EXPERTS (FY 1992)

1. Material Compatibility

JICA Expert : Dr. Fumio Yoshii

Duration : 16 June to 10 July 1992 (23 days)

Job Description :

1.1 Melt Flow Index tests (MFI) of irradiated PP.

1.2 Dissolution test and analysis of extracted materials.

1.3 Determination of molecular weight by intrinsic viscosity.

2. Microbiology

JICA Expert : Mr. Yuhei Watanabe

Duration : 19 August to 5 September 1992 (16 days)

Job Description :

2.1 Sensitivities of standard microbes to EB for sterilization

2.2 Effects of environments on the standard microbes.

3. Radiation Technology

JICA Expert : Mr. Hiroyuki Tachibana

Duration : 20 October to 9 November 1992 (19 days)

Job Description :

3.1 Survey of an adequate packaging method for surgical rubber gloves.

3.2 Optimization of irradiation conditions using conveyor system.

EQUIPMENTS

FY 1990
1. Tester Sangyo Geer Oven
2. Crystallization Rate Analyzer
3. Rockwell Hardiness Tester
4. Universal Tensile Machine
5. Izod Impact Tester
6. Dumbbell cutter
7. Sampling Machine

FY 1991
1. Melt Flow Indexer
2. Dissolution Tester
3. High Performance Liquid Chromatography (HPLC)

FY 1992
1. Chemiluminescence
2. Dynamic Mechanical Analyzer (DMA)
3. Mixing Roll (Two Rolls)
4. Adhesion Strength Tester

The equipments supplied in FY 1990 and 1991 are in good condition.

The Third UTN - JICA Joint Committee on the Radiation Applications Project

Review of Project Implementation in FY 1992 Radiation Curing of Surface Coatings

Presented by Nik Ghazali Nik Salleh

INTRODUCTION

The development of more powerful and efficient electron accelerators, the progress made in photo-chemistry technology and the increasing availability of wide range of acrylic acid derivatives have all contributed to the achievement of high speed polymerizing systems.

Two fundamental differences distinguish radiation-cured systems from conventional system based on polymers in solution or aqueous dispersions. These are as follows :

i. the absence of volatile solvents and

ii. the mechanism of polymerization of the components of the formulation under the influence of irradiation.

A chemical process (the formation of chemical bonds) is substituted for a physical process (the evaporation of solvents). The polymer molecules in the dried conventional coating are already present as such in the wet product due to crosslinking. In irradiation curing, the polymer is formed from monomers and prepolymers at the time of curing. The choice of 'solvents' (polyfunctional acrylates) and of prepolymers having specific chemical functions will dictate the final properties of the film obtained by irradiation. Polymerizable formulations are thus mixtures of unsaturated prepolymers diluted with monomers.

The main reasons for using irradiation technology are :

i. no pollution : absence of volatile solvents,

ii. instantaneous start and stop of production,

iii. excellent coating properties which are difficult or impossible to obtain with conventional technologies,

iv. room temperature curing : heat sensitive substrates can be coated,

v. high productivity : higher production speed from less working space,

vi. economy of processing : lower finishing costs per square meter, better properties from thinner coatings,

vii. energy savings.

OBJECTIVES

To generate technical knowhow on electron beam radiation curing of surface coatings and to develop new resins preparation using the indigenous materials.

Specific Area of Interest

i. Irradiation technology

To study the effect of different oxygen concentrations in the curing chamber on the efficiency of electron beam radiation curing of surface coatings.

ii. Coating formulations

By using commercially available acrylic oligomers, studies will be carried out to determine the most suitable formulations for electron beam curable resins preparation.

iii. Development of new resins

To develop a process of epoxy acrylates resins preparation from indigenous materials and to look into the resins applications.

i. IRRADIATION TECHNOLOGY

The main components used in preparing the formulation of radiation curable coating materials are as follow :

i. Prepolymer/oligomer

Aromatic urethane diacrylate (EBECRYL 210) used in the coating formulations was supplied by UCB Radcure.

Viscosity at 60°C : 3,900 mPa.s
Molecular weight : 1,500 g/mole

ii. Monomers

a. Monofunctional monomer

Cyclohexyl acrylate (CHA) was supplied by TCI, Tokyo Kasei.

Molecular weight : 154 g/mole

b. Difunctional monomers

1,6 - Hexanediol diacrylate (HDDA) was supplied by UCB Radcure.

Viscosity at 25°C : 10 mPa.s
Molecular weight : 226 g/mole

Tripropylene glycol diacrylate (TPGDA) was supplied by UCB Radcure.

Viscosity at 25°C : 15 mPa.s
Molecular weight : 300 g/mole

c. Trifunctional monomer

Trimethylolpropane triacrylate (TMPTA) was supplied by UCB Radcure.

Viscosity at 25°C : 115 mPa.s
Molecular weight : 298 g/mole

Experimental

Since acrylated urethane resin (EBECRYL 210) was 100 percent polymer solids, it was dissolved in several reactive diluents i.e. mono, di and trifunctional monomers, in order to achieve the required viscosity of the resin and the composition ratio is 1:1 (by weight).

The samples of different coating formulations were prepared by the used of automatic film applicator, Model PI-1210 (Tester Sangyo) with a bar coater size # 30. The thickness of all the films was about 70 μm. They were then irradiated by low energy electron beam accelerator, Model EBC-200-20-15 (Curetron, NHV). The beam voltage and the beam current were set at 200 kV and 2 mA respectively. The conveyor speed was fixed at 15 m/min and the dose per pass

was 15 kGy. All the samples were irradiated under nitrogen atmosphere at 100, 300, 500 and 800 ppm oxygen content and the doses given at 15, 30, 45 and 60 kGy for each formulations.

The coated plates were dried overnight to make the test piece for pendulum hardness measurement and gel content determination. First, the hardness of the cured films were measured by the pendulum hardness tester (Labotron-Byk) and using the glass calibration plate as its standard. In the second test, films of certain quantity were taken out from the glass plates. They were weighed and then placed in wire mesh. Initially, they were soaked in acetone and then placed in the soxhlet extractor. They were extracted for sixteen hours at the boiling temperature. The residues were taken out from the wire mesh after extraction process. They were vacuum dried and simultaneously heated up to 50℃ in vacuum oven to constant weight for several hours.

Results and Discussion

In this experiment one monofunctional, two difunctional and one trifunctional monomers were used in the coating formulations. A straight aromatic urethane acrylate (EBECRYL 210) was the main prepolymer/oligomer used in this system (see Table 1.0). This EBECRYL resin can be used in combination with polyester acrylates and epoxy acrylates such as epoxidized palm oil acrylate (EPOLA) and liquid epoxidized natural rubber acrylate (LENRA) in order to improve their flexibility. For monitoring the curing progress of the coating system, the pendulum hardness and the non-extractible gel content have been tested.

The first formulation (AP-1) used cyclohexyl acrylate because of the lower percentage of shrinkage during polymerization i.e. 12.5 percent shrinkage of homopolymer. Table 2.0 shows the effect of inerting atmosphere to the hardness of coating materials. The surfaces of all the films from the above sample were little tacky/sticky and could not be measured by the pendulum hardness tester. Figure 1.0 shows the effect of oxygen concentration to the curing of coating formulation. At 15 kGy, the gel content of this sample is below 85 percent at different oxygen concentration. But from 30 kGy onward, the gel content of these films is more than 97 percent i.e. difference by 12 percent from the above dose. The values of gel content between 30 kGy to 60 kGy did not reflect the actual curing progress and hardness of the cured films. It shows that this technique i.e. the gel content determination is not the best method to monitor the EB-curing of resins.

Samples AP-2A and AP-2B contain difunctional monomers i.e. 1,6-hexanediol diacrylate (HDDA) and and tripropylene glycol diacrylate (TPGDA) in the coating formulations. HDDA is a very low viscosity monomer characterized by its high diluting power and excellent adhesion. Whereas, TPGDA is a relatively low viscosity, a good cure speed and one of the most widely used monomer in the UV/EB formulation. Figure 2.0 and 4.0 show the effect of oxygen concentration to the hardness of the cured films at different doses. Sample AP-2A shows some changes in the pendulum hardness of the cured films at different dose and oxygen concentration. For example at 30 kGy, there is about 10 percent difference in hardness between 100 ppm and 800 ppm of oxygen content. The gel content of the above sample is about 99 percent at 30 kGy onwards (see Figure 3.0). Whereas in sample AP-2B between 30 kGy and 60 kGy, there is slight changed (variation) in the pendulum hardness i.e. less than 5 percent due to the effect of oxygen

concentration to radiation curing and the gel content is more than 98 percent (see Figure 5.0). From these formulations, sample AP-2A (HDDA) gave better percentage of pendulum hardness than sample AP-2B (TPGDA).

Sample AP-3 contain trifunctional monomer i.e. reactive diluent. Trimethylol propane triacrylate (TMPTA) is used in the formulations where high cure speed, chemical and/or abrasion resistance are required. From Figure 6.0, there is slight changed in the pendulum hardness i.e. about 5 percent due to the effect of oxygen concentration at 15 kGy and 30 kGy. As the dose given to the sample increases, there is not much changed in the hardness of the cured films. The hardness of this sample at 60 kGy is about 46 kGy and is the highest among the four formulations. Values from the gel extraction confirmed the hardness of the above sample. From Figure 7.0, at 30 kGy onwards the gel content of the cured films is more than 98 percent.

ii. COATING FORMULATIONS

The aim of this experiment is to find the best formulation of radiation curable resin with excellent properties such as hardness, abrasion, adhesion, glossiness, resistance to chemical and lower dose to cure. This experiment also include the compatibility study of coating materials with suitable substrates for the application of surface coating technology.

Parameters affecting the curing process :

i. the effect of monomer reactivity (acrylate/methacrylate)

ii. the effect of monomer content (ratio)

iii. the effect of monomer functionality

iv. the effect of different type of oligomer

The main components used in the formulation of radiation curable coating materials are :

i. Prepolymer/oligomers

Aliphatic urethane acrylate	(EBECRYL 270)
Aromatic urethane diacrylate	(EBECRYL 210)
Aromatic urethane acrylate	(UX 4101)

ii. Diluents/monomers

a. Monofunctional monomers

1-Vinyl-2-pyrrolidone	(NVP)
2-Ethylhexyl acrylate	(EHA)
2-Hydroxyethyl acrylate	(HEA)
Hydroxypropyl acrylate	(HPA)
Vinyl acetate	(VAc)

b. Difunctional monomers

1,6-Hexanediol diacrylate	(HDDA)
Neopentyl glycol diacrylate	(A-NPG)
Tripropylene glycol diacrylate	(TPGDA)
Dianol diacrylate	(DDA)
Triethylene glycol diacrylate	(TEGDA)
Ethylene glycol dimethacrylate	(1G)
Diethylene glycol dimethacrylate	(2G)
Triethylene glycol dimethacrylate	(3G)
Polyethylene glycol dimethacrylate	(4G)
1,3-Butylene glycol dimethacrylate	(BG)
1,6-Hexanediol dimethacrylate	(HD)

Experimental

Since the above prepolymer/oligomers are very viscous, there is a need to mix them with reactive diluents/monomers in order to achieve the required viscosity of the resin for the desired coatings. The number of monofunctional monomers used this year increases because they can offer better properties especially in viscosity, adhesion and physical properties.

The properties of the cured films were measured by the pendulum hardness tester (Labotron-Byk) and the percentage of crosslinking of polymers were determined by the gel extraction. Viscosities of the above formulations were measured at 25℃ by the cone/plate viscometer, Model DV 11 (Brookfield).

Chemical resistance test was done on the cured films using several chemicals such as 3 percent of Na_2CO_3, 10 percent of H_2SO_4, 5 percent CH_3COOH and 10 percent NaOH. Glossiness of the cured films was measured by the glossmeter, Model 101 (Sheen) at 60° angle which refer to 93.2 as a standard.

Adhesion test was carried out according to ASTM (D) 2571-71 method. The coated films were cut with a sharp knife in 25 squares with 2 mm on edge. Cellophane tape was applied and then rapidly peeled off from the coated film. The value of adhesion for each films was calculated by counting the number of squares remained on the substrate. While the degree of abrasion for the

above samples were measured by the Taber type abrasion tester, Model AB-101 (Tester Sangyo). The abrasion index of the sample were calculated from the weight lost (in mg) after 500 revolutions on the table with the abrasive wheels and load (in kg) applied to them.

Results and Discussion

Effect of Pendulum Hardness

The results show that dimethacrylate monomers are less reactive than diacrylate monomers and the former need a higher dose to cure the coating films (see Figure 8.0). But dimethacrylate system give higher percentage of pendulum hardness when they are irradiated at optimum dose. It is due to the the inductive effect imparted by the $-CH_3$ group to the acrylated double bond. These molecules of the methacrylate monomers need more activation energy for making free radicals and once they are formed, the curing speed is increased (faster). They also produce a relatively hard and more crosslinking films. For formulation 270/DDA, the percentage of pendulum hardness is very low because dianol diacrylate monomer is less reactive.
Reactive diluents/monomers also can increase the hardness of cured films. Another factor is that the monomer content in the coating formulation can influence the hardness of the cured films i.e. as monomers content increase, the hardness of the films also increase. For example, A-NPG monomer is more reactive than TPGDA when dissolves in the urethane acrylate resin. Hardness property of the former is higher than the latter.

The hardness of the cured films also depend on the type of prepolymer/oligomer used in the coating formulations i.e. aliphatic urethane diacrylate (EBECRYL 270) or aromatic urethane diacrylate (EBECRYL 210). The hardness of the cured film from the above formulations can be summarized as follow :

EBECRYL 210/Monofunctional	: NVP>EHA>VAc>HPA
EBECRYL 270/Monofunctional	: EHA>BA>HPA>NVP>VAc/HEA
EBECRYL 210/Difunctional	: A-NPG>HDDA>TPGDA/TEGDA>DDA
EBECRYL 270/Difunctional	: A-NPG>HDDA>TPGDA>TEGDA>DDA

From the above results, it is found that most acrylated monomers are more reactive than acetate monomer i.e. vinyl acetate. Films of urethane acrylate (UX 4101) derived from HEA-IPDI-(diol-polycaprolacton)-IPDI have also been tested but give a very soft films. Curing progress of the cured films were also monitored by the used of infrared spectrophotometer, Model IR-700 (JASCO). The disappearance/conversion of the double bond/functional group was observed at band range 1620-1640 cm^{-1}. The double bonds of diacrylate type disappeared at lower dose than dimethacrylate type i.e. 20 kGy and 60 kGy respectively.

Gel Content Determination

Analysis of gel content was carried out only to certain/selected formulations. Most of the samples have gel content between 95-97 percent except formulation which contain dianol diacrylate (DDA) monomer with gel content between 85-89 percent. The hardness of the cured films of urethane acrylates/DDA is less than 10 percent i.e. very soft although the dose have been increased up to 50 kGy.

Effect of Chemical

All the cured films of EBECRYL 270 with different types of monomers were resistance to several chemicals such as 5 percent of acetic acid, 3 percent of sodium carbonate, 50 percent of ethanol, 10 percent of sulphuric acid and 10 percent sodium hydroxide except formulation of EBECRYL 270/HPA, EBECRYL 270/HEA and EBECRYL 270/NVP (see Table 5.0 and 6.0).

Effect of Adhesion

From the results of adhesion test, it is found that most of the combination of EBECRYL 270 with monofunctional monomers show better adhesion to the substrate than the combination of difunctional monomers i.e. 100 percent and less than 60 percent adhesion respectively (see Table 7.0).

Glossiness Measurement

Table 3.0 shows the percentage of glossiness at 60° of clear coating from the cured films. The glossiness of the EBECRYL 270/difunctional monomers is over than 85 percent and should be considered as satisfactory compared to EBECRYL 270/dimethacrylate in the range of 65-77 percent with the exception of two coating formulations i.e. EBECRYL 270/2G and EBECRYL 270/4G.

iii. DEVELOPMENT OF NEW RESINS

Three main areas to investigate the epoxidized natural rubber (ENR) :

i. Depolymerization of ENR,

ii. Synthesis of acrylated liquid epoxidized natural rubber (LENRA) from depolymerization process,

iii. Application of acrylated liquid ENR in radiation curing.

Preparation of LENRA

In this investigation, two types of epoxidized natural rubber i.e. ENR-25 and ENR-50 have been used. For the depolymerization of ENR, some works have been done in collaboration with the Chemistry Department, National University of Malaysia (UKM). Rubber Research Institute of Malaysia (RRIM) has also been working on the same area and some of the liquid ENR-50 samples have been used for comparison purposes.

It is proven that the depolymerization of ENR does not destroy all the epoxy groups available. Therefore subsequent acrylation reaction of ENR is possible. The acrylation reaction takes place through the ring opening of the epoxy group to form liquid epoxidized natural rubber acrylate (LENRA) as suggested by the equation 1.

The infrared data as shown in Figures 15.0 to 17.0 confirm this observation. Only three functional groups are importance to us i.e. epoxy groups (the peaks at ca. 1250, 1081 and 872 cm^{-1}), acrylate (the peaks at 1664, 1637, 986 and 809 cm^{-1}) and hydroxyl group (broad peak at 3454 cm^{-1}). Except for a broad peak between 3600 and 3200 cm^{-1}, ENR-50 shows the same infrared spectrum as in ENR-25.

