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The Effects of Electron Beam Radiation on Cellulose

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THE EFFECTS OF ELECTRON BEAM RADIATION ON CELLULOSE

by

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ABSTRACT

This experiment was designed to show the effects of time and storage conditions on electron beam irradiated paper. The thirty four pound James River Waterleaf samples were irradiated at levels of 0 / 2 / 5 / and 10 Megarads. The samples were kept in a conditioned room, an evacuated, desiccated jar, and a Nitrogen purged jar. The samples were tested for viscosity, as well as wet and dry zero span tensile over a period of time. Burst and tensile were also run at one point in time.

Time following irradiation and storage conditions showed no significant effect on either zero span tensile or viscosity tests. Burst and tensile tests showed no difference in bonding levels due to storage conditions.

KEY WORDS: Electron Beam, Radiation, Cellulose Degradation, Drying, Curing, Paper Strength

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INTRODUCTION

With energy becoming an ever increasing part of a product's production expense, a major effort has been made to find more efficient alternatives. Electron beam (EB) curing is one of the possible alternatives in the field of coated papers.

EB curing involves exposing a substrate coated with reactive monomers or oligomers to between one and five Megarads of energy. The major benefits of this system are as follows: (1)

1. It allows the use of 100% reactive solids as a coating. This means that there is no vehicle to drive off, which results in a ten fold savings in energy.
2. The lack of a vehicle means that there is less air pollution to contend with.
3. EB allows excellent smoothness and coverage by limiting "blow out" and penetration into the substrate.

The electrons in EB radiation initiate free radicals uniformly throughout the coating's monomer and oligomer constituents. The cure, or degree of additional polymerization, proceeds to a point

determined by the treatment levels and reaction rates.

Drawbacks to the use of EB include the degradation of the cellulose substrates, a lack of compatible chemical coating systems, and high capital expense for equipment.

One of the obsacles to the widespread use of EB is a lack of knowledge about its effects.

It is the purpose of this thesis to further define those effects.

BACKGROUND

EB EQUIPMENT

Electrons for use in EB equipment are generated by the use of a heated wire inside a vacuum tube. Electrons must be accelerated inside a vacuum in order to prevent them from scattering off of gas molecules. A voltage of several hundred volts is used to extract the electrons from the wire. These electrons are then accelerated by an electric field of up to three hundred thousand volts. Increasing the field voltage increases the speed of the electrons (1).

Since the main energy transfer mechanism is the scattering of incoming electrons by electrons in the target, the ability to penetrate

is roughly proportional to the target material's density. It is for this reason that penetrating ability is quoted in distance of unit density material. This is given in meters X grams per meter^3, which reduces to grams per meter^2. This is conveniently the same unit as the basis weight of paper. For an EB unit using 300 kilovolts of processor voltage the penetration depth is roughly 400 grams per meter^2. This means that penetration is not a limiting factor in most cases. The major factor is electron speed, which is directly proportional to the ability to penetrate, and the target material's density, which is also proportional to penetration.

The accelerated electrons, moving at almost the speed of light, are then sent through a metallic foil window and into the atmosphere. The product must be close to the foil window in order to prevent the electron energy from being dissipated by collision with air molecules.

The EB process does emit some radiation, and causes some ozone generation. The radiation hazard is eliminated by proper shielding and the ozone hazard is minimized by inerting the process field with a N_2 gas purge.

Terms commonly used in the EB industry include Beam Current which is the number of electrons per second received by the product. Dose

to Cure, which is the amount of energy per unit mass of that coating required to obtain a cure. Megarad, which is a unit of radiation equal to 4.4 BTU per pound or 2.4 calories per gram. Free Radical Site, refers to a chemical bonding modification so that an unpaired electron is left associated with the molecule.

USES OF EB CURING

In spite of the energy savings offered by EB curing, its use has not become widespread. One reason for this is the lack of appropriate chemistry. The recent development of low viscosity formulations have just recently allowed the use of more gravure operations. The advantages of gravure coating have expanded the field of products possible.

One of these fields is the area of vacuum metallizing, due to the extremely smooth surfaces produced. Another significant use of EB is in the field of laminating. Almost instantaneous cures are possible, which allows the use of heat sensitive substrates. Four or more substrates can be combined into one laminate structure and cured in a single pass due to the high penetration achieved with the use of EB. No solvents are required to be removed or are left entrained in the substrate (1).

THE EFFECTS OF EB

The EB processor works by direct breaking of the chemical bonds due to the negative charge and energy of acceleration associated with the electrons. Another secondary reaction is due to the electrons freed by the initial reaction. These electrons react in the same fashion as the electrons generated in the EB equipment (7).

Due to the energy transfer that takes place, dehydrogenation takes place, as well as oxidative depolymerization. The energy absorbed by these reactions can be made less damaging by modifying the cellulose via substitution. The substituent groups must have π-electron type structures. These include benzenoid, furanoid, and thiophene groups which can selectively absorb the energy and re-emit it as heat or light.

The dehydrogenation and depolymerization reactions result in cellulosic radical formation. These radicals are formed predominately on the C-5 or C-6 sites. Although the radicals occur independently of lattice type, the radicals formed in the amorphous cellulose regions are scavenged much faster than those radicals formed in the more structured areas. Radicals in the crystal lattice have remained for up to four years following irradiation (6).

The radicals can be scavenged by reactions with the coating, reaction with water vapor, or with other reactive chemicals (usually oxygen). The reactions with oxygen generally cause chain scissions by oxidative depolymerization. Total Dose, not dose rate, is the most important factor. Following irradiation by more than 100 Megarads of radiation, the cellulose is completely fragmented. Following the disintegration of the fragments, hydrogen, carbon monoxide, and carbon dioxide is evolved.

