percent change in bending strength(from untreated wood)	Percent decrease in moisture absorption(from untreated wood)	Percent decrease in water absorp- tion (from untreated wood)
1	76% styrene 22.5% methanol	4.5	105	8,24	hr	. 90	÷ 46.5	69	79
2	1.5% water	9.0	n	11	11	95	+ 38.8	68	82
3	52% styrene 43.5% methanol	1.35	0 1050	2 ,24	h r .	60	÷ 50.1	æ	-
<u> </u>	4.5% water	2.70	n	U	11	60	+ 42.7	-	-
5	52% styrene 43.5% methanol 4.5% water	4.5	D	11	12	70	÷ 48.9	66	67
6	u u n	9-0	11	11	п	70	+ 33.0	65	69
7	11 11 11	Di.h	11	II.	я	70	+ 21.2	63	7).
8	ti it it	18.9	11	н	- 11	70	- 5.5	62	78
9	30, styrene 61, methanol	4.5	(1	17	18	38	✤ 29.6	48	43
10	y Water II II II	9.0	(1	п	11	40	+ 17.8	48	45

Continued

TABLE L continued

Series	Impregnant (by weight)	Irradi- ation (mega rads)	Therm treat	al ment	Weight increase (%)	Percent change in bending strength (from untreated wood)	Percent decrease in moisture absorption (from untreated wood)	Percent decrease in water absorp- tion (from untreated wood)
11	76% styrene 22.5% methanol 1.5% water	nil	1058,	24 h	r. 42	+ 27.4	43	ц 6
12	81 F2 E8	nil	11	Ħ	" 80	+ 41.3	58	74
13	76% styreng 22.5% methanol 1.5% water + 0.2% on	nil	11	Ŧ	" <u>4</u> 6	+ 27.0	45	կ7
	volume of Benzoyl peroxide catalyst							
זת	57 82 Tr	nil	11	11	" 74	+ 41.7	62	65

Results of Polymerization of Styrene in Methanol-Water Solution in Wood

Serie (Same as Ta	s ble L)	Polymer extracted*
1		19.1
2		20.1
3		24.8
4		20.3
5		19.0
6		21.4
7		23.0
8		19.1
9		4.8
10		5.7
11		62.8
12		63.0
13		81.2
11		81.8

(Benzene Extraction of Polymer)

* weight of polymer extracted per 100 grams of polystyrene formed per 100 grams of dry wood.

1.4

impregnant resulted predominantly in homopolymerization.

The styrene solution found to be most suitable for obtaining graft co-polymerization and optimum improvement in properties contained 22.5 percent (W) of methanol and 1.5 percent (W) of water. A total dose of 4.5 mega rads is optimal.

Table 6 and Figs. 5 and 6 summarise the various properties of such a grafted cellulose-polystyrene wood. The maximum water absorption of the treated wood in a 30 day period was not greater than 25 percent as compared to 150 percent for the untreated. The treated wood also absorbed less than 1/3 as much moisture as the untreated wood (Fig. 5).

The volumetric shrinkage in going from a swollen to the ovendry state was reduced by about 80 percent. Similarly, the shrinkage taking place on drying the conditioned sample (conditioned at 76 percent relative humidity and 25° C) was reduced by about 80 percent. The swelling of wood when it was saturated with water was reduced by about 85 percent (Table 6).

A typical stress-strain diagram of the treated wood is compared with that of untreated one in Fig. 6. It can be seen that the modulus of elasticity of the treated wood was significantly altered. The untreated wood exhibited a proportionality limit which is the true measure of the strength of material. With treated wood, there was no proportionality limit and the stress was proportional to the strain till the break point.

4. Treatment with Styrene-Methanol solution

The use of water in the impregnating solution above was based on
Shrinkago and Swelling of Wood Treated Under Optimum Conditions

Percent volumetric shrinkage (based on conditioned volume)	Percent volumetric swelling (based on oven-dry volume)	Percent total shrinkage (based on volume of swollen sample)	Percent increase in volume of wood on treat- ment
5.0	15.0	12.0	•
0.90	1.0	2.5	8 - 9
	Percent volumetric shrinkage (based on conditioned volume) 5.0 0.90	Percent volumetric shrinkage (based swelling (based on conditioned on oven-dry volume) volume) 5.0 15.0 0.90 1.0	Percent volumetric shrinkage (based on conditioned volume) 5.0 15.0 12.0 1.0 2.5









claims in the literature (20) that water was essential for grafting of styrene on to cellulose. In order to verify this statement in the present case, an impregnation was carried out with the exclusion of water in the solution. The results are shown in Table 7. Practically no effect due to absence of water was observed with respect to improvement in machanical and water and moisture absorption properties. However, the amount of polymer extracted in each case was significantly greater than that obtained with styrene-methanol-water system. This may suggest that water helps to increase the extent of grafting though the effect was not as pronounced as the case noted in the literature.

