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RADIATION-INDUCED GRAFTING OF 2-HYDROXYETHYL METHACRYLATE ONTO POLYPROPYLENE FOR BIOMEDICAL APPLICATIONS. I. EFFECT OF SYNTHESIS CONDITIONS

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ABSTRACT

Graft copolymerization of 2-hydroxyethyl methacrylate onto polypropylene monofilament was carried out by using a simultaneous gamma radiation technique from a ^{60}Co source, so that the hydrogel polypropylene-*g*-polyhydroxyethyl methacrylate thus produced by grafting could be used as a biocompatible suture material. The influence of various parameters, such as dose rate, total dose, and monomer concentration, on the degree of grafting was determined. It was found that the degree of grafting increases with an increase in monomer concentration. However, for a constant dose under optimum monomer concentration (1.5–2.0 mol/L), a low dose rate produces better graft levels. The studies showed that grafting is strongly influenced by the reaction medium. The optimum conditions for the system were determined. The grafting was ascertained by infrared spectroscopy and color formation with methylene blue.

The grafted monofilament showed very good swelling behavior in water due to the incorporation of hydrophilicity in the copolymer monofilament.

INTRODUCTION

Hydrogels have been tested for use in a variety of surgical, prosthetic, and implantation applications [1, 2]. A number of opinions have been forwarded for the biocompatibility of polymeric hydrogels [3–5]. However, the biological compatibility of these hydrogels to a living system may be due to their excellent swelling behavior in aqueous medium. This swollen matrix then makes a continuous pathway by permeation and diffusion for low molecular weight metabolites in the tissues.

Hydrogels show very weak mechanical characteristics, particularly in the presence of moisture and, hence, in considering their suture application, it is necessary to graft them on some polymeric support such as polyesters, nylons, and polypropylene. Polypropylene possesses attractive features such as good dimensional stability, chemical resistance, and thermal stability up to 165–170°C, and it has been tested for its suture application *in vivo* [6]. However, a tissue reaction has been reported in esophageal and gastrointestinal operations [7]. Therefore, it is expected that polypropylene with the surface properties of a hydrogel would perform the function of a biocompatible suture material. Tollar et al. [8] prepared a hydrogel system for surgical materials by using a coating of hydrophilic polyhydroxyethyl methacrylate. Several other studies have been carried out on the radiation-induced grafting of such monomers as 2-hydroxyethyl methacrylate (HEMA), acrylic acid, acrylamide, and *N*-vinyl pyrrolidone onto inert polymers to produce a material with the surface properties of a hydrogel and with the better mechanical characteristics of the composite substrate [9–11]. This led us to confine our studies for the preparation of a suture material to polypropylene, which not only shows biocompatible and antimicrobial properties but also retains its strength during clinical applications. Hydrogels prepared from HEMA have shown good compatibility in a variety of surgical applications [12, 13]. Based on these studies, HEMA was chosen as a most suitable monomer for grafting onto polypropylene monofilament.

The present study attempts to graft copolymerize HEMA onto polypropylene monofilament by using a direct radiation technique and to determine the influence of various parameters on the degree of grafting.

EXPERIMENTAL

Materials and Grafting Technique

Polypropylene (Extrusion grade) used for this study was supplied by Indian Petrochemicals Corporation Limited, Gujrat, India. The monofilament was obtained by melt spinning on a laboratory melt spinning unit. Spinning was carried out at 230°C under nitrogen atmosphere to prevent thermal degradation. The monofilament was collected on bobbins and was further drawn to a 1 : 3 ratio to achieve better tensile properties and a fine diameter of 0.21 mm.

Chlorobenzene, benzene, and dichloroethane (Glaxo Laboratories) were used as received without further purification. HEMA (Fluka) was distilled at 70°C/20 mmHg and stored at refrigerator temperature.

All the grafting experiments were carried out with ^{60}Co rays from a gamma radiation chamber by using the simultaneous irradiation technique.

