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# Radiation grafting of hydrophilic monomers onto plasticized poly(vinyl chloride) sheets

## Part III. *Physical and mechanical properties of migration resistant sheets*

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Medical grade poly(vinyl chloride) (PVC) sheets were surface modified by grafting a combination of 2-hydroxyethyl methacrylate (HEMA) and N-vinyl pyrrolidone (NVP) or NVP alone using gamma radiation in an effort to retard the migration of the plasticizer from the PVC matrix. Presence of cupric ions at a concentration of 0.005 M was found to be optimal in not only preventing the homopolymerization of the monomers but also producing the highest graft yield at all monomer concentrations used for grafting. The grafted PVC was characterized for its water absorption properties. Surface morphology of the grafted surface was examined using scanning electron microscopy (SEM). PVC sheets grafted on both sides as well as on one side were characterized for their physical and mechanical properties in order to assess their suitability in biomedical applications. While the tensile strength and percentage elongation values of PVC sheets grafted on both sides showed a downward trend with increasing graft yield, these properties were not drastically affected by surface modification on one side only at graft yields pertinent to prevent the migration of the plasticizer. Measurement of Shore A hardness and optical transparency of the migration resistant sheetings showed that such properties were not seriously affected by surface modification thus rendering them suitable for their intended applications.

## 1. Introduction

The migration of plasticizers from flexible PVC based medical devices and storage bags into physiological fluids has been widely reported [1–3]. Phthalate esters, especially di(2-ethylhexyl) phthalate (DEHP), are the most extensively used plasticizers in the manufacture of flexible PVC. The production of this plasticizer in the United States alone is estimated to be around 500 000 tons per year [4]. The toxicity of phthalate plasticizers has been a matter of serious concern [5–7]. Alarming reports questioning the safety of using DEHP as a plasticizer in PVC based medical devices have been surfacing since the early eighties [8–10]. Recent studies have indicated that DEHP is capable of producing adverse effects on pituitary gland tissues, cause liver abnormalities and testicular damage [11, 12]. A study conducted by the US Cancer Institute in 1981 has indicated possible chances of DEHP or its metabolites produced in contact with blood acting as a potential carcinogen [13].

Attempts have been made to find a suitable alternative to plasticized PVC or to use alternate plasticizers [14, 15]. Glow discharge treatment of PVC sheets have been reported to retard the migration to a certain extent [16]. Recent studies reported from our laboratories [17, 18], have demonstrated that migration of the plasticizer could be prevented by a significant extent by grafting hydrophilic monomers on to flexible PVC using radiation from a $Co^{60}$ source. Grafting a 1:1 combination of HEMA and NVP from a 5% solution of these monomers was able to prevent the migration of DEHP into a simulated biological extractant such as cotton seed oil completely. Even migration into potential organic extractants such as n-hexane was found to be less than 4% of the migration from unmodified control sheets. Drastic reduction in the migration of DEHP could also be achieved by grafting a homopolymer of NVP on to the PVC surface. Nevertheless, a combination of HEMA and NVP was found to be the best for preventing the migration of the plasticizer. For such modified PVC sheetings to be of any practical use in medical devices such as blood storage bags, the physical, mechanical and optical properties of the grafted sheets should be comparable to sheetings presently being used for the manufacture of such devices. As hydrophilic polymers

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have also been known to offer better blood compatible surfaces [19, 20], surface modification by grafting hydrophilic monomers on to PVC is expected to improve only the blood compatibility of the trunk polymer. In this paper, we therefore report our results on the analysis of the mechanical, optical and water absorption properties of the migration resistant graft modified PVC sheetings.

## 2. Experimental details

PVC sheeting of 0.4 mm thickness (received as a gift from Technoport Co., Japan) was used in all the experiments. The identity of the plasticizer present in the sheetings was determined by extraction and characterization using chromatographic and spectroscopic methods. Extraction of the plasticizer was carried out using methanol and carbon tetrachloride (Spectroscopic grade, E. Merck, India) in the ratio 1:2 by volume in a Soxhlet apparatus for 16 h. The procedure followed was as per ASTM D-3421-75. The plasticizer extracted was characterized using a Perkin–Elmer IR spectrophotometer (Model 597), a Shimadzu UV-Vis spectrophotometer (Model 240) and a Waters High Performance Liquid Chromatograph having a UV detector (Model 440). The refractive index was measured using a Model 3T ABBE refractometer (Atago, Japan).