5. Three-stage Treatment of Wood

It was noted earlier that pure styrene was not able to penetrate to the cellulose in wood. This was because non-polar liquids like styrene are incapable of swelling the structure. Such non-polar liquids could, however, replace swelling liquids in the swollen structure of wood to a large extent, provided the liquid to be removed is completely miscible with the one replacing it (2h). Such a procedure was used by Huang and others (19) to study graft co-polymerization in pure cellulose. They claimed that by successive treatment of cellulose with water, methanol and styrene, the styrene got "included" in the structure. A similar impregnation procedure was tried in the present instance. Wood was first swollen in water and the owollen wood placed in methanol for 65 hours. The methanol was intended to replace all the The wood was then subsequently immersed water in the wood structure. in pure styrene for 50 hours. Replacement of methanol by styrene could take place because of the complete miscibility of the two liquids. The

Results of Polymerization of Styrene in Methanol Solution (No Water) in Wood

(Properties of Treated Wood and Benzene Extraction of Polymer)

Irradiation - 9×10^6 rads Thermal treatment - $105^{\circ}C_{0}$, 24 hr.

Series	Impregnant (by weight)	Weight in- crease (%)	Percent change in bending strength(from untreated wood)	Percent decrease in moisture absorp- tion (from un- treated wood)	Percent decrease in water absorp- tion (from un- treated wood)	Polymor extracted*
				X		
1	77.5% styrene 22.5% methanol	95	+ 46.6	68	84	26.4
2	5h.0% styrene 46.0% methanol	70	+ 35.8	64	73	26.8
3	33.5% styrene 66.5% methanol	ЦО	+ 14.4	<u>ц</u> 6	L 8	14.8

* weight of polymer extracted per 100 grams of polystyrene formed per 100 grams of dry wood. polymerization of styrene was effected by a combination of irradiation and thermal treatment. The results of the experiment are shown in Table 8. As could be seen from the table, the replacement was not very effective, for the permanent increase in weight was only around 49 percent. Adequate improvements in bending strength and degree of grafting were not observed. The technique, being a time-consuming operation, may not have much practical usefulness.

6. Treatment of Wood with Methyl methacrylate and Acrylonitrile Monomers

It was observed that pure methyl methacrylate monomer did not penetrate the wood structure. Even with the use of a swelling agent like methyl alcohol in conjunction with the monomer the penetration was not satisfactory. The extent of polymerization was only of the order of 20 - 25 percent. There was considerable polymerization of the monomer on the surface of the wood specimen.

With Acrylonitrile in methanol-water solvent mixture the penetration was better and the extent of polymerization was of the order of 60 percent. In this case also, it was observed that there was a considerable tendency for homo polymerization to occur. Some of the results obtained are summarized in Table 9.

TABLE	8

Results of Polymerization of Styrene in Wood by "Inclusion Technique"

Series	Irradiation (mega rads)	Thermal treatment	Percent weight increase	Percent change in bending strength (from un- treated wood)	Polymer extracted*
1	4.5	105°C 30 hrs.	49	÷ 13.0	29.8
2	9.0	105°C 30 hrs.	49	- 10.0	48.1

* weight of polymer extracted per 100 grams of polystyrene formed per 100 grams of dry wood.