Grafting Procedure

Grafting was carried out according to the procedure reported earlier [14]. A weighed amount of monofilament was put into a tube containing the monomer and the grafting medium. An inert atmosphere was created by passing nitrogen through the tube for a sufficient time. Samples were then put into a gamma chamber for a specified period. After exposure, the samples were Soxhlet extracted with methanol for 8 h to remove any adhering homopolymer. The samples were dried under vacuum at 60°C. The degree of grafting and the grafting efficiency were obtained from the following relationships [14]:

$$\text{degree of grafting} = \frac{\text{weight of grafted PHEMA}}{\text{original weight of sample}} \times 100$$

$$\text{grafting efficiency} = \frac{\text{weight of grafted PHEMA}}{\text{total polymer yield}} \times 100$$

Infrared Spectroscopy

Infrared spectra of the samples were recorded on a Perkin-Elmer instrument [15].

Color Reaction with Methylene Blue

The modified polypropylene monofilaments were put in the aqueous solution of methylene blue of 1 g/L concentration. The solution pH was maintained at 5.5 by using acetic acid. The bath temperature was maintained at 100°C, and the samples were subjected to coloring for 8 h [16].

Swelling Measurements

The swelling of monofilaments was determined by putting the samples in distilled water at 35±2°C according to the procedure adopted by Wilson [17]. The percent swelling was obtained as follows:

$$\%\ \text{swelling} = \frac{W_s - W_d}{W_d} \times 100$$

where W_s is the weight of the swollen sample and W_d is the weight of the dry sample.

RESULTS AND DISCUSSIONS

Polypropylene monofilament as obtained directly from the spinneret contains a large percentage of amorphous content. This monofilament was subjected to further drawing to obtain a monofilament with the better tensile strength required for suture application. After drawing, the tensile strength increases because of the increase in orientation of the molecular chains in the amorphous region. This oriented monofilament was subjected to grafting carried out at monomer concentrations varying from 0.5 to 2 mol/L at various doses and dose rates.

Figure 1 shows the effect of dose rate on the degree of grafting and on grafting efficiency. It was found that for a constant dose and monomer concentration, the degree of grafting and grafting efficiency decrease with the increase in dose rate. A similar behavior was observed in our earlier studies of methacrylic acid grafting onto polypropylene fibers [14]. This behavior may be explained by the fact that irradiation produces monomer radicals in the grafting system which have the option to either initiate polymerization at the macromolecular backbone or to interact with other monomer radicals in the system. At higher dose rates the number of free radicals generated is also higher. However, all these radi-

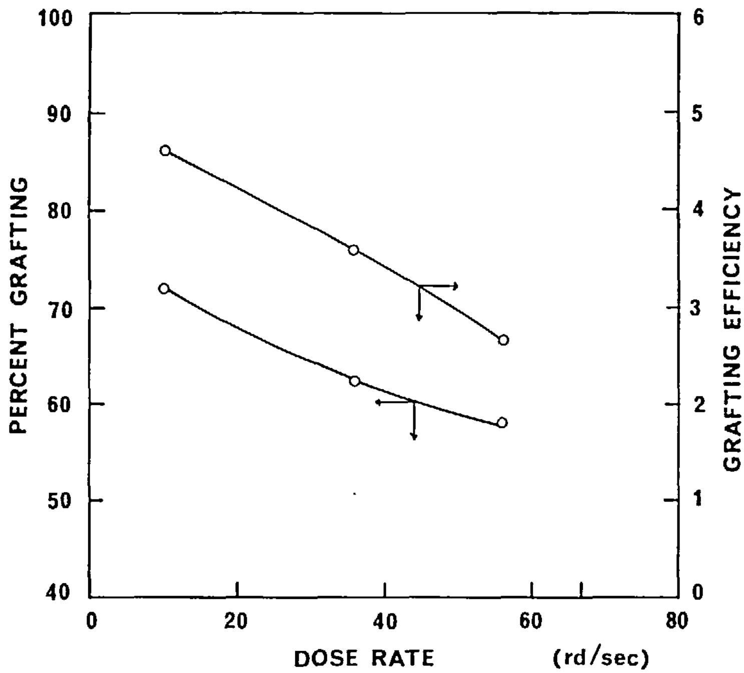

FIG. 1. Variation of percent grafting and grafting efficiency with dose rate of radiation. Monomer concentration, 1.5 mol/L; dose, 0.2 Mrd; solvent, chlorobenzene.

cals are unable to initiate grafting on the PP backbone, and most of them terminate by mutual recombination, leading to the formation of a homopolymer. This results in a decrease in the degree of grafting and in grafting efficiency. It was found that the percentage of homopolymer formed is higher at a higher dose rate, thereby suggesting that the monomer recombination reaction is favored more at higher dose rates. As a result, grafting efficiency decreases because of greater homopolymerization. At a lower dose rate, radical generation is very low, and grafting continues steadily for a longer time with relatively less depletion of monomer compared to higher dose rates where the time period is short.

