RADIATION-INDUCED SIMULTANEOUS GRAFTING OF 2-HYDROXYETHYL-METHACRYLATE (HEMA) ONTO NATURAL RUBBER (NR) TUBES

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ABSTRACT

RADIATION-INDUCED SIMULTANEOUS GRAFTING OF 2-HYDROXYETHYL-METHACRYLATE (HEMA) ONTO NATURAL RUBBER (NR) TUBES. An attempt has been made to obtain a graft copolymer of natural rubber (NR) with 2-hydroxyethyl-methacrylate (HEMA). The graft copolymer (NR-g-PHEMA) was synthesized with radiation-induced simultaneous grafting of HEMA monomer onto NR tubes.Following the selection of appropriate solvent for the grafting,effects of monomer concentration, temperature, irradiation dose, and dose rate were studied. It was found that the grafting proceeds effectively in the present of carbon tetrachloride (CCl_4) as a solvent. At a given monomer concentration of 20 Vol%, the degree of grafting increases with the increasing of temperature, irradiation dose and dose rate. The rate of grafting was found to be proportional to 0.68 power of dose rate. An apparent activation energy was calculated to be 4.50 kcal/mol and the grafting efficiency of 4.90 % was achieved. The result of blood compatibility test on the graft copolymer showed that it was slightly improved.

ABSTRAK

RADIASI GRAFTING SIMULTAN 2-HIDROKSIETILMETAKRILAT (HEMA) PADA KARET ALAM (NR). Telah dicoba untuk mendapatkan graft kopolimer karet alam (NR) dengan 2-hidroksietilmetakrilat (HEMA) melalui cara radiasi grafting simultan. Setelah dilakukan pemilihan pelarut, maka ditentukan pengaruh konsentrasi monomer, suhu, dosis dan laju dosis iradiasi terhadap kemampuan serta efisiensi grafting.

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Karbon tetraklorida (CCl_4) digunakan sebagai pelarut dan konsentrasi monomer HEMA sebesar 20 vol% dapat memberikan kadar grafting optimum. Kadar grafting meningkat dengan kenaikan suhu, dosis dan laju dosis iradiasi, serta efisiensi grafting mencapai 4.90 %. Laju grafting didapatkan berbanding langsung dengan pangkat 0.68 laju dosis ($R_p = C.I^{0.68}$) dengan energi pengaktifan (Ea) dihitung sebesar 4.50 kcal/mol. Uji kompatibilitas dengan darah menunjukkan bahwa kompatibilitas hasil grafting dengan darah sedikit meningkat.

INTRODUCTION

Radiation induced grafting of hydrophilic monomer onto polymeric and elastomeric materials has been studied in detail by many investigators (1-3). The grafting is usually aimed to modify the surface properties of certain materials. For example, in the case of preparation of ion-exchange membranes and biomaterials (4-6).

It has been reported previously (7-8) that blood compatibility of natural rubber (NR) tubes could be enhanced significantly by grafting of hydrophylic monomers of N,N dimethylacrylamide (DMAA) and N,N dimethylamino ethylacrylate (DMAEA). The efficiency of grafting of those monomers onto NR tubes, however is almost less than 1 % (8). Attempt has been continued to obtain hydrophilic monomers with higher grafting efficiency.

In the present work, a hydrophilic monomer, i.e. 2-

hydroxyethyl-methacrylate (HEMA) is used to be grafted onto natural rubber (NR) tubes. The monomer is selected to be studied because polyhydroxyethylmethacrylate (PHEMA) is well known as a biocompatible material (9 -10). Therefore, grafting of HEMA onto NR tube is expected to improve the blood compatibility of NR tube.

This article reports the kinetics of grafting of HEMA onto NR tubes using radiation-induced simultaneous grafting technique. Blood compatibility of the obtained grafted NR tubes is also mentioned.

MATERIALS AND METHODS

Materials. Commercially available natural rubber (NR) tube (Komine Rubber Mfg.Co.Ltd.) of 1 mm thick (inner diameter 3.5 mm and outer diameter 5.5 mm) was cut into pieces of 35 mm length. The NR tubes were thoroughly washed with tap water and subsequently washed with acetone and distilled water in an ultrasonic cleaner for 15 min. The NR tubes were then dried in vacuo at room temperature and weighed. 2-Hydroxyethylmethacrylate (HEMA) monomer was purchased from Yoneyama Chem.Ind.Ltd and used as supplied. The other chemicals of reagent grade were used without further purification.