According to a study by Delides (3), the negative effects of EB radiation can be seen at dose levels as low as one Megarad. The initial effect is the development of cracks parallel to the spiral angle of the fiber wall. These cracks become longer and deeper with increasing radiation dosage, and may be due to the fracture of molecular bonding between fibrils. Another major consequence of irradiation is chain scission, primarily due to the oxidative depolymerization reaction. Studies by Imamura and Venn (5), indicate that chain scission is directly proportional to the total dose.

The above reactions are probably the reason for the strength decrease noted in irradiated cellulose. These reactions are affected by several

factors, including the presence of oxygen, moisture, additives, sensitizers, protecting groups, the dose rate (very minor), and the total dose (the most important factor) (5).

The mechanical properties used to determine radiation effects include: tensile strength, elongation at break, modulus of elasticity, and others. The exponential decrease in tensile strength with total dose (proposed by Winogradoff) was confirmed in a study by Delides (3). The equation is:

$$Y=Y_{\cdot}EXP(-R/R_{\cdot})$$

where Y and $Y_{\cdot}$ are the tensile strength and/or the elongation at break, before and after irradiation of R Megarad, respectively. $R_{\cdot}$ is a constant determined by the least squares method. Fortunately, according to Guthrie (6), the radiation dose required to start deterioration of cellulose is usually at least thirty times that needed for grafting.

TEST PROCEDURE

In a recent report by Janes (21), a thesis by McEnroe (23), and several other articles (5) (6), cellulose radicals have been described as being of two types. The types are described as being divided into long and short radicals, depending upon their position in the crystal lattice. No mention of the half life of the respective types was found. One of the questions to be investigated is the time-radical decay relationship.

Articles by Blouin (15), Arthur (2), Guthrie (5), and Delides (3), and others (6) (20), have referred to the scavenging of radicals by various means. Research indicates that the compounds most responsible for the quenching of free radicals are oxygen and water vapor. Most of the information indicates that water vapor if favored. Oxygen, although not favored in this reaction, is a primary cause of oxidative depolymerization. This depolymerization and its resultant chain cleavage is responsible for at least part of the strength loss experienced by irradiated cellulose.

A study by Arthur and Blouin (15) showed that the ratio for carbonyl formation, carboxyl formation, and chain cleavage is 20:1:1 in a nitrogen

atmosphere and 19:.5:1 in an oxygen atmosphere. Guthrie (5) claims that in the absence of air no degradation was experienced as a result of irradiation. The rate of radical scavenging by oxygen and water vapor, and their effects on irradiated cellulose is the other question that this thesis is intended to answer.

Another reason for investigating this aspect is the possibility that water vapor may scavenge radicals faster, and with less damage to the cellulose, than oxygen. If the decrease in oxidative depolymerization is substantial, then there may be a measurable advantage to running the web thru a high humidity region following irradiation.

The questions attempted to be answered are as follows:

a. What is the relationship between time and radical decay?

b. What role does oxygen play in (a) above?

c. What role does moisture vapor play in (a) above?

d. What role does oxygen play in strength degradation vs time, and can water vapor help prevent this degradation?

The paper chosen was James Rivers' 34 pound water leaf. This paper was chosen because it does not use fillers, sizing agents, or other

chemicals. This prevents additives from affecting the final results.

The paper samples were irradiated at Energy Sciences Incorporated of Woburn, Massachusetts. The actual irradiation was done by the staff under the direction of Mr. E.P. Tripp III. The samples were returned by express mail in order to minimize the time lag between irradiation and testing.

The samples were kept under the following conditions, prior to testing.

Sample A: Conditioned at 50% Relative Humidity at 73^{o}F.

Sample B: Conditioned in an evacuated dessicator jar

Sample C: Conditioned in a vacuum dessicator jar with a nitrogen purge.

The intention with sample A was to see the radical decay rate-time effects under standard conditions. The intention with sample B was to see the effect of water vapor, and sample C was used to see the effect of oxygen.

The samples were conditioned in the constant humidity room and shipped double-bagged in heavy duty Ziplock plastic bags. They were then irradiated at levels of 2, 5, and 10 Megarads. A non-irradiated sample was also tested. Tests were run at 2,5,11, and 30 days following

irradiation. The tests included wet and dry zero span tensile, as well as viscosity (TAPPI T 230 os 76). In a belated effort to see the effects on paper bonding strength, burst and tensile were evaluated one time only.

