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Surface Modification of Polyurethane with Acrylamide by Plasma Radiation and its Cellular Investigations

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ABSTRACT

Poly urethane as a biomaterial used for medical applications. In this study, polyurethane surface grafted with to acrylamide by oxygen plasma radiation. Grafted surface were investigated by ATR-FTIR, SEM, Zeta potential and cell culture analyses. ATR-FTIR results and SEM images showed presence of acrylamide groups and successful grafting on the polyurethane surface. Cellular culture results showed more adhesive and proliferate of fibroblast cells on the acrylamide grafted polyurethane surface than the control groups. The acrylamide grafted polyurethane surface can be used for tissue engineering and medical applications.

Key words: Polyurethane, Acrylamide , Grafting , Plasma radiation, Surface modification.

INTRODUCTION

Polyurethane (PU) is a hydrophobic polymer without bioactive fragments, which might limit its *in vivo* application. To achieve positive cell–biomaterial interaction, functional groups or biomacromolecules have been immobilized onto polymer for direct tuning of surface without altering their bulk properties.[1-6] Biomaterials wettability is an important factor in the surface modification of materials. Surface modification of hydrophobic polymer surfaces can be achieved by wet (acid, alkali), dry (plasma) and radiation treatments (ultraviolet radiation and laser).[7-10] Non thermal and low pressure plasma have been used in a series of surface treatment applications. The majority of plasma-assisted technologies are based on low pressure processes.[11] The treatment of polymeric materials with plasma is a frequently-used technique to accomplish surface modifications that affects chemical composition as well as surface topography. Moreover, microwave discharges are routinely employed in the processing of materials to deposit films as well as coatings.[12,13] In this work , the modified polyurethane were obtained with acrylamide grafting through the plasma radiation method with oxygen gas. The samples were evaluated by attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR), scanning electron microscope (SEM), and zeta potential, and also the cell culture with fibroblast cells.

MATERIAL AND METHODS

Twenty five ml solution of dimethylformamide (Sigma Co.) poured in 50 ml tube then 2.5 g polyurethane (Bayer Co.) added to the solution and was well stirred for 12 h in order to obtained homogeneous solution. The solution poured in Petri dish and kept at 25°c for a few days to remove the solvent. In our current experimental observation, we used a plasma source (K1050x and Emitech) to modify the surface of polyurethane samples. The samples were placed in plasma chamber and exposed to oxygen gas for 60, 120 and 180s. The irradiated samples at various times were investigated by structural analysis and microscopic investigations. The plasma surface treatment was reached in induced plasma with

surface wave at power level of 60 W. The acrylamide solution with to distinctive concentration were poured in a baker, then the modified polyurethane samples were placed in and immersed in the acryamide solution. The samples degassed by nitrogen. This process was followed to increase the efficiency of the free radical polymerization, Then, the samples were brought out and washed by distilled water and were put in distilled water for 72 hours and Soxhleted for removing the ungrafted monomer, then were taken out for analysis

ATR - FTIR Analysis

For surface identification of modified samples, the samples were studied before and after surface modification by an infrared spectrometer device (Bruker IFS 48). For this study, the samples must be cleaned before being used in the study.

Scanning electron microscopy

The surface characteristics of various grafted and ungrafted films were studied by scanning electron microscopy (SEM; Cambridge Stereo-scan, model S-360; Cambridge Instruments, Wetzlar, Germany) to analyze the changes in the surface morphology. The films were first coated with a gold layer (Joel fine coat, ion sputter for 2 hours) to provide surface conduction before their scanning.

Zeta potential study

Zeta potential of surfaces was studied by Anton Paar analyzer. The samples were sectioned in distinctive dimension (thickness: 300 micron; length:40 mm and width:20 mm) and analyzed at 25°c and Ph:6.5-7.

Cellular study

For cellular analysis, fibroblast cell suspension (L929) from mouse tails was prepared according to International Organization for Standardization 10993 standards. The polyurethane surfaces were well cleaned and sterilized. Individual samples were placed in Petri dishes using a sterilized pincer; 3 cc of the cell suspension was removed by pipette and poured into the control and experimental samples. Thereafter, all of the samples were placed separately in a Memmert incubator at 37°C for 48 hours. The samples in the polystyrene Petri dish were removed from the incubator after 48 hours and studied using an Eclipse TS-100 photonic microscope (Nikon, T-B 2.5x, Japan).

RESULTS

ATR-FTIR Study

ATR-FTIR spectra results of the un-grafted and acrylamide grafted polyurethane samples have been shown in Fig. 1. The ATR-FTIR spectrums of polystyrene surface have been shown below Fig. 1a. The Polyurethane picks characteristics include 3300-3500 cm^{-1} indicating primary amine groups and 1690-1730 cm^{-1} indicating C=O groups and 2800-3000 cm^{-1} indicating CH3 groups. All these picks are found in acrylamide grafted polyurethane samples but secondary amine groups indicated 3300-3500 cm-1 for the acrylamide grafted samples (Fig. 1b). This conclusion shows grafting between the acrylamide and the polyurethane surface occurs by activation of plasma radiation.