Grafting Procedure. Simultaneous radiation grafting technique was used as a grafting procedure. In this grafting technique, the NR tube sample was placed in a special glass ampoule and then a given monomer-solvent composition was added. The glass ampoule was then connected to a vacuum line system, degassed with freezing and thawing technique. It was then irradiated at a given dose and dose rate of gamma-rays from a ^{60}Co source at room temperature. The dosimetry was performed using ferrosulphate (Fricke) dosimeter. After irradiation, the NR tube was taken out, washed thoroughly with tap water and soaked overnight in distilled water. The NR tube was then boiled in distilled water for 5 h to extract and to remove residual monomer and homopolymer in the NR tube. The NR tube was then dried in vacuo at room temperature for 24 h and weighed. The remaining monomer solution in the glass ampoule was transferred to a beaker glass and then the homopolymer was precipitated by pouring an excess diethylether to the beaker. The homopolymer obtained was dried in vacuo at room temperature until a constant weight was achieved (48 h in most cases).

The degree of grafting was determined by the percentage of increase in weight :

$$\text{Degree of grafting (wt\%)} = \frac{(W_g - W_0)}{W_0} \times 100$$

where W_0 and W_g represent the weights of initial and grafted NR tube, respectively.

The efficiency of grafting was calculated by the following equation :

$$\text{Grafting efficiency (wt\%)} = \frac{(W_g - W_0)}{(W_g - W_0) + P} \times 100$$

where P represents the weight of homopolymer.

Infra-red Measurement. Infra-red spectra of the grafted NR tube was taken using attenuated total reflection (ATR-IR) technique. The ATR-IR spectra was taken at an incident angle of 45^o using a JASCO-IRA 2 spectrophotometer.

Water Up-Take Measurement. The grafted NR tube was split into two parts and weighed. One part of the NR tube was immersed in distilled water at 25 ^oC until equilibrium was reached (24 h in most cases), and then, the excess water deposited on the surface was quickly taken up with blotting paper and weighed. The water up-take percent was calculated as follows :

$$\text{Water up-take (wt\%)} = \frac{(W_s - W_i)}{W_i} \times 100$$

where W_s and W_i represent the swelling and initial weights of the half parts of NR tube.

Blood Compatibility Assessment. The assessment of blood compatibility of the grafted NR tube was carried out using a whole blood contacting in-vitro test. In this method, one end of the grafted NR tube was clamped and immersed in saline solution prior to use to avoid blood-air interface. Fresh canine (dog) blood was filled into the tube and kept standing for 15 minutes at room temperature. The clamp was released and the blood was flushed out using saline solution. The blood clot remain on the surface of the NR tube was inspected. The least amount of clot means the best blood compatibility.

RESULTS AND DISCUSSION

Solvent for Grafting. The role of solvent is very important in radiation-induced simultaneous grafting technique. This is because the solvent should be able to diffuse the monomer molecules into the polymeric substrate. Therefore, the grafting reaction will be more effective immediately after the active centers or radicals of polymeric substrate are formed during irradiation (10). In many cases, a higher degree of grafting can be obtained when the polymeric substrate is swollen enough in monomer solution with or without solvent. In case of NR tube as polymeric substrate and HEMA as grafting monomer, it was found that the NR tube did not swell enough in HEMA. Therefore, an appropriate solvent should be selected in order to get a higher degree of grafting. Table 1 shows effect of different solvents on the grafting of HEMA onto NR tubes. As can be seen in Table I, among the solvents examined, carbon tetrachloride (CCl_4) gives the highest degree of grafting. The same effect of solvent was also exhibited by radiation grafting of dimethylacrylamide (DMAA) onto NR tube (1). Considering the necessity of sample with higher grafting yield, CCl_4 was then selected as the solvent for grafting of HEMA onto NR tube.

Effect of Monomer Concentration. Effect of monomer concentration in the grafting of HEMA onto NR tube can be seen in Figure 1. The degree of grafting increases as the monomer concentration increases and reaches an optimum at monomer concentration of 20 Vol%. It indicates that diffusibility of HEMA into NR tube matrix is perfect at 20 Vol % HEMA concentration, and consequently a higher degree of grafting is obtained. The dependence of the grafting on monomer concentration demonstrates a three-halves-order dependence. These results indicate that degree of grafting depends not only upon the amount of radicals formed in NR tube but also on the diffusibility of HEMA into NR tube.

Effect of Temperature. The relationship between degree of grafting and irradiation time at various temperatures is shown in Figure 2. It is obvious that graft polymerization is largely affected by irradiation temperature, and that the higher tempe-rature, the higher the grafting rate. It can be explained that the increase in temperature facilitates monomer diffusibility and it causes the increase in initial grafting rate. On the other hand, the increase of temperature affects also the increase of chain segment mobility and this favors the bimolecular termination of primary and growing chain radicals. Consequently, the higher the temperature, the faster the grafting levels off.