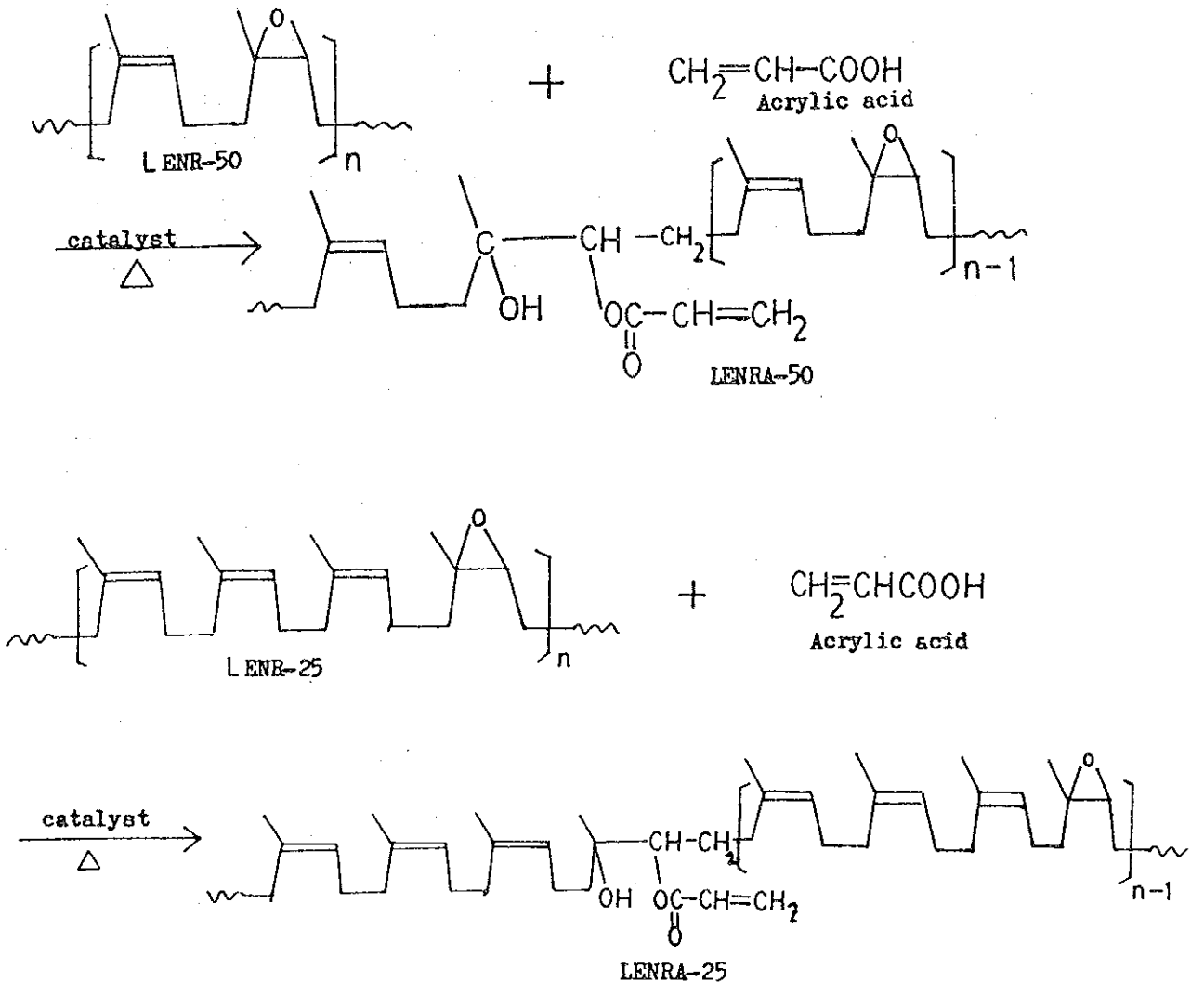
There are several important factors that govern the reaction between liquid ENR and acrylic acid. These factors need to be observed in order to minimise the risks of gelation during synthesis. The most important parameters are found to be the reaction temperature, inhibitor, catalyst, reactant ratio, concentration of liquid ENR and reaction time. Table 8.0 summarizes the synthesis data of the liquid ENR as a result of these conditions.

Application of LENRA

For radiation curing studies, liquid epoxidized natural rubber (based on ENR-50) sample supplied by RRIM was reacted with acrylic acid for twelve hours with the reaction ratio of one mole epoxy group to 0.2 mole acrylic acid. 4-Methoxyphenol and trimethylamine were used as inhibitor and catalyst respectively,

The basic formulations necessary for liquid epoxidized natural rubber acrylate (LENRA) to be used as radiation curable resins are summarized in Table 9.0 and 10.0 i.e. data of the formulation works. Table 9.0 represents the formulations based on 20 percent of LENRA and 80 percent reactive diluents and Table 10.0 is based on 20 percent of LENRA, 20 percent of EPOPA and 60 percent of reactive diluents. Three reactive diluents used were 2-hydroxyethyl acrylate (monofunctional), tripropylene glycol diacrylate (difunctional) and trimethylolpropane triacrylate (TMPTA). The samples were coated on the glass plates, size 10 cm x 10 cm, using a bar coater and cured by the low energy electron beam accelerator (Curetron, NHV). The conditions of the machine were adjusted to give 20 kGy per pass at 200 keV voltage, 5 mA current and 18.2 m/min conveyor speed.

Figure 18.0 represents the infrared spectrum of the cured liquid epoxidized natural rubber acrylate film. From this spectrum, it can be observed that the peaks attributable to acrylate double bond have been used up.



Equation 1: The acrylation reactions of LENR-50 and LENR-25.

The gel contents of the cured films are found to be high i.e. more than 90 percent as shown in Figures 20.0, 22.0, 24.0 and 26.0. They indicate that the formation network almost reaches the maximum at the dose of 40 kGy. It is observed that the gel content of the formulations using LENRA show slightly higher than the ones using the mixture of LENRA and EPOPA i.e. epoxidized palm oil acrylate.

The pendulum hardness of the cured films increases as the monomer content of TMPTA increases and at the same time it makes the formulations to be more sensitive to radiation as illustrated in Figures 19.0 and 20.0. By adding 40 to 50 percent of TMPTA monomer, the hardness can be increased up to more than 50 percent but the viscosity also increases. Additional of 2-hydroxy ethyl acrylate to the formulations is to reduce the viscosity. Formulations using LENRA again show better hardness than the ones using the mixture of LENRA and EPOPA as shown in Figure 19.0 and 23.0. It is a characteristic of the epoxidized palm oil acrylate to give soft cured films.

From the formulations of liquid epoxidized natural rubber acrylate with different type of monomers, the cured films give glossiness values in the range of 50 to 86 percent (see Tables 9.0 and 10.0). Whereas, the LENRA-EPOPA mixed formulations give higher gloss compared to the ones without epoxidized palm oil acrylate.

Finally, the cured films are also resistance to certain chemicals such as acetic acid, sodium carbonate, ethanol, sulphuric acid and sodium hydroxide.

ACKNOWLEDGEMENTS

Thanks for the cooperation and support to all the members of the Nuclear Energy Unit (UTN) Surface Coatings Group.

FORMULATION
of
RADIATION CURABLE COATINGS

Sample Nos.	EBECRYL 210 (Radcure)	CHA	HDDA	TPGDA	TMPTA
AP-1	50 %	50 %			
AP-2A	50 %		50 %		
AP-2B	50 %			50 %	
AP-3	50 %				50 %

Table 1.0
Composition ratio of radiation curing systems for coatings (aromatic urethane diacrylate system).

EFFECT OF OXYGEN TO RADIATION CURING

PENDULUM HARDNESS

Ebecryl 210/CHA

Absorbed Doses	Oxygen Concentn. 100 ppm	300 ppm	500 ppm	800 ppm
15 kGy	sticky	sticky	sticky	sticky
30 kGy	sticky	sticky	sticky	sticky
45 kGy	sticky	sticky	sticky	sticky
60 kGy	sticky	sticky	sticky	sticky

Table 2.0
Effect of oxygen concentration to the hardness of coating materials.

PUA 270	1G	2G	3G	4G	BG	HD	A-NPG	HDDA	DDA	TPGDA
40 40 40 40 40 40 40 40 40 40	60	60	60	60	60	60	60	60	60	60
Dose to cure (kGy)	80	40	50	40	60	60	10	10	10	10
Average Gloss % (at 60°)	77.3	91.0	76.3	82.1	70.1	65.9	87.2	87.4	90.1	88.0
Viscosity ,cps	60	102	109	179	91	75	145	102	very viscous	254
% P.Hardness	45.5	22.1	40.2	16.9	49.3	25.2	25.7	18.4	4.4	9.7

Table 3: Curing studies of different type monomers (diacrylate & dimethacrylate)

OLIGOMERS			MONOMERS									% P.H at20kGy
PUA 270	PUA 210	UX 4101	NVP	HPA	HEA	VAC	A-NPG	TPGDA	HDDA	A-HD	TEGDA	
60	-	-	40	-	-	-	-	-	-	-	-	9.4
60	-	-	-	40	-	-	-	-	-	-	-	17.6
60	-	-	-	-	40	-	-	-	-	-	-	7.3
60	-	-	-	-	-	40	-	-	-	-	-	8.7
60	-	-	-	-	-	-	40	-	-	-	-	29.1
60	-	-	-	-	-	-	-	40	-	-	-	12.9
50	-	-	-	-	-	-	-	50	-	-	-	14.2
50	-	-	-	-	-	-	50	-	-	-	-	41.4
40	-	-	-	-	-	-	60	-	-	-	-	49.4
40	-	-	-	-	-	-	-	60	-	-	-	13.8
-	60	-	40	-	-	-	-	-	-	-	-	22.0
-	60	-	-	40	-	-	-	-	-	-	-	4.6
-	60	-	-	-	40	-		-	-	-	-	7.5
-	60	-	-	-	-	40	-	-	-	-	-	6.5
-	60	-	-	-	-	-	40	-	-	-	-	19.8
-	60	-	-	-	-	-	-	40	-	-	-	9.1
-	60	-	-	-	-	-	-	-	40	-	-	14.2
-	60	-	-	-	-	-	-	-	-	40	-	21.1
-	60	-	-	-	-	-	-	-	-	-	40	12.6
-	-	60	40	-	-	-	-	-	-	-	-	7.7
-	-	60	-	40	-	-	-	-	-	-	-	6.3
-	-	60	-	-	40	-	-	-	-	-	-	6.1
-	-	60	-	-	-	40	-	-	-	-	-	5.6
-	-	60	-	-	-	-	40	-	-	-	-	25.6
-	-	60	-	-	-	-	-	40	-	-	-	11.5

Table 4: Curing studies with different oligomers polyurethane acrylate

Chemical	Monomers								
	A-NPG	HDDA	TPGDA	DDA	BA	HPA	HEA	NVP	Vac
Acetic acid 5%	Y	Y	Y	Y	Y	Y	Y	Y	Y
Ethanol 50%	Y	Y	Y	Y	Y	Y	Y	Y	Y
Sodium carbonate 3%	Y	Y	Y	Y	Y	Y	Y	Y	Y
Sulphuric acid 10%	Y	Y	Y	Y	Y	Y	Y	Y	Y
Sodium hydroxide 10%	Y	Y	Y	Y	Y	Y	Y	Y	Y

Table 5 : Chemical analysis for aliphatic urethane acrylate (PUA 270/monomers) in ratio oligomer/monomer : 60/40

* Y for pass the test

* N for fail the test

Chemical	Monomers				
	A-NPG	TPGDA	HDDA	DDA	TEGDA
Acetic acid 5%	Y	Y	Y	Y	Y
Ethanol 50%	Y	Y	Y	Y	Y
Sodium carbonate 3%	Y	Y	Y	Y	Y
Sulphuric acid 10%	Y	Y	Y	Y	Y
Sodium hydroxide 10%	Y	Y	Y	Y	Y

Table 6 : Chemical analysis for aliphatic urethane acrylate (PUA 270/monomers) in ratio oligomer/monomer : 50/50

* Y for pass the test

* N for fail the test

Formulations	Oligomer/monomers ratio	% adhesion
270/HPA	60/40	100%
270/HEA	60/40	100%
270/EHA	60/40	100%
270/BA	60/40	100%
270/NVP	60/40	87%
270/HDDA	60/40	30%
270/DDA	60/40	28%
270/TPGDA	60/40	20%
270/A-NPG	60/40	10%

Table 7 : Adhesion test for the formulations of aliphatic urethane acrylate PUA 270/monomers

Table9 : Formulations, using oligomer LENRA

Sample No.	LENRA,%	TMPTA,%	TPGDA,%	HEA,%	Viscosity, cps	Average Gloss, % (at 60°)
H2A	20	60	20	0	1360	55.0
H2B	20	50	30	0	1280	70.7
H2C	20	40	40	0	890	64.0
H2D	20	30	50	0	613	67.9
H2E	20	20	60	0	340	70.5
H2F	20	50	20	10	1100	53.3
H2G	20	40	30	10	684	54.0
H2H	20	30	40	10	360	68.7
H2I	20	20	50	10	236	69.5

Table 10 Formulations, using oligomers LENRA & EPOPA

Sample No.	LENRA,%	EPOPA,%	TMPTA,%	TPGDA,%	HEA,%	Viscosity, cps	Average Gloss, % (at 60°)
J2A	20	20	50	10	0	1200	79.0
J2B	20	20	40	20	0	850	73.4
J2C	20	20	30	30	0	940	68.2
J2D	20	20	20	40	0	714	62.8
J2E	20	20	10	50	0	552	84.7
J2F	20	20	0	60	0	500	74.4
J2G	20	20	10	40	10	370	49.8
J2H	20	20	20	30	10	560	68.4
J2J	20	20	30	20	10	694	70.7
J2K	20	20	40	10	10	900	86.4
J2L	20	20	0	50	10	322	49.1

EFFECT OF OXYGEN TO RADIATION CURING

GEL EXTRACTION

Ebecryl 210/CHA

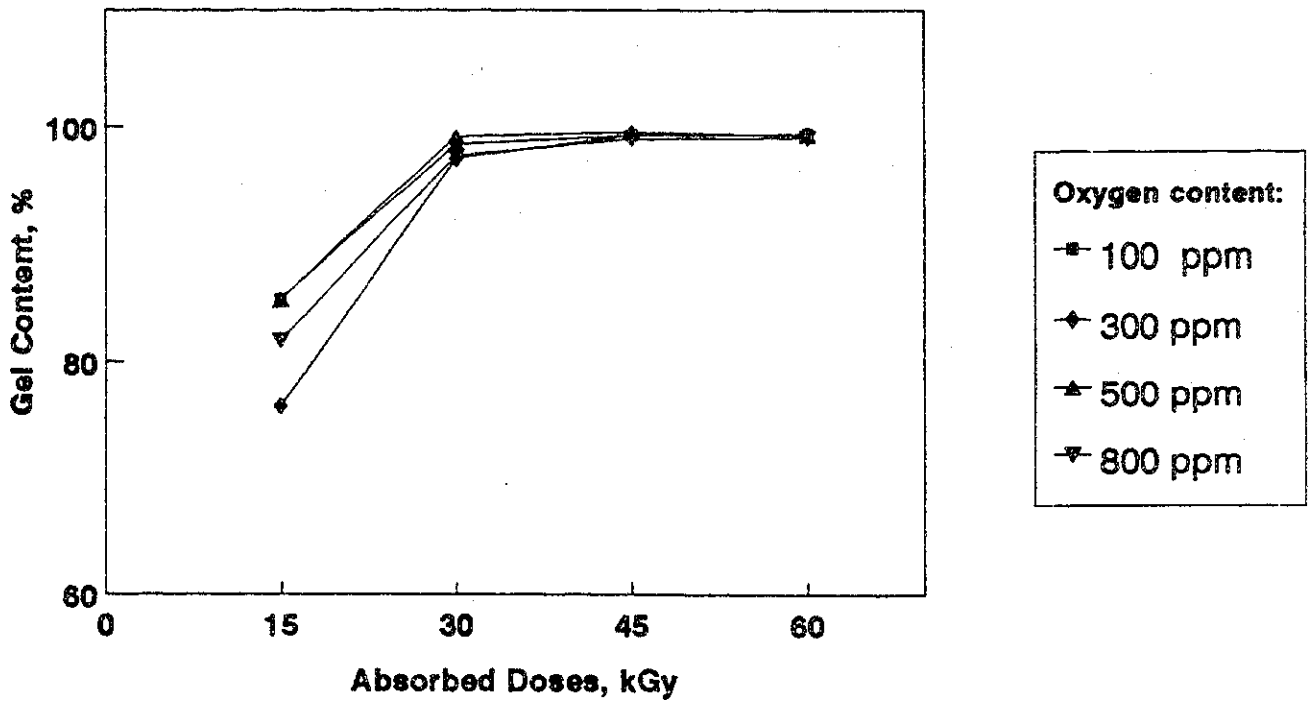


Figure 1.0
Effect of oxygen concentration to the curing of coating formulation.

EFFECT OF OXYGEN TO RADIATION CURING

PENDULUM HARDNESS TEST

Ebecryl 210/HDDA

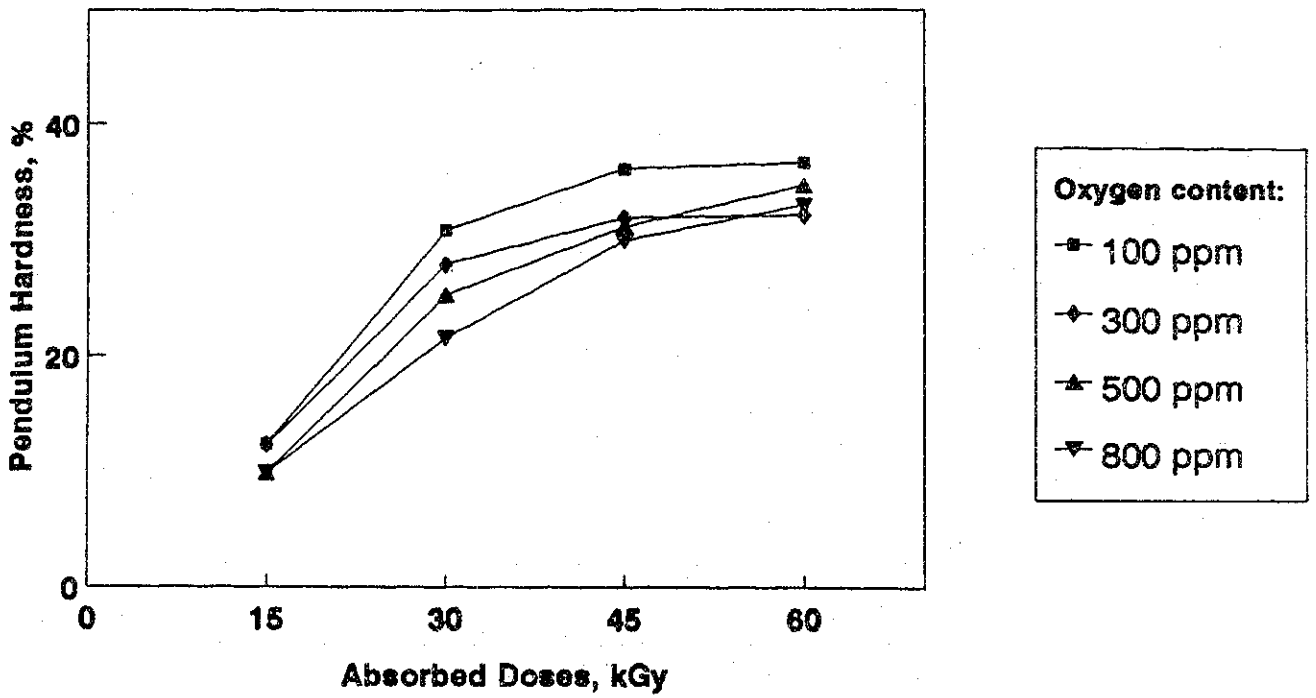


Figure 2.0
Effect of oxygen concentration to the hardness of coating materials.