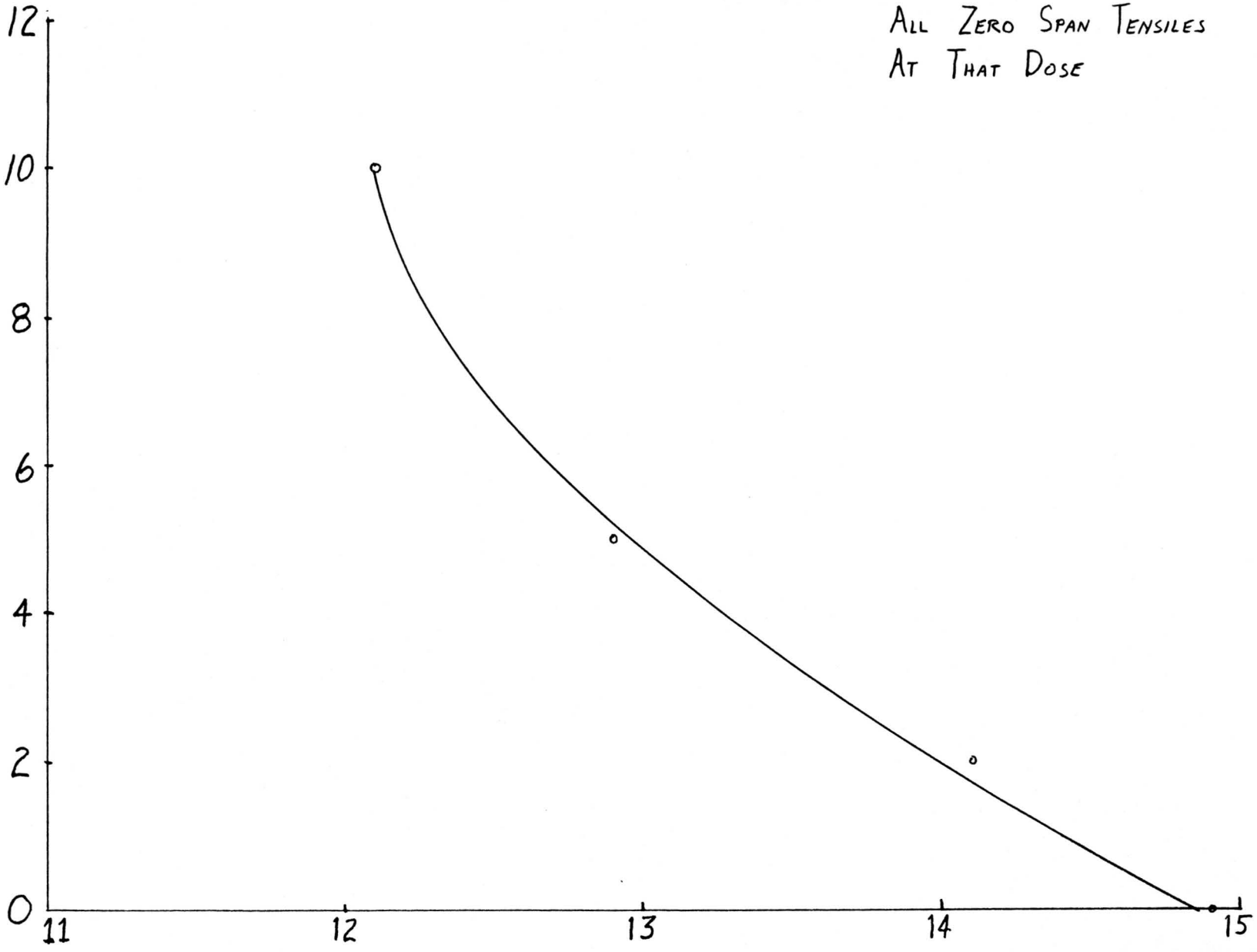
All samples were allowed to condition in the constant temperature and humidity room (23°C, 50% R.H.) for one hour after being removed from their storage conditions. The samples were then tested after this conditioning period.

RESULTS AND DISCUSSION

The effect of electron beam radiation can be seen in graphs one and two. Graph one shows the average zero span tensile as a function of total dose and graph two shows viscosity as a function of total dose.

Although Guthrie (5) claims that the rate of chain cleavage is directly proportional to the dose, the above graphs indicate that damage to the cellulose is more pronounced at lower radiation levels and tends to lessen in rate as the total radiation dosage increases. One reason for this may be the rapid scavenging and subsequent depolymerization of the free radicals in the less crystalling regions of the cellulose. As these radicals are scavenged, the free radicals located in the more crystalline regions begin to represent a higher percentage of the total number of free radicals available. These radicals are relatively inaccessable. They therefore contribute little to depolymerization of the cellulose until the dose is increased to the point where total breakdown of the fiber occurs.