Arrhenius plots for this grafting system are shown in Fig.3. Activation energy for the grafting process was calculated and found to be 4.50 kcal/mol.

Effect of Irradiation Dose and Dose Rate. Fig.4 shows the effect of irradiation dose and dose rate on the grafting yield. It appears that degree of grafting increases with dose and dose rate. The higher irradiation dose (time) and the higher dose rate results the higher degree of grafting. It suggests that the formation of free radicals increases with dose and dose rate. These radicals lead to initiate the grafting reaction and then produce a higher degree of grafting.

Dependence of radiation-induced grafting rate of HEMA onto NR tube on dose rate is depicted in Fig.5. As can be seen in Fig.5, the graft rate increases almost linearly up to about 100 wt%. From the slope of this linear plot, the dependency of the initial rate of grafting on dose rate was calculated and found to be proportional to the 6.50 power of dose rate. This value demonstrates that grafting was terminated by both uni- and bi- molecular reactions.

Efficiency of Grafting. The efficiency of grafting of HEMA onto NR tube has been determined at a constant dose rate, temperature and at a given monomer concentration.

Table 2 summarises the efficiency of grafting of HEMA onto NR tube. As can be seen in Table 2, the efficiency of grafting is 4.90 wt% in average. This value is not affected by the degree of grafting.

In fact, the efficiency of grafting of HEMA onto NR tube was found to be approximately five times higher than that of grafting of DMAA onto NR tube (11).

Infra-red Measurement. Besides gravimetrical measurement, the evidence of grafting was also proofed with infra-red measurement. Fig.6 shows the spectra of grafted NR tube (NR-g-PHEMA) and ungrafted (virgin) NR tube.

Infra-red spectra of NR-g-PHEMA has two peaks in which at 3300 cm^{-1} corresponds to -OH stretching vibration, and at 1720 cm^{-1} corresponds to -C=O stretching vibration of HEMA. Those peaks confirm that HEMA is grafted onto NR tube.

Water Up-take Measurement. Water uptake of polymeric sub-strate is usually studied to indicate the hydrophylicity of the substrate. The higher water uptake means the higher hydrophylicity. This is particularly important in the characterization of blood compatible material. It was assumed that a polymeric material with a higher water uptake may exhibit a good blood compatibility.

Fig. 7 shows the water uptake curve of NR-g-PHEMA tube. As can be seen, the water uptake increases with degree of grafting. In this grafting system, the water uptake of 10 wt% is achieved then the sample contains 60 wt% degree of grafting. This value is relatively low as compared to that of NR-g-DMAEA (8).

Blood Compatibility Assessment. Table 3 shows a typical result of blood compatibility assessment of NR-g-PHEMA tubes. It indicates that the blood compatibility of NR-g-HEMA tubes improves as the degree of grafting increases.

However, eventhough the NR-g-PHEMA has a degree of 60 wt% grafting, its blood compatibility is not good enough. This is strongly related to the hydrophilicity behavior of NR-g-PHEMA. In fact the hydrophilicity of NR-g-PHEMA is relatively low as shown in its water uptake curve (Fig.7). This is one reason why the blood compatibility of NR-g-HEMA is not comparable to that of NR-g-DMAEA (8).

In case of NR-g-DMAEA (8), a good blood compatibility was exhibited at 30 wt% degree of grafting in which the water uptake of around 40 wt% was achieved.

CONCLUSION

A hydrophilic monomer 2-hydroxyethylmethacrylate (HEMA) can be grafted onto Natural Rubber (NR) tubes by using radiation induced simultaneous grafting technique.

The appropriate grafting condition was found to be 20

Vol% HEMA in CCl_4 at irradiation dose rate of 0.84 kGy/h at room temperature. The apparent activation energy was calculated to be 4.50 kcal/mol, and a grafting efficiency of 4.90% was achieved. The grafted NR-g-HEMA tubes exhibited a relatively low water uptake (around 10 wt%) eventhough it contained a relatively high degree of grafting (60 wt%). Blood compatibility of the grafted NR tubes was found to be only slightly improved, probably due to its low water uptake.