Surface morphology study

Fig. 2 show SEM images from the un-grafted polyurethane and plasma modified samples and the grafted sample in the different radiation times. The Fig. 3 shows the surface morphology (cross-section) for the grafted sample in the different radiation times. The SEM image of un-treated polyurethane sample shows white spots and surface roughness due pollution and production process. The Fig. 2b shows the smooth surface morphology for the plasma modified polyurethane. The Fig. 2c-e show surface roughness due acrylamide grafting on the plasma modified polyurethane. The graft thickness average for the

Table 1: Zeta potential of the un-grafted and plasma modified and the grafted samples.

Sample	un-grafted PU	plasma modified PU	grafted PU
Zeta potential (mv)	-18.59	-25.89	-16.53

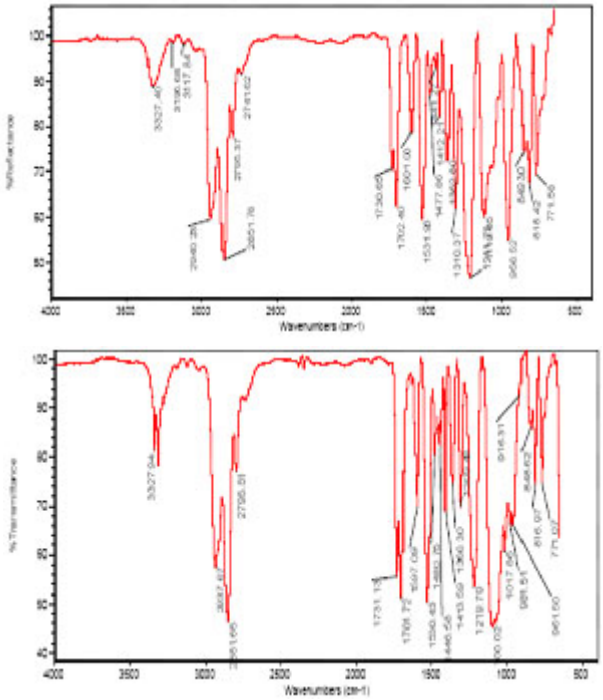

Fig. 1: Spectra of ATR-FTIR of normal polyurethane (A), Acrylamide grafted polyurethane at 180 s (B).

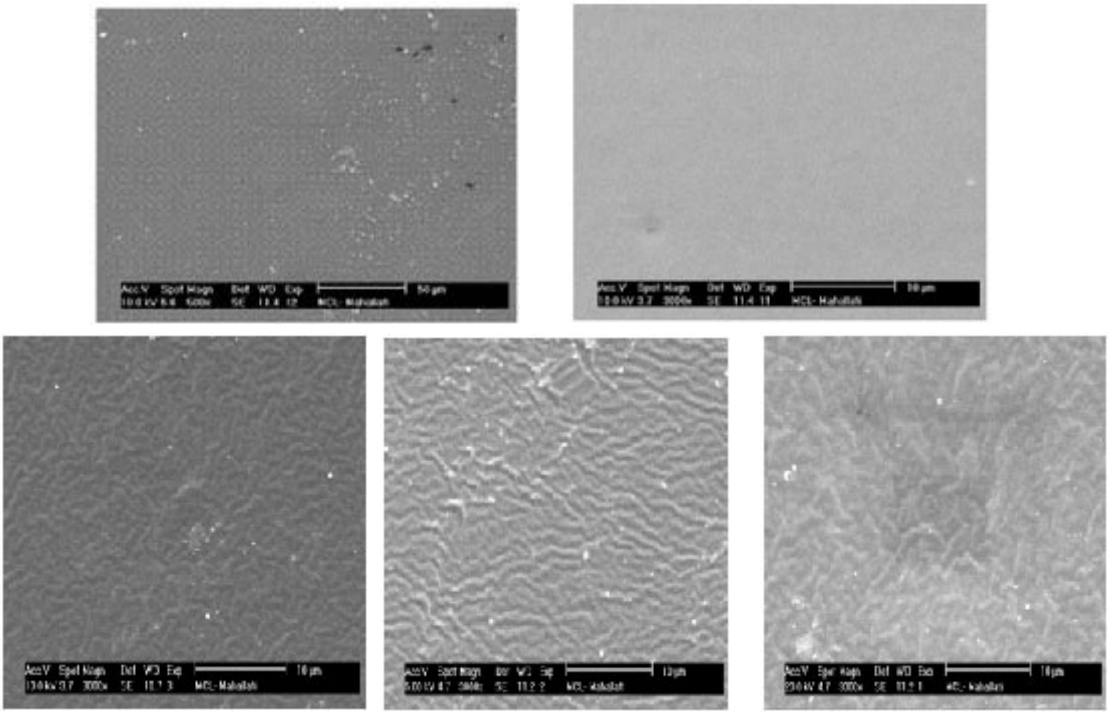

Fig. 2: Scanning electron microscopy of untreated polyurethane (a) oxygen-plasma modified polyurethane(b) acrylamide grafted polyurethane surface at different radiation times 60s (c) ; 120 s (d) and 180 s (e). MAG:3000X .