The influence of irradiation dose on the degree of grafting is presented in Fig. 2. Grafting was carried out for doses of 0.05 to 0.3 Mrd at 56

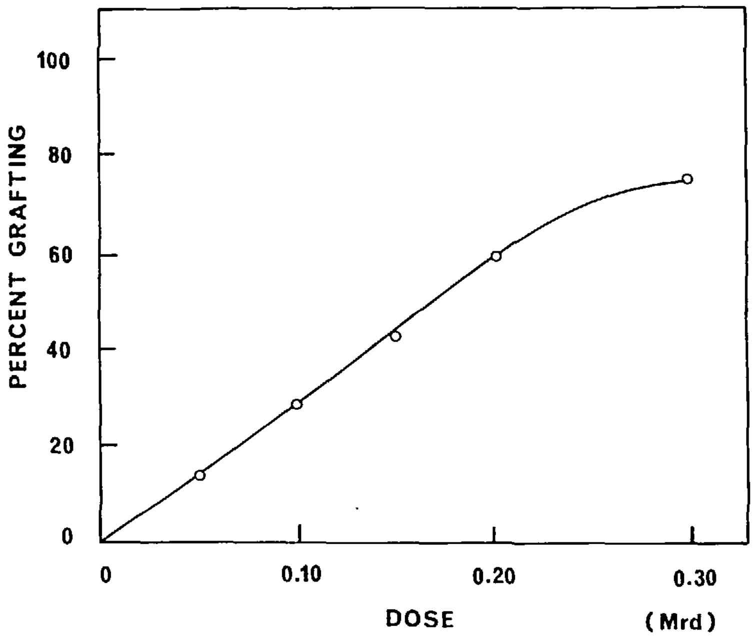

FIG. 2. Variation of percent grafting with the dose of radiation. Monomer concentration, 1.5 mol/L; dose rate, 56 rd/s; solvent, chlorobenzene.

rd/s. The graft yield increases sharply for the initial doses and then starts leveling off beyond 0.20 Mrd.

Hoffman et al. carried out the grafting of HEMA on polyethylene films where complex kinetic behavior involving an induction period followed by a short autoacceleration was observed [18]. The authors attribute this to the partitioning of the polar monomer solution with the nonpolar polyethylene surface. However, in our system no such induction period was observed probably due to the use of chlorobenzene as the grafting medium, because it acts as a swelling agent and facilitates diffusion of monomer into the PP matrix. The increase in percent grafting with an increase in the irradiation dose is essentially due to the higher generation of free radicals at higher doses. However, the degree of grafting tends to level off beyond a dose of 0.2 Mrd. It appears that with the progressing dose of irradiation, a certain graft level is attained where the grafted chains are long enough to cause hindrance to monomer diffusion into the swollen polymer matrix [19]. Therefore, the radicals terminate by mutual recombination before reaching and reacting with the primary radicals at the polymer backbone. A similar observation was made for the preparation of hydrogels by the grafting of HEMA onto PVC films [20]. It appears that in the present system it is a dose of 0.20 Mrd at which optimum grafting is attained and beyond which graft levels start leveling off due to the restrictions imposed on monomer diffusion by grafted chains.