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Tabel 1. Effect of solvent on grafting of HEMA onto NR tube by simultaneous irradiation method*

Solvent	Monomer conc. (vol %)	Total dose (kGy)	Degree of grafting (wt %)
Water	20	0.37	0.00
Methanol	30	2.24	0.00
Ethyl acetate	30	0.93	1.48
Tetrahydrofuran	20	1.12	4.60
Benzeme	20	1.12	14.91
Chloroform	20	1.12	30.46
Carbon tetrachlorida	20	1.12	58.46

* Dose rate : 2.25 kGy/h
Irrad. temperature : 24°C

Tabel 2. The efficiency of grafting of HEMA onto NR tubes by simultaneous irradiation method

Sample	Total dose* (kGy)	Degree of grafting (wt %)	Efficiency of grafting (wt %)
GE 1-7	68.33	31.75	4.96
GE 1-8	186.11	51.10	4.60
GE 1-9	205.00	54.34	5.10
GE 2-1	136.66	23.15	4.94
GE 2-2	136.66	22.84	4.91

* Dose rate : 0.82 kGy/hr
HEMA concentration : 20 vol % in CCl_4
Irradiation temperature : 24°C

Table 3. A typical results of blood compatibility assessment of NR-g-PHEMA tubes

Sample	Degree of grafting (wt %)	Appearance	Remarks*
Original NR	0	Clot	Poor
HEMA-11	5.30	Clot	Poor
HEMA-21	12.01	Clot	Poor
HEMA-22	20.61	Clot	Poor
HEMA-19	31.64	Few clot	Fair
HEMA-15	60.60	Few clot	Fair

* The blood compatibility is catagorized into three explanation, namely, poor, fair and good. Only in case where the appearance of NR-g-PHEMA without any clot means good in blood compatibility.

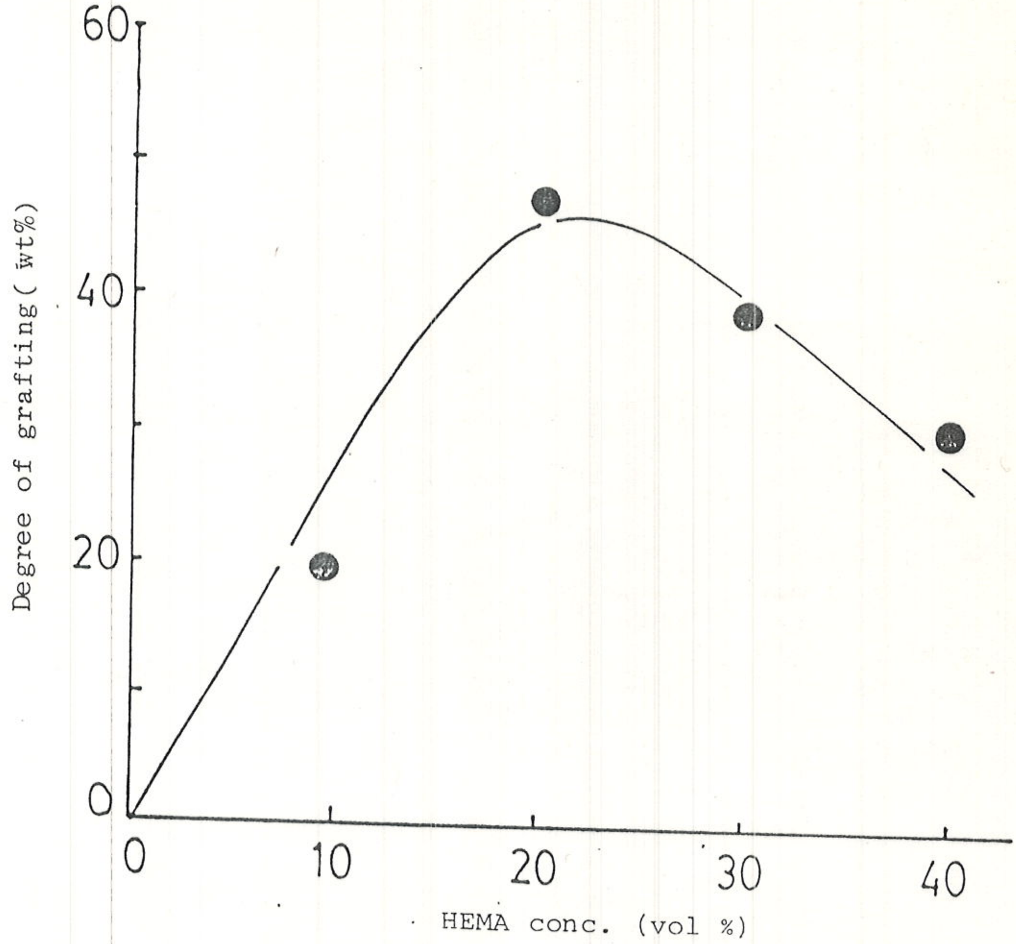

Figure 1. HEMA concentration vs degrre of grafting of HEMA onto NR tube.
Dose rate 2.25 kGy/h, solvent CCl_4, Irradiation time 10 min, irradiation temperature 23^{o}C.

