Characterization of Poly(Vinyl Alcohol) Grafted with Acrylic Acid and Methylmethacrylate Using a Ce(IV) Glucose Redox System

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ABSTRACT: Poly(vinyl alcohol) (PVA) is a well-known biomedical polymer and is biocompatible. Methylmethacrylate and acrylic acid monomers were grafted onto PVA using a Ce(IV)–glucose redox system at three different temperatures (35, 45, and 55°C) under nitrogen atmosphere. More than 80% grafting could be achieved in the process. The grafted PVA was characterized through infrared spectra, thermal decomposition studies [thermogravimetric analysis (TGA) and decomposition thermal grafting (DTG)], differential scanning calorimetry (DSC), and scanning electron microscopy (SEM). The thermal stability and other properties of grafted PVA related to medical applications was found to be better than those of ungrafted PVA. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 677–683, 1999

Key words: PVA; grafting; TGA; DTG; DSC; SEM

INTRODUCTION

Biomedical polymers play an important role in the functioning of biological systems.[1,2] Biodegradable polymers and their applications have been reviewed by Sudesh Kumar.[3] One of the most important universal requirements of a biomedical polymer is its biocompatibility. Bachtsi et al.[4] examined the use of crosslinked poly(vinyl alcohol) (PVA) as a control delivery device for enzymes. PVA is a water-soluble polymer with no known health hazards. Considerable scope exists for effective improvement in the application of bioabsorbable polymers, such as methylmethacrylate (MMA)- and acrylic acid (AA)-grafted PVA. Method of chemical initiation permits surface modification of the matrix polymer. Graft copolymerization of MMA and AA onto PVA has been carried out with the initiating system involving Ce(IV) and glucose. Mechanisms of grafting have been clearly demonstrated.[5,6] Characterization of grafted polymers has been done using techniques of infrared (IR) spectra, thermal decomposition studies [thermogravimetric analysis (TGA) and decomposition thermal grafting (DTG)], differential scanning calorimetry (DSC), and scanning electron microscopy (SEM).

EXPERIMENTAL

MMA was washed with 5% NaOH solution followed by conductivity water. The monomers are dried with anhydrous $CaCl_2$, distilled under reduced pressure, and stored in the refrigerator for use. Ammonium ceric sulfate, glucose, PVA, and other reagents were used as received. Graft copolymerization was carried out at the desired temperature in a constant temperature bath with an accuracy of ± 0.1°C. PVA was soaked with a requisite quantity of monomer (MMA or AA) for about 15 min. Reactions were carried out in Pyrex

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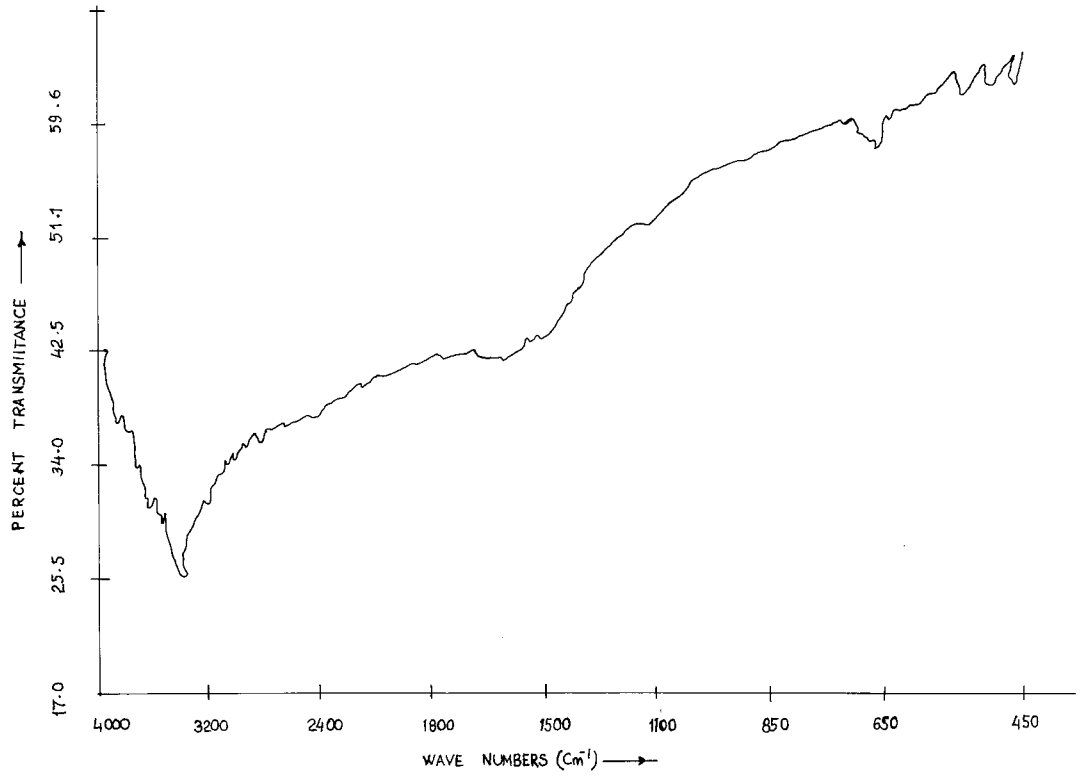