The sheets were cleaned and radiation grafted with combinations of NVP and HEMA in different proportions (v/v%) (NVP25–HEMA75, NVP50–HEMA50, NVP75–HEMA25 and NVP alone), as described before [17, 18]. Sheets were grafted on one side as well as on both sides. For one side grafting, bags were fabricated from the sheets, filled with the monomer(s) solution of the required concentrations and irradiated at the desired dose. For both sides grafting, strips immersed in the monomer solutions were irradiated. Grafting with HEMA alone was not attempted as the monomer tended to homopolymerize heavily thereby making the retrieval and cleaning of the grafted sheets very difficult. Copper sulphate at concentrations of 0.0025 M, 0.005 M, 0.0075 M and 0.01 M were used in the grafting media to prevent homopolymerization of the monomers on irradiation. The graft yield was determined using the method of Ratner [22] and the homopolymer formation, if any was observed visually.

The tensile strength and elongation of the test samples were measured using an Instron Model 1193 Universal Testing Machine according to the ASTM standard D-882. Grafted strips of 10 cm (L) × 1 cm (W) were used for all the measurements maintaining a gauge length of 6 cm. A cross-head speed of 500 mm min$^{-1}$ and a chart speed of 500 mm min$^{-1}$ were used (magnification ratio = 1). The strips were hydrated before the measurements by equilibrating them in distilled water for more than 48 h.

Shore A hardness values were estimated for all the grafted samples and the control using ASTM D-676-69T procedure. A minimum of 6 estimations were carried out for each sample. The transparency of the grafted specimens was checked by measuring the percentage transmission of light in the 700–350 nm region using a UV-VIS (Shimadzu Model 240) spectrophotometer.

The percentage water of hydration present in the total polymer as well as in the graft was determined using gravimetric methods after equilibrating the grafted polymer in distilled water for a minimum of 48 h. The following relations were employed [22].

$$\text{Percentage water}_{\text{total}} = \frac{(\text{Wt of hydrated graft polymer}) - (\text{Wt of dry graft polymer})}{(\text{Wt of hydrated graft polymer})} \times 100$$

$$\text{Percentage water}_{\text{graft}} = \frac{(\text{Wt of hydrated graft polymer}) - (\text{Wt of dry graft polymer})}{(\text{Wt of hydrated graft polymer}) - (\text{Wt of ungrafted polymer})} \times 100$$

The weighings were performed using a high precision analytical balance (Ohaus) having a sensitivity of 0.1 mg. The hydrated samples were pressed in between two Whatman filter papers applying very little pressure before weighing so as to remove the surface adherent water.

SEM examination of the grafted and ungrafted PVC surfaces was carried out using a Jeol instrument (JSM 35C). Specimens were mounted on aluminium stubs using double sided tape, coated with gold and examined in the microscope at 15 kV.

## 3. Results and discussion

Extraction of the plasticizer using methanol and carbon tetrachloride for 16 h from PVC sheets yielded nearly 15% of the total weight of the sheeting as plasticizer. Infrared spectrum of the extracted plasticizer shown in Fig. 1 was found to correspond with the standard spectrum of DEHP [23] exhibiting all its characteristic absorption peaks. UV spectral data showed absorption maxima at 274 nm characteristic of DEHP. HPLC analysis of the plasticizer showed a

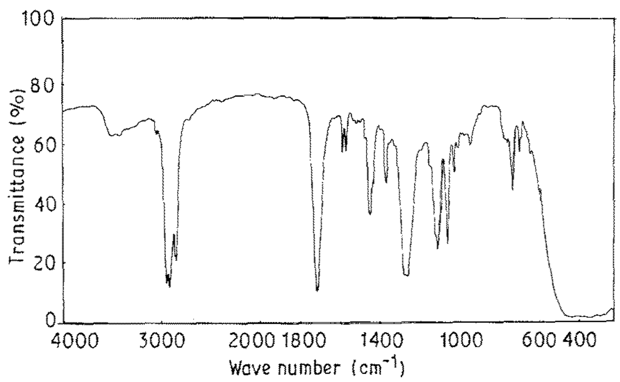


*Figure 1* Infrared spectrum of the extracted plasticizer di(2-ethylhexyl) phthalate.