EFFECT OF OXYGEN TO RADIATION CURING

GEL EXTRACTION

Ebecryl 210/HDDA

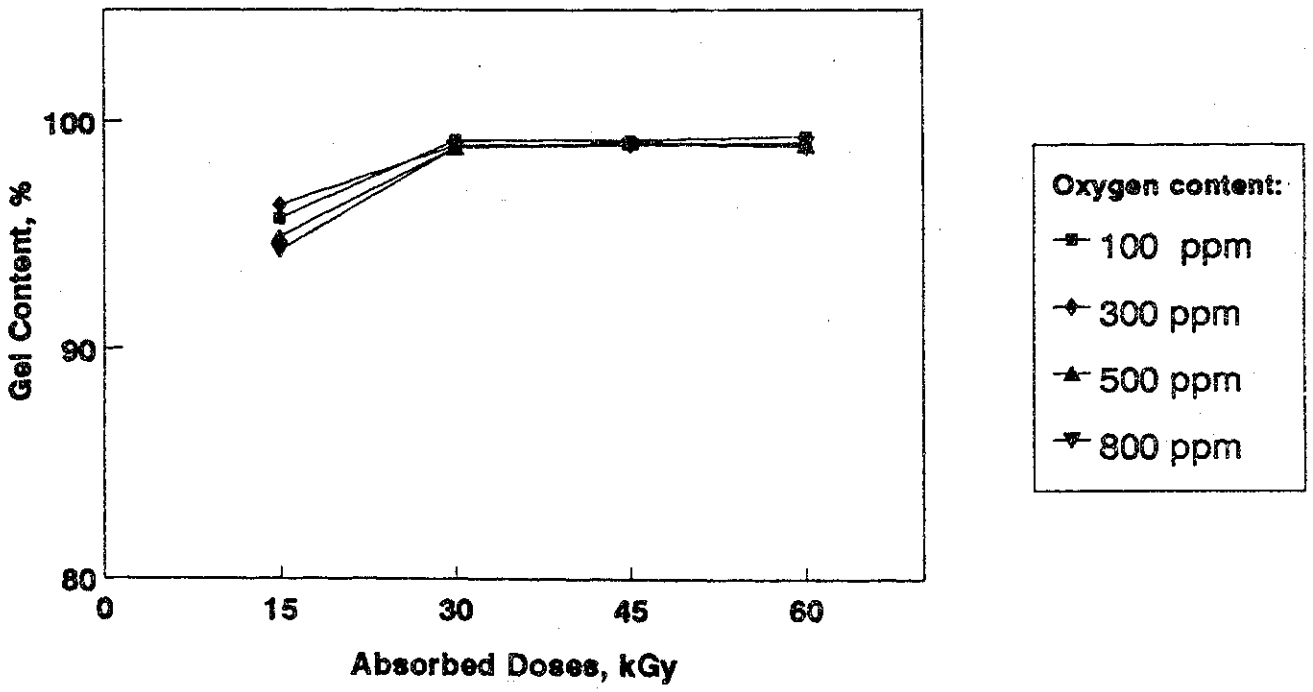


Figure 3.0
Effect of oxygen concentration to the curing of coating formulation.

EFFECT OF OXYGEN TO RADIATION CURING

PENDULUM HARDNESS TEST

Ebecryl 210/TPGDA

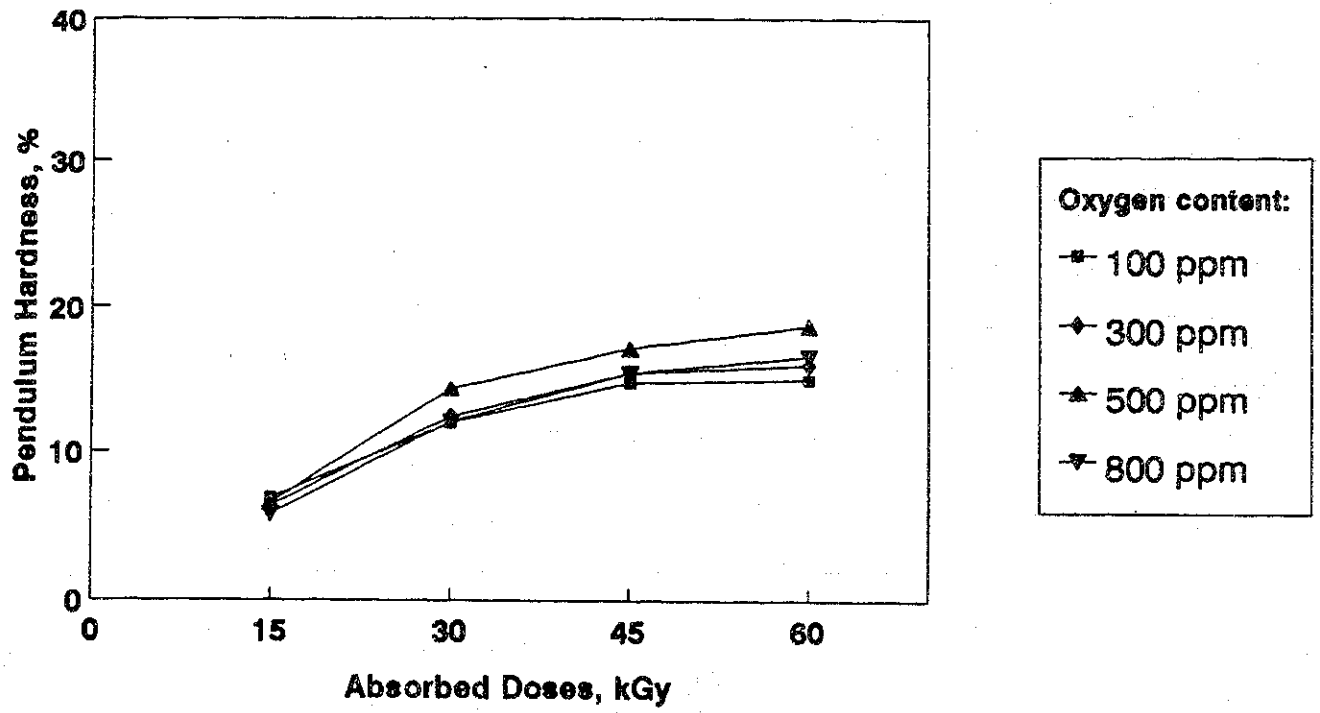


Figure 4.0
Effect of oxygen concentration to the hardness of coating materials.

EFFECT OF OXYGEN TO RADIATION CURING

GEL EXTRACTION

Ebecryl 210/TPGDA

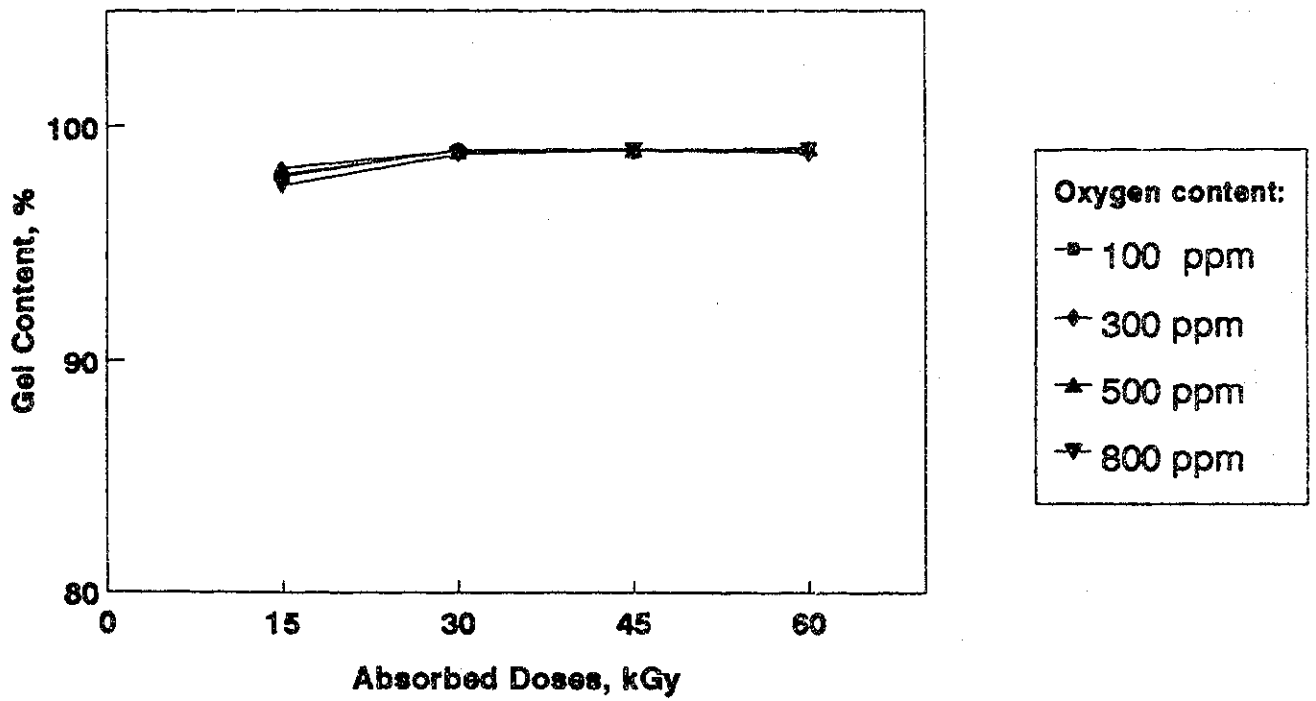


Figure 8.0
Effect of oxygen concentration to the curing of coating formulation.

EFFECT OF OXYGEN TO RADIATION CURING

PENDULUM HARDNESS TEST

Ebecryl 210/TMPTA

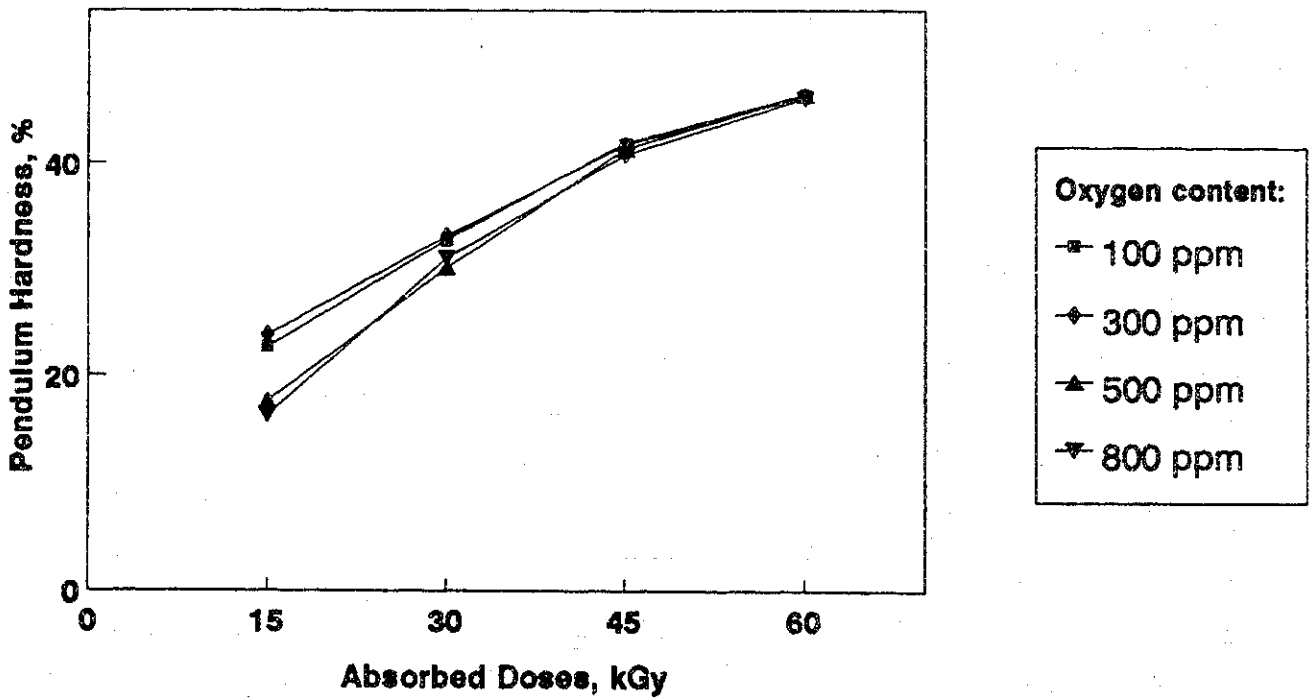


Figure 6.0
Effect of oxygen concentration to the hardness of coating materials.

EFFECT OF OXYGEN TO RADIATION CURING

GEL EXTRACTION

Ebecryl 210/TMPTA

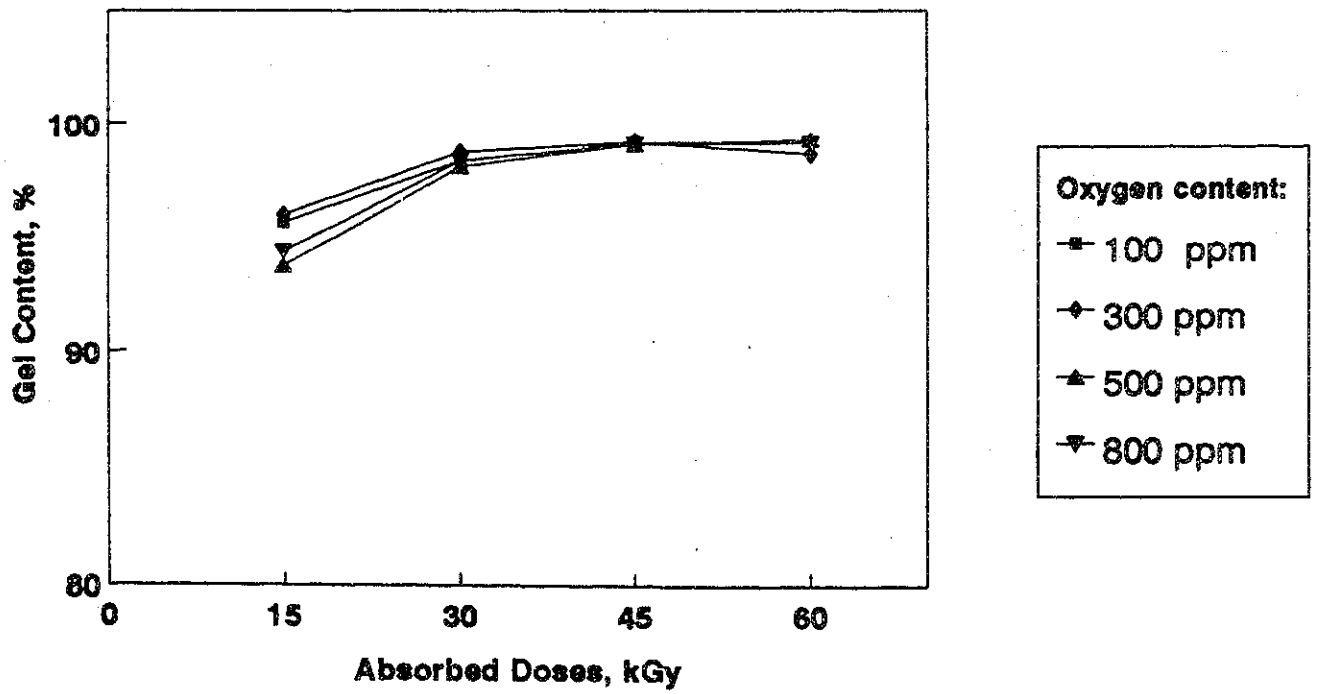


Figure 7.0
Effect of oxygen concentration to the curing of coating formulation.