Figure 1 IR spectra of ungrafted PVA.

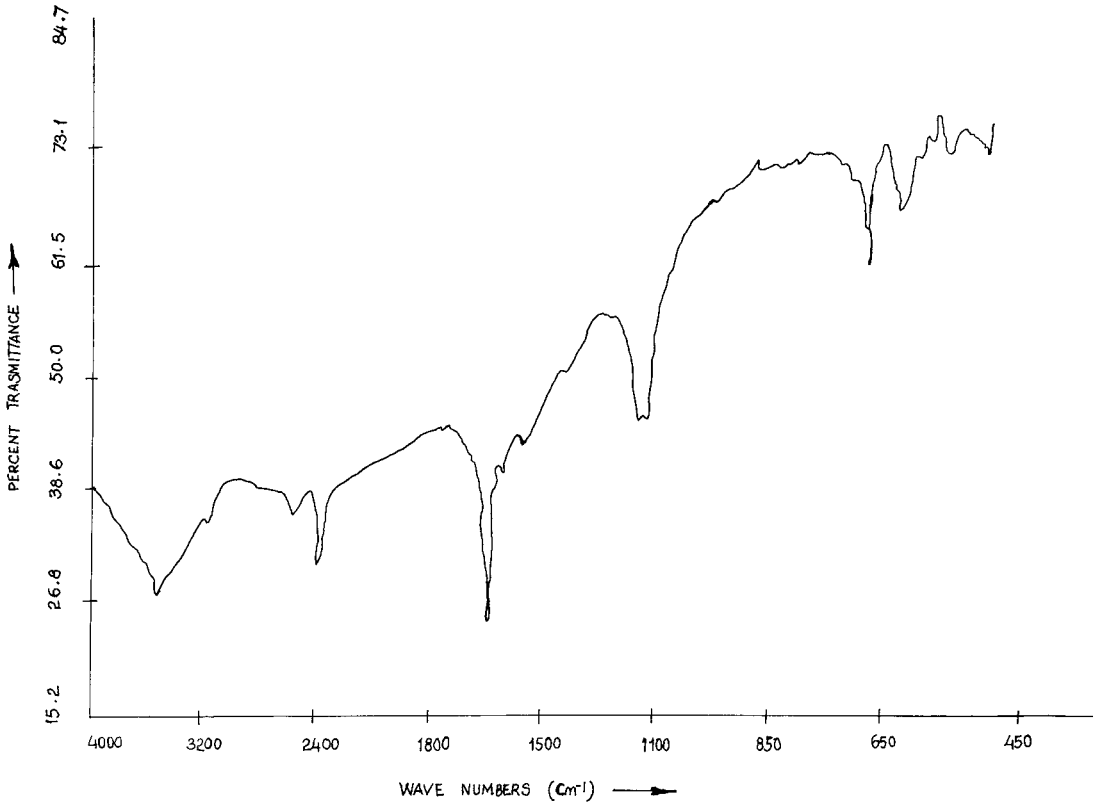

Figure 2 IR spectra of MMA-grafted PVA · $GY = 110\%$.

