Graft Copolymerization of PU Membranes with Acrylic Acid and Crotonic Acid Using Benzoyl Peroxide Initiator

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ABSTRACT: To improve water wettability of polyurethane (PU), graft copolymerization with acrylic acid (AA) and crotonic acid (CA) was performed using a benzoyl peroxide (BO) initiator. The grafting reaction was carried out by placing the membranes in aqueous solutions of AA and CA at constant temperatures. Variations of graft yield with time, temperature, initiator, and monomer concentrations were investigated. The optimum temperature, polymerization time, monomer, and initiator concentrations for AA were found to be 70°C; 3 h; 1.5 *M;* 5.0×10^{-2} *M,* and for CA 70°C; 1 h; 1.5 *M;* 4.0×10^{-2} *M,* respectively. The grafting membranes were characterized by FTIR spectroscopy and scanning electron microscopy (SEM) analysis, and the effect of grafting on equilibrium water content (EWC) of PU membranes was obtained by swelling measurements. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 2690–2695, 2001

Key words: graft copolymerization; polyurethane membranes; acrylic acid; crotonic acid; SEM; FTIR; equilibrium water content

INTRODUCTION

Segmented polyurethanes (PU) are widely used in both commercial and experimental blood-contacting applications, such as catheters, heart assist pumps, and chambers for artificial hearts because of their physiological acceptability, relatively good blood tolerability, excellent stability over long implant periods, and excellent physical and mechanical properties.[1–4] According to their properties, PU are useful as wound dressing and controlled release materials.[5–7] These properties are related to the surface chemistry and physics of the PU implants, and vary as a result of variation in the composition of the prepolymer and also the casting procedure. Besides all of these positive properties, hydrophobicisity of PU is a disadvantage in some medical and industrial applications.

In our previous studies, we had investigated structural and surface characterization, interaction with antimicrobial agent, response to cell attachment, and growth and drug diffusion behaviors of a series of PU membranes.[8–13] In this study, we aim to develop the wettability of those PU membranes in via graft copolymerization with some hydrophilic vinyl monomers.

There is much interest in modifying the surface of common polymers to make them more hydrophilic. Example benefits of such modifications include having wettable surfaces for dye adsorption, better adhesion to metal films, enzyme immobilization, weathering, blood compatibility, and less tissue damage for intraocular lenses.[14] Several different methods may be used for surface modification, for example, oxidation by chromic acid, flame or corona discharge, plasma treatment, and surface grafting of polar monomers.[15] Surface grafting may proceed by a free radical

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mechanism where the free radicals abstract hydrogen atoms from the polymer. Macroradicals are then formed and these radicals can act as grafting sites for vinyl functional monomers. Free radicals can be generated by several different methods, for example, UV or γ-radiation, Ce^{+4} ions, H_2O_2 or peroxide initiators.[15–18]

It is known that the graft copolymerization of hydrophobic polymers with various hydrophilic vinyl monomers is a suitable method to obtain more hydrophilic polymeric materials.[14–18] Therefore, in this presented study, we aim to modify hydrophobic PU membranes via graft copolymerization with acrylic acid (AA) and crotonic acid (CA) monomers using benzoyl peroxide (BO). Our previous studies were focused to develop and characterize a series of PU membranes. This is an interesting related study for the materials PU-AA and PU-CA pairs, which are used for the first time.

EXPERIMENTAL

Preparation of PU Membranes

PU membranes were prepared by solvent-casting procedure performed with polyether urethane (Pellethane® 2363-80A, Up-John) using dioxane (Aldrich) solvent. According to the literature, equal volumes of polymer–dioxane solutions of 8% (g/100 mL) concentration were poured into identical Petri dishes and left at 25°C until the solvent was completely evaporated to obtain a homogenous structure.[8,9] Obtained membranes were removed from the surface of Petri dishes, washed thoroughly with distilled water, cut into equal pieces, dried at 40°C under vacuum for 48 h, and weighed.

