

Surface Structure of Radiation-Grafted Polyethylene-g-Polyacrylamide Films

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Received 22 January 2001; accepted 30 January 2002

ABSTRACT: Modification of polyethylene films was carried out by radiation-induced graft polymerization of acrylamide using a preirradiation method. The surface behavior of grafted films as a function of the degree of grafting was determined using contact angle measurements, attenuated total reflectance (ATR), and scanning electron microscopy (SEM). In spite of the presence of hydrophilic polyacrylamide chains, grafted films still showed high hydrophobicity on the surface. ATR results revealed the presence of a polyacrylamide moiety in the surface layer of the films.

Interestingly, the contact angle of grafted films did not change much for the entire range of degree of grafting. SEM results showed that the roughness is introduced on the film surface irrespective of the nature of the additive. However, the addition of acetone to the grafting medium was the most effective in increasing the surface roughness. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 1118–1122, 2002

Key words: polyethylene; surface; acrylamide; membrane; radiation grafting

INTRODUCTION

Modification of polymeric films has received significant attention for many technologically important areas such as in adhesion, immobilization, and membranes.^{1–4} One of the ways to modify polymers is the radiation grafting of a specific monomer into a film that leads to a copolymer structure in which the backbone is represented by the base polymer and the branches are formed out of the polymerized monomer.^{5–9} The most interesting aspect of the radiation grafting is that the extent of modification may be controlled by the proper selection of the radiation dose, dose rate, and reaction conditions. The grafting has been observed to introduce both the structural and the morphological changes in the polymer matrix as well as on the surface. The magnitude of these changes strongly depends on the nature of the monomer and the degree of grafting. Therefore, the method offers an attractive way to develop a polymer structure for the specific application by proper selection of the radiation and grafting parameters.^{10–16}

We have been working in the area of the development of membranes by radiation grafting of acrylic acid and acrylamide into polyethylene films.^{6,17–19} In these studies, we investigated the influence of not only the grafting and radiation conditions but also the

physical properties on the degree of grafting. These grafted films have been observed to undergo considerable changes in the crystalline/amorphous ratio, aqueous swelling, and resistivity as a function of the degree of grafting.^{19,20} These grafted membranes show excellent binding capacity for toxic metal ions such as mercury. Finally, it is a matter of interest to monitor the surface changes that follow the radiation grafting process. In the present study, both the chemical and the morphological changes at the polyethylene surface developed by the grafting of acrylamide have been investigated.

EXPERIMENTAL

Materials

Polyethylene films of 40- μm thickness, processed from chips (Grade F19010, MFI 1.0), were supplied by Reliance Industries, India. Acrylamide monomer (Sisco, India) was used as received without any further purification. Acetone, methanol, and Mohr's salt were supplied by Merck, India. Distilled water was used in all experiments.

Irradiation

A ⁶⁰Co gamma-radiation source (900 Ci) was used for the irradiation of PE films. The dose rate of irradiation was 0.36 kGy/h. The irradiation was carried out in air and the exposed films were stored at -4°C before grafting experiments.

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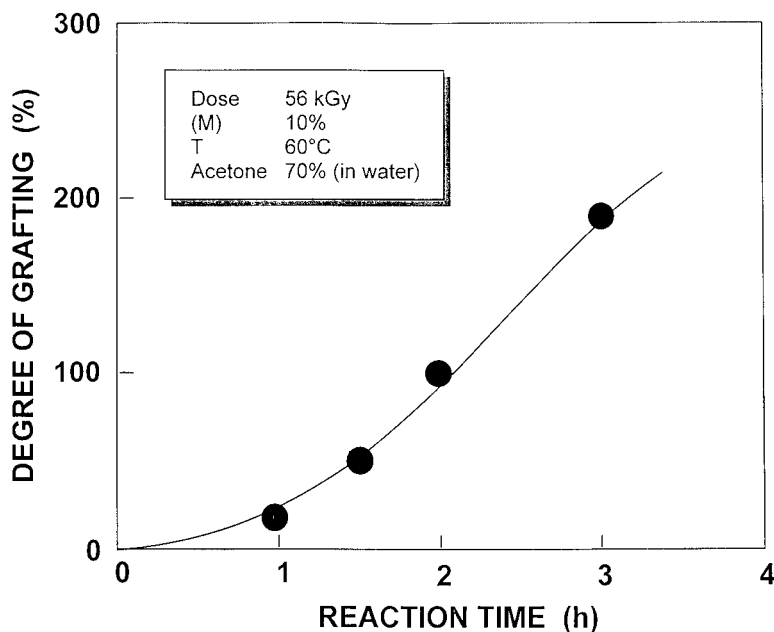


Figure 1 Variation of the degree of grafting with the reaction time.