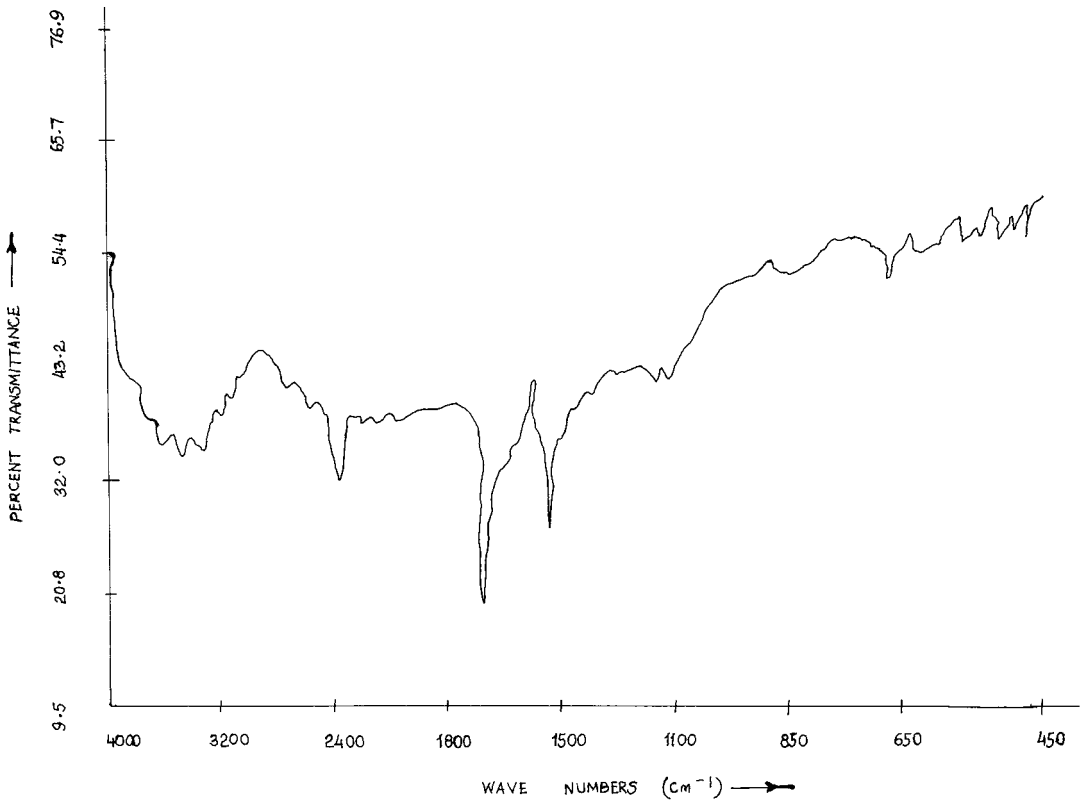

Figure 3 IR spectra of AA-grafted PVA · $GY = 82\%$.