Graft Polymerization

Graft polymerization procedure were performed according to the literature.[15–18] To obtain the effect of polymerization temperature (T) on grafting yield, polymerization reaction was investigated by changing the temperature from 30 to 90°C at constant polymerization time (t = 3 h), monomer [M] and initiator [BO] concentrations (1.5 M and 4.0×10^{-2} M). PU membranes at known mass were placed into polymerization tubes containing 1.5 mL benzoyl peroxide (BO)–acetone (Merck) solutions of 4.0×10^{-2} M. The polymerization tubes were placed into water bath at constant temperature (30–90°C). After thermal equilibrium is reached 28.5 mL monomer (Aldrich)–water solutions of 1.5 M concentration was added into polymerization tubes, and the polymerization procedure was performed for 3 h. At the end of the polymerization time the grafted membranes were taken out. Residual solvent, monomer, and homopolymer were removed from the membranes by washing with water until constant weight. The grafted membranes were dried at 40°C under vacuum for 48 h and weighed. The graft yields (%) were calculated from the equation given below

$$\text{Graft yield } (\%) = \frac{m - m_o}{m_o} \times 100 \qquad (1)$$

where m_o and m are masses of the ungrafted and grafted membranes, respectively.[19–21]

To obtain the effect of polymerization time, monomer, and initiator concentrations on grafting yield, the procedure were repeated by changing polymerization time (20–240 min.), concentrations of the monomer (0.5–3.0 M) and initiator (1.0×10^{-2}–6.0×10^{-2} M), and the percent yields were calculated by using eq. (1).

Scanning Electron Microscopy (SEM) Analysis

SEM analysis of 200 Å gold-coated ungrafted and grafted membranes were performed by using a JEOL model JSM 840A SEM.

FTIR Spectrum

FTIR spectra of AA and CA and grafted membranes were recorded using a Perkin-Elmer 1710 model spectrophotometer.

Equilibrium Water Content (EWC) Determination

The EWC values were determined from the wet (m_w) and dry (m_d) mass of the grafted membranes. To calculate the EWC values, the equation were used given below. m_w and m_d values were determined from swollen membranes in distilled water at room temperature to constant weight and dried membranes at 40°C for 48 h, respectively.[19–21]

$$\text{EWC } (\%) = \frac{m_w - m_d}{m_d} \times 100 \qquad (2)$$

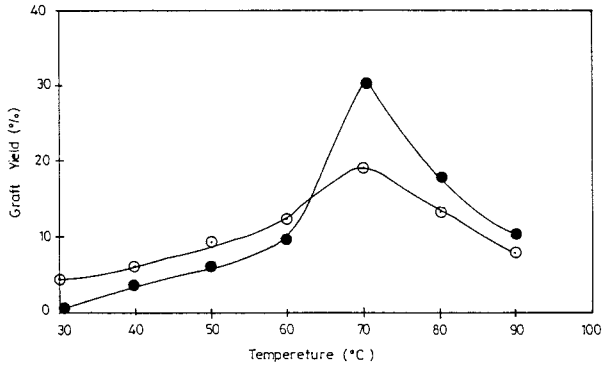

Figure 1 Effect of temperature on graft yield of AA (●) and CA (○) monomers (t = 3 h, [M] = 1.5 M, [BO] = $4.0 \cdot 10^{-2}$ M).