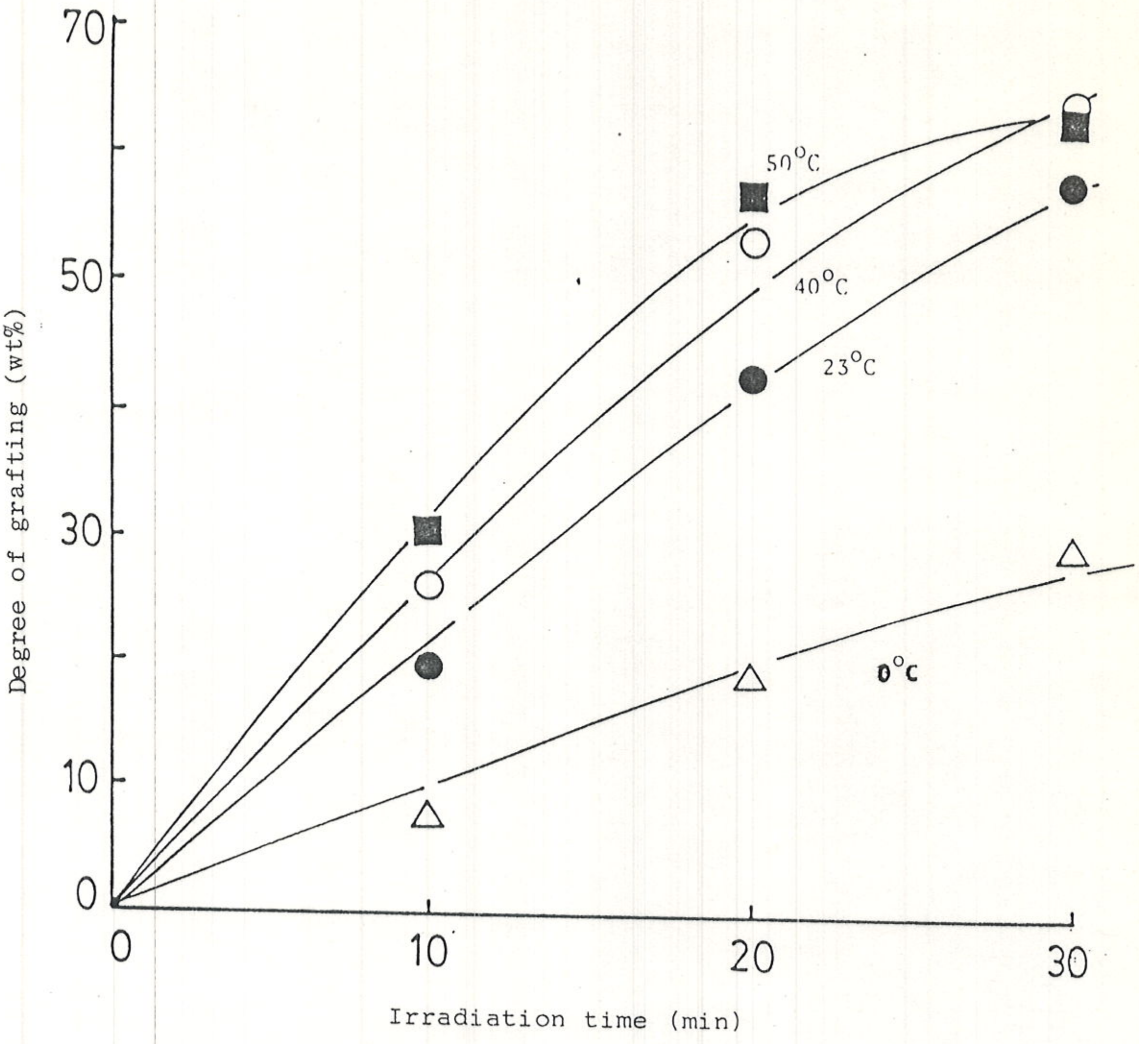

Figure 2. Effect of temperature on radiation induced grafting of HEMA onto NR tube
Monomer concentration 20 Vol % in CCl_4, dose rate, 0.84 kGy/h