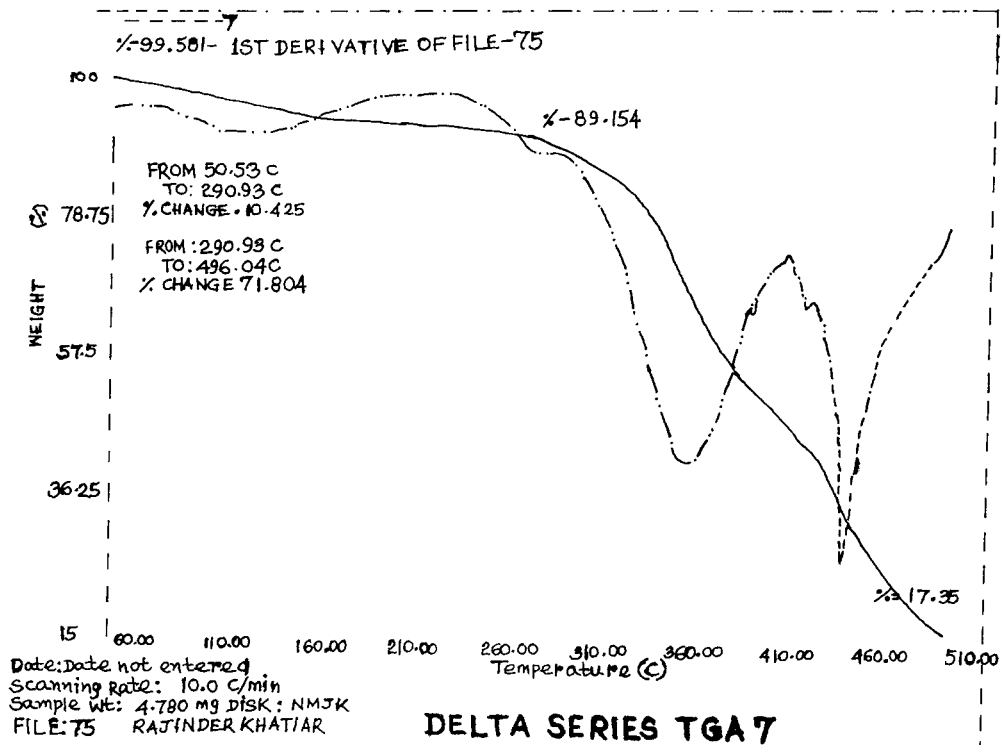

Figure 4 TGA and DTG of ungrafted PVA.