RESULTS AND DISCUSSION

Effect of Polymerization Temperature

The effect of temperature on the graft polymerization of PU membranes was studied within the range of 30–90°C. As the temperature was increased from 30 to 90°C the yields increased first, reached a maximum value, and then decreased (Fig. 1). The increase in the graft yield may be attributed to the increase of the mobility and diffusion rate of monomer and initiator molecules. The maximum graft yield was observed at 70°C for both monomers. The grafting yield of AA was found to be higher than the grafting yield of CA at the temperature higher than 70°C. The decrease of the graft yield after that temperature was due to the favored chain-termination reactions and increase in the formation of homopolymer, which plays a more important role than does graft copolymerization at high temperatures. Similar results were also reported in the BO and H_2O_2-initiated graft copolymerization of AA on poly(ethylene terephatalate) fibers.[19,20]

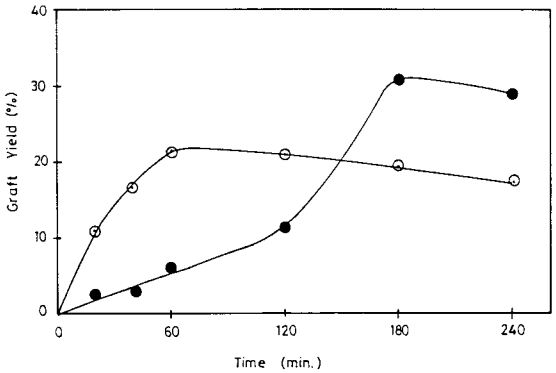

Figure 2 Variation of graft yield of AA (●) and CA (○) with polymerization time (T = 70°C, [M] = 1.5 M, [BO] = $4.0 \cdot 10^{-2}$ M).

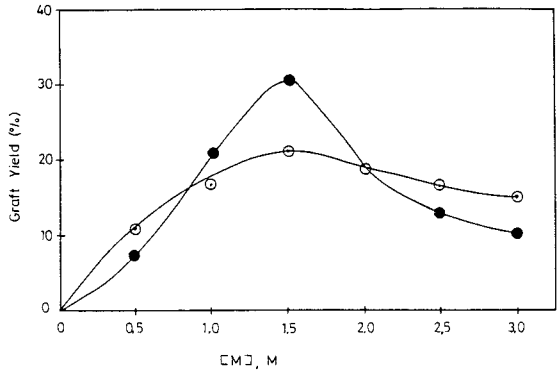

Figure 3 Variation of graft yield of AA (●) and CA (○) with monomer concentration, [M] (T = 70°C, [BO] = $4.0 \cdot 10^{-2}$ M, t = 3 h for AA and 1 h for CA).

Effect of Polymerization Time

The effect of polymerization time on grafting yield was investigated by changing the polymerization time (from 20 to 240 min) at constant polymerization temperature (70°C), monomer (1.5 M), and initiator (4.0×10^{-2} M) concentration. As shown in Figure 2, graft yields were first increased with an increase in polymerization time and than reached a saturation grafting value at 3 and 1 h for AA and CA, respectively. The maximum grafting values were obtained 30.22% for AA and 21.0% for CA at 70°C. The results are similar to the literature.[15–20]

Effect of Monomer and Initiator Concentrations

Effect of monomer concentration on graft yield was studied by changing the concentration from

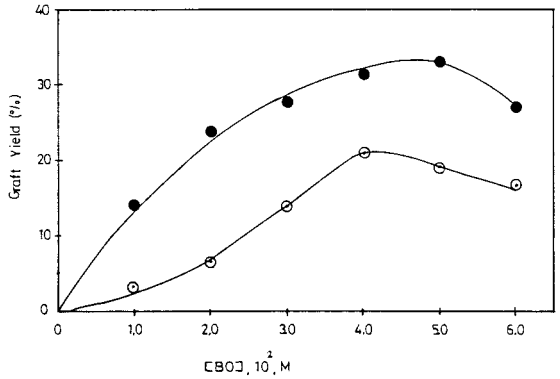

Figure 4 Variation of graft yield of AA (●) and CA (○) with initiator concentration, [BO], (T = 70°C, [M] = 1.5 M, t = 3 h for AA and 1 h for CA).