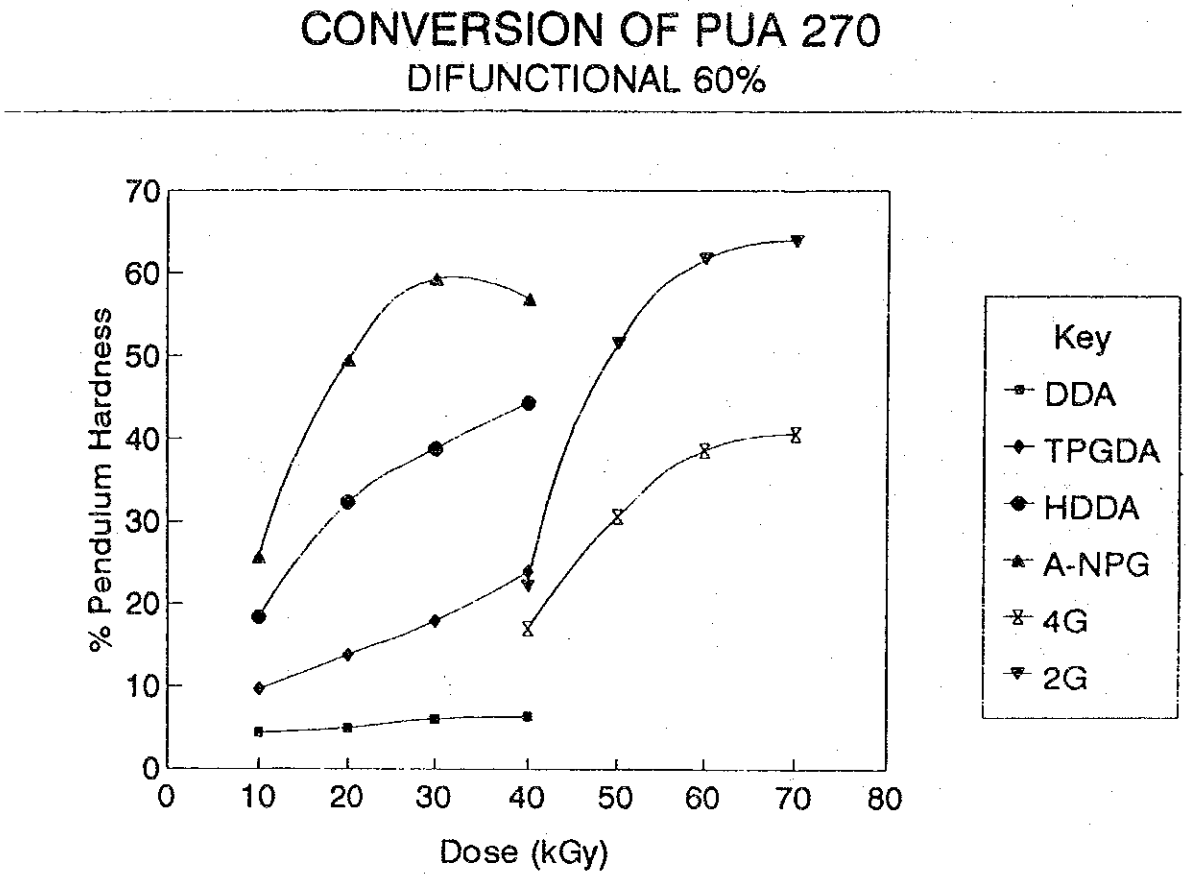


Fig 8 : The effect of difunctional monomers (acrylate/methacrylate) on to the % pendulum hardness.

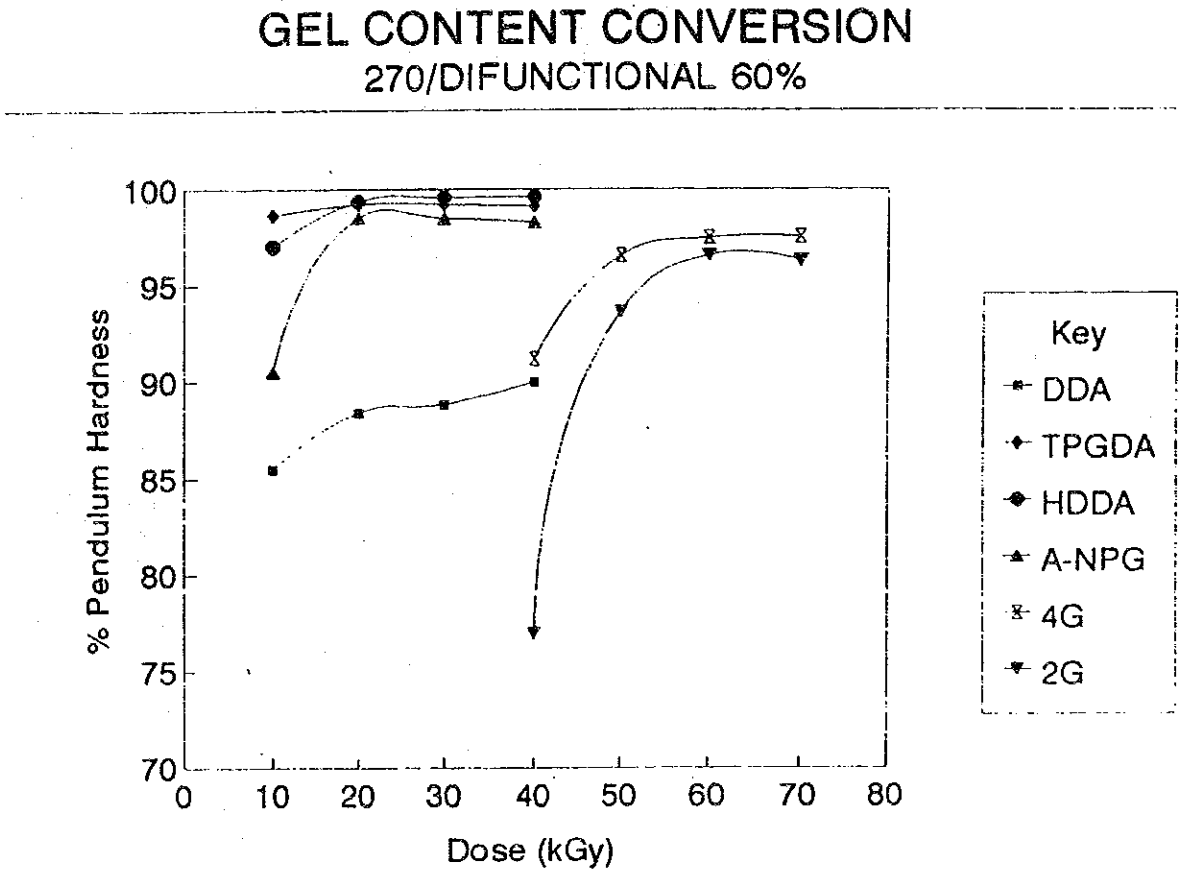


Fig 9 : Gel content conversion of aliphatic urethane acrylate formulations (diacrylate/dimethacrylate).

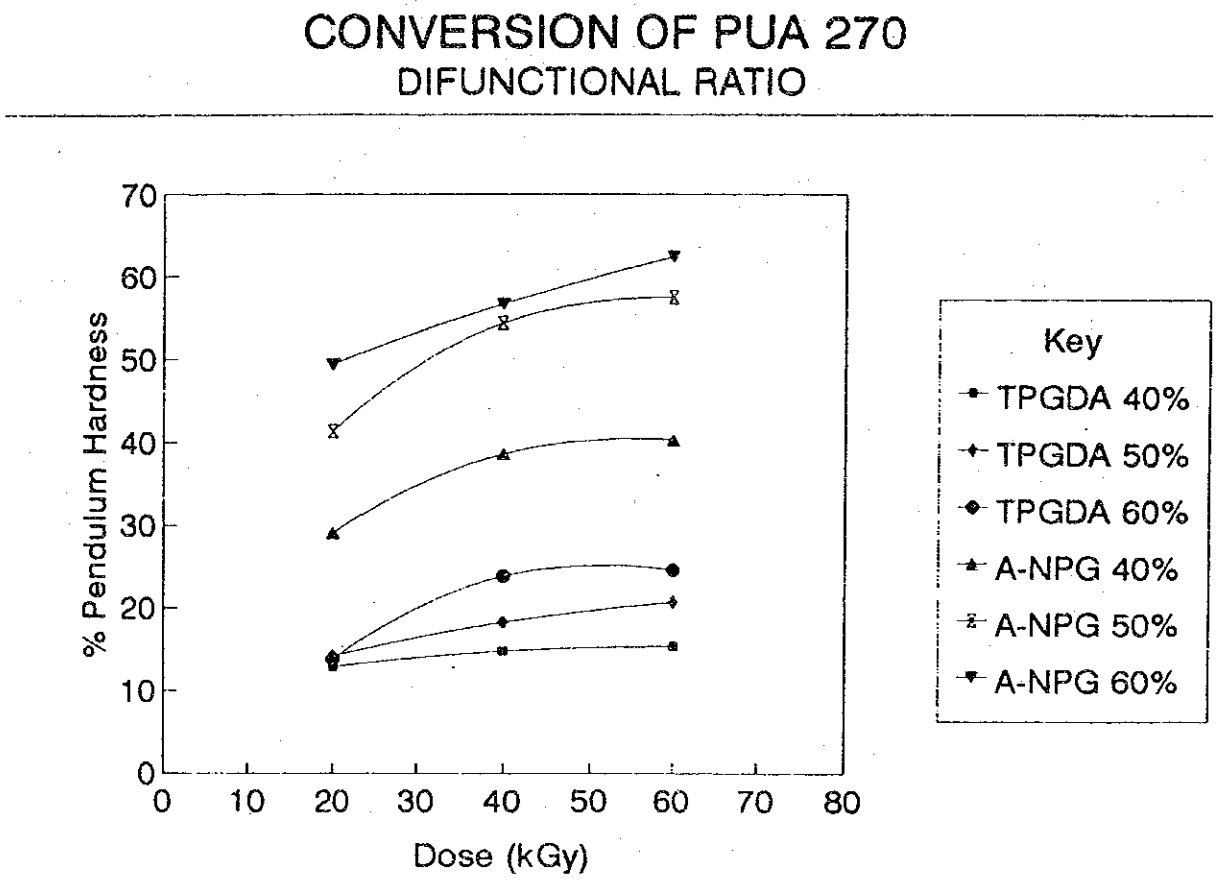


Fig 10: The effect of using difunctional monomers with different ratio on to the % pendulum hardness.

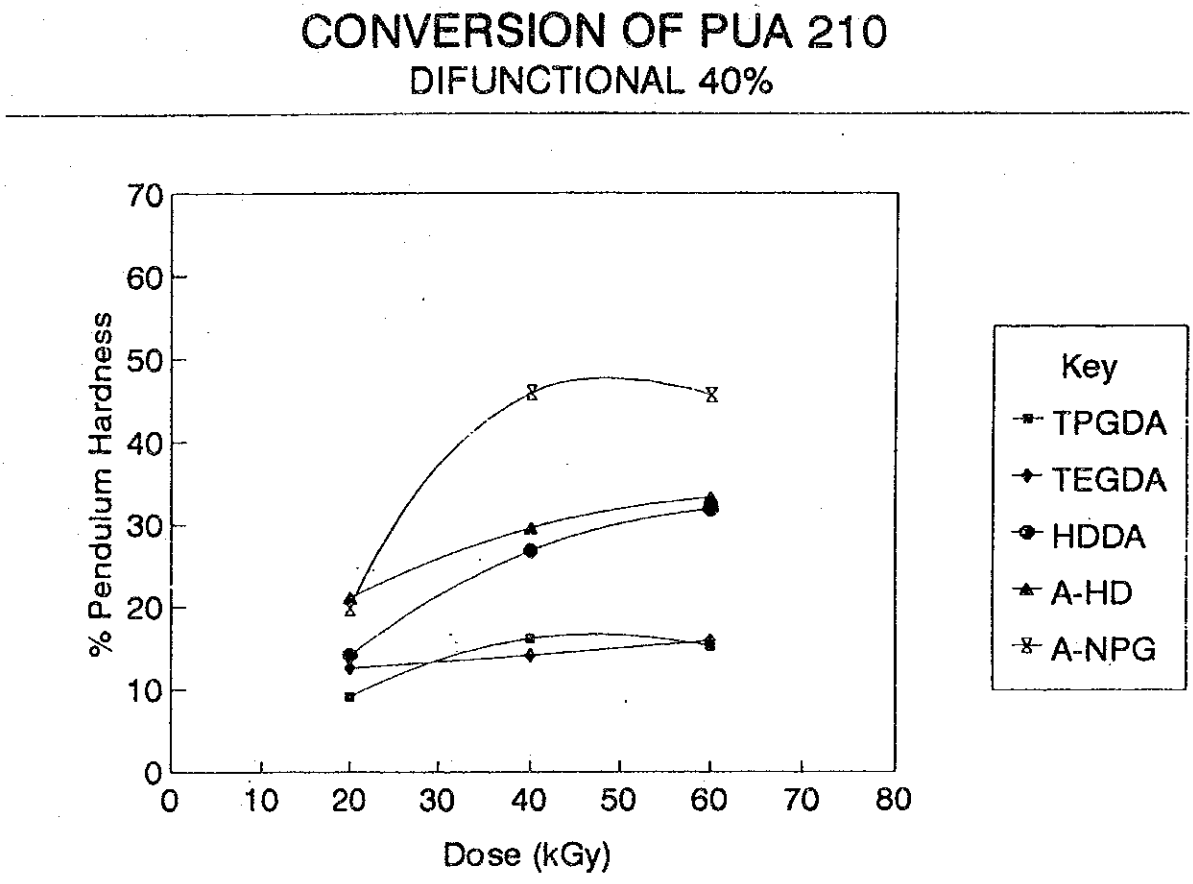


Fig 11 : The effect of using difunctional monomers on to the % pendulum hardness

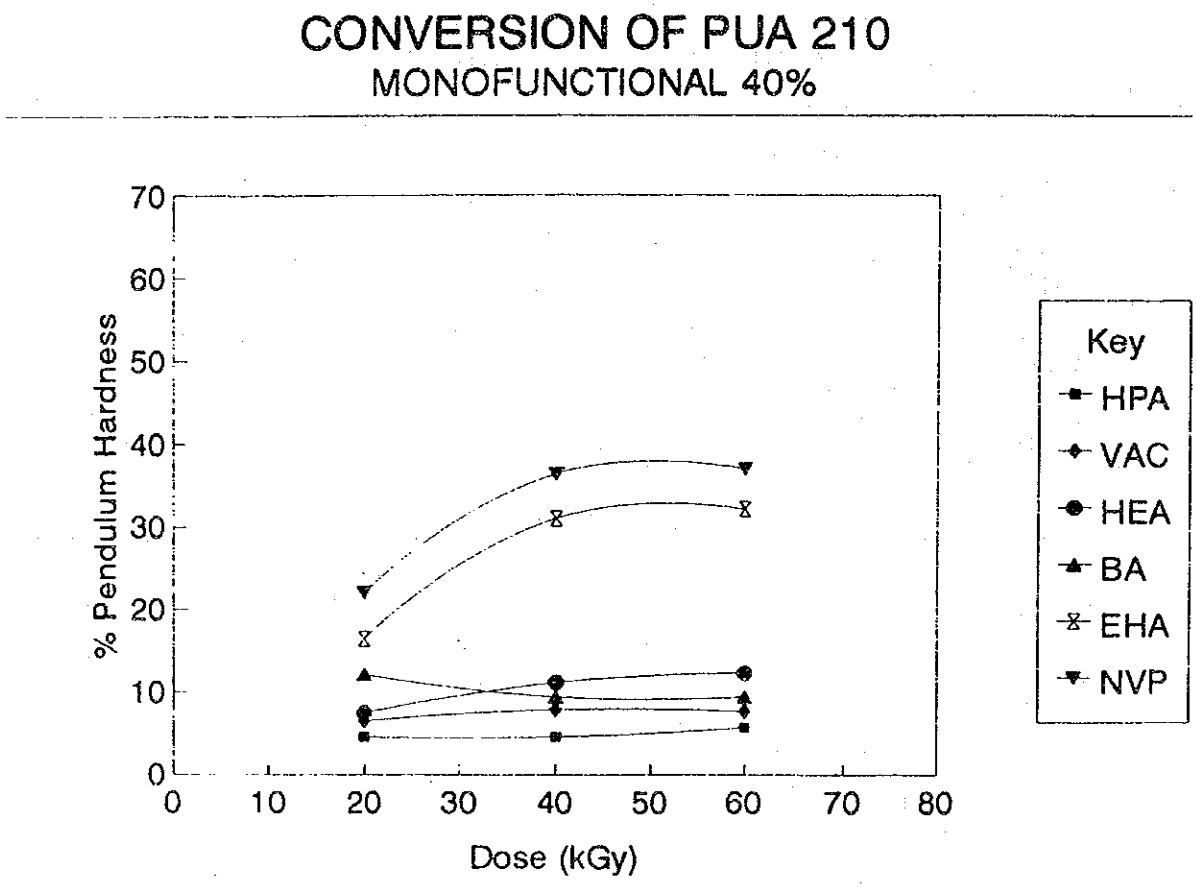


Fig 12: The effect of using monofunctional monomers with aromatic urethane acrylate on to % pendulum hardness.

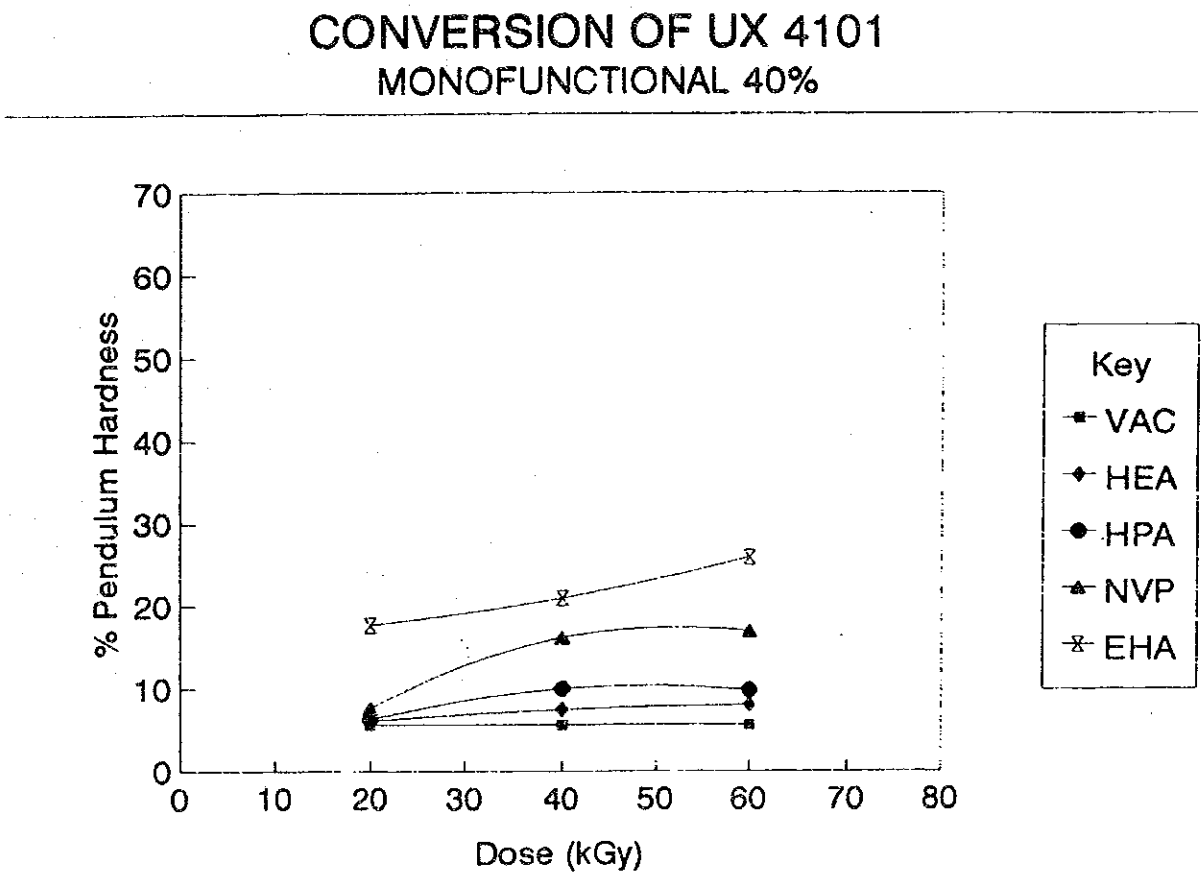


Fig 13 : The effect of using monofunctional monomers with aromatic urethane acrylate on to the % pendulum hardness.