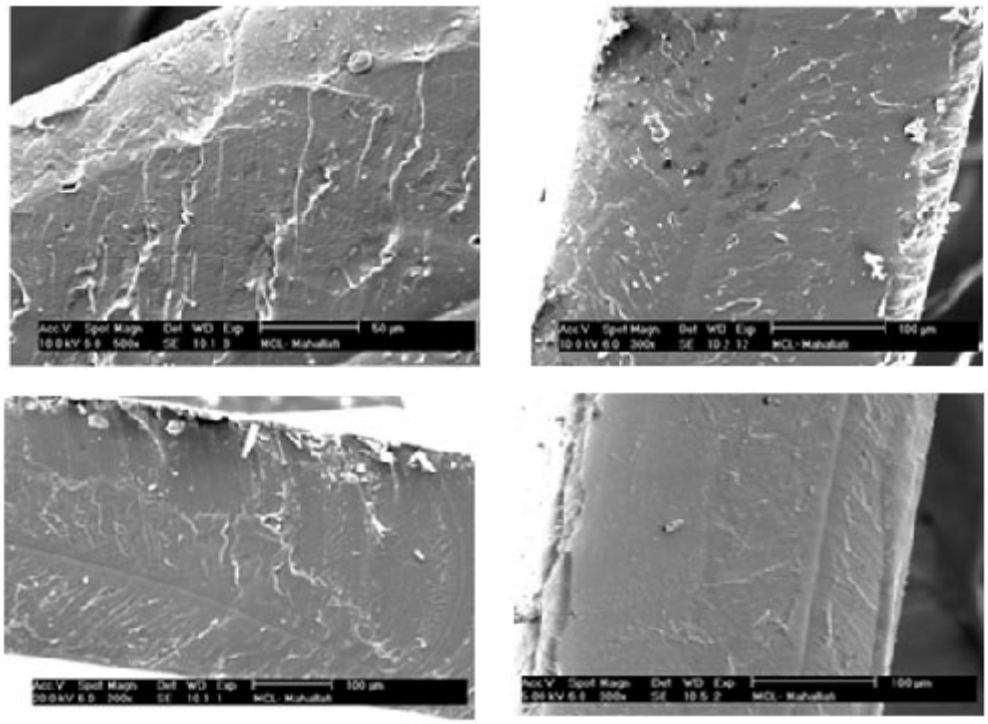

Fig. 3: Scanning electron microscopy from cross- section of acrylamide grafted polyurethane surface at different radiation times. Un treated (a) ; 60s (b) ; 120 s (c) and 180 s (d).

Fig. 4 : The culture of fibroblast cells on the control sample (a); Un treated PU (b) ; plasma modified PU at 60 s (c); plasma modified PU at 120 s (d); plasma modified PU at 180 s (e); acrylamide grafted polyurethane surface at different modified times (60s (f) ; 120 s (g) and 180 s (h)).

grafted samples obtained about 8 micrometer that grafting showed in Fig. 3.

Zeta potential results

Table 1 shows zeta potential of the un-grafted polyurethane and plasma modified samples and the grafted sample. The zeta potential of the un-grafted polyurethane obtained -18.59 mv and for the plasma modified samples about -26 mv. This result demonstrated presence of oxide and peroxide negative groups on the oxygen plasma modified polyurethane surface. The grafted polyurethane samples have positive potential than the other samples due acrylamide grafting on the polyurethane surface.

Cellular results

Fig. 4 shows cellular assay for TCPS (control, 4a), un-treated PU film (4b), plasma modified at different times (60, 120 and 180 s) and acrylamide grafted PU surface. The results showed high viability for plasma modified and acrylamide grafted samples than un-treated polyurethane. The modified samples with plasma in longer times showed a better viability. Cellular Images showed high cell growth on the grafted surfaces, especially those grafted with active gas in longer times.

CONCLUSION

In this study, polyurethane surface modified with to oxygen plasma radiation and acrylamide and investigated by different analyses. The ATR-FTIR and SEM and zeta potential analyses well demonstrated presence of acrylamide grafting on the modified surface. Microscope images showed much surface roughness of modified and grafted samples at higher times. These differences could be related to the physical modification or roughness of modified samples with oxygen plasma , also much radical sites at higher times. Cellular investigations with fibroblast cells showed better adhesion, growth, and viability of acrylamide grafted PU, especially acrylamide grafted PU at 180s modification with oxygen plasma. Therefore, the results indicated that cell adhesion increased by acrylamide grafting on the polyurethane surface. These modified surfaces could be used as biomaterials in medical application.

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