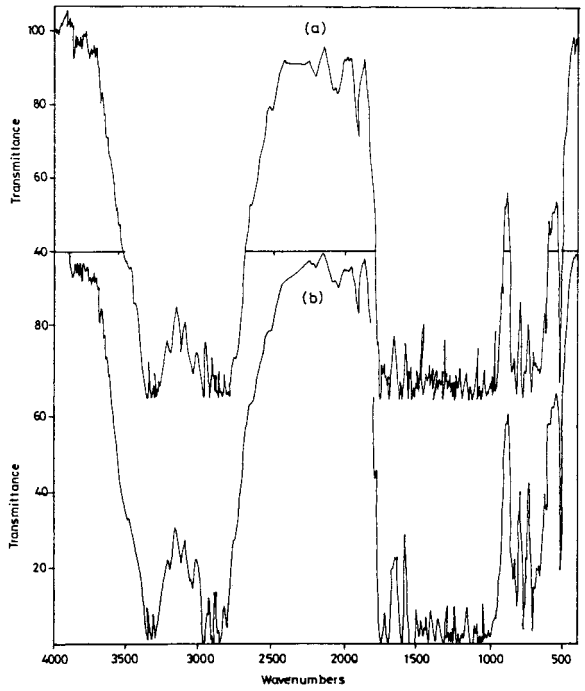

Figure 5 FTIR spectra of AA (a) and CA-grafted (b) membranes.

0.5 to 3.0 *M* at constant temperature (70°C), time (3 h for AA and 1 h for CA), and initiator concentration (4.0×10^{-2} *M*). As shown from the results graphed in Figure 3, grafting yields were increased first with increasing the monomer concentration, reached a maximum value, and than decreased. As the monomer concentration increases, the diffusion of monomer molecules into the PU structure increases, leading to a higher graft yield. Decreasing in the grafting values can be explained by the enhancement of homopolymer formation at high monomer concentrations.[18–20] The maximum graft yield were obtained for both monomers at the concentration of 1.5 *M*.

Table I Variation of EWC % Values of AA and CA-Grafted Membranes with Grafting Temperature

Temp. (°C)	30	40	50	60	70	80	90
AA	4.7	6.5	8.7	10.2	14.1	11.0	8.4
CA	2.9	4.6	5.9	6.3	9.8	6.5	5.7

Figure 4 represents the effect of initiator concentration on grafting yield. Evidently, the percent grafting increased significantly as the BO concentration increased from 1.0×10^{-2} to 6.0×10^{-2} *M*. A further increase in BO concentration decreased the graft yield. The free radicals occurred as a result of the decomposition of BO taking place in various reactions in the polymerization media. The increase in the concentration of BO increases the chance of hydrogen abstraction from PU backbone and the chain transfer reactions of poly(AA)/or poly(CA) homopolymer chains with PU. In both cases the graft yield increases. However, the exess increase in the concentration of BO causes the free radical species formed from decomposition of BO ($C_6H_5COO^{\bullet}$