TABLE I Effects of copper ion concentration in the grafting medium on the graft yield at various monomer concentrations at 0.25 Mrad

| NVP/HEMA monomer ratio | Monomer conc. (vol %) | Graft yield (%) 0.0025 M | 0.005 M | 0.0075 M | 0.01 M |
|---|---|---|---|---|---|
| NVP25/HEMA75 | 1 | 0.00 | 0.69 | 0.35 | 0.46 |
| | 3 | 1.89 | 2.43 | 1.80 | 1.92 |
| | 5 | 5.53 | 6.52 | 4.59 | 3.59 |
| | 7 | 6.45 | 12.00 | 6.88 | 5.50 |
| NVP50/HEMA50 | 1 | 0.00 | 0.97 | 0.18 | 0.00 |
| | 3 | 1.66 | 2.99 | 1.79 | 1.83 |
| | 5 | 3.38 | 7.01 | 3.95 | 4.30 |
| | 7 | 7.19 | 9.81 | 6.02 | 5.88 |
| NVP75/HEMA25 | 1 | 0.17 | 0.77 | 0.00 | 0.35 |
| | 3 | 1.13 | 4.17 | 1.56 | 2.28 |
| | 5 | 3.25 | 7.91 | 4.91 | 3.96 |
| | 7 | 12.03 | 11.40 | 8.39 | 7.77 |
| NVP | 1 | 0.83 | 1.06 | 0.26 | 0.56 |
| | 3 | 3.15 | 2.83 | 1.72 | 2.61 |
| | 5 | 5.58 | 9.75 | 5.15 | 2.72 |
| | 7 | 9.77 | 14.73 | 4.14 | 5.71 |

single prominent peak having strong absorption at 254 nm and elution time (nearly 4 min) similar to that of control DEHP. The refractive index value was measured as 1.4828 which corresponded with the reference value of DEHP [24] confirming the identity of the plasticizer.

Table I shows the graft yield values obtained when the PVC sheetings were grafted using various ratios of NVP/HEMA at different concentrations in the presence of varying amounts of $Cu^{2+}$ in the grafting medium. All grafting experiments were carried out at a radiation dose of 0.25 Mrad. Molarity of the $Cu^{2+}$ ions in the grafting medium was varied from 0.0025 to 0.01 M, while monomer concentrations of 1, 3, 5 and 7 vol % were employed for grafting. The graft yield was found to increase with increase in monomer concentration for all the systems studied. However, samples grafted in the presence of 0.005 M copper sulphate showed the highest graft yield values in all systems compared to other concentrations. This is analogous to the observations made by Ratner *et al.* [21] for the grafting of hydrophilic monomers onto silicone rubber and is likely to be the critical copper ion concentration for (NVP/HEMA)–PVC and NVP–PVC systems too. The homopolymer was found to be present in traces where the $Cu^{2+}$ ion concentration in the grafting medium was 0.0025 M. The solutions were all clear with no homopolymerization in other grafting systems. We have already shown by atomic absorption measurements that residual copper concentrations in the polymer grafted with HEMA/NVP in the presence of 0.005 M $Cu^{2+}$ is well within safety limits recommended for blood contact applications [17]. Thus the incorporation of cupric ions in the grafting medium prevents homopolymerization and facilitates cleaning procedure of the grafted material to a significant extent.

Scanning electron micrographs of the virgin and grafted PVC surfaces are shown in Fig. 2a and b. The virgin PVC sheeting appears to have a rough, irregular, non-uniform surface as seen in the photomicrograph. The surface grafted using a 5% solution of 1:1 NVP/HEMA shows fine layers of the grafted hydrophilic polymer thus changing the surface morphology of the polymer altogether. The shrinking of these hydrophilic graft layers on contact with hydrophobic solvents such as n-hexane is believed to be responsible for the retardation of plasticizer migration from the PVC matrix.