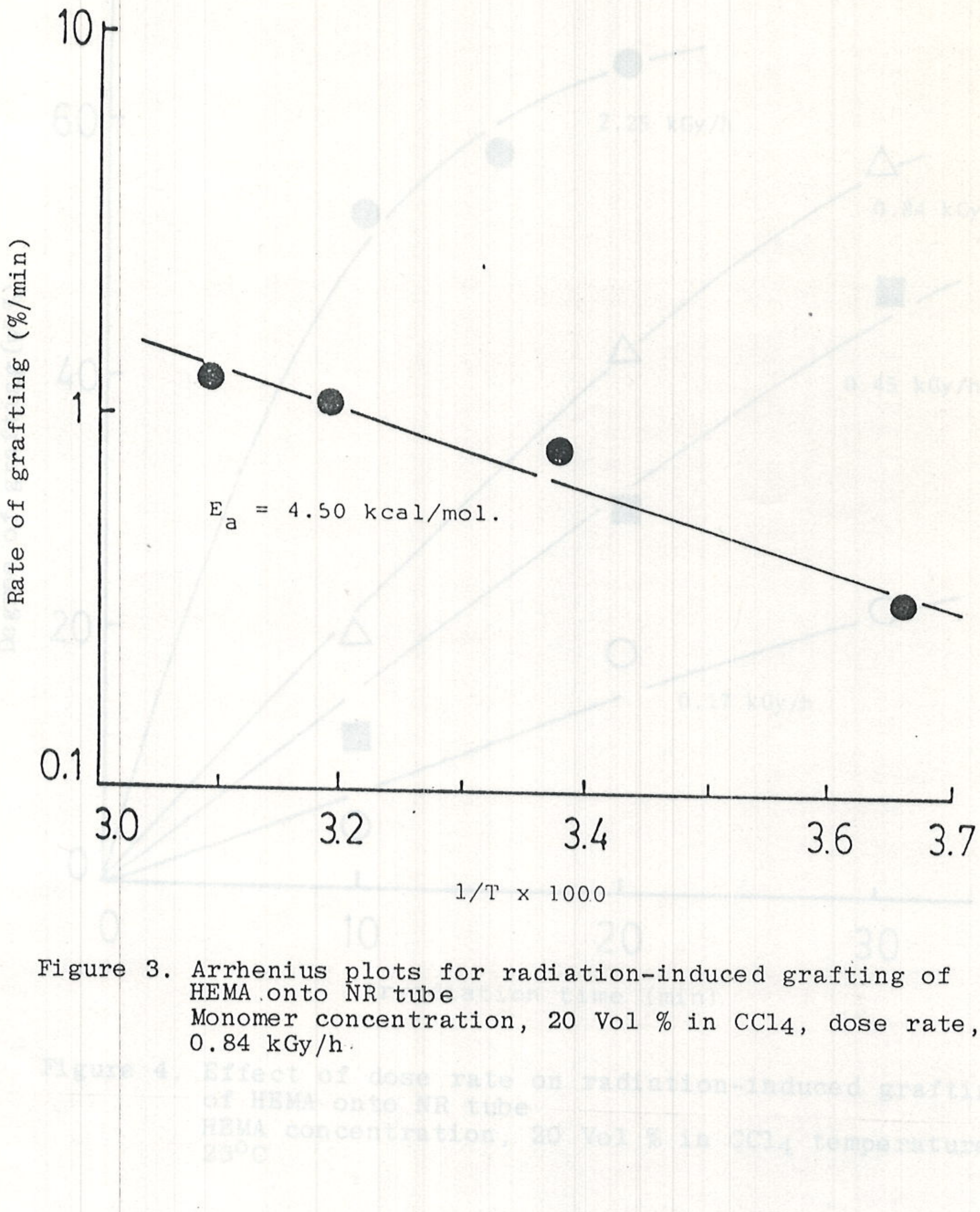

Figure 3. Arrhenius plots for radiation-induced grafting of HEMA onto NR tube
Monomer concentration, 20 Vol % in CCl_4, dose rate, 0.84 kGy/h