All Zero Span Tensiles
At That Dose



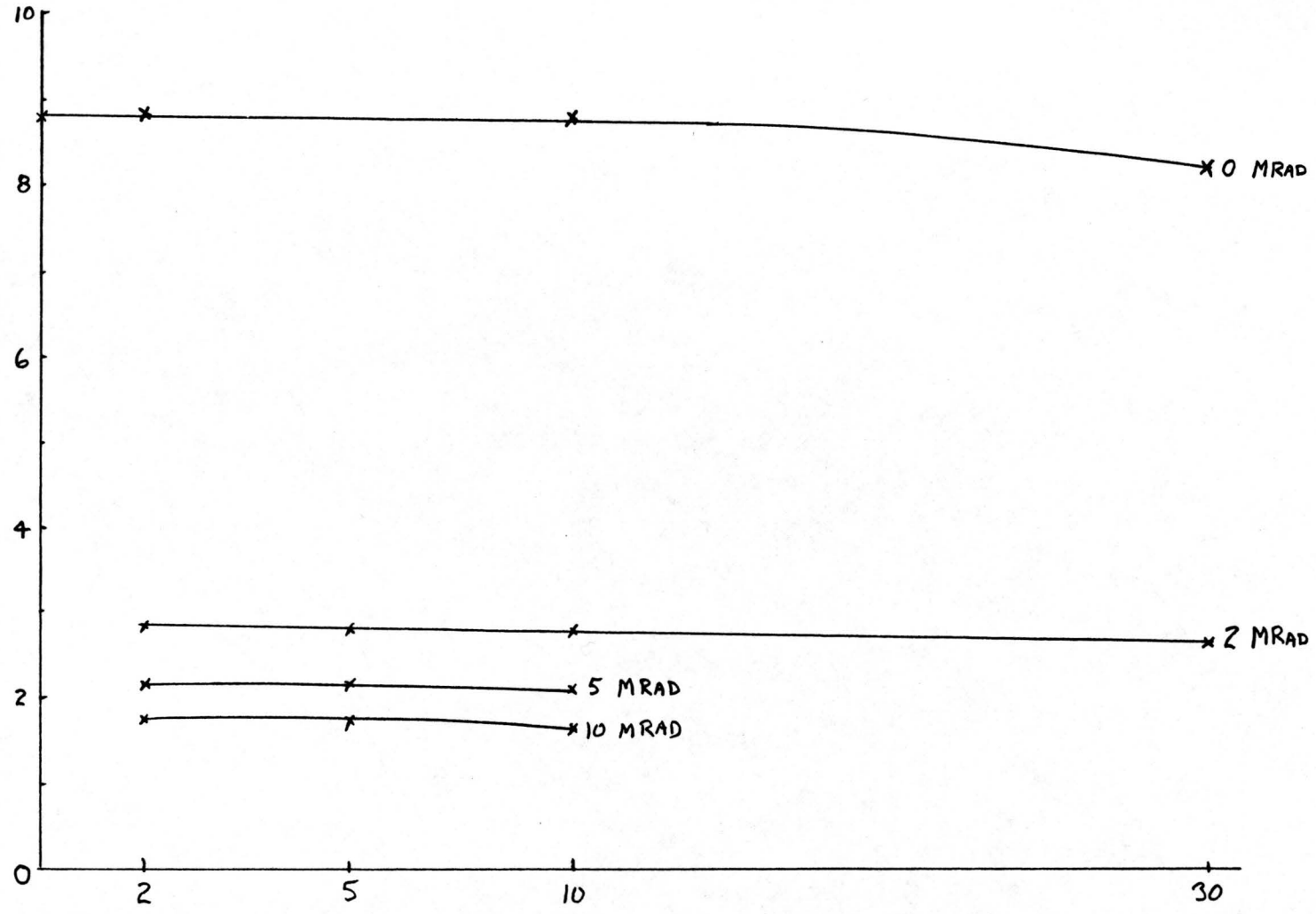
Dose In
Mega Rads

Average Zero Span Tensile In P.S.I.

Graph 1

The effect of time can be seen in graph three and graph four. Graph three shows the viscosity-time relationship. This graph indicates that time has little or no effect on viscosity. This may indicate that the initial scavenging of radicals takes place prior to the first test point at two days following irradiation. This conflicts with graph four. Graph four, which shows the zero span tensile-time relationship, indicates an increase in strength with time for the samples exposed to two and five megarads of electron beam radiation. One possible explanation is that some cross linking between fibers may be occuring. This would cause an increase in tensile strength without affecting molecular length as indicated by viscosity. The reason for the decrease in tensile strength of the samples exposed to zero and ten megarads (without affecting viscosity) is not known.

GRAPH 3 - VISCOSITY VS TIME

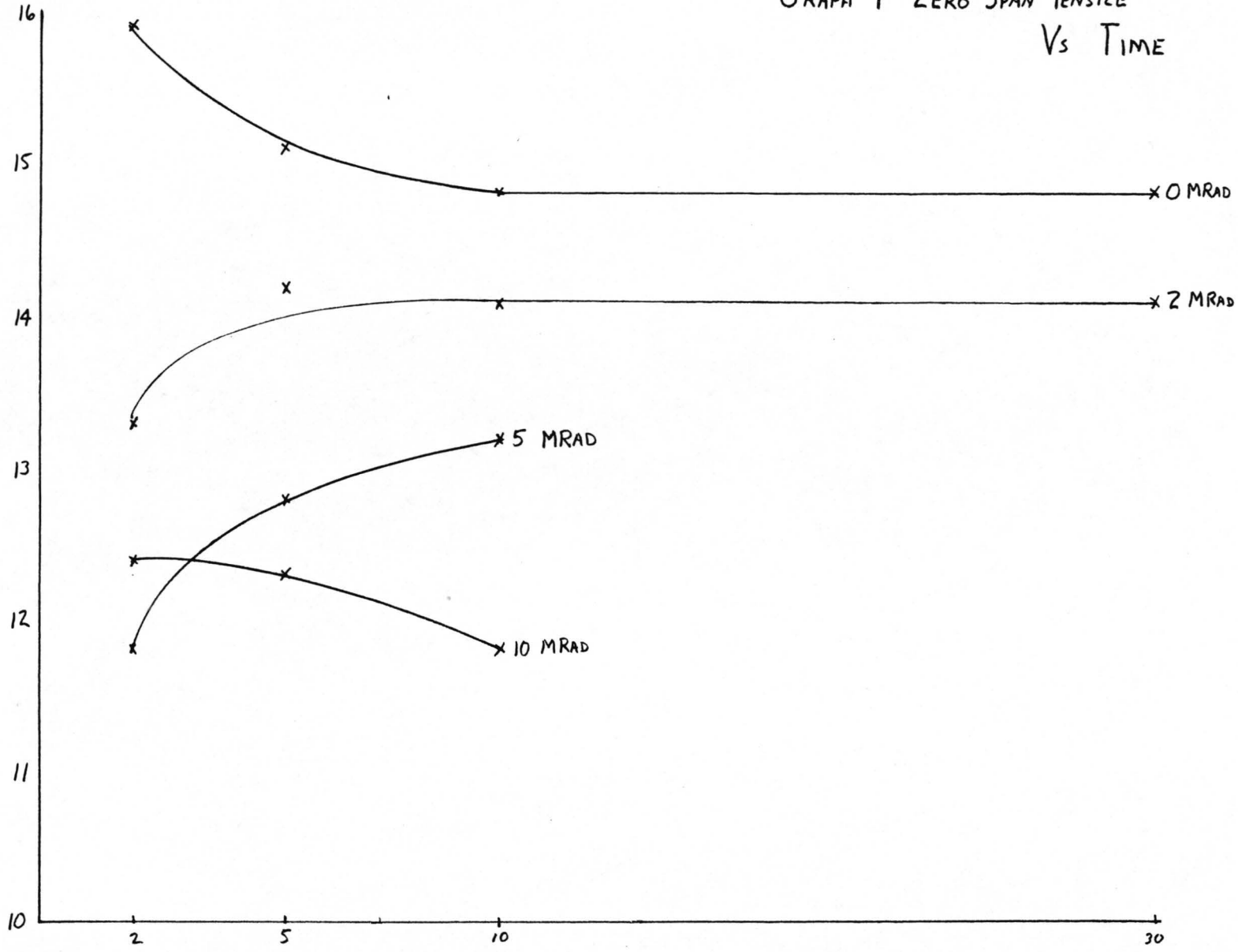


VISCOSITY IN CENTIPOISE

DAYS FOLLOWING IRRADIATION

GRAPH 3

GRAPH 4 ZERO SPAN TENSILE VS TIME



ZERO SPAN TENSILE (PSI)