Graft polymerization

Graft polymerization was carried out on irradiated polyethylene (PE) films by placing them in a glass tube containing a monomer solution of the desired concentration. Nitrogen was introduced into the glass tube to remove air from the grafting solution. Subsequently, the glass tube was placed in a water bath maintained at 60°C. After the desired period, the glass tube was removed and the grafted films were extracted with hot water to remove traces of any homopolymer adhering to the film surface. The grafted films were dried in an air oven at 60°C and weighed. The degree of grafting of PE films was calculated from the following equation:

$$\text{Degree of grafting (\%)} = \frac{W_g - W_0}{W_0} \times 100$$

where W_0 and W_g are the weights of ungrafted and grafted films, respectively.

Contact angle measurements

The contact angle of PE films was as measured by goniometer (Ramé-Hart, Mountain Lakes, NJ). All measurements were performed at 22°C using deionized water. A water droplet of 10 μL was placed on the film surface and the contact angle was measured 30 s after the application of the droplet. Six measurements were taken at different places on the film surface and averaged.

Attenuated total reflectance (ATR) measurements

ATR measurements on samples were carried out on a Nicolet Magna IR-560 (Nicolet Instruments, Madison, WI). The samples were analyzed in the reflectance mode in the range of 400–4000 cm^{-1} .

Scanning electron microscopy (SEM)

The topographical studies on the film surface were carried out using a scanning electron microscope (Stereoscan 300; Cambridge Biotech, Worcester, MA). Samples were coated with silver before scanning.

RESULTS AND DISCUSSION

The radiation-induced graft polymerization of acrylamide into PE films using an acetone–water mixture as the medium is presented in Figure 1. Although the grafting kinetics in this system was studied up to 16 h, the short-duration (up to 3 h) grafting variation is presented here. Films with the degree of grafting in the range of 19 to 198% were obtained using different grafting mediums and investigated by contact angle measurements, ATR, and SEM. All these techniques are surface-selective and thus a careful monitoring of the surface by these methods would lead to noteworthy information on the graft modification of PE films.

The variation in the contact angle with the degree of grafting in PE-g-PAAm films synthesized under various reaction mediums is presented in Figure 2. The contact angle shows very little decrease with the increase in grafting. Interestingly, for a specific graft

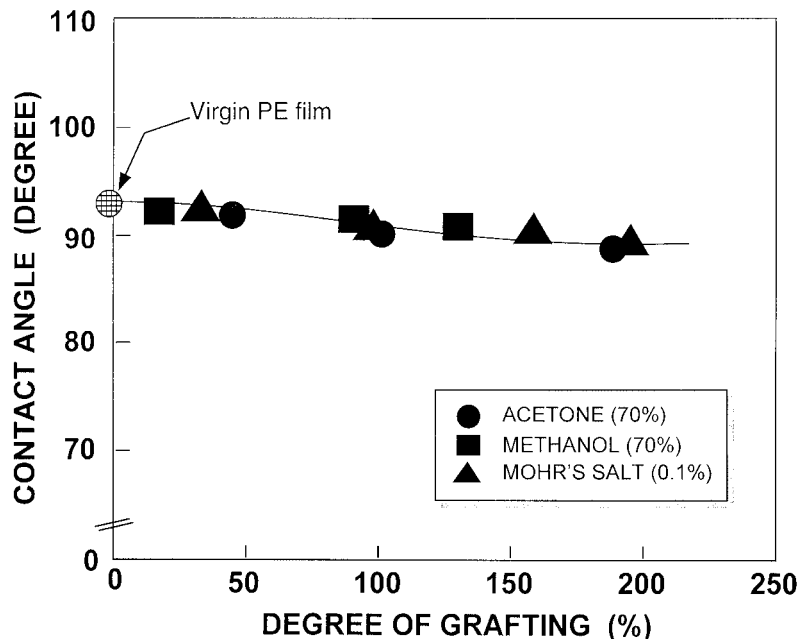


Figure 2 Variation of the contact angle with the degree of grafting.