Results of Polymerization of Methyl methacrylate and

Acrylonitrile Monomers in Mood

Series	Impro (Pero velg	egnar cent cht)	ıt by	Irradiation (Mega rads)	Thern	al ment	Percent weight increase	Percent change in bending strength (from un- treated wood)
l	Pure meth	e Met nacry	hyl late	1.8	24 hrs	.60 ⁰ C	9	+ <u>L</u>
2	57	n	17	9.0	12	B	1]1	nil
3	55 Me metha + 45 alcoh	ethyl Acryl Heth Nol	ate yl	4.5	24 hrs	••75 [°] C	20	+ 12
4	13 T	r	tł	9.0	11	17	23	+ 12
5	63 Ac nitri 21 Me alcor 16 wa	erylo ile + athyl nol + ater	160-	2.3	24 hrs	.100°C	59	+ 25.0
6	fi T	1	n	4.5	17	11	62	+ 15.0
7	f7 T	I	12	9.0	81	17	65	nil

DISCUSSION OF RESULTS

1. Irradiation of Wood

Although gamma-irradiation causes depolymerization of cellulose, wood will withstand a moderate radiation dosage without significant The ability of wood to withstand larger dosages reduction in strength. than pure cellulose is probably the result of the hemicelluloses, which "". constitute about 25 percent of the wood substance as well as the protective character of lignin. The hemicelluloses do not contribute to //~ the strength properties at all being of low degree of polymerization (25). It is quite likely that the initial radiolytic attack is mostly confined to these hemicelluloses with but little alterations in strength; \mathcal{L} cellulose is the primary contributor to the bending strength. Degradation of d -cellulose may start only after all hemicelluloses are Support for this argument is contained in the observation destroyed. made with respect to mechanical behaviour of irradiated pure cellulosic materials where it has been shown (13) that most of the radiolytic damage occurs during the initial stages of irradiation.

2. Mechanical Properties

The improvement in bending strength of wood resulting from the treatment can be due to reduction in equilibrium moisture content and increase in specific gravity. It has been known that the strength of wood increases with increasing specific gravity and decreasing moisture content below the fibre saturation point (26).

The stress-strain behaviour of wood treated with styrenemethanol-water solution (Fig. 6) suggests that the cellulose chains have been modified by the grafting of polystyrene. In the untreated wood the force required to move the cellulose chains with respect to one another is that necessary to overcome weak Van der Waal's forces between hydroxyl groups in adjacent chains. However, in the modified wood the forces to be overcome are in addition to above, primary valence forces introduced by the side chains of polystyrene.

3. Water Absorption Properties

When the wood structure is not swollen during the impregnation as is the case obtained with pure styrene as impregnant, most of the polystyrene may be assumed to fill in cell cavities and intercellular spaces since it could be extracted by benzene (Table 3). The reduced water vapour and liquid water absorption (Table 2) is due to the coating of the surface of the cells with polystyrene film which acts as a barrier to the entry of water into the amorphous regions of cellulose. Swelling and shrinkage are also thereby minimized in refer.

When the wood structure is swollen by incorporation of methanol and water in the impregnant, most of the styrene finds access to the amorphous regions in cell walls due to increase in the effective diameter of the transient capillaries formed by the amorphous regions. The benzene extraction results (Table 5) indicate that the polystyrene does not exist in a free form but presumably grafted on to the cellulose chains. The reduction in water vapour and liquid water absorption of wood (Table 4) could be attributed to these hydrophobic grafts of polystyrene along the cellulose chain. The cellulose is thus kept in a

suclien state by the side-chain substituent. This may account for the 8 - 9 percent increase in the volume of wood resulting from the treatment under optimum conditions (Table 6).

In both cases of treatment complete dimensional stability is not possible because water molecules can always reach regions inaccessible to bigger styrene molecules. Whether there is homo polymerization in cell cavities or grafting with cellulose chains, the improvement in water absorption properties seems to depend on the degree of permanent increase in weight attained by the treated material (Tables 2 and h).

The suclien wood definitely displayed a greater ease in reaction in that during heating following irradiation, the samples did not exhibit heterogeneity observed with the non-swollen samples. This heterogeneity in the latter case is demonstrated by the extrusion of bubbles appearing on the surface of wood and depositing as a thin film. Where samples have received lower radiation dosages the extrusion is increased to such an extent as to cause the pieces of wood to stick together.

In general, it can be said that the polystyrene grafted wood exhibited a better physical appearance after treatment than the wood containing the homo polymerized styrene.

4. Grafting Process

Free radicals must be present in order to initiate the grafting reaction. When a synthetic polymer like polyethylene is irradiated, the primary reaction is the loss of hydrogen atom and formation of polymer radicals. Some of these radicals get trapped in the structure as demonstrated by Sinohara and Tomioka (27) who detected them by electron spin resonance spectroscopy. With oxygen present during irradiation peroxides and hydroperoxides can be formed by reaction of the radicals with oxygen. These are fairly stable at ordinary temperatures. On heating, however, they decompose to form free radicals. The radicals formed on a polymeric back-bone by either one or both of the above methods can react with a reactive monomer present at the radical site to form a graft co-polymer.