The effect of monomer concentration on percent grafting is presented in Fig. 3. The grafting was carried out at 56 rd/s for monomer concentrations of 0.5 to 2.0 mol/L. It can be seen from the results that the degree of grafting increases with an increase in monomer concentration for all radiation doses. However, the plots show a slight leveling off at higher monomer concentrations. The increase in percent grafting with increasing monomer concentration may be understood from the fact that more

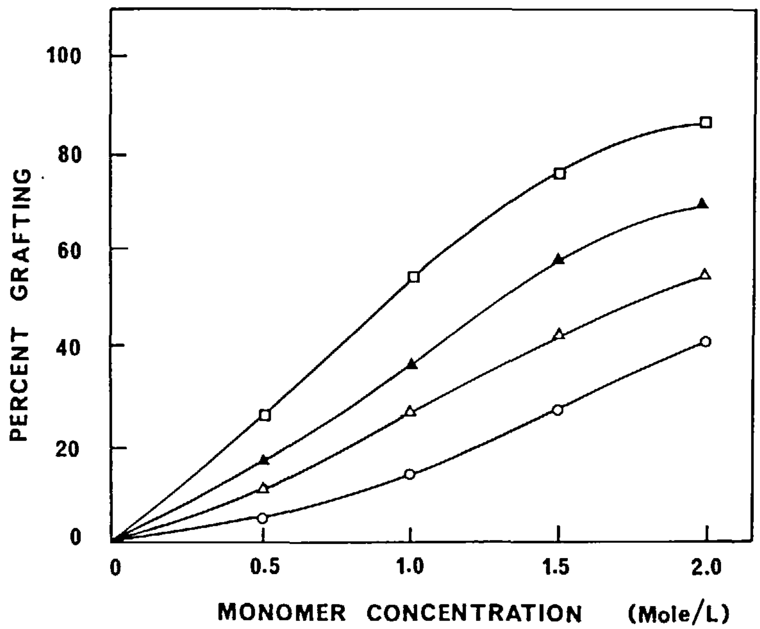

FIG. 3. Variation of percent grafting with monomer concentration at different doses: (○) 0.1 Mrd, (△) 0.15 Mrd, (▲) 0.2 Mrd, (□) 0.3 Mrd. Dose rate, 56 rd/s; solvent, chlorobenzene.

monomer is made available to the grafting sites. The grafting appears to be diffusion controlled in the present system. The grafted layer is initially formed on the film surface and then gradually moves inward into the polymer. This means that the monomer diffuses into the polymer bulk, followed by grafting to the active site. It seems that the grafted PHEMA chains restrict monomer diffusion to the initiating sites on the polymeric backbone only after a graft level of 60–65% is attained, i.e., at a monomer concentration of 1.5 mol/L, resulting in leveling off [14].

Figure 4 shows the effect of various solvents on the degree of grafting. Chlorobenzene was found to produce the greatest extent of grafting of all the solvents; water the least. Benzene and dichloroethane (DCE) gave intermediate amounts of grafting. The higher graft yields in chlorobenzene may be due to the higher swelling of monofilament which results in the availability of the maximum possible area for monomer diffusion

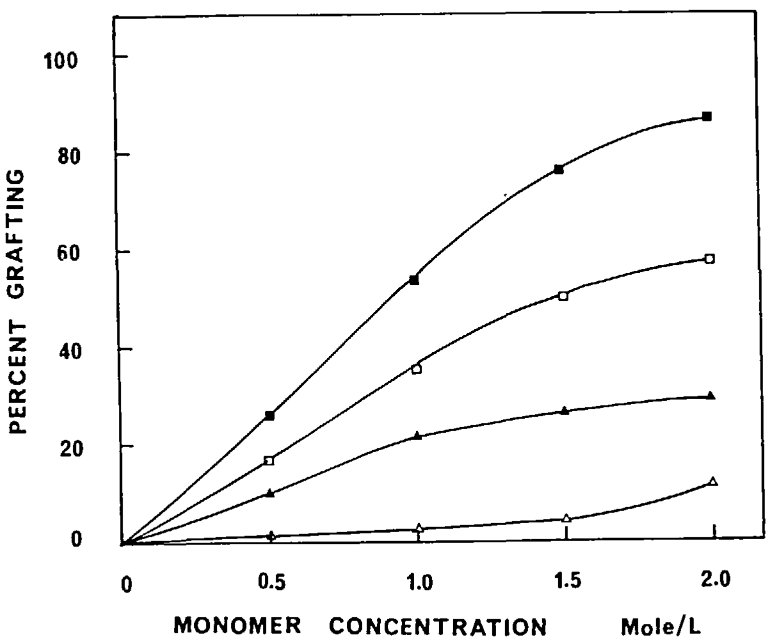

FIG. 4. Variation of percent grafting with monomer concentration in different solvents. (△) Water, (▲) dichloroethane, (□) benzene, (■) chlorobenzene; dose rate, 56 rd/s; dose, 0.3 Mrd.

into the polymer matrix. Benzene and DCE show less swelling and, hence, the degree of grafting is lower. Water shows very little graft yield even at 3.0 mol/L. This may essentially be due to the grafting taking place at the fiber surface since there is no swelling of monofilament in water.