level, the contact angle remains identical, irrespective of the nature of the additive. Considering the hydrophilicity of the polyacrylamide domain it may be expected that the wettability and thus the surface energy of the modified film would increase, which could lead to a decrease in the contact angle at the film surface. A decreasing trend has been observed for the grafting of acrylamide into polyethylene films by several workers.^{21,22}

The high contact angle of grafted films in our investigation indicates that the graft management on the surface and within the matrix of the film proceeds in

such a way that the surface remains devoid of any significant polyacrylamide grafts. Probably, it is the solvent composition that plays a major role during the course of the grafting reaction. The grafting in our system was carried out in an acetone–water mixture consisting of 70% acetone and 10% methanol. We have observed that the medium constituting the acetone fraction more than 30% in the acetone–water mixture and more than 5% methanol in methanol–water mixture inhibits the homopolymerization of acrylamide in the grafting solution, although the grafting reaction continues to take place. A similar trend is obtained in

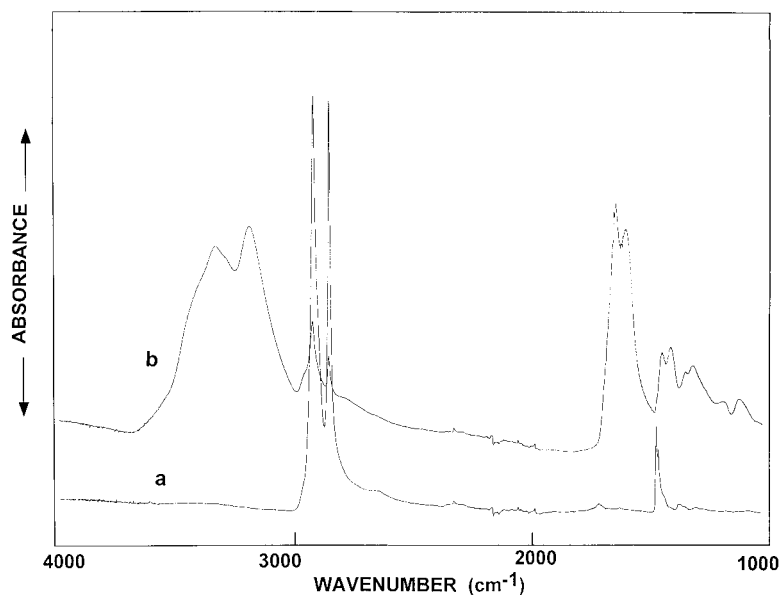


Figure 3 ATR spectra of (a) ungrafted PE film and (b) PE-g-PAAm film with 54% degree of grafting.