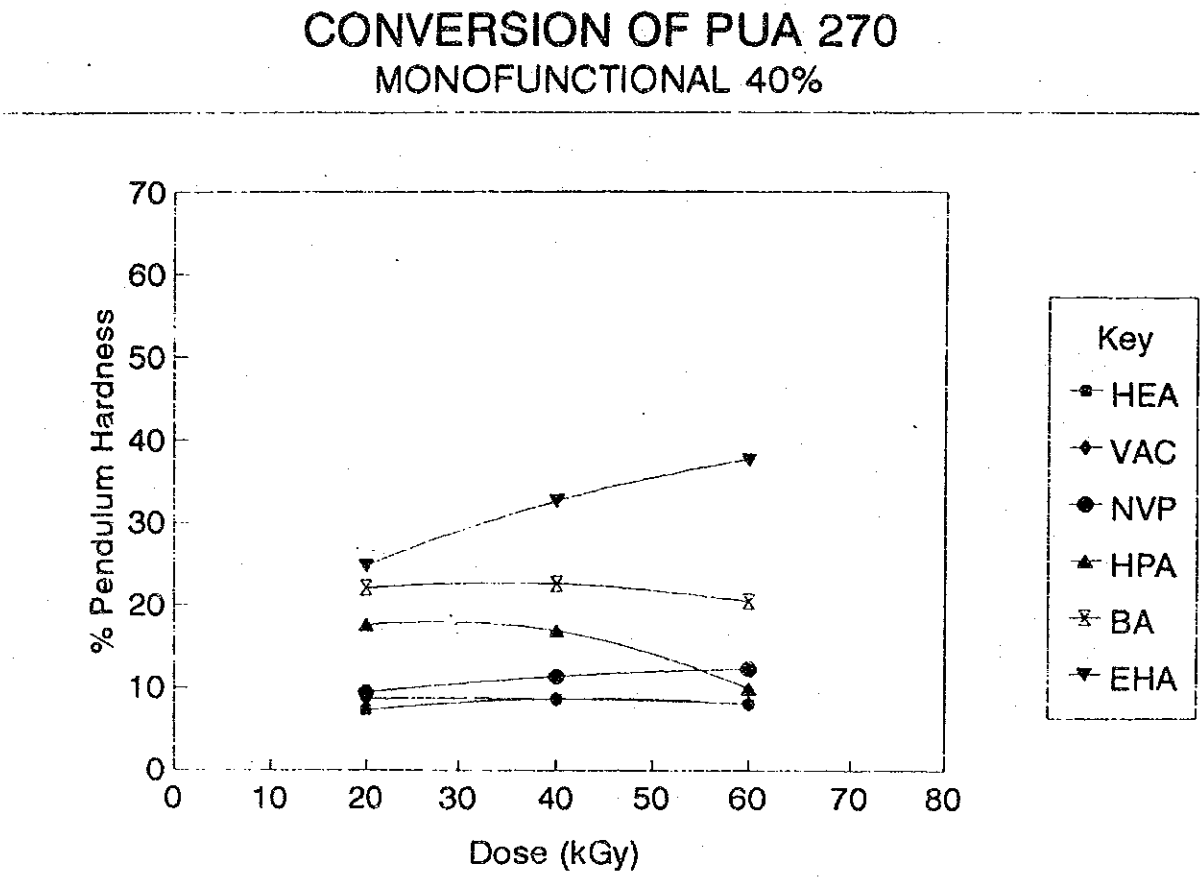


Fig 14: The effect of using monofunctional monomers with aliphatic urethane acrylate on to % pendulum hardness.