The modified monofilament gave an intense blue color with methylene blue, which suggests the presence of PHEMA grafts in the polymer. The unmodified PP monofilament did not give any color with methylene blue. The color reaction of grafted monofilament is due to the polar interaction between methylene blue and the —OH group of the grafted PHEMA chain.

Further confirmation of grafted structure in polypropylene monofilament was obtained from IR spectroscopy. The spectra of grafted PP-*g*-PHEMA are presented in Fig. 5. The spectra of grafted samples show a strong band at 3000–3400 cm^{-1}, characteristic of the OH group of the grafted moiety. Another band at 1720 cm^{-1} in the spectra of the grafted sample is the carbonyl group of the ester linkage.

The swelling behavior of grafted monofilament is presented in Fig. 6. All samples show a degree of swelling which increases with an increase in percent grafting. These swelling characteristics suggest that the monofilament could perform as a polymeric hydrogel for suture application.

On the whole, the process of grafting HEMA onto PP monofilament

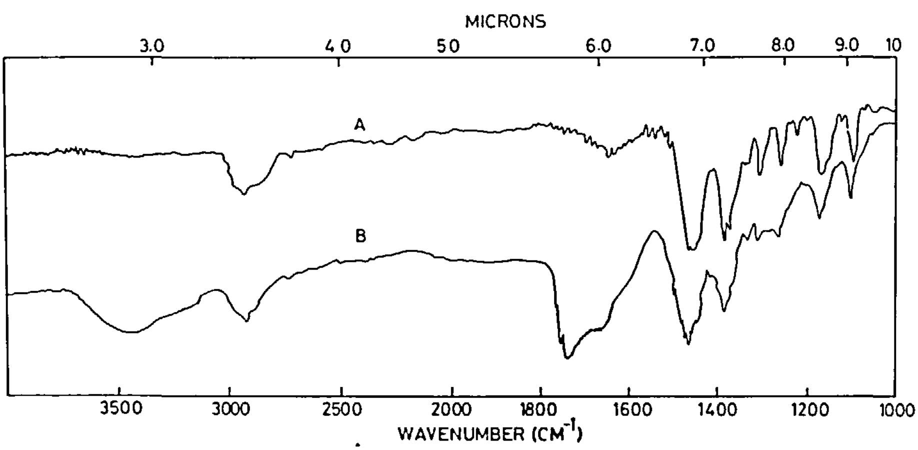

FIG. 5. Infrared spectra of unmodified polypropylene (A) and grafted polypropylene monofilament (B).