When cellulose is irradiated, the main effect is the degradation of cellulose due to breakdown of the 1,4 - glucosidic linkage. However, free radicals are also formed and some of them get trapped in the structure and their presence has been detected by electron spin resonance spectroscopy by Abraham and Whiffen (28). It was mentioned earlier that Glogg and Kertesz (9) obtained an "after-effect" from cellulose irradiated in air. Glegg (29) attributed this to the interaction of trapped free radicals with oxygen which resulted in further degradation of cellulose as indicated by intrinsic viscosity measurements.

Radiation grafting on to cellulose can, therefore, proceed via both free radical and peroxide mechanisms as in the case of polyethylene irradiated in air. The free radicals formed on irradiation of wood either directly or from decomposition of peroxides and hydroperoxides are presumably located along the cellulose chains in the amorphous and crystalline regions. The grafting reaction can take place when the monomer is present along these radical sites. The diffusion of the monomer to the amorphous regions of cellulose in wood is facilitated by a swollen structure. It has been demonstrated by several workers (18, 19, 20) that successful inner-layer grafting with cellulose can take place only when opportunity is afforded for the

monomer thoroughly to penetrate the interstitial regions of the fibre. The efficiency of grafting is thus related to the accessibility of the monomer to regions in the structure where radical formation takes place.

In view of the above, it is not surprising that homo polymerization of styrene predominates when pure styrene is used as the impregnant because styrene is not penetrating to radical sites in the amorphous regions. However, a certain amount of grafting can take place with the cellulose chains exposed to the surface of the fibre. This is found to be so and corresponds to the amount of polymer not extracted by benzene (Table 3). As can be seen from the table, the amount of surface grafting increases with increasing dose which may presumably be due to increasing concentration of radicals formed at higher doses. It has been demonstrated (27) that the concentration of free radicals produced on irradiation is proportional to the total dose.

With styrene-methanol-water solution as impregnant, it is quite likely that a certain amount of surface grafting takes place. However, it may also be assumed that a fair degree of inner-layer grafting with cellulose occurs because of the swollen structure.

Homo polymerization of styrene also accompanies grafting as can be seen from the results in Table 5. It is not considerable as observed with acrylonitrile solutions. This is due to the low 'G' value of styrene for radical production compared to that of the main chain polymer (cellulose). It has been shown (h) that the feasibility of a graft

> 'G' value represents the number of free radicals formed per 100 e.v. of energy absorbed in a material of unit density.

co-polymerization reaction depends upon the relative ability of the polymer and the monomer to form free radicals when subjected to ionizing radiation. If the rate of free radical production is smaller in the monomer to be grafted than the polymer, the amount of graft co-polymer may be large compared to the homo polymer. Styrene having a low 'G' value for radical production (30) is thus very effective for graft co-polymerization.

PART II

While direct experimental evidence for the linking of polystyrene on to cellulose is lacking in the results so far obtained, it has been possible to obtain positive proof for the presence of free radicals over a long period after irradiation of wood. This has been made possible by electron spin resonance spectroscopy and the following portion of the thesis is concerned with this work.

ELECTRON SPIN RESONANCE TECHNIQUE (ESR)

A free radical may be defined as an atom or molecule containing one or more unpaired electrons. The unpaired electron, which occupies a single orbital, has a spin and a resulting magnetic moment. If the electron is placed in a magnetic field there occurs a procession of the spinning electron. This gives rise to a splitting of the electronic energy level into two energy levels having a constant separation.

A finite probability exists for transition between these two energy levels and this change in the energy state can be accomplished by supplying an external radio-frequency magnetic field. The frequency at which absorption takes place is governed by the expression (31)

$$\mathcal{U} = \frac{\mathcal{G}\mathcal{B}\mathcal{H}}{\mathcal{L}}$$

where \mathcal{U} is the frequency of the wave at resonance
'g' is the gyromagnetic ratio,
' \mathcal{B} ' is the Bohr magneton

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H is the field strength

and 'h' is Planck's constant.

In the measurement of this paramagnetic resonance absorption, the common procedure is to hold the frequency of the applied electromagnetic radiation constant and to measure the intensity of absorption when the magnetic field is modulated.