The tensile strength and elongation values for PVC sheets grafted on both sides tend to decrease with higher graft content compared with control values in all four systems studied (Figs 3 and 4). Higher HEMA content in the graft copolymer is found to favour this decrease as evidenced by the tensile strength values which are in the order NVP100 > N75–H25 > N50–H50 > N25–H75. The percentage elongation in all cases was found to decrease with increase in the graft content. This phenomenon is not surprising in view of the fact that graft modification of the surface using high energy radiation produces a highly cross-linked three dimensional network of the graft polymer on the surface thereby restraining the surface from stretching. The change in mechanical properties of PVC grafted with NVP alone was negligible. This is presumably due to the higher hydrophilicity achieved by the NVP graft compared to that of NVP/HEMA.

A comparison of the tensile strength and percentage elongation values of PVC sheets grafted only on one side versus that of sheets grafted on both sides is very interesting with respect to the practical use of such modified surfaces in PVC based devices and storage bags. This was carried out only for PVC grafted using a 1:1 ratio of NVP/HEMA and pure NVP in view of the fact that surfaces grafted with even a 1% solution of the monomer was able to prevent the plasticizer migration drastically [17]. While the monografts of the NVP/HEMA system showed no loss in tensile strength up to a monomer concentration of 5%, there was a slight decrease in the tensile properties beyond this concentration. The percentage elongation values also followed more or less the same trend up to this concentration and thereafter showed a decrease in value. Sheetings grafted on both sides however showed rapid decrease in their tensile strength values with increasing monomer concentration (and therefore increased graft yield). The percentage elongation also decreased with increasing monomer concentration

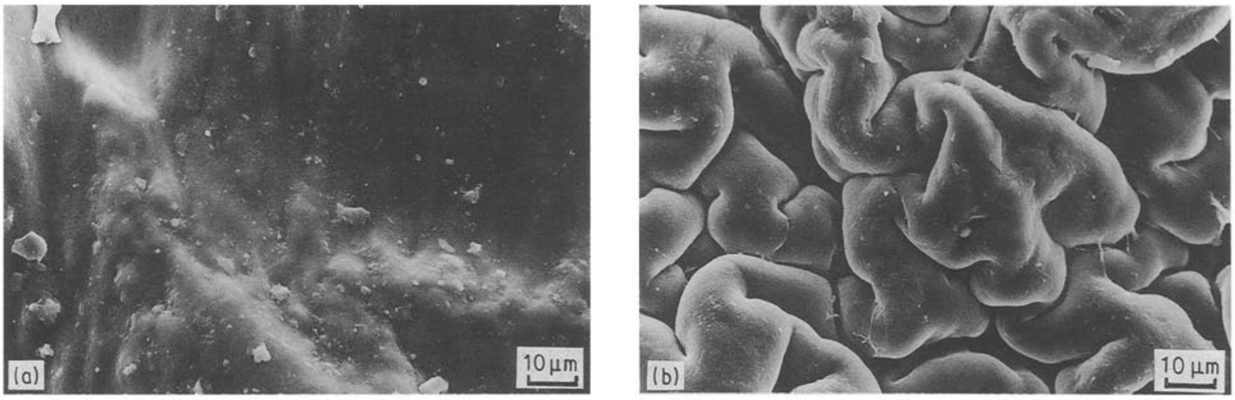


*Figure 2* Scanning electron photomicrographs of (a) ungrafted PVC surface and (b) surface grafted using 5 vol % NVP/HEMA (50:50) at 0.25 Mrad.

TABLE II Comparison of tensile strength values of PVC sheets grafted on both sides and only on one side at a radiation dose of 0.25 Mrad at different monomer concentrations

| Monomer conc. (vol %) | Tensile strength (kg $cm^{-2}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | N50–H50 | | | | NVP | | | |
| | Mono | SD | Bi | SD | Mono | SD | Bi | SD |
| Control | 189.42 | 9.99 | – | – | – | – | – | – |
| 1 | 194.69 | 13.16 | 172.86 | 3.33 | 172.50 | 6.61 | 184.17 | 10.10 |
| 3 | 197.50 | 6.61 | 130.45 | 3.36 | 160.00 | 6.37 | 175.00 | 5.00 |
| 5 | 196.67 | 9.38 | 130.97 | 8.19 | 145.50 | 12.33 | 177.92 | 5.90 |
| 7 | 172.50 | 11.32 | 83.71 | 2.09 | 122.50 | 19.23 | 167.92 | 1.91 |

though this change was not pronounced at a monomer concentration of 1%. In the case of pure NVP grafted sheetings, both monografts and bigrafts showed a decreasing trend in their tensile strength values unlike the NVP/HEMA combination. The elongation values were also found to decrease with increasing monomer concentration in the case of both monografts and bigrafts though the change at 1% concentration does not justify this trend. The values obtained are tabulated in Tables II and III. The fact that monograft properties are comparable to control values at monomer concentrations, which are pertinent to retard the migration of the plasticizer when grafted, is very encouraging since it offers an opportunity to modify the surface of PVC based medical devices to prevent the plasticizer migration without affecting the mechanical properties of the polymer matrix adversely.