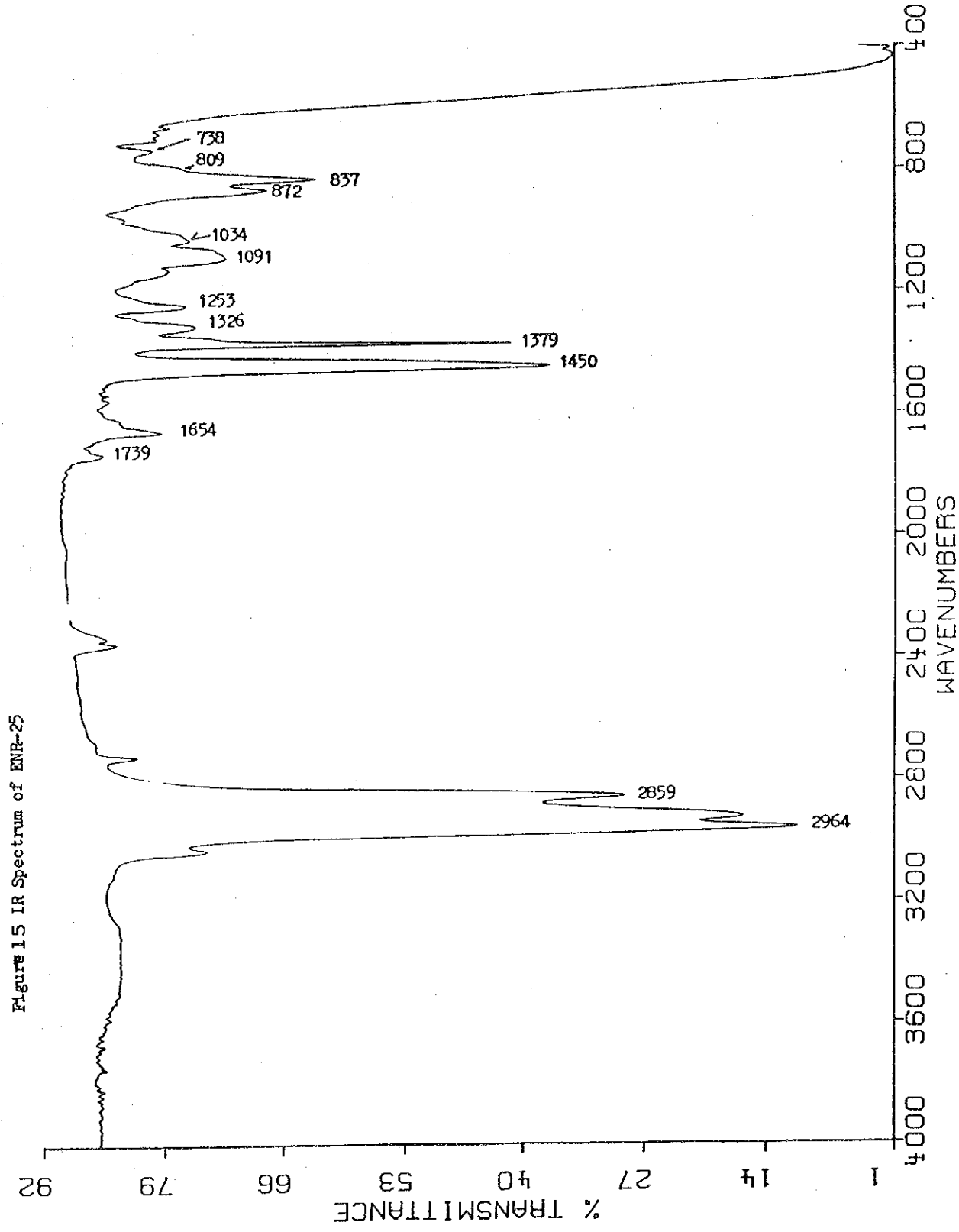


Figure 15 IR Spectrum of ENR-25

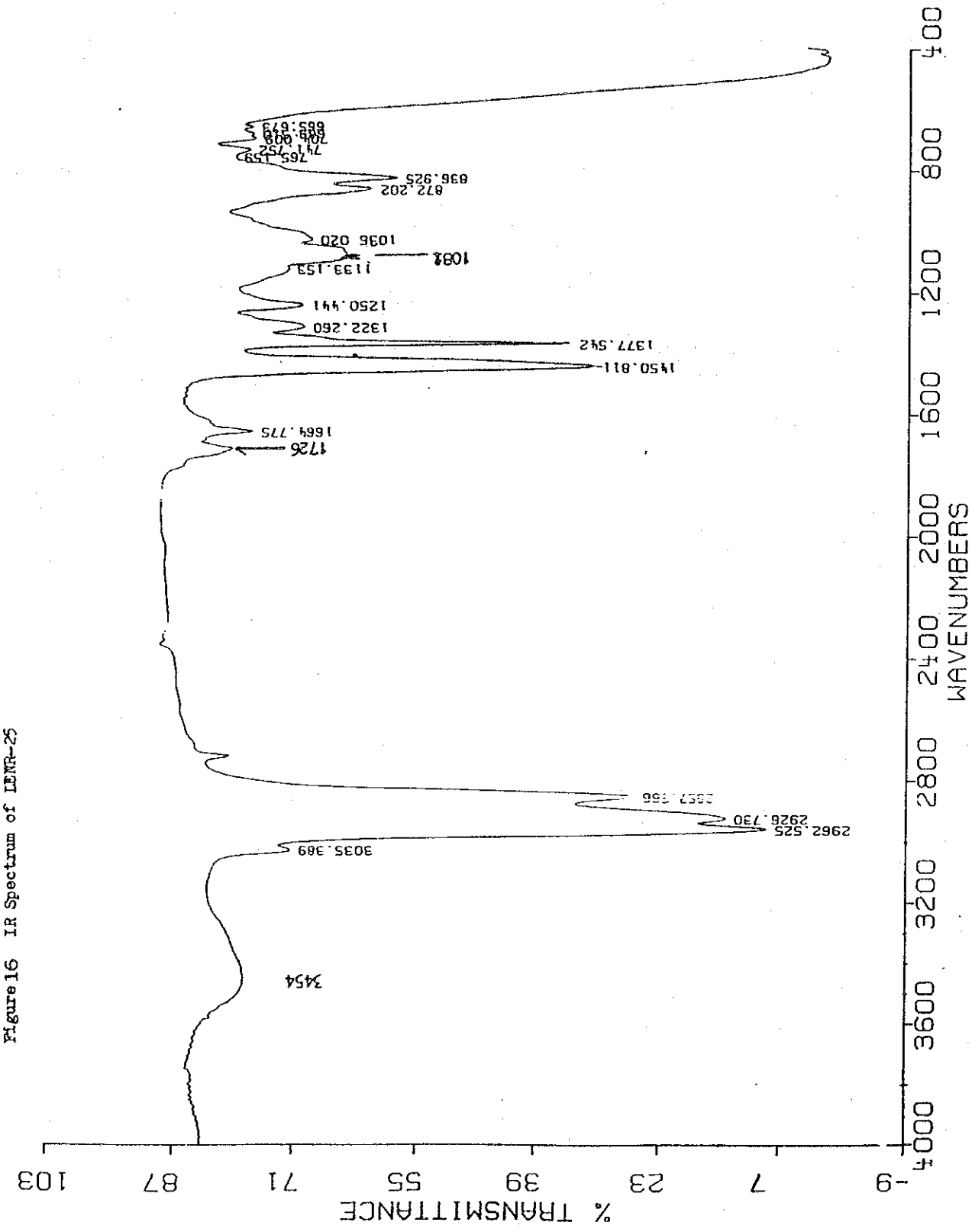


Figure 16 IR Spectrum of LENR-25

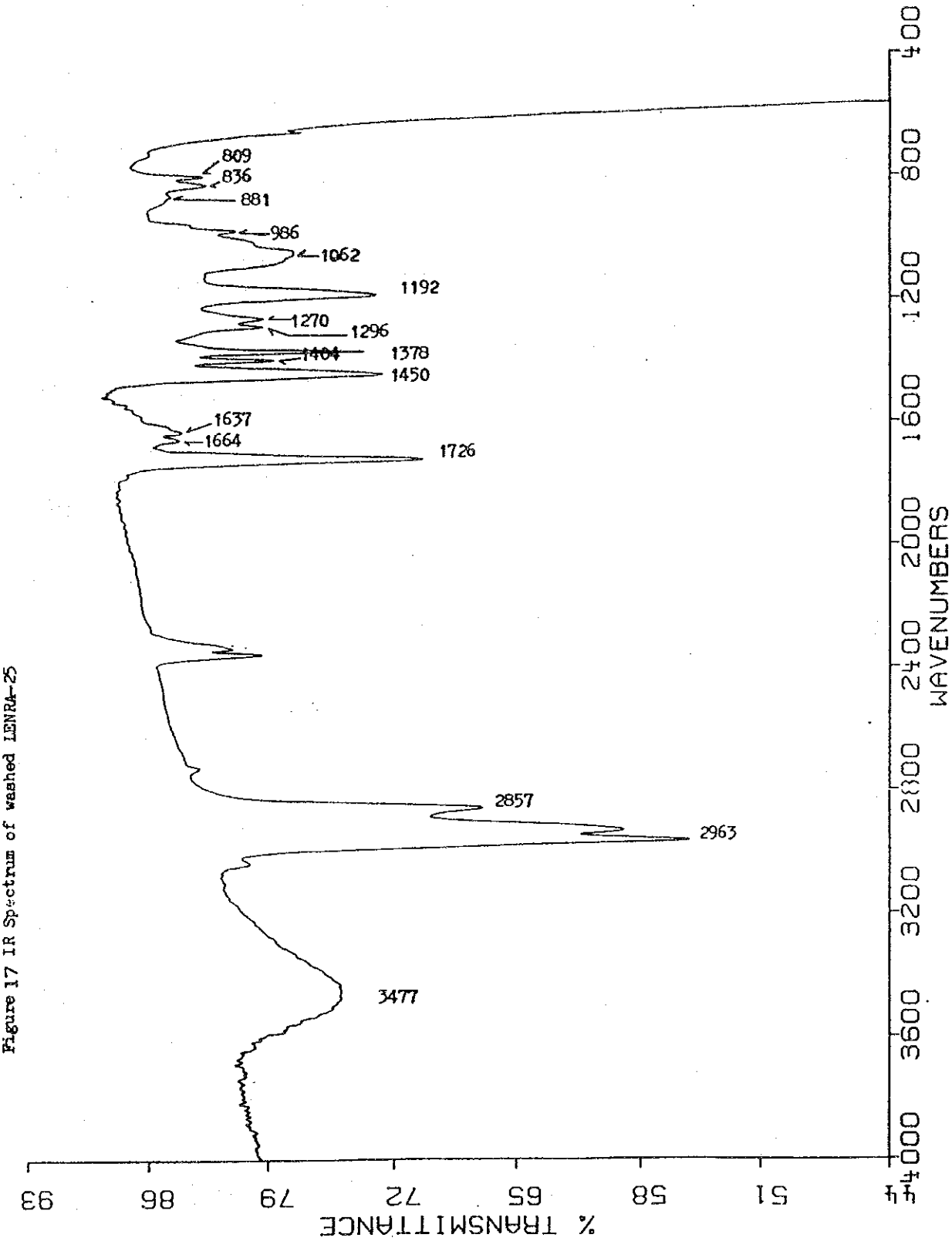


Figure 17 IR Spectrum of washed LDNRA-25

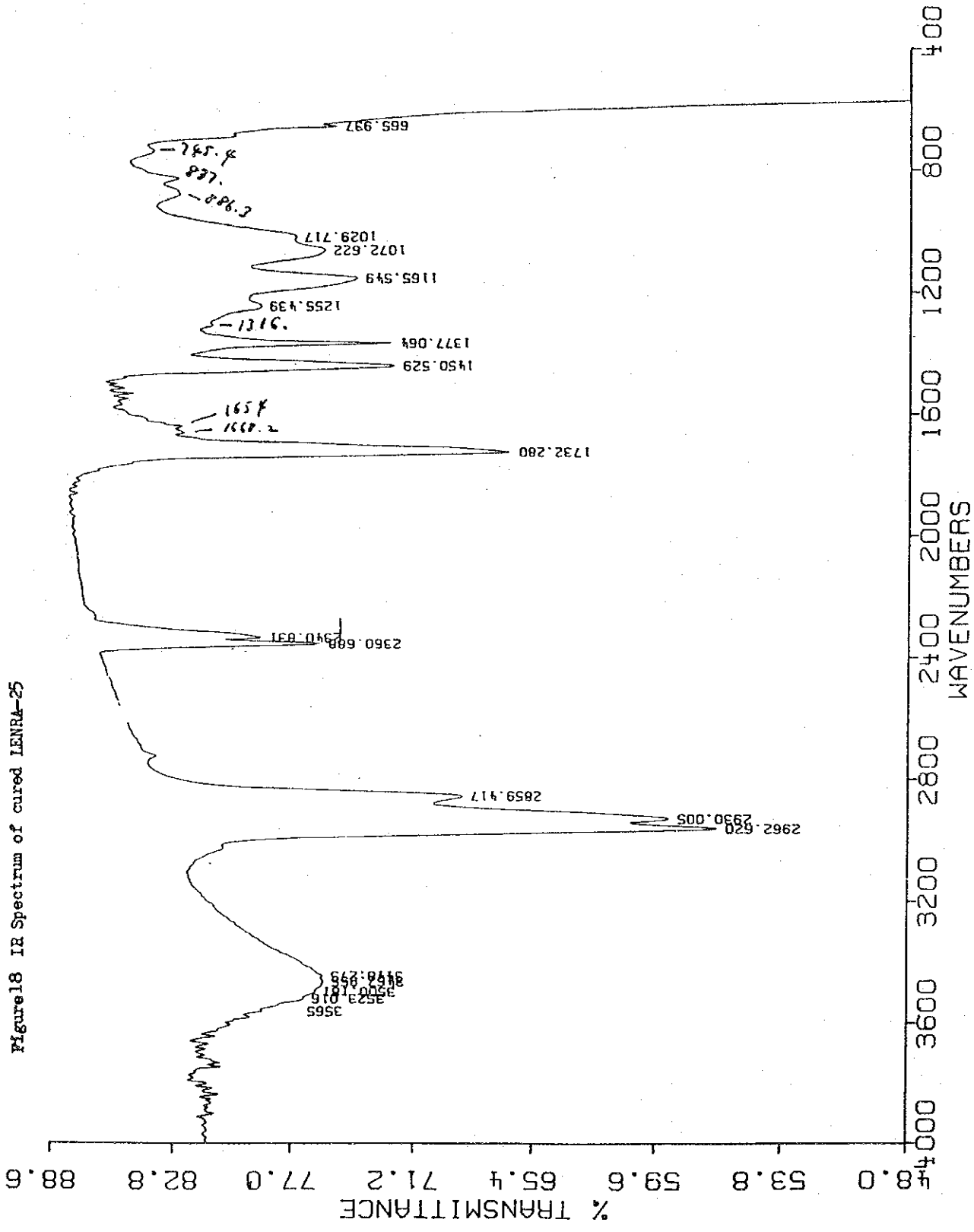


Figure18 IR Spectrum of cured LENRA-25

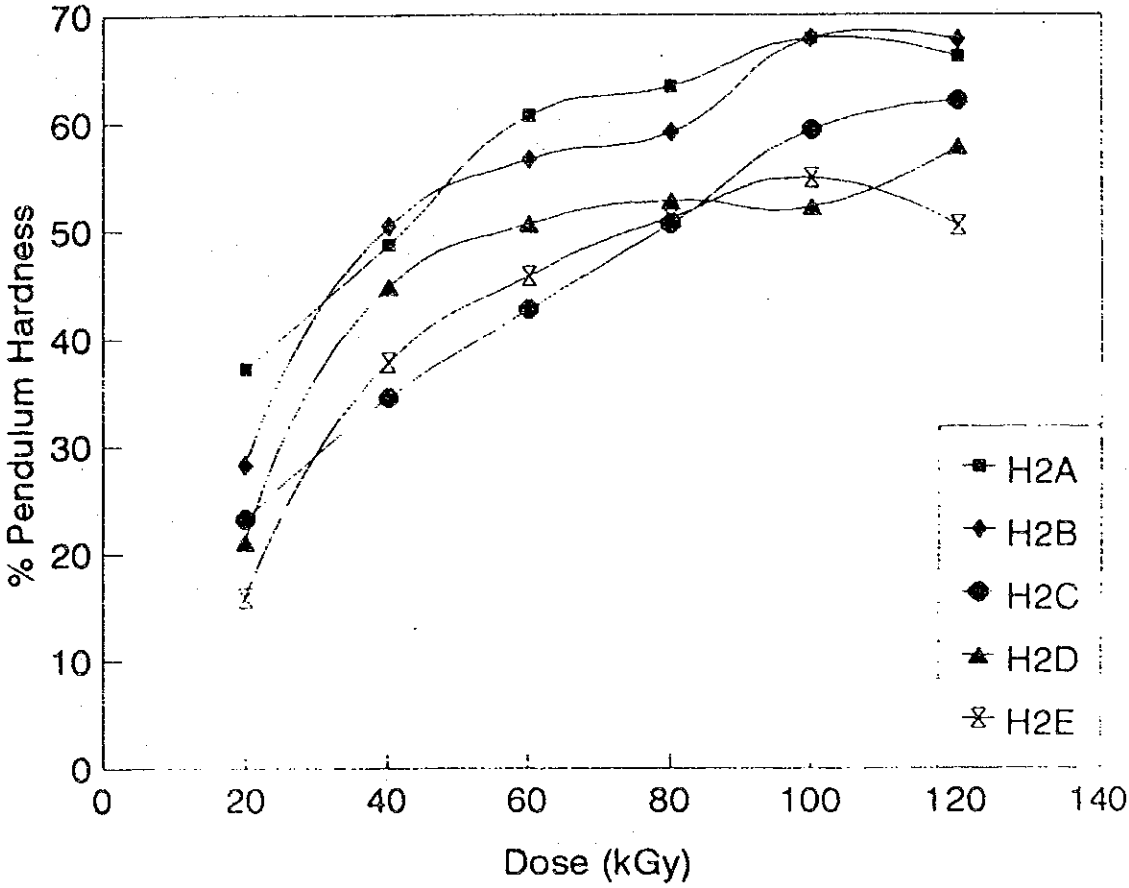


Fig.19 : The effects of monomers on Pendulum Hardness.

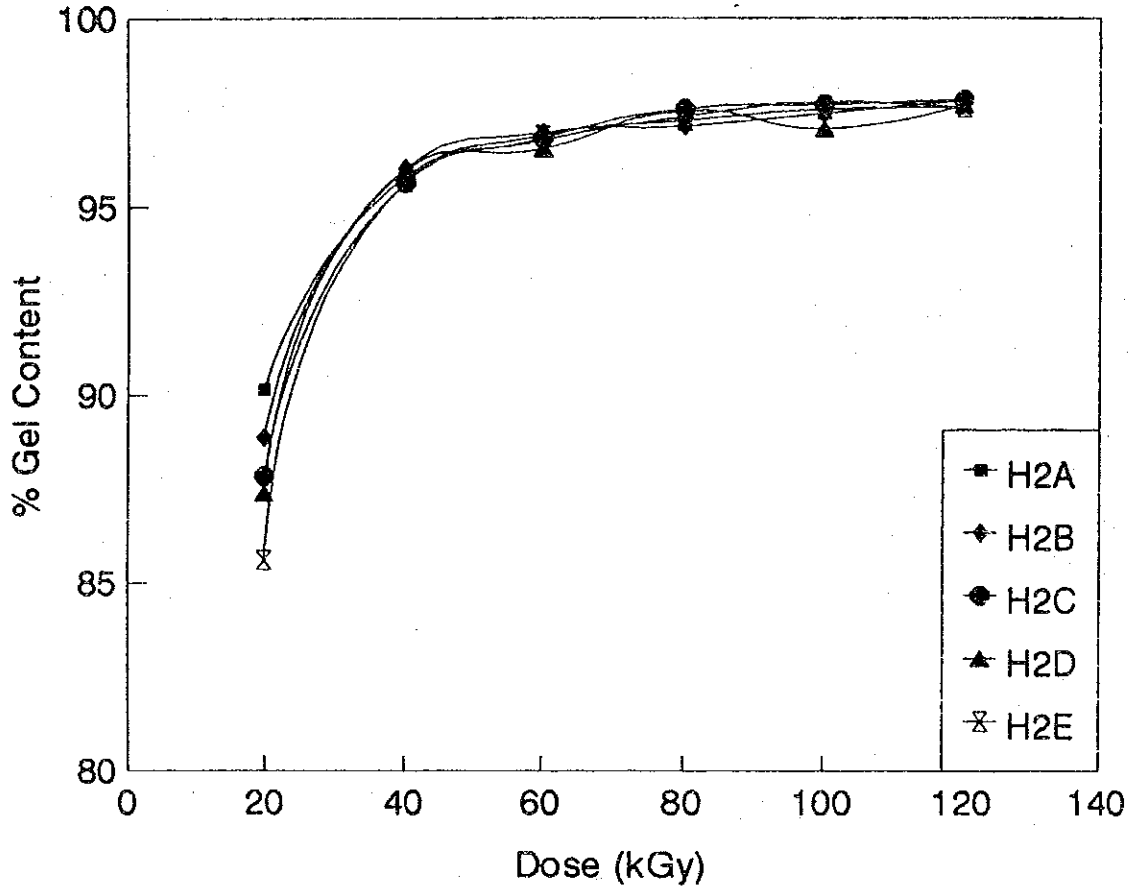


Fig. 20 : The effects of monomers on gel content.

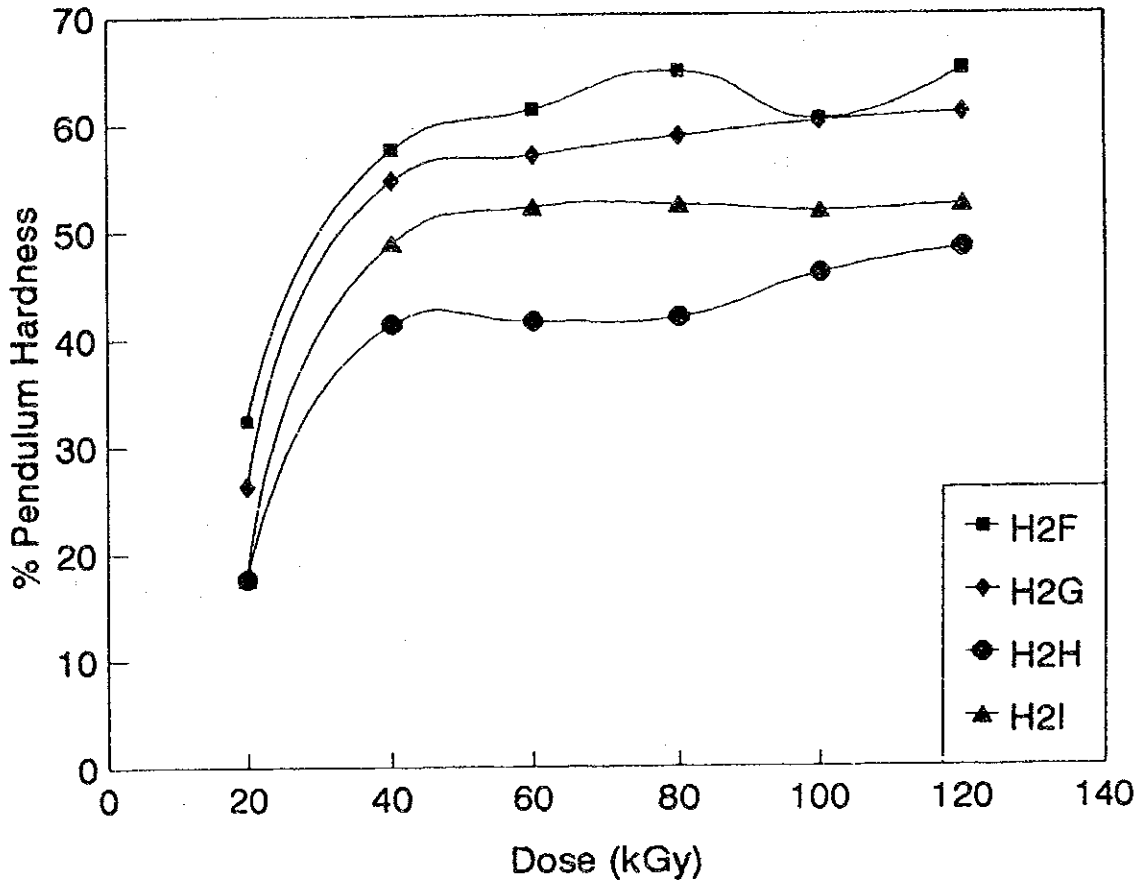


Fig. 21: The effects of HEA on Pendulum Hardness.

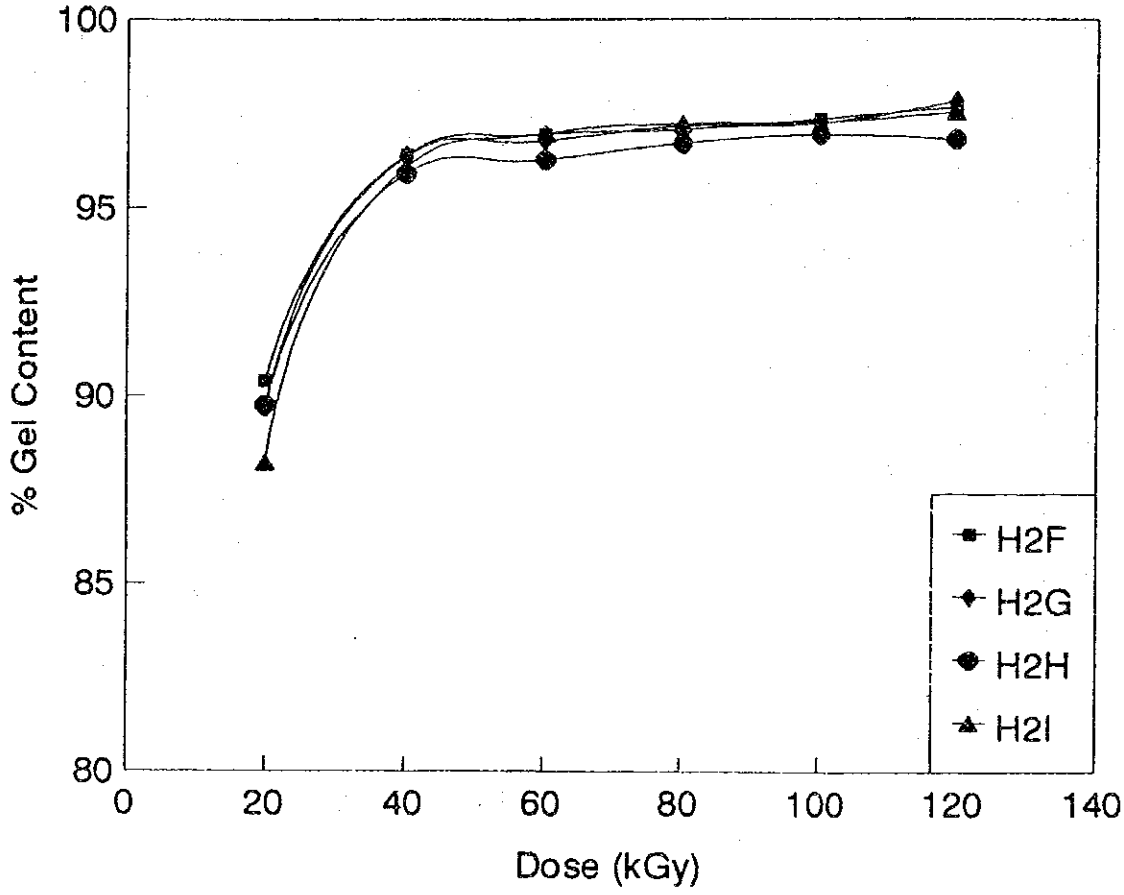


Fig.22 : The effects of HEA on gel content.

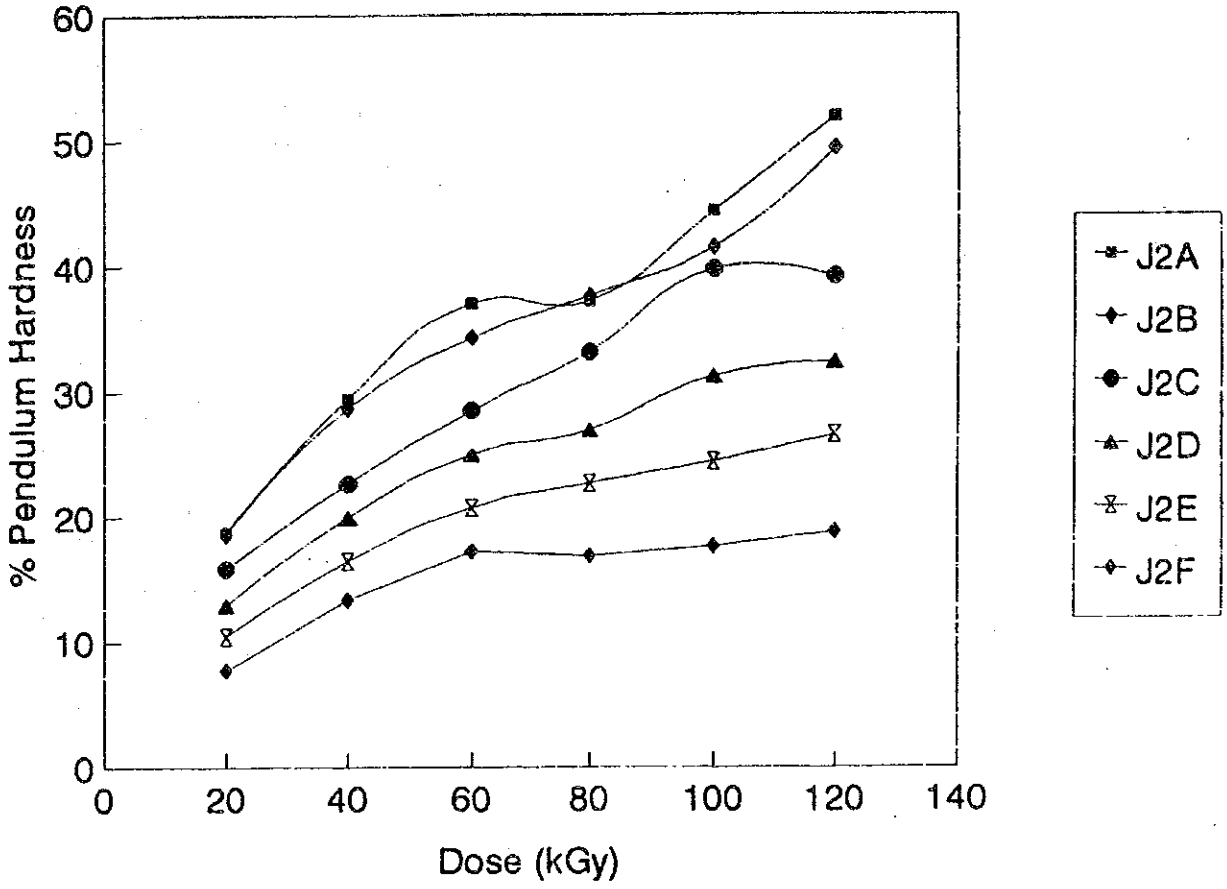


Fig.23 : The effects of EPOPA on Pendulum Hardness.