EXPERIMENTAL

Procedure for Irradiation

In order to ascertain the change of free radical concentration with time, it was desirable to start the electron spin resonance measurements immediately after irradiation. However, the wood samples were sufficiently radioactive as to render them unsafe to handle before several hours had elapsed; this was due principally to radioactivity induced in the manganese in wood by neutrons emanating from the reactor core. The problem of recovering the wood samples immediately after irradiation, therefore, became the problem of irradiating with a neutron-free gamma beam.

In order to screen out the thermal neutrons a cadmium cylinder was fitted to the front face of the irradiation truck (Fig.2); the cylinder had a diameter of 1 10/16 inches, a height of 82 inches and was formed from cadmium sheet 1/32 inch thick.

The wood sample, 5 mm x 11 mm x 1 mm was enclosed in a polythene capsule suspended on a weighted line (Fig. 7) and was positioned in the centre of the cadmium cylinder by means of a polythene slab which rested in a notch in the top of the cylinder. The sample was lowered into the reactor within this screen, and the whole assembly positioned in the desired radiation flux. By this device, the sample could be irradiated at a dose rate of 19.0 mega rads per hour and recovered with a residual radioactivity of less than 10 milli curies. Irradiation of all samples was done for half an hour.





Capsule for irradiation of small wood sample

After irradiation, the sample was brought to the surface of the reactor pool leaving the now radioactive cylinder behind. The sample was then removed from the capsule and enclosed in cellophane so as to be able to use it directly in the cavity of the spectrometer for measurement of the e.s.r. spectrum.

Electron Spin Resonance Measurements

E.S.R. measurements were made at a frequency of 9 kilo mega cycles/sec. using an automatic recording spectrometer which records the first derivative of the true resonance curve.

Standardisation of the Spectrometer

In order to make estimates of radical concentrations it was necessary to have a standard radical source. Diphenyl picrylhydrazyl (DPPH) was used as the standard. Heasurements were made with different concentrations of the standard. It was found that 0.01 mgm of the standard corresponding to a radical concentration of 1.5×10^{16} spins resulted in a fairly satisfactory signal in the desired sensitivity range. This was used as a standard spectrum for comparison in all experiments.

Calculation of Radical Concentration in the Samples

The e.s.r. spectrum of the samples were recorded at periodic intervals following irradiation. The derivative curves obtained were graphically integrated to give the true resonance curves. Radical concentrations in the samples were evaluated by comparing the area of the sample curves with that of the standard. For any sample the actual integration of the resonance curve and calculation of area was done only for one signal. The areas of subsequent signals were evaluated from the peak heights. It was assumed, provided the sample is the same, that the area of the curve is directly proportional to the peak height of the signal.

EXPERIMENTAL RESULTS

The preliminary series of experiments was concerned only with a qualitative detection of free radicals in irradiated air-dry wood, and wood impregnated with styrene-methanol-water solution. Strong resonance signals were obtained in both cases immediately after irradiation. After 20 hours the intensity of the signal was moderate. Only very slight resonance was observed after 40 hours.

1. Estimate of Radical Concentration

Since positive results were forthcoming, a series of experiments was planned to enable an estimate of radical concentration after irradiation of air-dry wood, wood impregnated with styrene alone and wood impregnated with styrene-methanol-water solution. The results of the measurements are shown in Tables 10, 11 and 12 and Figs. 6 and 9.

In all the cases investigated it was found that there was an initial rapid decay of radicals which continued for a period of $\mu = 5$ hours with a nearly constant rate, followed by a slow decay, the rate of which depended on the nature of the substrate. In the case of untreated wood the second process is much more prolonged than that for the treated wood (Fig. 9).

Effect of Heating after Irradiation on Radicals In the modification of wood by the process described in Part I,

Results of E.S.R. Measurements on Irradiated Wood

No.	Time clapsed after completion of irradiation	No. of spins or radical centras/ gm. of wood x 10 ⁻¹⁷
_		10.05
1	55 min.	75.00
2	2 hrs. 5 min.	8.79
3	2 hrs. 55 min.	7.56
2,	l hrs. 25 min.	6.51
5	5 hrs.	6.36
6	35 hrs. 10 min.	5.82
7	76 hrs. 15 min.	5.19
б	171 hrs.	5.19
9	363 hrs.	4.05

(Estimate of Radical Concentration)

Concentration at zero time obtained by extrapolation = 15.10×10^{17} spins/gm. of wood.