Measurement of Shore A hardness of the grafted and ungrafted PVC sheetings showed that grafting did not change this property significantly. The data obtained with specimens grafted with different concentrations of the monomers are shown in Table IV. However, the transparency measurements at 700 nm show a steady decrease in transparency with increase in graft yield. However, this is not likely to affect the

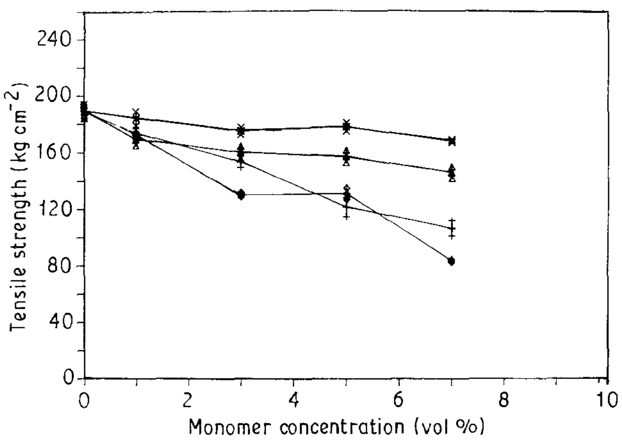


*Figure 3* Tensile strength values of hydrated PVC strips grafted on both sides using various monomer concentrations at a radiation dose of 0.25 Mrad in the presence of 0.005 M $Cu^{2+}$ in the grafting medium; (+) N25–H75, (◆) N50–H50, (▲) N75–H25 and (x) NVP100.

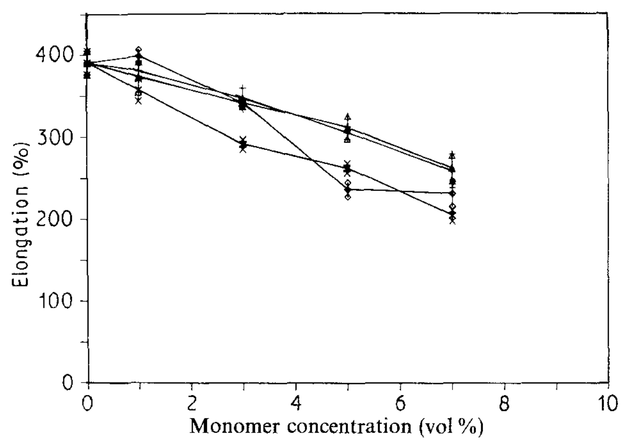


*Figure 4* Percentage elongation values of hydrated PVC strips grafted on both sides using various monomer concentrations at a radiation dose of 0.25 Mrad in the presence of 0.005 M $Cu^{2+}$ in the grafting medium; (+) N25–H75, (◆) N50–H50, (▲) N75–H25 and (x) NVP100.

TABLE III Comparison of percentage elongation values of PVC sheets grafted on both sides and only on one side at a radiation dose of 0.25 Mrad at different monomer concentrations

| Monomer conc. (vol %) | Elongation (%) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | N50–H50 | | | | NVP | | | |
| | Mono | SD | Bi | SD | Mono | SD | Bi | SD |
| Control | 390.95 | 29.18 | – | – | – | – | – | – |
| 1 | 444.58 | 14.23 | 398.61 | 16.21 | 456.66 | 31.79 | 357.56 | 26.75 |
| 3 | 404.45 | 8.55 | 341.06 | 8.42 | 350.67 | 21.91 | 291.11 | 11.70 |
| 5 | 336.11 | 37.28 | 236.39 | 17.40 | 321.67 | 34.30 | 262.22 | 11.70 |
| 7 | 293.30 | 24.56 | 231.39 | 30.87 | 235.00 | 58.91 | 204.45 | 13.47 |