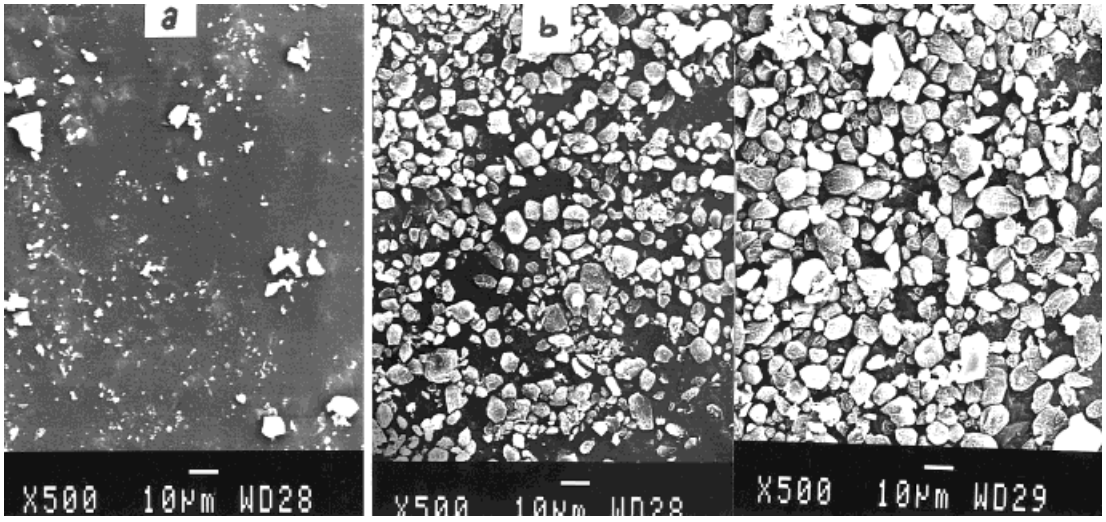

Figure 6 SEM photographs of ungrafted (a), AA grafted (b), and CA-grafted (c) membranes.

Table II Variation of EWC % Values of AA and CA-Grafted Membranes with Grafting Time

Time (min)	20	40	60	120	180
AA	2.6	2.9	4.8	6.2	14.1
CA	7.2	8.9	9.8	8.7	8.2

and/or $C_6H_5^{\bullet}$) to give termination reactions with PU macroradicals or growing polymer chains or combination reactions between them, and consequently, the graft yield decreases.[19–23]

FTIR Spectrum

FTIR spectra of AA and CA grafted membranes were presented in Figure 5. Both of the spectra have similar absorption peaks at 1070–1150 cm^{-1} (C—O stretching); 1690–1740 cm^{-1} (urethanes groups); 1650–1710 cm^{-1} (C═O stretching); 2880–2890 cm^{-1} (C—H stretching). In addition to the above absorptions, AA and CA-grafted PU membranes are also characterized with the adsorption at 3300–3500 cm^{-1} (N—H stretching in primary amide groups) and 2850–2960 cm^{-1} (CH_3 groups); 1260–1410 cm^{-1} (O—H bendings), respectively.[24]

SEM Analysis

Scanning electron micrographs of ungrafted, AA, and CA-grafted membranes were presented in Figure 6. It was observed from the SEM results that the ungrafted PU membrane surfaces have a smoother and more homogeneous appearance than grafted membranes. Heterogeneous appearance of AA and CA grafted surfaces are another proof of grafting.

Equilibrium Water Content (EWC) Determination

EWC values calculated from the eq. (2) are presented in Tables I–IV. EWC percent of ungrafted PU membrane is found to be 2.1%. As seen from the results, EWC % values of both grafted membranes increases according to the grafting percent. It is found that the hydrophilicities of AA grafted membranes are higher than CA-grafted membranes. These results show that the grafting with AA and CA increases hydrophilic character of PU membranes.

Table III Variation of EWC % Values of AA and CA-Grafted Membranes with Monomer Concentration, [*M*]

[*M*], (*M*)	0.5	1.0	1.5	2.0	2.5
AA	5.2	9.2	14.1	11.2	9.8
CA	4.2	6.7	9.8	8.6	8.2

Table IV Variation of EWC % Values of AA and CA-Grafted Membranes with Initiator Concentration, [BO]

[BO] · 10^{+2}, (M)	2.0	3.0	4.0	5.0	6.0
AA	6.2	9.2	11.0	14.1	12.2
CA	2.7	5.6	9.8	7.4	6.1

CONCLUSION

In this study, the graft copolymerization of PU membranes with AA and CA monomers by using BO initiator were performed. The polymerization conditions were investigated, and the optimum conditions were found to be 70°C and 1.5 *M* of monomer concentration. The maximum graft yield values were obtained 30% (for AA) and 20% (for CA) approximately. The existence of graft polymerization was proved in via FTIR spectra and SEM analysis. The effect of grafting on EWC of the grafted membranes was also determined.

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