Results of E.S.R. Measurements on Wood

Treated with Styrenc-Methanol-Water Solution

(Estimate of Radical Concentration)

No.	Time elapsed after completion of irradiation	No. of spins or radical contres/ m. of wood x 10 ⁻¹⁷
1	27 min.	12.58
2	l hr 22 min.	10.09
3	3 hrs 2 min.	8.61
<u>)</u> .	4 hrs h2 min.	8.17
5	23 hrs 27 min.	6.77
6	52 hrs 37 min.	4.82
7	147 hrs 52 min.	2.65
8	335 hrs	1.10

Concentration at zero time obtained by extrapolation = $1h.6 \times 10^{17}$ spins/gm. of wood.

Results of E.S.R. Measurements on Wood Treated with Pure Styrene

No.	Time elapsed after completion of irradiation	No. of spins or radical centres/ gm. wood x 10 ⁻¹⁷
1	55 min.	12.39
2	2 hrs 5 min.	8.78
3	3 hrs 10 min.	7.23
4	h hrs 20 min.	6.72
5	26 hrs 55 min.	0.20
ó	125 hrs 55 min.	3.30
7	318 hrs	0.56

(Estimate of Radical Concentration)

Concentration of zero time obtained by extrapolation = 15.10 x 10¹⁷ spins/gm. of wood.







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the samples, after irradiation, were heated at 105°C for 24 hours to complete the reaction. In order to see what happens during the heating step to the radicals formed on irradiation, an experiment was performed in which air-dry wood sample and wood impregnated with styrenemethanol-water solution were irradiated, the respective spectra (e.s.r.) measured, then heated for 2 hours at 105°C and the spectre again taken. The results are shown in Figs. 10 and 11. It can be seen that heating results in a considerable diminution in the concentration of radicals in both cases.

3. Hyperfine structure

In the e.s.r. spectra of air-dry and impregnated wood samples irradiated for half hour period, in addition to the Main signal, smaller subsidiary signals were also observed (Figs. 12(a), (b) and (c), although they were not very well defined. It was thought that irradiation for a longer period night reveal any hyperfine structure since the radical concentration increases with dose and if the smaller signals were due to radicals it would show up more distinctly when the radical concentration is increased. Accordingly a wood sample impregnated with styrene-methenol-water solution was irradiated for 3 hours giving a total dosage of nearly 60 mega rads. The e.s.r. spectrum of this sample was measured following irradiation. Fig. 12(d) represents the spectrum obtained. The spectrum indeed reveals a hyperfine structure.





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FIG. II E.S.R SPECTRUM OF WOOD IMPREGNATED WITH STYRENE-METHANOL-WATER SOLUTION AND IRRADIATED FOR Y2 HR.

E.S.R SPECTRUM OF THE SAME SAMPLE AFTER HEATING FOR 2 HRS. AT 105'C.



 (a) Air-dry wood Irradiated for 1/2 hour Spectrum obtained 55 minutes after Irradiation.



(c) Wood impregnated with pure styrene

Irradiated for 1/2 hour

Spectrum obtained 55 minutes after Irradiation.







 (d) Sample same as (b) Irradiate: for 3 hours
Spectrum obtained 40 minutes atter Irra liation.

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DISCUSSION OF RESULTS

The nature of the decay curves (Fig.9) suggests that two different radical species are involved in the process, one of which is characterised by a rapid rate of decay and the other by a much slower rate. It is not possible to say anything conclusive about the origin of these radicals. Since the radical concentration at the completion of irradiation, obtained by extrapolation of decay curves (Fig. 8), in air-dry wood is substantially the same as that for wood impregnated with styrene, the radicals may be thought to arise from wood itself and not from any polystyrene formed during irradiation. Wood is heterogeneous and the two main constituents are cellulose and lignin. It is quite likely that radicals originate from both, though there is no reference in literature as to whether lignin gives rise to long-lived radicals at all on irradiation or not. It may be assumed, therefore, that the radicals arise from cellulose. Abraham and Whiffen (20) obtained an asymmetric pattern for e.s.r curve for irradiated pure cellulose and they attributed this to the presence of several different radicals. Later Kuri and Ueda (32) also obtained a similar pattern on irradiation of powdered wood pulp. In both these cases the irradiation was done in vacuum and therefore there were no complications introduced by the presence of air as is the case in our experiments. Since the pattern of the e.s.r. spectrum obtained from irradiated wood bears a resemblance to the pattern observed for pure cellulose and also that

radical formation from lignin has not been reported it is reasonable to assume that the radicals detected in these experiments originate in the cellulose. Also the hyper fine structure suggests that more than one radical species is involved.