TABLE IV Shore A hardness values of grafted and control PVC sheetings in the dry and in the hydrated state

| Sample | | Hardness (Shore A) | | | |
|---|---|---|---|---|---|
| | | Dry | | Hydrated | |
| | | Mean | SD | Mean | SD |
| PVC control | | 87.50 | 0.55 | 87.5 | 0.55 |
| N25–H75, | 1 vol % | 92.33 | 1.03 | 91.50 | 0.55 |
| | 3 vol % | 92.00 | 1.10 | 91.00 | 0.89 |
| | 5 vol % | 93.00 | 0.63 | 92.33 | 0.52 |
| | 7 vol % | 93.67 | 0.52 | 92.50 | 0.55 |
| N50–H50, | 1 vol % | 90.33 | 1.03 | 91.17 | 0.41 |
| | 3 vol % | 90.33 | 1.86 | 92.17 | 0.41 |
| | 5 vol % | 92.83 | 0.75 | 92.17 | 0.75 |
| | 7 vol % | 93.00 | 0.89 | 92.00 | 0.63 |
| N75–H25, | 1 vol % | 91.50 | 0.55 | 89.83 | 1.57 |
| | 3 vol % | 91.83 | 0.41 | 91.33 | 0.52 |
| | 5 vol % | 93.00 | 0.89 | 89.83 | 0.98 |
| NVP | 1 vol % | 91.33 | 0.52 | 90.67 | 1.51 |
| | 3 vol % | 90.67 | 0.82 | 91.83 | 1.47 |
| | 5 vol % | 90.50 | 1.05 | 91.17 | 1.17 |

TABLE V Percentage transmission values at 700 nm for control and grafted PVC samples

| System | | Transmission (%) | |
|---|---|---|---|
| | | Dry | Hydrated |
| PVC control | | 8.08 | 8.08 |
| N25–H75, | 1 vol % | 3.60 | 3.30 |
| | 3 vol % | 3.70 | 2.60 |
| | 5 vol % | 3.50 | 2.44 |
| | 7 vol % | 1.65 | 1.94 |
| N50–H50, | 1 vol % | 6.12 | 6.00 |
| | 3 vol % | 5.72 | 4.40 |
| | 5 vol % | 5.64 | 5.70 |
| | 7 vol % | 4.52 | 3.60 |
| N75–H25, | 1 vol % | 4.10 | 3.96 |
| | 3 vol % | 3.80 | 2.44 |
| | 5 vol % | 3.90 | 2.50 |
| N100 | 1 vol % | 6.68 | 5.76 |
| | 3 vol % | 5.36 | 10.80 |
| | 5 vol % | 4.88 | 9.20 |

final product significantly because the control sample itself was showing only about 8% transmission at this wavelength. The percentage transmission values also do not show considerable change when the samples were subjected to measurements in the dry state and in the hydrated state. Data on the percentage transmission measurements are given in Table V.

Determination of the water absorptivity of the grafted PVC sheetings was carried out on both one side grafted and two sides grafted sheetings. The water content in the total polymer $H_2O_{total}$, was found to increase with increasing monomer concentrations in the grafting medium i.e., increasing graft yield, for all the four systems studied irrespective of whether the sheet was grafted only on one side or on both sides (Figs 5 and 6). The water content present in the graft for PVC sheetings grafted on both sides $H_2O_{graft}$, however tended to decrease with increasing graft content for all the NVP–HEMA systems whereas for samples grafted with NVP alone this effect was not pronounced. Fig. 7 shows this trend. This was expected since the absorption of water is to increase with increasing graft yield since the graft polymers of both HEMA and NVP possess high hydrophilicity.

## 4. Conclusions

1. Grafting of hydrophilic monomers on to PVC by gamma radiation in the presence of cupric ions at specific concentrations prevents the homopolymerization of the monomers in the grafting medium thus facilitating the grafting and cleaning of the trunk polymer. Graft yield is found to be the highest at an optimum $Cu^{2+}$ concentration of 0.005 M.