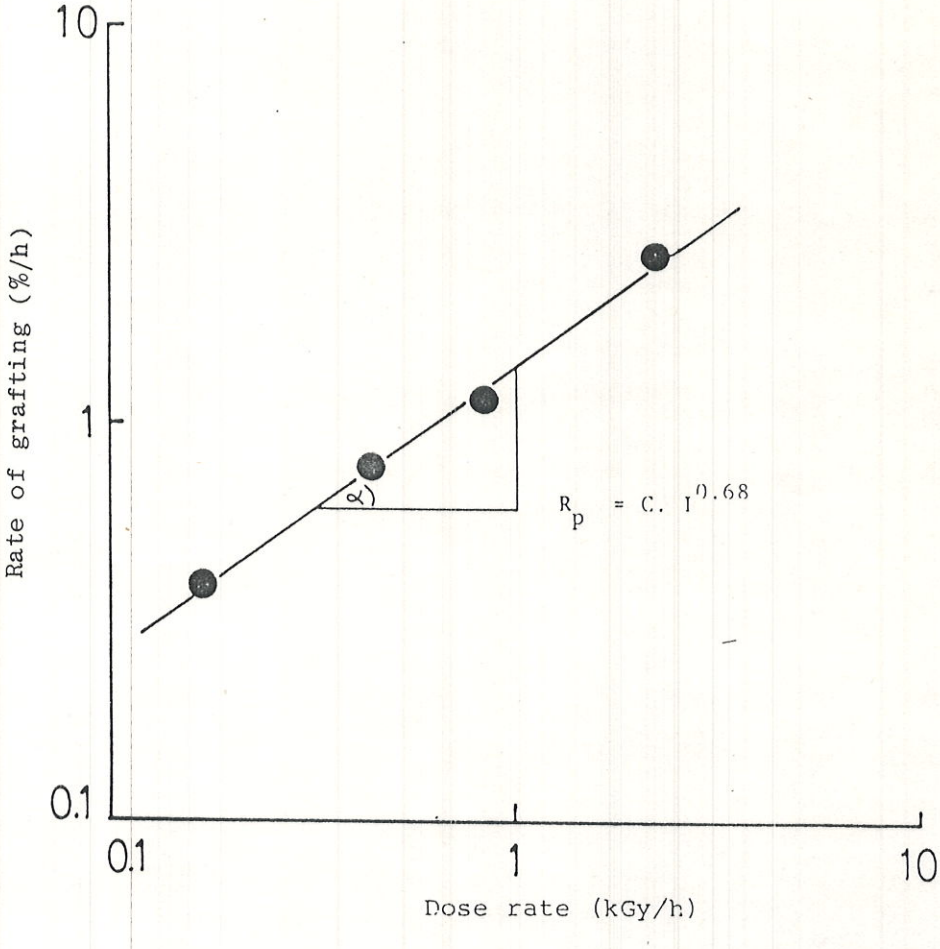

Figure 5. Log-log plots of the rate of grafting and dose rate

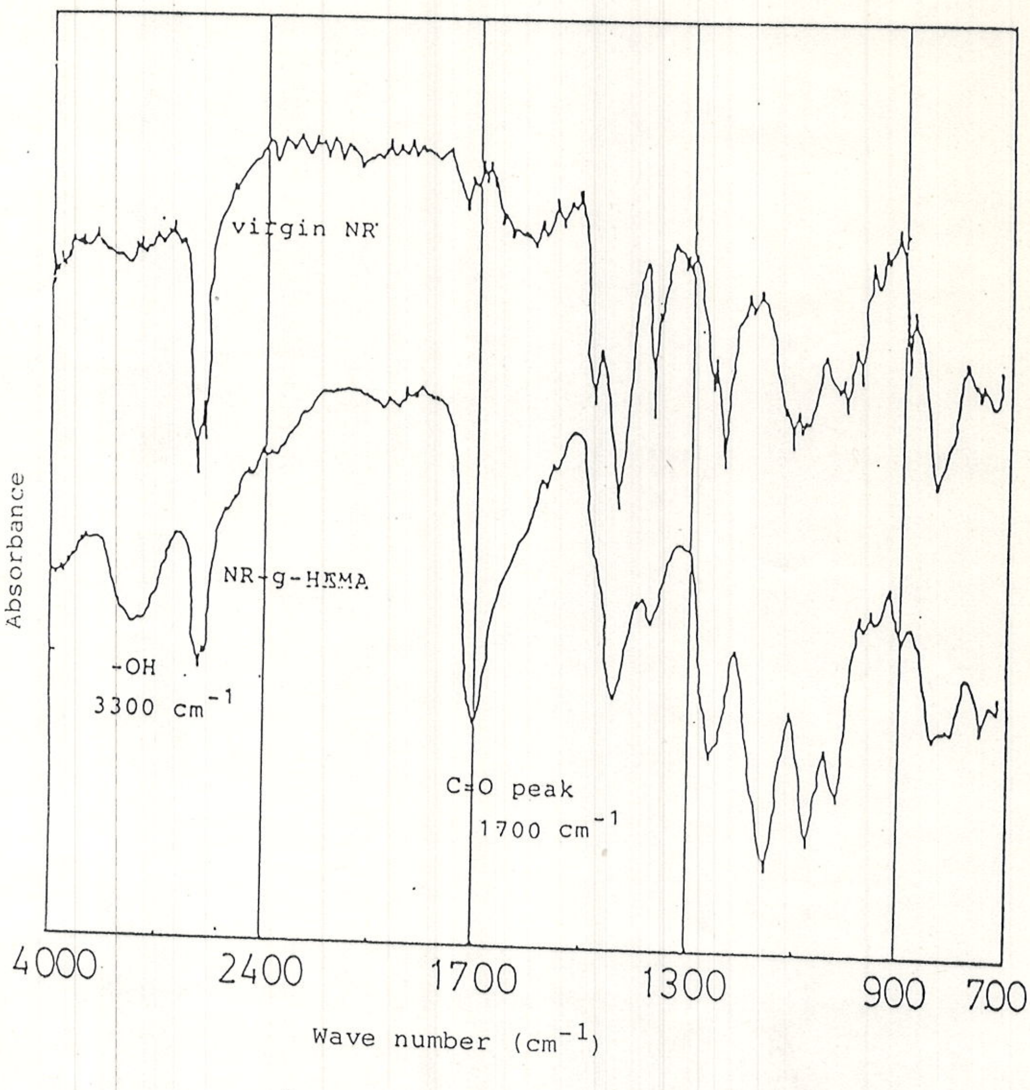

Figure 6. IR spectra of NR-g-HEMA and virgin NR