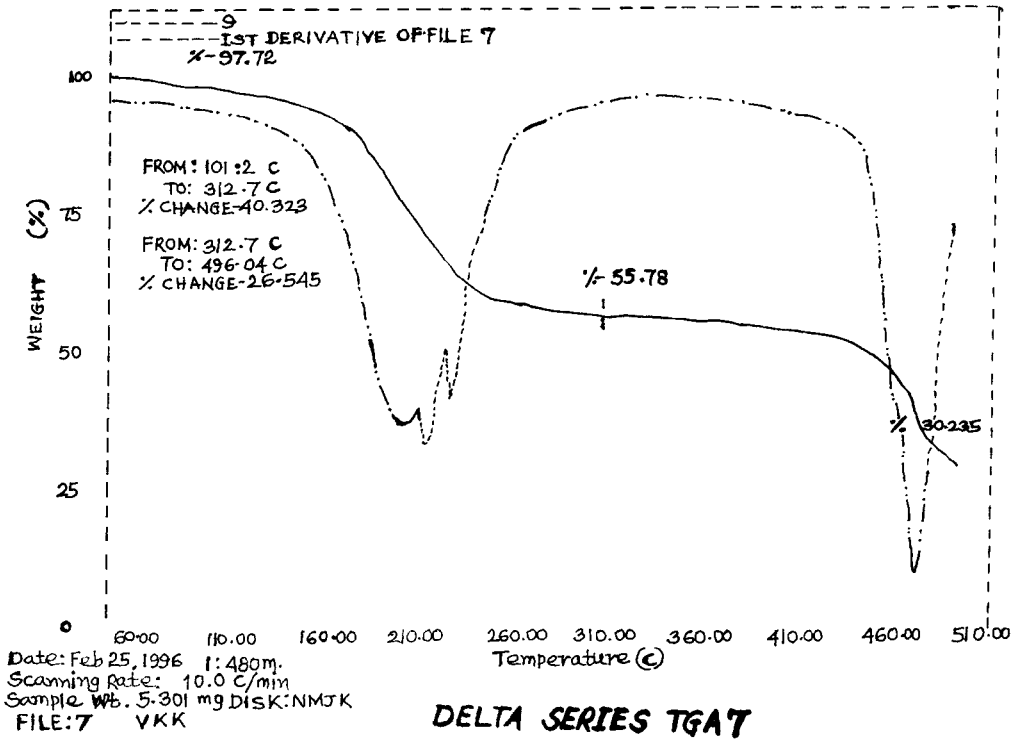

Figure 5 TGA and DTG of AA-g-PVA (GY) = 82%.

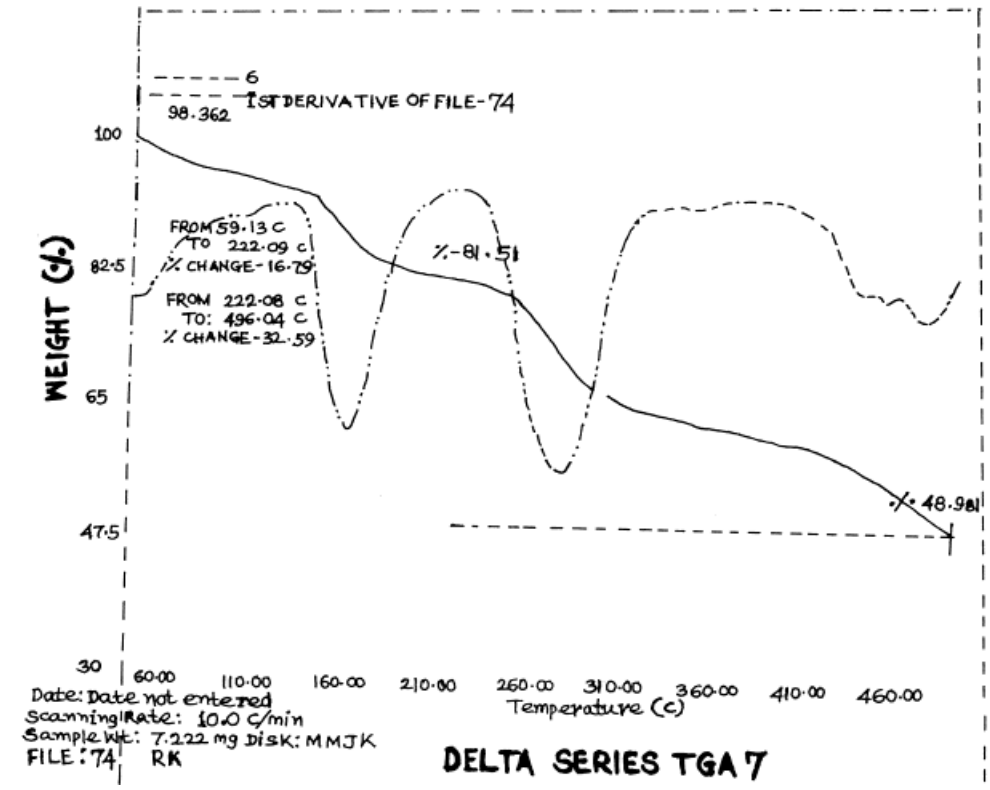

Figure 6 TGA and DTG of MMA-g-PVA (GY) = 95%.