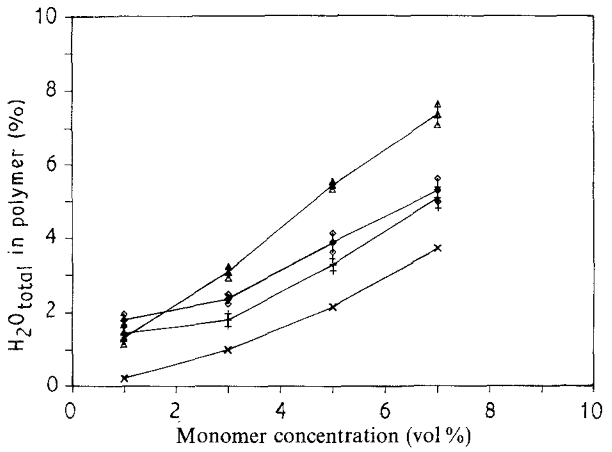


*Figure 5* Water of hydration in total polymer (both sides grafted) plotted against various monomer concentrations used for grafting at 0.005 M $Cu^{2+}$ in the grafting medium; (+) N25–H75, (◆) N50–H50, (▲) N75–H25 and (×) NVP100.

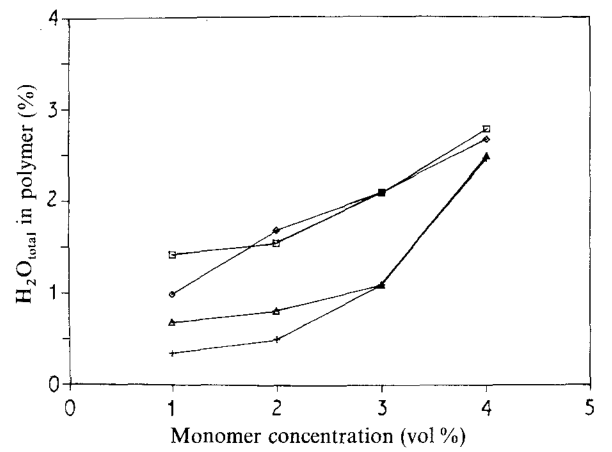


*Figure 6* Water of hydration in total polymer (single side grafted) plotted against various monomer concentrations used for grafting at 0.005 M $Cu^{2+}$ in the grafting medium; (□) N25–H75, (+) N50–H50, (◇) N75–H25 and (△) NVP100.

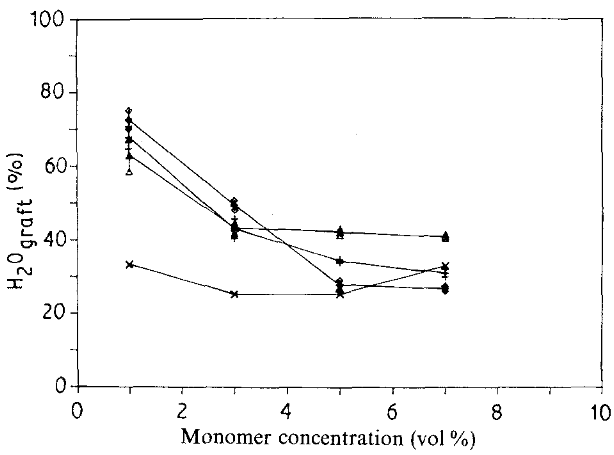


*Figure 7* Water of hydration in graft polymer (both sides grafted) plotted against various monomer concentrations used for grafting at 0.005 M $Cu^{2+}$ in the grafting medium; (+) N25–H75, (◆) N50–H50, (▲) N75–H25 and (×) NVP100.

2. Both tensile strength and percentage elongation values of PVC strips grafted on both sides and hydrated tend to decrease slightly compared to the control values with increase in graft yield whereas the reduction is negligible with strips grafted only on one side. The hardness values tend to show a slight increase compared to control.

3. Optical transparency of the sheetings decreases slightly for the grafted samples though it does not seem to affect the appearance of the material to any significant extent.

4. As percentage of water of hydration in the total polymer tend to increase with increase in graft yield, the total water present in the graft tend to show a gradual decrease as expected.

5. Migration resistant PVC sheetings prepared by grafting hydrophilic monomers such as NVP and HEMA on to their surface by gamma irradiation appear to be suitable for their intended biomedical applications as most of the physical and mechanical properties of the trunk polymer are not adversely affected by surface modification.

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