The chemical nature of radicals formed during irradiation of cellulose has not been revealed so far and is subject only to conjecture. They are believed to te polymeric in nature. It has been shown by Kuri and Ueda (32) that O_2 and SO_2 are able to transform some high polymer radicals into such species as RSO_2 and RO_2 where R. denotes the primary radical formed from the polymer. The same workers have also shown that the e.s.r. spectra of cellulose irradiated in vacuum, irradiated in vacuum followed by introduction of SO_2 gas and irradiated in SO_2 atmosphere are all identical. They conclude that the radicals produced in polymers containing hydroxyl groups have scant activity. This lack of reactivity towards SO_2 has been explained as being due to intra and inter-molecular hydrogen bonds.

There seems to be no reason to believe that the radicals formed from cellulose are similarly unreactive towards oxygen when irradiation is done in presence of air. It is quite likely that oxygenated radicals of the type ROO. are formed and such radicals derived from other synthetic polymers like Poly Vinyl chloride are reported to be very stable (33). Abraham and Whiffen (20) observed that radicals of the type ROO. obtained from polymers like polychlorotrifluoroethylene irradiated in vacuum and subsequently opened to the atmosphere undergo a reversible decay

 $RO_2 \iff R. * O_2$

According to these observations, it seems likely that in the irradiation of wood at least two distinct radical species are formed from cellulose of the type R. and RO_2 . The rapid decay may be due to radicals of the R. type which can easily undergo recombination. The much slower decay may be due to RO_2 . type radicals. With impregnated wood samples the second decay rate seems to be larger than that for the untreated air-dry wood. This may be due to the consumption of these RO_2 . radicals by styrene which initiate its chain growth. That polymerization of styrene takes place during this period is demonstrated by the observation that wood treated with styrene-methanol-water solution irradiated and kept at room temperature for about a month had an appreciable permanent gain in weight.

The effect of heating is apparently the decomposition of the RO₂. radicals. The observation of a residual spectrum (Figs. 10 and 11) after heating the samples for 2 hours at 105°C may offer support to the observation made by Abraham and Whiffen (28) that the decay of this type of radical is reversible.

A more complete elucidation of the nature of the persistent radical species and of the polymerization process is beyond the scope of the present work and indeed beyond the capacity of the electron spin resonance equipment employed. This study is to be pursued in the next phase of this investigation.

CONCLUSIONS

Gamma-irradiation can be employed effectively in the initiation of graft co-polymerization of styrene with the cellulose in wood. The dosage necessary (about 5 mega rads) is sufficiently low that the degradation of cellulose by radiation is not significant as to deleteriously affect the strength properties of the wood. As a result of this graft co-polymerization, several desirable modifications in properties of the wood result. The bending strength is increased by Reteof about one half. Penetration of water vapour and liquid are drastically dimensional changes with water absorption are correspondingly reduced: raduced. It should be pointed out that the improvement in physical properties for wood containing graft co-polymer is of the same magnitude as that observed with wood containing homopolymerized styrene. The only significant difference in property is in physical appearance (the sample containing the graft co-polymer has a more uniform surface sheen).

The transient species associated with the graft co-polymerization have been identified by electron spin resonance spectroscopy as free radicals. Since the radical concentration in irradiated wood is substantially the same as that for wood impregnated with styrene, the radicals are thought to arise from wood and probably from the cellulose, in viewof the grafting which occurs. Radical concentrations are significant for a long period of time after irradiation. No differentiation

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has been established between long-lived radicals and pervistence of the radical species; it may well be that the radicals detected after a long time interval arise from thermal decomposition of peroxides formed in the wood structure. Attempts to detect any peroxides in wood by titrimetric methods were unsuccessful.

Several experiments are suggested by this exploratory work. Irradiation of the full-sized wood specimen behind the cadmium screen would be an interesting experiment, since the temperature could be elevated and graft co-polymerization completed during the period when the radical concentration was at its height. This will decidedly result in improved grafting efficiency. Quantitative estimation of radical concentrations is now indicated as a first step to elucidating the mechanism of the graft co-polymerization process. Further study of other monomers is necessary, and of course a study of the feasibility of using other woods and laminated constructions as substrates is attractive.

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