Table I DSC Results of Polymer Samples

Sample Name and No.	Peak Maximum Temperature (°C)	Peak Start Temperature (°C)	Peak Area (Heat of Fusion) (J/gm)
PVA-1	195.03	180.23	34.76
PVA-2	193.36	178.65	35.27
PVA-3	191.33	175.02	33.20
AA-g-PVA (50%)			
(1)	152.85	133.51	33.09
(2)	150.64	128.31	43.30
(3)	148.20	131.16	47.85
AA-g-PVA (70%)			
(1)	159.91	123.69	57.58
(2)	154.46	125.32	25.44
(3)	154.22	115.62	147.05
AA-g-PVA (82%)			
(1)	149.70	130.09	29.88
(2)	151.83	139.58	24.06
(3)	149.82	129.89	25.50
MMA-g-PVA (67%)			
(1)	129.93	121.60	05.06
(2)	133.18	124.05	09.03
(3)	133.52	124.18	08.04
MMA-g-PVA (83%)			
(1)	139.27	126.21	114.07
(2)	241.27	221.06	99.09
(3)	241.44	221.63	91.31

vessels with $B_{24/29}$ standard joints equipped with gas inlet and outlet tubes. An appropriate quantity of reaction mixture containing PVA, monomer, glucose, H_2SO_4, and water was taken in the reaction vessel, and nitrogen gas was passed for 30 min. The requisite amount of ceric ammonium sulfate solution was added, and the time was noted. The reaction was carried out at three different temperatures: 35, 45, and 55°C. After the specified time interval, the reaction was arrested by quenching with ice-cold water. To remove homopolymer, samples were precipitated out with acetone. Finally, the samples were refluxed with acetone for about 6 h, or until a constant weight of grafted PVA was obtained:

$$\% \text{ graft yield} = \frac{(\text{dry weight of grafted PVA} - \text{dry weight of original PVA})}{\text{dry weight of original PVA}} \times 100$$

RESULTS AND DISCUSSION

Various techniques have been used to establish the evidence for real chemical grafting.

IR Spectra

IR spectra of ungrafted PVA, MMA-grafted PVA, and AA-grafted PVA were recorded by a Shi-

Table II SEM of Different Samples

Sample	Graft (%)	Magnification
PVA (two or more particles)		×50
PVA (surface of one particle)		×200
AA-g-PVA	82	×35
AA-g-PVA	82	×200
MMA-g-PVA	91	×150
MMA-g-PVA	91	×50
AA-g-PVA	69	×500
AA-g-PVA	69	×200
MMA-g-PVA	67	×500

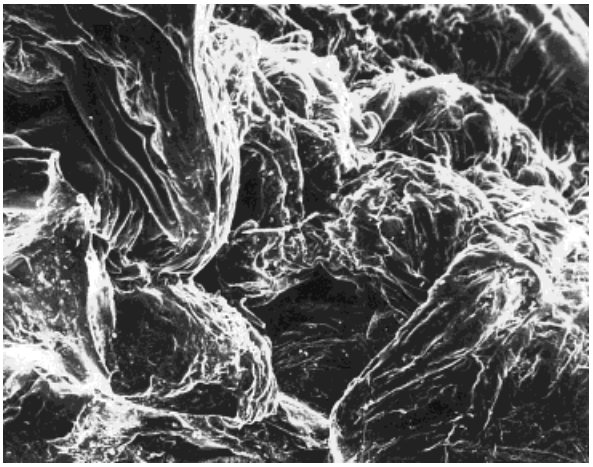

Figure 7 SEM of AA-g-PVA (GY = 82%) at ×35 on JSM-T330 A; recorded at 30 kV.

matzu IR 408 spectrophotometer in the form of nujol paste (Figs. 1–3). The spectrum of MMA-grafted PVA alcohol shows a characteristic band at 1720 cm^{-1}, indicating the presence of an easter group. The AA-grafted PVA reveals a characteristic band at about 1700 cm^{-1}, due to the presence of an acid group.

Thermal Decomposition Studies

Recently introduced high-resolution TGA[7] permits determination of kinetic data such as energy of activation and reaction order for each step. In the present investigation, the thermogravimetric experiments were carried out using a DuPont 951 TGA analyzer in a nitrogen atmosphere at a heating rate of 10°C/min. In the case of ungrafted PVA, the decomposition starts at 60.5°C (Fig. 4) whereas AA-grafted PVA starts decomposing at a higher temperature [e.g., 101.2°C (Fig. 5)]. This result indicates that grafting increases the decomposition temperature and heat resistance of PVA. However, MMA-grafted PVA, having a low decomposition temperature (59.1°C), does not contribute to the thermal stability of grafted polymer (Fig. 6).