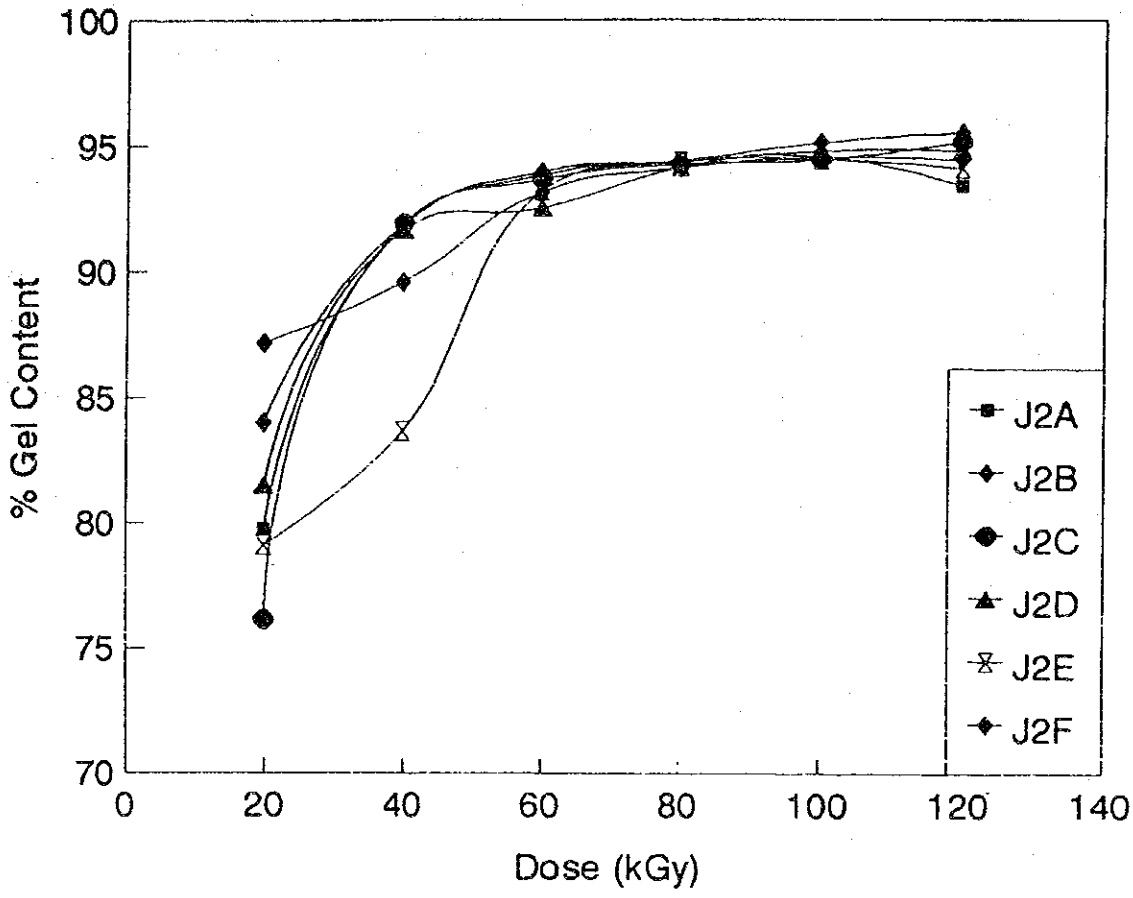


Fig. 24 : The effects of EPOPA on gel content.

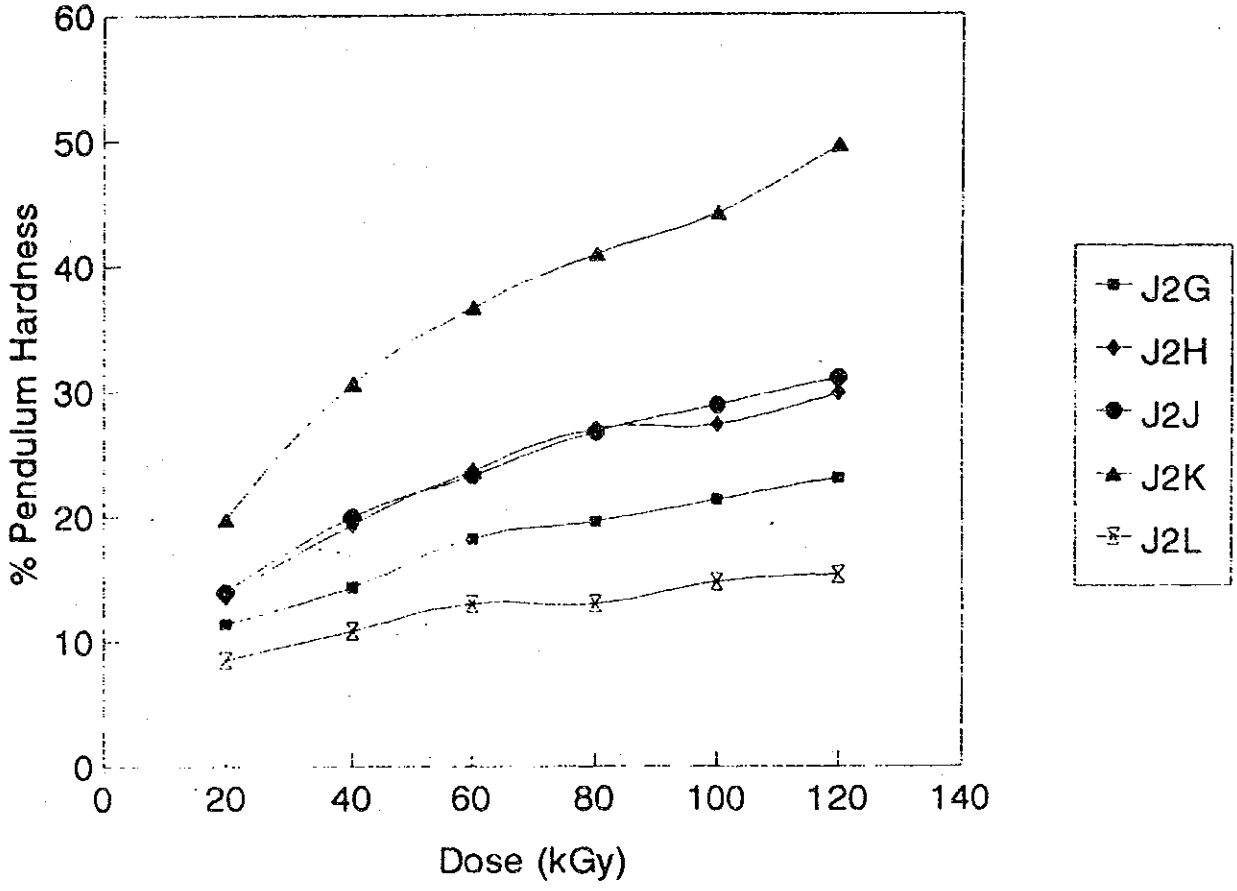


Fig.25 : The effects of HEA on formulations using mixture of LENRA & EPOPA.

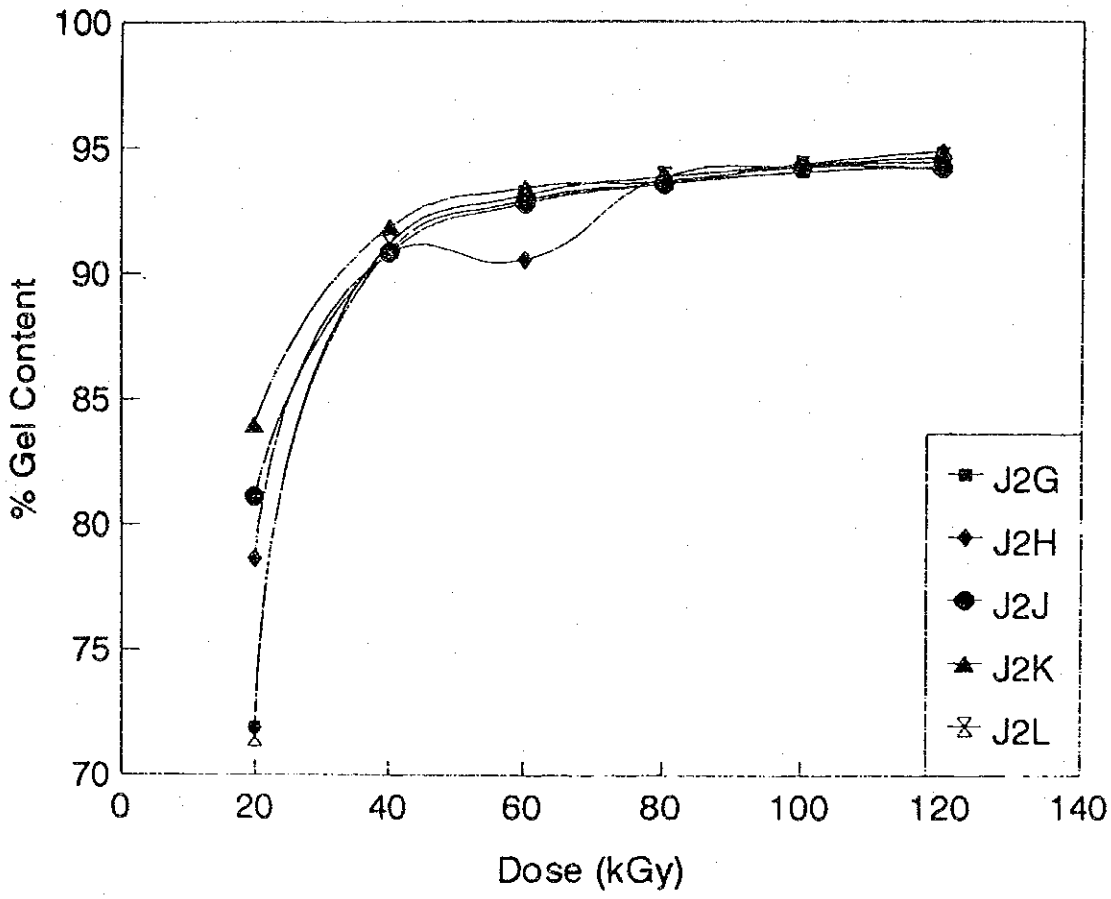


Fig.26 : The effects of HEA on formulations using mixture of LENRA & EPOPA.

Appendix 9

REVIEW OF THE OVERALL PROJECT IMPLEMENTATION IN FY 1992

Table 1. List of Experts in FY 1992

Name	Organiz.	Period	Purpose
Takashi Sasaki	JAERI	06.05.92 - 30.05.92	Resin Formulation Surface Coat. I
Yoshio Yamamoto	TOSOH	06.05.92 - 13.05.92	Commissioning GPC
Shinichi Kajiya	TOSOH	06.05.92 - 13.05.92	Commissioning GPC
Yasuhiro Kurauchi	TOSOH	06.05.92 - 13.05.92	Commissioning GPC
Humio Yoshii	JAERI	16.06.92 - 07.07.92	Radiat. Damages
Kazuyoshi Mikihara	NHV	07.07.92 - 25.07.92	EBM Maintenance
Takao Kanazawa	JAERI	21.07.92 - 01.08.92	Data Logger Syste
Yuhei Watanabe	JAERI	19.08.92 - 05.09.92	Biological Study
Kazuyoshi Mikihara	NHV	09.09.92 - 18.09.92	EBM Repair Work
Masayuki Kashiwagi	NHV	09.09.92 - 18.09.92	EBM Repair Work
Keizo Hayashi	NHV	05.10.92 - 23.10.92	EBM Repair Work
Hiroyuki Tachibana	JAERI	20.10.92 - 09.11.92	Rad. Technology
Hiromi Sunaga	JAERI	12.11.92 - 25.11.92	EBM Dosimetry
Not Fixed	-	Sept/Oct. 1992	Surface Coat.II
Not Fixed	-	January 1993	Prod. Charactn
Not Fixed	-	March 1993	Surface Coat.III
Not Fixed	-	February 1993	Sterilization, QC
Not Fixed	-	March 1993 POSTPONED TO FY 93	Comm.Chemiluminesc

Table 2: List of Trainee in FY 1992

Name	Period	Field
Mr. Mohd. Hilmi Mahmod	21.09.92 - 18.12.92	Rad.Curing
Mr. Shari Jahar	21.09.92 - 18.12.92	Acc.Maintenance
Ms. Mek Zah Salleh	15.03.93 - 12.09.93	Rad. Curing

Table 3: List of Donated Equipments in FY 1992

Equipment	Estimated Price (10^3 Yen)	Purpose
1.Chemiluminescence Analyzer	13.000	Sterilization
2.Adhesion Strength Tester	6.200	Curing/Sterili.
3.Calender Roll (2 rolls)	6.360	Sterilization
4.Mixing Roll (3 rolls)	1.310	Sterilization
5.Tackiness Tester	2.700	Curing
6.Dynamic Mechanical Tester	12.000	Steilization
7.UV-Vis. Spectrophotometer	3.500	Dosimetry
8.Data Processing System for CTA Dosimeter	3.600	Dosimetry
9.Acc.Accessories & Supplies	6.286	EBM Maintenance

Table 4: Progress of the Project in FY 92 (Research Activities)

	1992												1993			
	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3	4
Accelerator Operation (1) 3 MV EBM	Maintenance											Maintenance				
(2) Curetron	Handing Over						Maintenance			Repair						
(3) Dosimetry	O_2 Valve									Ion Gauge						
Curing of Surface Coating																
(1) Study of Substrates and Coating Materials																
(2) Coating and Lamination Technology (including Pretreatment)																
(3) Coating Formulation Study																
(4) Gas Inerting																
(5) Product Characterization (Hardness, Glossy, Weathering Test, etc.,)																
(6) Product Evaluation (Quality Control)	NOT STARTED															
Medical Products Sterilization (1) Study of Product Items	FINISHED															
(3) Dose Requirement Study (Biological Study) (Dose Rate Effect)																
(4) Radiation Damage of Products																
(5) Radiation Technology (Packaging, Dose Uniformity, Conveyor System)																
(6) Test Production (Quality Control)																

Table 5: Progress of the Project in 1992 (Mission & Trainee)

	1991		1992												1993			
	11	12	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3	4
Mission Joint Committee			2nd Meeting — 13/01-15/01												3rd Meeting — 13/01 - 15/01			
Opening Ceremony				— 20/02														
Trainee (1) EBM - High Energy Operation and Maintenance														21/09 - 18/12			3 Months	
(2) Curing of Surface Coating Coating Formulation														21/09 - 18/12				
(3) Curing of Suface Coating Product Characterization																	6 Months	13/03 - 12/09
Trainee of FY 91 (1) EBM Operation and Maintenance	24/09 - 17/12																	
(2) EBM Management of Radiation Safety	22/10 - 17/12																	
(3) Surface Coating Substrates and Coating Materials									2/03 - 1/06									

Progress of the Project in 1992 (Experts) (Continued)

	1991		1992												1993			
	11	12	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3	4
Short Term Expert (Continued)																		
(9) Sterilization Test Production																═══		
(10) Sterilization Biological Study											═══	═══						
(11) EBM Noise Control						═══ Cancelled												
(12) Seminar Lecturers (4 Lecturers)											═══ Cancelled							

Table 6: Progress of the Project in 1992 (Experts)

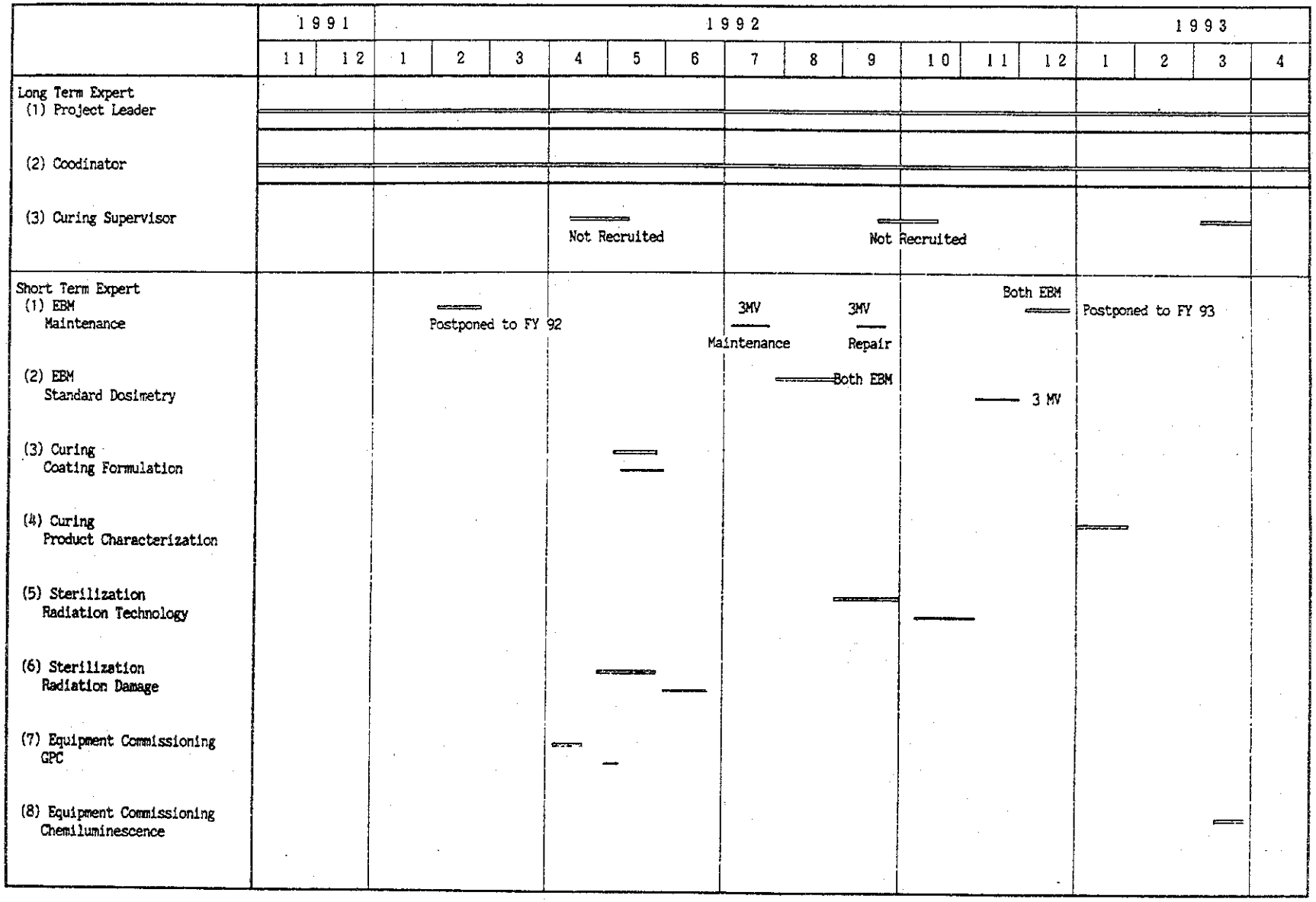


Table 7: Progress of the Project in FY 92 (Provision of Equipment and Woeks)