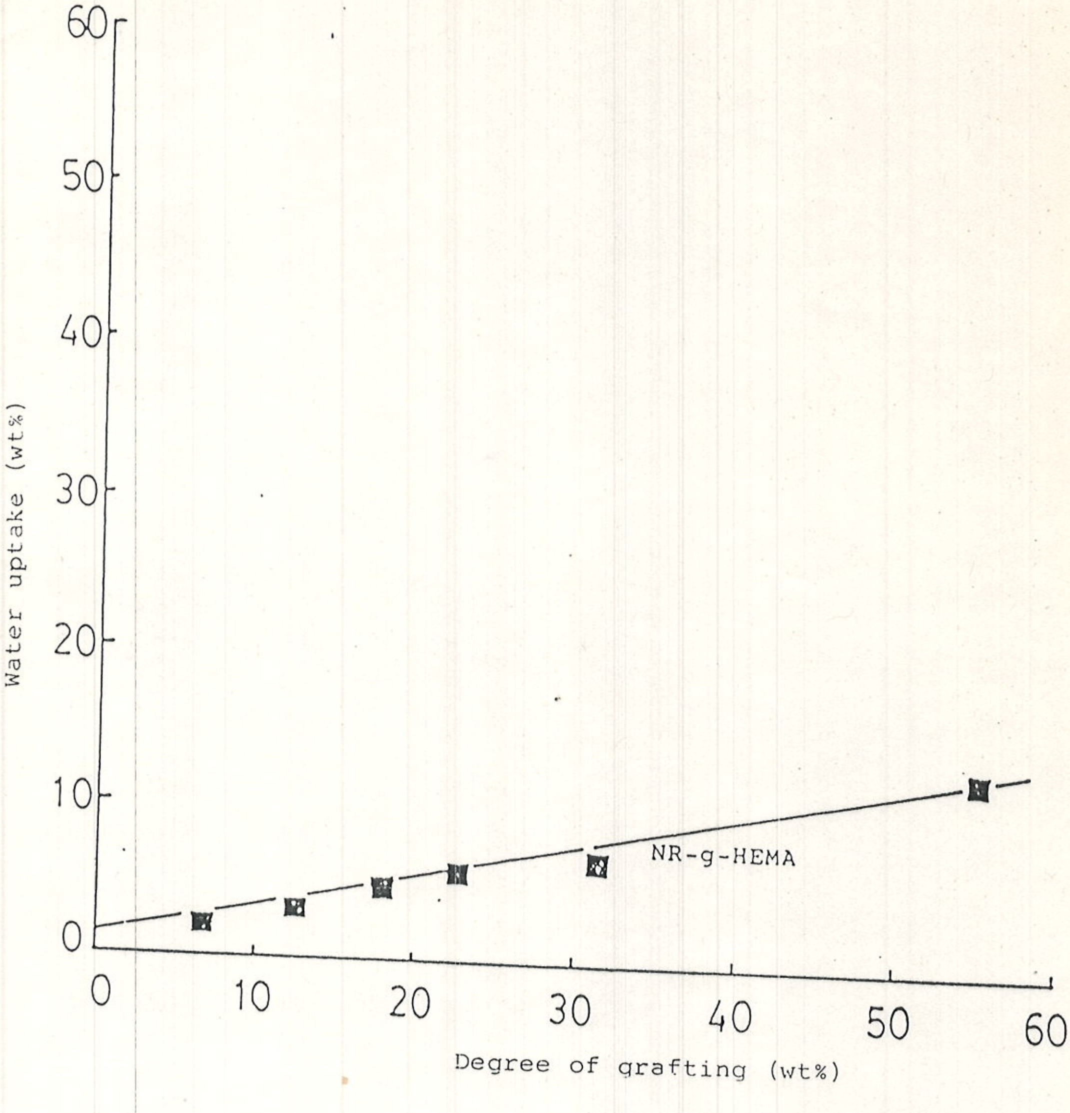

Figure 7. The water uptake curves for all grafting systems of NR tube studied

PAIR / P.472 / 1991

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NO. KP. 268