DSC

The ungrafted PVA, AA-grafted PVA, and MMA-grafted PVA with different graft yields were taken for the study of DSC thermograms. Peak starting temperature, peak maximum temperature, and peak area from the thermograms are given in Table I.

In the case of grafted copolymers, these values were found to be different for three samples of the same grafted polymer. The dependence of these parameters on graft yield cannot be generalized with increasing or decreasing order. This nature

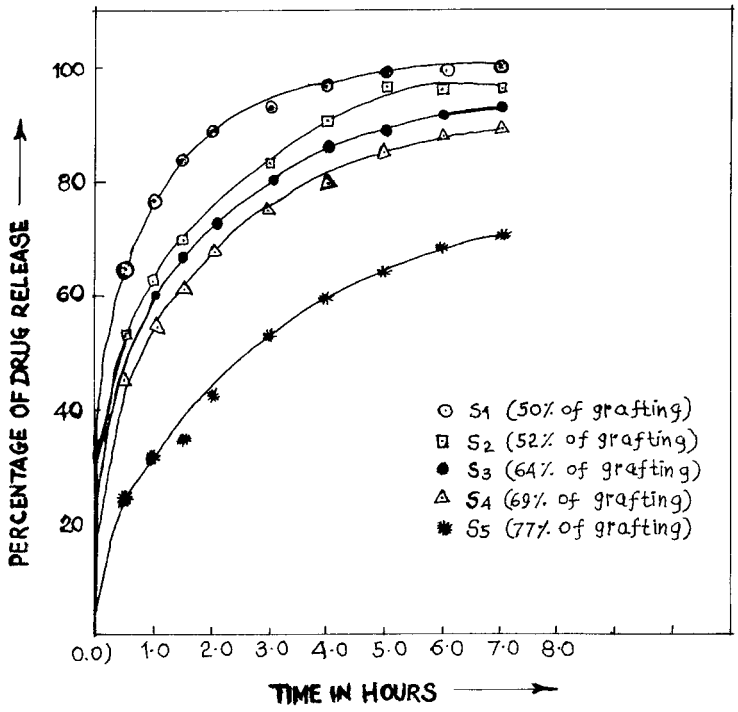

Figure 8 Cumulative percentage of tetracycline released from drug-immobilized AA-g-PVA.

of graft copolymer indicates nonhomogeneity in the sample of grafted PVA. However, grafting decreases the glass transition temperature of the polymeric samples.

SEM

The grafted and ungrafted PVA samples were coated with a thin layer of gold on the surface of interest to provide electrical conductivity. A JSM T 330A scanning microscope was used for this coating. The micrographs were photographed at different view of the same sample at different magnification. Table II shows different conditions to which samples were subjected before being scanned under an electron microscope. The photomicrograph shows the distinct presence of grafts. The individual graft shoots are no longer visible; instead, a mass of smooth polymer covering is obtained. Figure 7 presents a photomicrograph showing the morphology of the grafted samples.

CONCLUSIONS

In addition to the various methods of characterization, allied experiments on release of drugs like tetracycline and microbial studies were carried out (Fig. 8). *In vitro* release of immobilized tetracycline was studied spectrophotometrically. In the present experiment, the elution or release of tetracycline was studied in 0.9% NaCl solution. The drug-immobilized sample was taken in 900 mL of 0.9% of NaCl solution in the tablet dissolution test apparatus. The experimental temperature was 37°C. The solution was mechanically stirred at a speed of 50 rpm. Drug release was studied periodically in an UV-VIS spectrophotometer. The release of drugs in the first few hours was followed by a slow release. On the other hand AA-grafted PVA shows greater inhibition than the ungrafted sample, possibly due to the antimicrobial property of poly(acrylic acid).

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