Provision of Equipment	1991		1992												1993			
	11	12	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3	4
Provision of Equipment and Works																		
(1) EB Machine			Maintenance			Operation							Maintenance		Operation			
			Handing-over			Operation			Maintenance			Repair		Noise Prtection			Operation	
(2) Curetron			Maintenance			Operation							Maintenance					
			Instal. O_2 Valves			Operation						Replace Ion Vacuum Gauge						
(3) Research Instruments (FY91) Disolution Tester, Melt Indexer, Data Logger, etc.	P/O (in August)		Delivery		Shipping	Delivery		Commissioning					Utilization					
(4) Research Instruments (FY92) Cemiluminescence Analyzer, Dynamic-Mechanical Tester, Mixing Roll, etc.,								P/O						Shipping	Delivery			
									P/O									Shipping

Proposed Workplan FY 1993

1. The mission and seminar

(1) National Seminar on EB Curing: August or September 1993, 1 week

(2) Survey Mission (Evaluation) : January, 1994

2. Despatch of the short-term experts

(1) Accelerator (Preventive maintenance) : 3 weeks (December, 93)

(2) 〃 (Standardization of Dosimetry) :4 weeks (July, 93)

(3) Surface coating (Resin Formulation Study) : 4 Weeks, (May, 93)

(4) 〃 (Characterization of Products): 4 weeks (January, 94)

(5) 〃 (General, not specified) : 4 weeks (October,93)

(6) Sterilization (Radiation Technology) : 4 weeks (Early October, 93)

(7) 〃 (Radiation Damage of Materials) : 4 weeks (Early May, 93)

(8) 〃 (Test Production) : 4 weeks (January, 94)

(9) 〃 (Biological Study) : 4 weeks (August, 93)

(10)Instruction of Equipment : 1 week (June, 93)
(Chemiluminescence)

(11) 〃 (Dynamic-Mech. Analyzer) : 1 week (December, 93)

(12)Seminar Lecturers (3 lecturers) : 1 week (August), 93)

3. Long-term expert

(1) Team Leader: Kenzo Yoshida

(2) Coodinator : Kiyoshi Honma (-24/05/93) and Successor

4. Trainee

(1) Accelerator (Operation & Maintenance): 3 months (July, 93 -)

(2) Curing (Product Characterization): 6 months (July, 93 -)

(3) Sterilization (Radiation Damage) : 3 months (Late October, 93 -)

5. Equipments to be donated

(1) 3 MV EBM Spare parts	4,000 ($\times 10^3$ yen)
(2) ITV Camera forIrrad. room	350
(3) X-ray Area Monitor Probe	1,150
(4) Curetron Spare parts	1,500
(5) Weather tester Spare parts	1,000
(6) GPC and HPLC Spare parts	2,000
Total	10,000,000 Yen

6. Keiko-Kizai

Total budget: 5.0 MYen

7. Local cost

(1) Seminar: 1.2 M-Yen

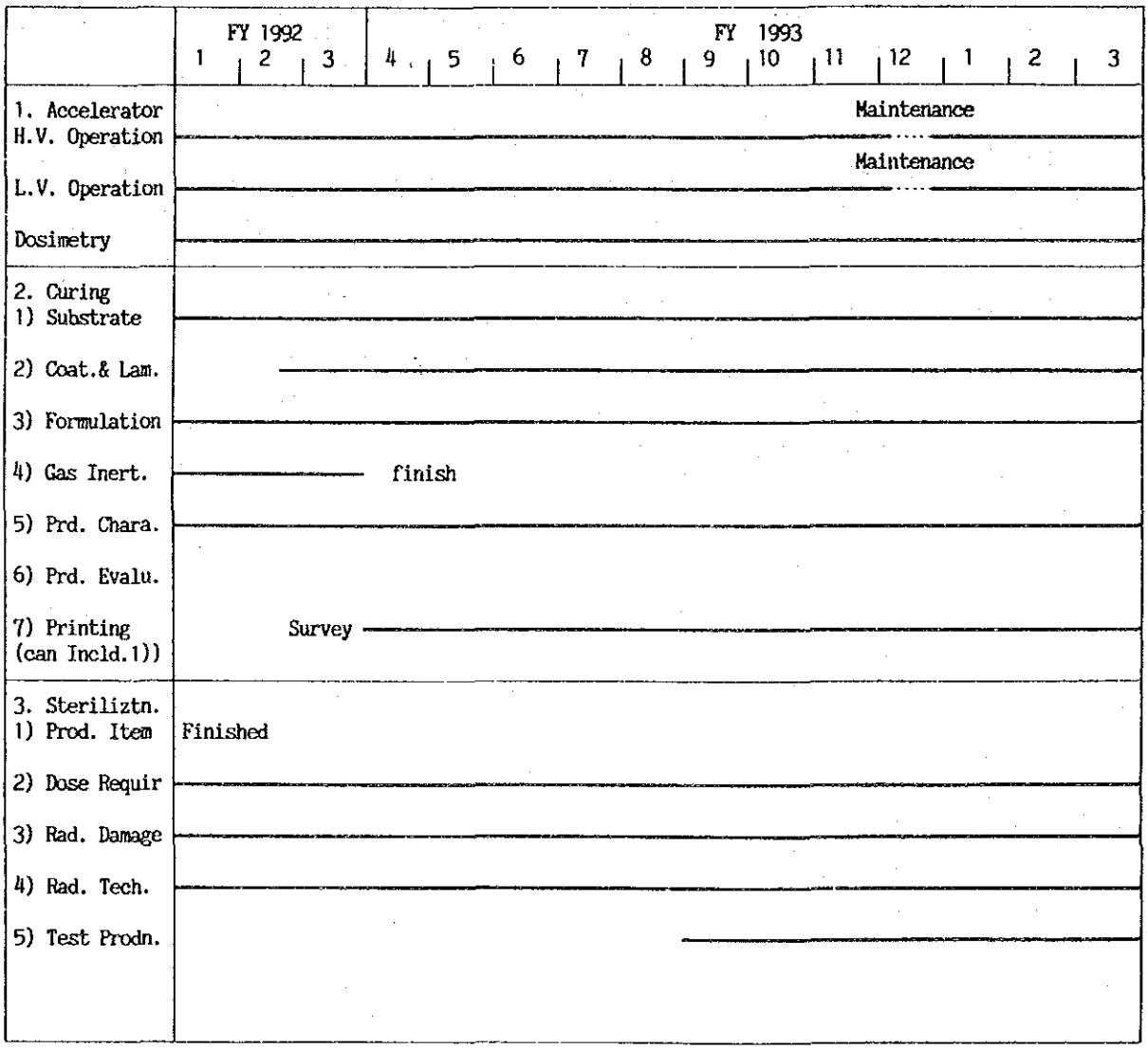
(2) Payment for Official car driver: 0.9 M-Yen

ANNUAL RESEARCH WORK PLAN - FY 1993

Ⅰ. Research Subjects

1. Accelerator Operation	2. Curing of Surface Coating	3. Sterilization of Medical Product
1) Operation 2) Maintenance 3) Dosimetry	1) Substrate, Material 2) Coating, Lamination 3) Coating Formulation 4) Gas Inerting 5) Product Characterization 6) Product Evaluation	1) Product Item Study 2) Dose Requirement(Biological)Study 3) Radiation Damage of Product 4) Radiation Technology 5) Test Production

Ⅱ. Schedule



Implementation Schedule in FY 93

		FY 1993: 4	5	6	7	8	9	10	11	12	1	2	3
Mission	Joint Committee									— 1 week			
Seminor	National						— 1 week						
Expert	Long Term 1. Leader	———											2 years
	2. Coordinator	———		———									2 years
	Short Term 1. Acc. Maintenance									—			
	2. Standard Dosimet.				—								
	3. Coating Formulat.	—											
	4. Product Charact.										—		
	5. Curing, General							—					
	6 Radiation Techn.							—					
	7 Radiation Damage	—											
	8. Test Production										—		
	9. Biological Study					—							
	10 Chemilumi. Commsn			—									
	11 Dynamic-Mech Comm									—			
	12 Seminar Lecturers						—						
	13												
	14												
	15												
Trainee	1. EBM Operation				———								
	2. Curing				———								
	3. Sterilization								———				

Proposed Workplan FY 1993

1. The mission and seminar

(1) National Seminar on EB Curing: August or September 1993, 1 week

(2) Survey Mission (Evaluation) : December, 1993

2. Despatch of the short-term experts

(1) Accelerator (Preventive maintenance) : 3 weeks (January, 94)

(2) Accelerator (Curetron Maintenance) : 1 week (January, 94)

(3) Accelerator (Dose Standardization) : 3 weeks (Sept. or Oct., 93)

(4) Surface coating (Resin Formulation Study) : 2 weeks (June, 93)

(5) 〃 (Characterization of Products): 2 weeks (January, 94)

(6) 〃 (General, not specified) : 4 weeks (October, 93)

(7) 〃 (General, not specified) : 4 weeks (After Oct., 93)

(8) Sterilization (Radiation Technology) : 3 - 4 weeks (Early October, 93)

(9) 〃 (Radiation Damage of Materials) : 3 - 4 weeks (Mid. May, 93)

(10) 〃 (Test Production) : 3 - 4 weeks (February, 94)

(11) 〃 (Biological Study) : 3 - 4 weeks (After Oct., 93)

(12)Instruction of Equipment : 1 week (Early May, 93)
(Chemiluminescence)

(13) 〃 (Dynamic-Mech. Analyzer): 1 week (July to Sept., 93)

(14)Seminar Lecturers (3 lecturers) : 1 week (August or Sept., 93)

3. Long-term expert

(1) Team Leader: Kenzo Yoshida

(2) Coodinator : Kiyoshi Honma (-24/05/93) and Successor

4. Trainee

(1) Accelerator (Operation & Maintenance): 3 months (Sept., 93 -)

(2) Curing (Product Characterization): 6 months (July, 93 -)

(3) Sterilization (Radiation Damage) : 3 months (Sept., 93 -)

5. Equipments to be donated

(1) 3 MV EBM Spare parts	4,000 ($x10^3$ yen)
(2) ITV Camera forIrrad. room	350
(3) X-ray Area Monitor Probe	1,150
(4) Curetron Spare parts	1,500
(5) Weather tester Spare parts	1,000
(6) GPC and HPLC Spare parts	2,000
Total	10,000,000 Yen

6. Keiko-Kizai

Total budget: 5.0 MYen

7. Local cost

(1) Seminar: 1.2 M-Yen

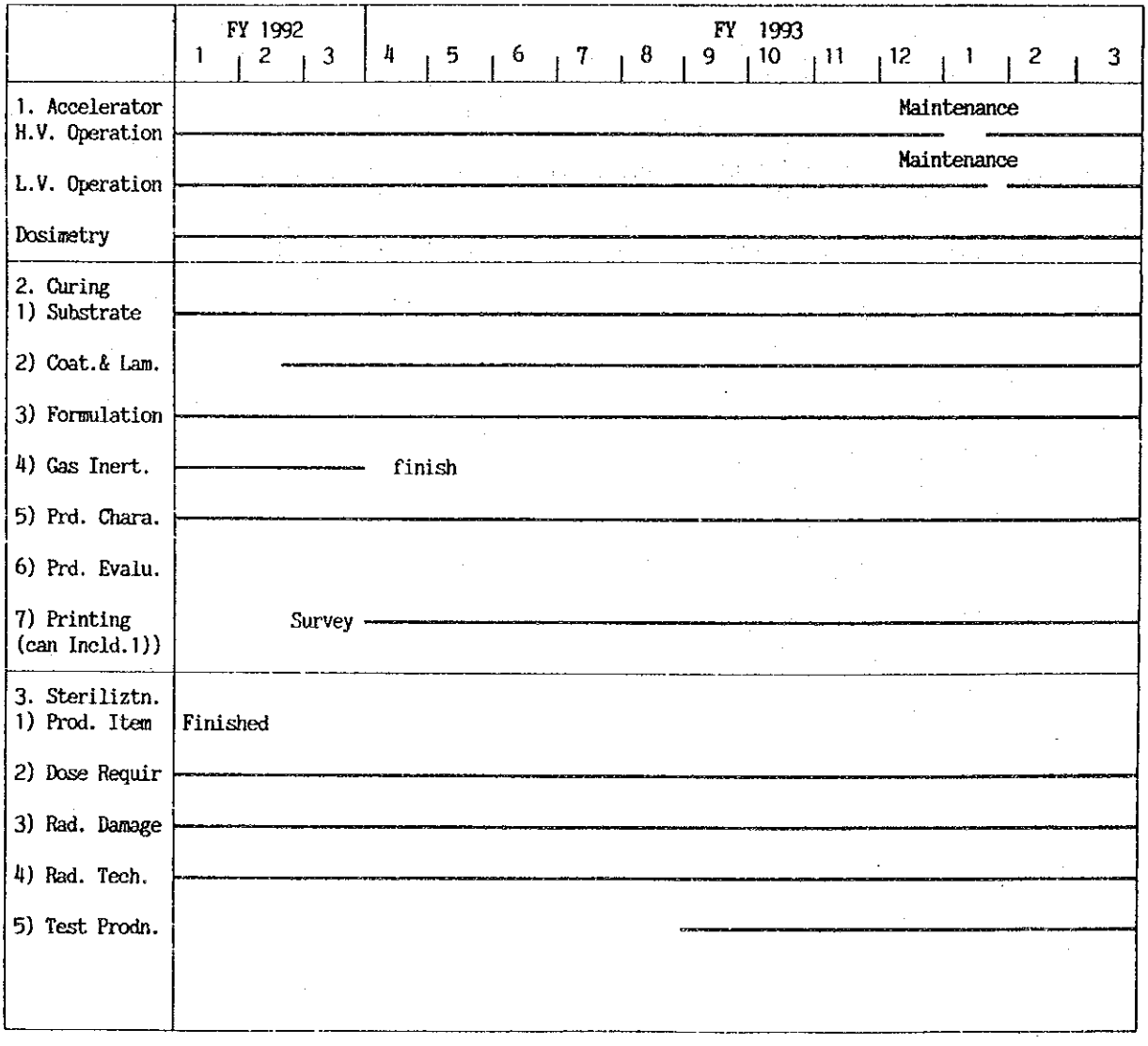
(2) Payment for Official car driver: 0.9 M-Yen

ANNUAL RESEARCH WORK PLAN - FY 1993

Ⅰ. Research Subjects

1. Accelerator Operation	2. Curing of Surface Coating	3. Sterilization of Medical Product
1) Operation 2) Maintenance 3) Dosimetry	1) Substrate, Material 2) Coating, Lamination 3) Coating Formulation 4) Gas Inerting 5) Product Characterization 6) Product Evaluation	1) Product Item Study 2) Dose Requiement(Biological)Study 3) Radiation Damage of Product 4) Radiation Technology 5) Test Production

Ⅱ. Schedule



Implementation Schedule in FY 93

		FY 1993 4 5 6 7 8 9 10 11 12 1 2 3
Mission	Joint Committee	— 1 week
Seminor	National	— 1 week
Expert	Long Term 1. Leader 2. Coordinator	2 years 1.5 years
	Short Term 1. Acc. Maintenance 2. Curetron Mainte.. 3. Dose Standardiza. 4. Formulation 5. Characterization 6 Curing , General 7 Curing, General 8. Rad. Technology 9. Rad. Damage 10 Test Prodction 11 Biological Study 12 Chemiluminescence 13 Dynamic Mech Anal 14 Seminar Lecturer 15	
Trainee	1. EBM Operation 2. Curing 3. Sterilization	

Project targets to be implemented

1. Accelerator and Dosimetry

(1) Accelerator
Preventive maintenance: every 1 - 2 year, CW-circuit, Window, ion pump
Supply of spare parts: rectifier, resistor, capacitor

(2) Dosimetry
Standard dosimetry (calorimetry for 3 MV),
Routine Dosimetry: CTA and RCD

2. Sterilization of Medical Products

(1) Biological Study
Identification and distribution of microorganisms contaminating medical products.
Confirmation of EB sterilization effect in the semi-commercial scale processing using surgical gloves.

(2) Radiation Damage of the Products
Materials degradation, dose-rate effect and product tests (comparison of EB and gamma processing)
Evaluation of material damage in the semi-commercial scale processing using surgical gloves.

(3) Radiation Technology
Dose distribution and Uniformity measurement of all samples in the irradiation box.
Determination of irradiation conditions and selection of irradiation box in the semi-commercial scale processing.