DAYS FOLLOWING IRRADIATION

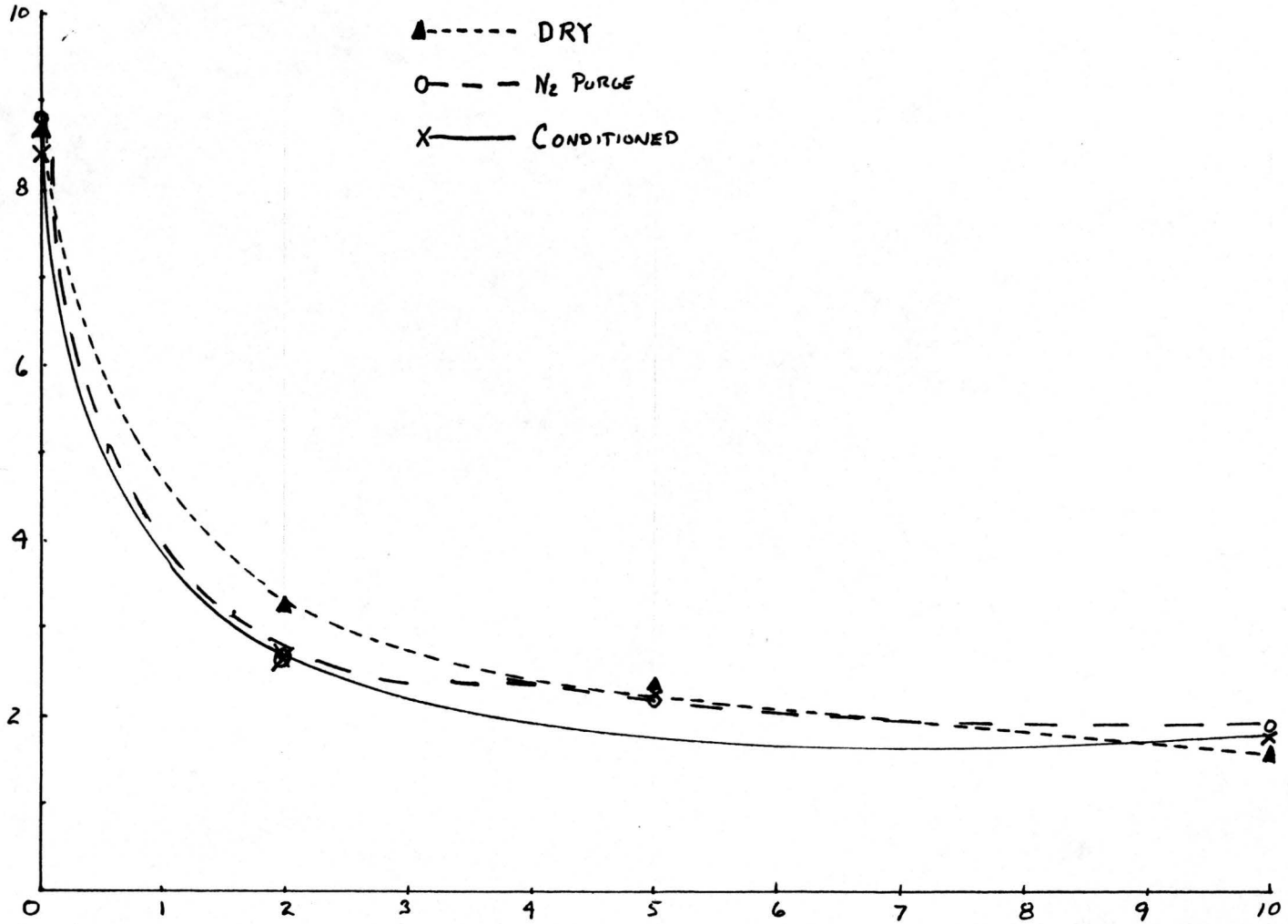
GRAPH 4

The effects of conditioning can be seen in graphs five through eight. Graph five shows the viscosity-dose relationship for each of the storage conditions used. This graph indicates that storage condition has little or no effect on the molecular weight of cellulose. This would be expected if the accessable radicals were scavenged prior to the first test point.

The effect of conditioning on zero span tensile can be seen in graph six. Again no significant differences due to type of storage condition can be observed. Note that test results obtained at the two megarad dose level do not fit the curve. In all cases the zero span tensile results were higher. This abnormality tends to reinforce the possibility of cross linking.

The effect of conditioning on burst can be seen in graph seven. All of the lines on this graph effectively fall on top of one another after the zero megarad point. This indicates that there is no difference in burst due to different storage conditions.