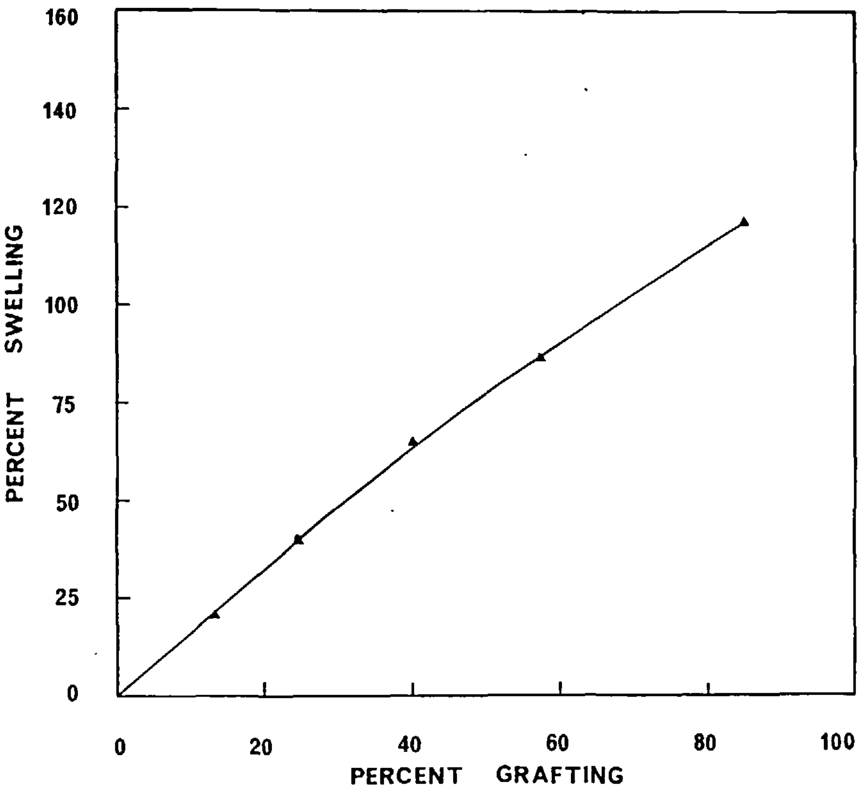

FIG. 6. Variation of percent swelling in water with degree of grafting.

provides an effective technique to produce colored sutures. A low dose rate accompanied by a low monomer concentration produces better graft levels and grafting efficiency. The further characterization of these suture materials by SEM and their biocompatibility evaluation *in vivo* is in progress.

REFERENCES

[1] M. F. Refojo, *J. Biomed. Mater. Res.*, *3*, 333 (1969).
[2] I. Michnevic and K. Kliment, *Ibid.*, *5*, 17 (1971).

[3] C. K. Akers, I. Dardik, and M. Wodka, *J. Colloid Interface Sci., 59*, 461 (1977).
[4] E. Nyilas, W. A. Morton, R. D. Cumming, D. M. Lederman, T. H. Chiu, and R. E. Bair, *J. Biomed. Mater. Res. Symp., 8*, 51 (1977).
[5] B. D. Ratner and A. S. Hoffman, *J. Appl. Polym. Sci., 18*, 3183 (1974).
[6] J. C. Delee, M. T. Smith, and D. P. Green, *J. Surg., 2*, 38 (1977).
[7] M. B. Orringer, H. D. Appleman, L. Argenta, E. Bove, and V. Cimmino, *Surg. Gynecol. Obstet. 144*, 67 (1977).
[8] M. Tollar, M. Stol, and K. Kliment, *J. Biomed. Mater. Res., 3*, 305 (1969).
[9] B. D. Ratner, A. S. Hoffman, and J. D. Whiffen, *J. Bioeng., 2*, 313 (1978).
[10] D. Cohn, A. S. Hoffman, and B. D. Ratner, *J. Appl. Polym. Sci., 31*, 1 (1987).
[11] H. B. Lee, H. S. Shim, and J. D. Andrade, *Am. Chem. Soc., Polym. Prepr., 13*, 729 (1972).
[12] C. M. Meaburn, J. L. Hosszu, and C. M. Coley, *Int. J. Appl. Radiat. Isot., 29*, 233 (1978).
[13] S. J. Gourlay, R. M. Rice, A. F. Heggeli, J. C. Eaton Jr., J. W. Hodge Jr., and C. W. R. Wade, *Trans. Am. Soc. Artif. Intern. Organs, 21*, 28 (1975).
[14] A. K. Mukherjee and B. D. Gupta, *J. Appl. Polym. Sci., 30*, 2643 (1985).
[15] A. K. Mukherjee and B. D. Gupta, *Ibid., 30*, 2253 (1985).
[16] A. K. Mukherjee and B. D. Gupta, *Ibid., 30*, 4455 (1985).
[17] J. E. Wilson, *J. Macromol. Sci.—Chem., A8*, 307 (1974).
[18] D. Cohn, A. S. Hoffman, and B. D. Ratner, *J. Appl. Polym. Sci., 29*, 2645 (1984).
[19] M. A. El-Azmirly, A. H. Zahran, and M. F. Barakat, *Eur. Polym. J., 12*, 195 (1976).
[20] Harpal Singh, PhD Thesis, Indian Institute of Technology, New Delhi, 1981.

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