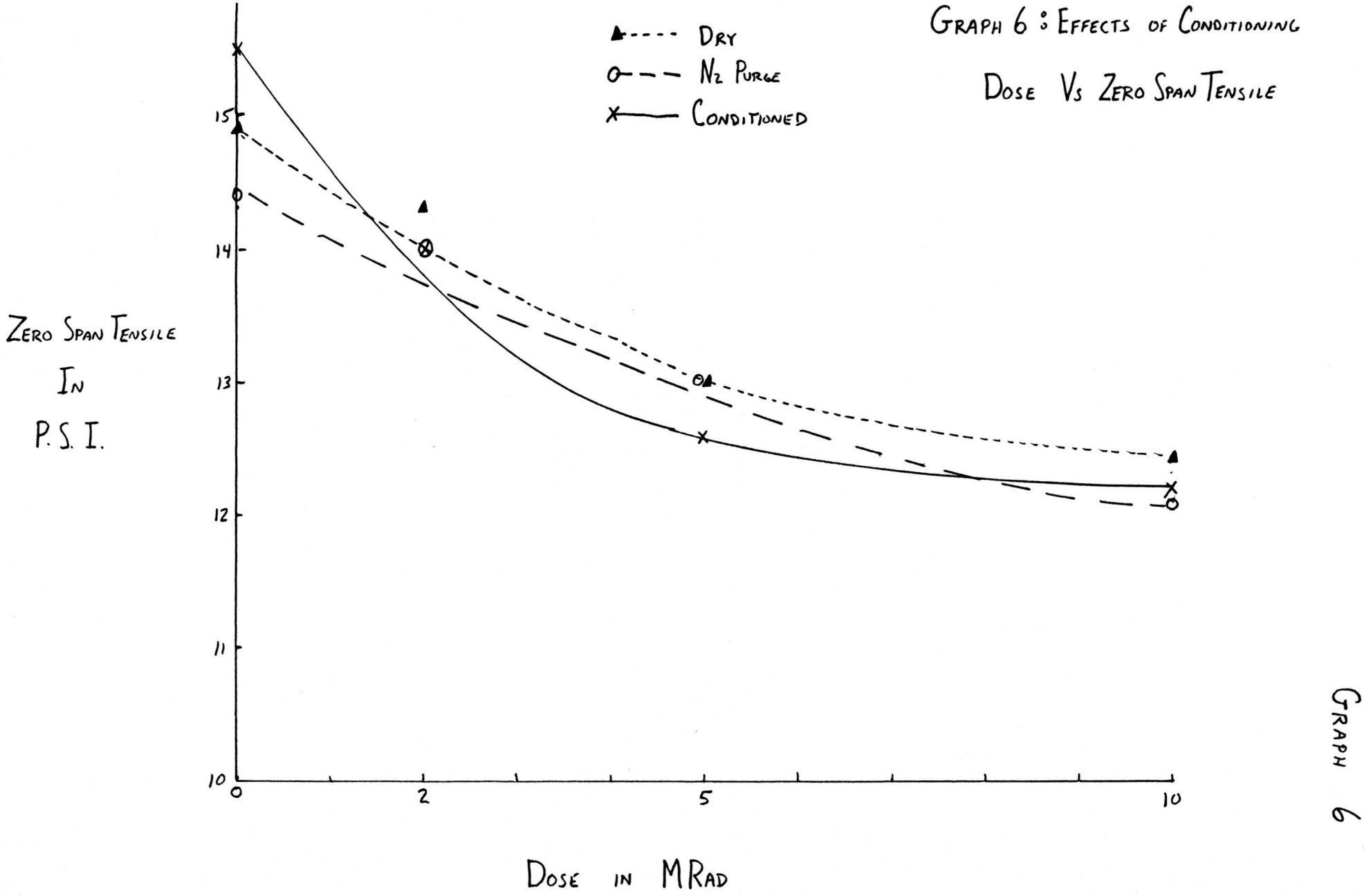
Viscosity Vs Dose



Graph 5

GRAPH 6 : EFFECTS OF CONDITIONING

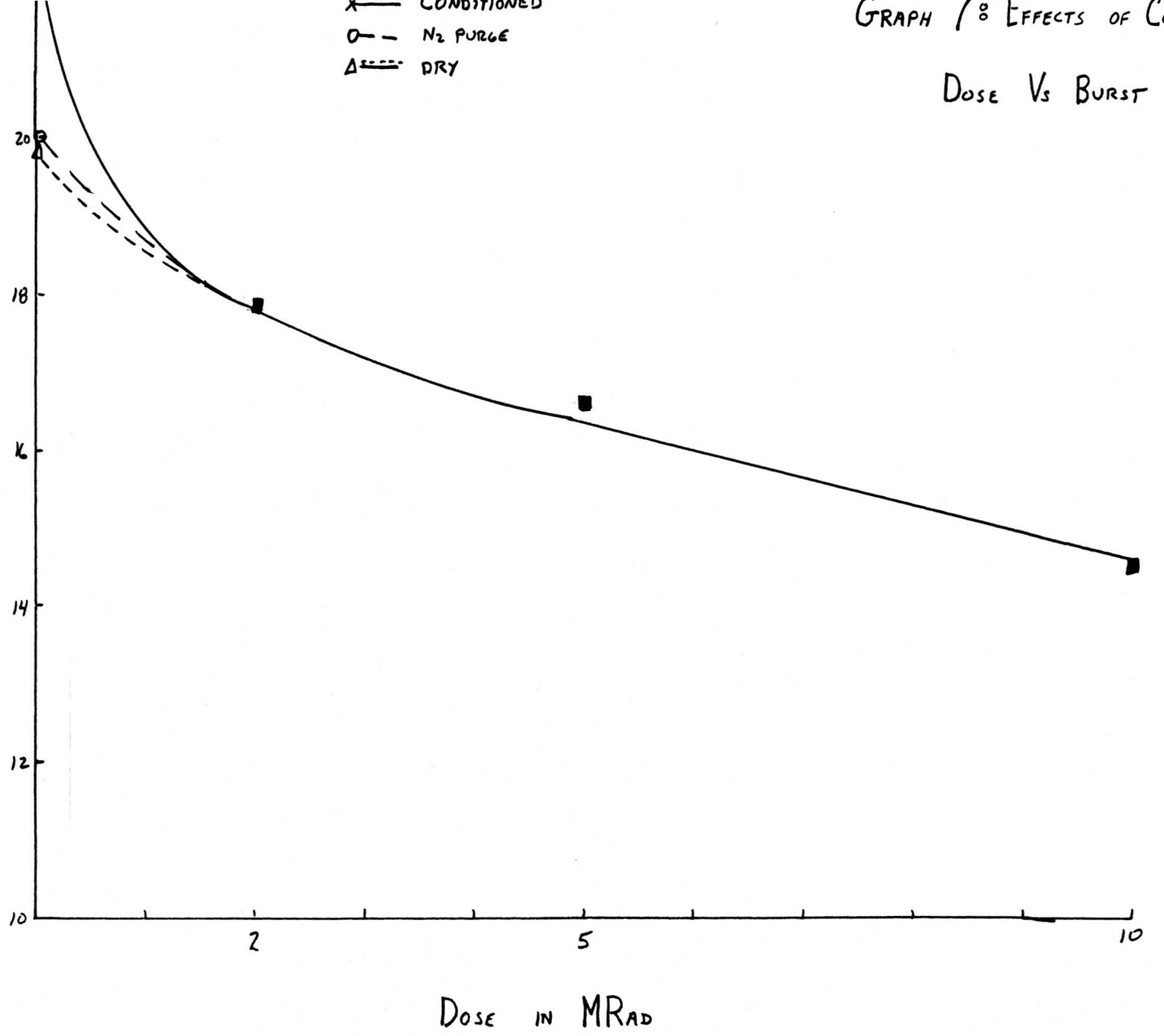
DOSE VS ZERO SPAN TENSILE



GRAPH 6

GRAPH 7 EFFECTS OF CONDITIONING

DOSE VS BURST

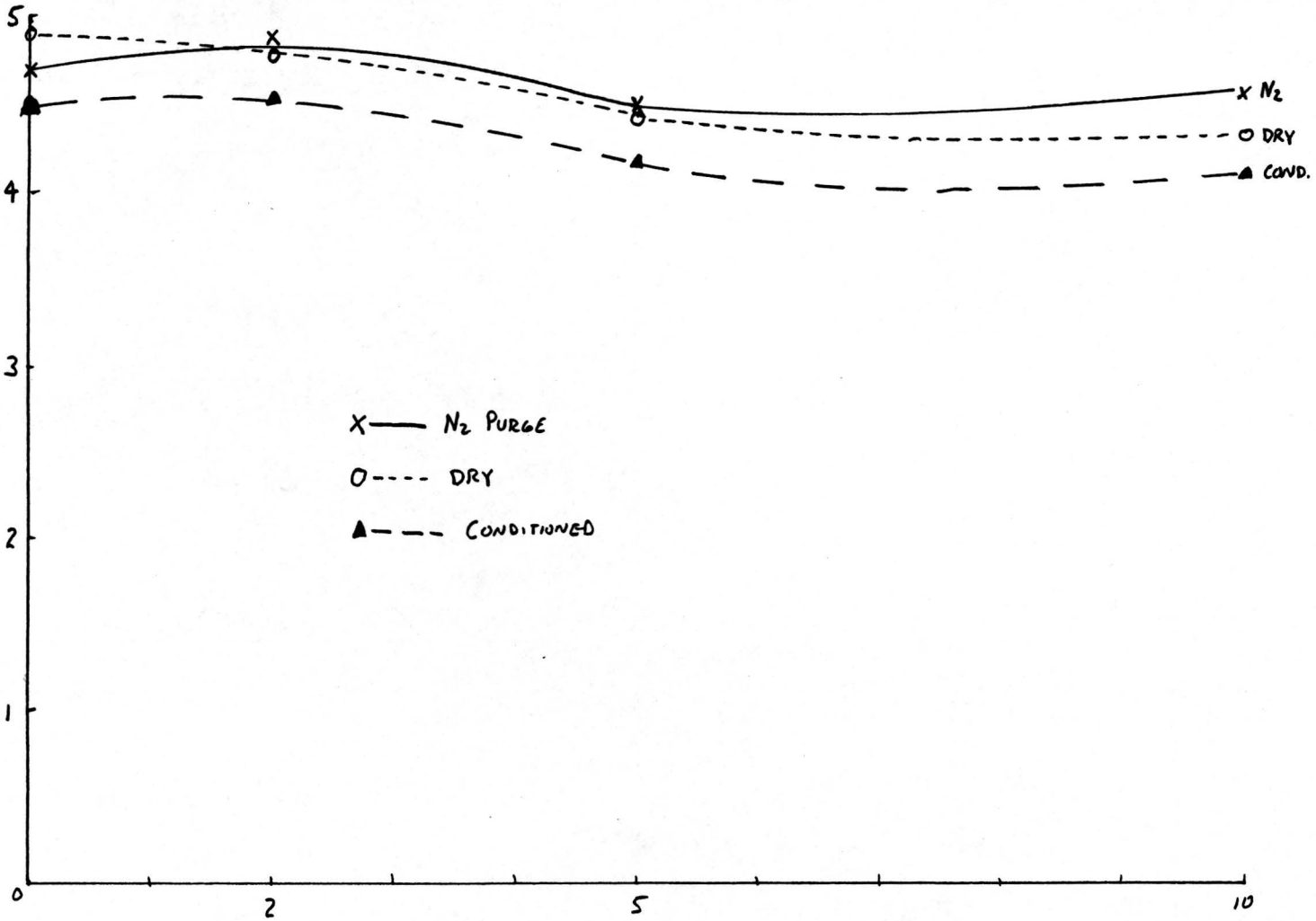


GRAPH 7

The effects of conditioning on tensile strength can be seen in graph eight. This graph indicates a decrease in tensile strength for the samples exposed to oxygen and water vapor, (the conditioned samples). This is most likely due to depolymerization. The graph also indicates some increase in tensile strength at the two megarad exposure level for the nitrogen purged and the conditioned samples. This is probably due to the same phenomenon that caused the increase in zero span tensile strength at the same dose level.

GRAPH 8: EFFECTS OF CONDITIONING

DOSE VS TENSILE



TENSILE IN KG.

DOSE IN MRAD

GRAPH 8

CONCLUSION

The Results Indicate Two Conclusions:

1. There is no benefit to be obtained by storing electron beam irradiated papers under special conditions.
2. Time has little effect on the molecular weight or zero span tensile strength of electron beam irradiated paper.

One possible explanation for these results is that the free radicals in the crystalline regions of the cellulose were not accessible to oxygen or water vapor. One flaw in this reasoning is that no explanation is given as to why water vapor or oxygen cannot penetrate over the relatively long period of time available. Since 45 to 60% of the free radicals occur in the crystalline regions, if any penetration occured it would have to affect the test results in some manner. (The 45 to 60% figure was based on the percentage of the cellulose structure that is crystalline. This assumes that the radicals occur independently of the lattice type, as the literature suggents.)

One other possibility is that a large percentage of the radicals in the crystalline regions were scavenged prior to testing. This would leave a small number of free radicals virtually inaccessible. These would be the ones present for up to two years following irradiation as

described in the literature.

The lack of effect of storage conditions is consistant with either of the above theorys. Both theories indicate that the paper should remain relatively stable over a period of time. These results may be of some value because it had been suspected that electron beam irradiated paper would continue to degrade with time. This research indicates that this is not the case and that there is no benefit to be obtained by utilizing special post irradiation storage conditions.

RECOMMENDATIONS

One area that would justify future research is the increase in tensile related strength at the lower (2 megarad) radiation levels. This increase may be due to crosslinking between fibers. It is suspected that the radiation levels at which this phenomenon occurs would vary with the type of substrate used.

Further research into the effects of storage conditions or the time-radical decay curve is not indicated unless more sophisticated equipment is available to accurately pinpoint the location and number of free radicals.

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APPENDIX

Average Values of Test Results

C= Conditioned
D= Dessicated
N= Nitrogen Purge

1. Zero Span Tensile (in PSI)

Days		2	5	11	30
0 Mrads	C	15,9	15.0	14.8	15.5
	N		14.6	14.8	13.9
	D		15.6	14.8	14.4
2 Mrads	C	13.3	14.1	14.4	14.3
	N		13.8	14.2	13.9
	D		14.8	13.8	14.2
5 Mrads	C	11.8	12.5	13.5	--
	N		13.1	13.1	--
	D		13.0	13.1	--
10 Mrad	C	12.4	12.1	11.9	--
	N		12.2	11.3	--
	D		12.5	12.2	--

2. Viscosity (in centipoise)

0 Mrads	C	8.80	8.78	8.78	8.31
	N		8.95	8.98	8.48
	D		9.00	8.99	8.37
2 Mrads	C	2.96	2.83	2.81	2.76
	N		2.81	2.85	2.71
	D		2.80	2.77	2.70
5 Mrads	C	2.43	2.42	2.37	--
	N		2.34	2.27	--
	D		2.36	2.39	--
10 Mrads	C	1.99	1.90	1.94	--
	N		1.98	1.98	--
	D		1.99	1.86	--

Burst and Tensile Results (tested April 14, 1983)

1. Conditioned Samples

	Burst (in PSI)	Tensile(1)	Time(2)
0 Mrads	19.9	4.5	--
2 Mrads	17.8	4.5	45
5 Mrads	16.4	4.2	21
10 Mrads	14.6	3.8	16

2. Nitrogen Purge

0 Mrads	21.3	4.7	--
2 Mrads	17.8	4.8	45
5 Mrads	16.5	4.4	21
10 Mrads	14.3	4.4	16

3. Dessicated Samples

0 Mrads	20.0	4.8	--
2 Mrads	17.9	4.7	45
5 Mrads	16.6	4.4	21
10 Mrads	14.4	3.8	16

1 = 15 mm strip, 2.0 cm/sec., in Kg.

2 = time following irradiation

Zero Span Tensile Results (in PSI)

Days			2	5	11	30
0 Mrads						
	C	wet	11.2	10.7	10.4	11.1
		dry	20.6	19.3	19.1	19.8
	N	wet		11.1	9.7	10.6
		dry		18.1	19.8	17.1
	D	wet		11.5	10.5	11.1
		dry		19.6	19.0	17.6
2 Mrads						
	C	wet	9.4	10.0	10.1	10.5
		dry	17.1	18.2	18.7	18.0
	N	wet		10.3	10.5	9.7
		dry		17.2	17.9	18.0
	D	Wet		9.8	9.3	11.9
		dry		19.8	18.3	16.4
5 Mrads						
	C	wet	8.6	8.5	9.6	
		dry	14.9	16.4	17.4	
	N	wet		8.9	10.1	
		dry		17.3	16.1	
	D	wet		9.0	10.0	
		dry		16.9	16.2	
10 Mrads						
	C	wet	8.2	8.7	8.4	
		dry	16.5	15.5	15.3	
	N	wet		8.4	8.2	
		dry		16.0	14.3	
	D	wet		8.7	8.4	
		dry		16.3	16.0	

8 GILL STREET
WOBURN, MASSACHUSETTS 01801
617-935-8020

Company Western Michigan Univ.

Name

Date 2-28-83

Time In 1 30 p Out

Sample No.	Coating	Substrate	Dose (Mrads)	Line Speed (ft/min)	Beam Current (mA)	Terminal Voltage (kV)	~~Oxygen (ppm)~~ N_2 (cfh)	Remarks
1	NONE	~~AS supplied~~	2	22	2	200	400 cfh	taped to cassette; 20 pcs (taped over top ≈ 1/4" side marked "2 MR")
							O_2 = 100 ppm or less	

R (2)

8 GILL STREET
WOBURN, MASSACHUSETTS 01801
617-935-8020

Company Western Michigan University

Name T. Clements

Date 3/24/83

Time In _____ Out _____

Sample No.	Coating	Substrate	Dose (Mrads)	Line Speed (ft/min)	Beam Current (mA)	Terminal Voltage (kV)	~~Oxygen (ppm)~~ N_2	Remarks
1	NONE	As Supplied	5	22	5	200	400 cfh	taped to carrier web 20 Samples

8 GILL STREET
WOBURN, MASSACHUSETTS 01801
617-935-8020

Company Western Michigan University

Name _____

Date 3-29-83

Time In _____ Out _____

Sample No.	Coating	Substrate	Dose (Mrads)	Line Speed (ft/min)	Beam Current (mA)	Terminal Voltage (kV)	~~Oxygen (ppm)~~ N_2	Remarks
1	none	As Supplied	10	22	10	200	400 CFH	taped to carrier web, 20 samples