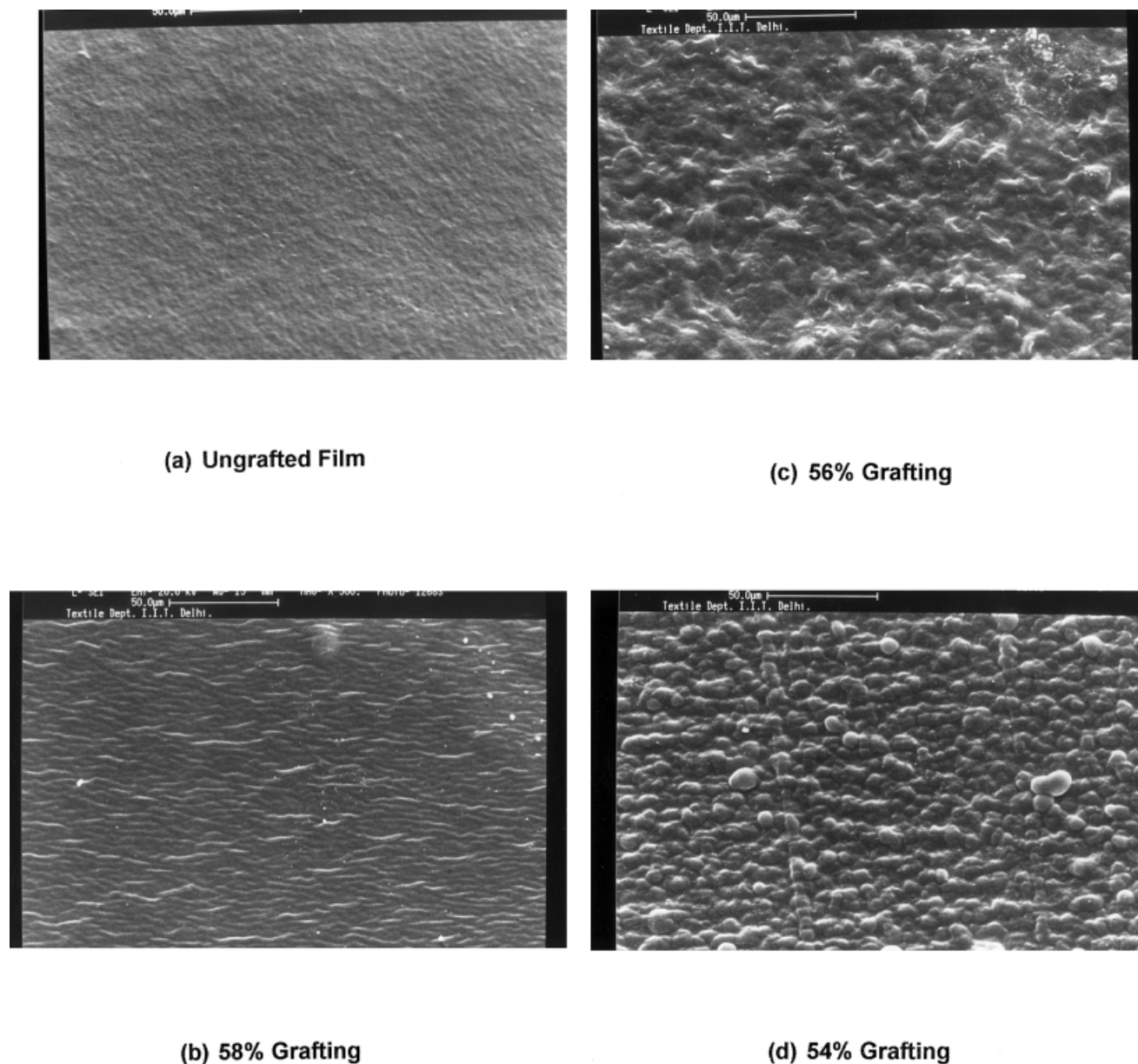


Figure 4 SEM images of (a) ungrafted PE film and PE-g-PAAm films prepared using different additives to the grafting medium; (b) Mohr's salt 0.1%; (c) methanol 10%; (d) acetone 70%.

the medium containing Mohr's salt as the additive. We wonder whether these additives inhibit the graft propagation on the film surface that remains in direct contact with the medium during the course of the grafting reaction. However, the amount of additives that diffuses within the bulk of the matrix may not be enough to exert any inhibitory action on the grafting within the film. This produces a matrix that becomes hydrophilic in composition but renders the surface hydrophobic in nature. The contact angle, as a result, does not show any appreciable change. However, the hydrophilicity of the grafted films is evident from the swelling behavior in aqueous water. A film with 54% degree of grafting shows 18% swelling in deionized

water as compared to nil for the ungrafted film.²⁰ This further substantiates the assumption that the polyacrylamide chains are predominantly located within the bulk of the matrix and participate in the swelling process in spite of a relatively hydrophobic surface.

ATR results on the ungrafted and grafted films are presented in Figure 3. The spectra of the grafted film show two clear distinctions from the ungrafted film. The peak at 1647 cm^{-1} may be assigned to the presence of carbonyl stretching of the amide group. At the same time, the peak at 1610 cm^{-1} may be ascribed to -N-H bending. The appearance of the peaks at 3326 and 3182 cm^{-1} may be attributed to the -NH_2 component in the amide group. These observations indicate

the presence of the polyacrylamide grafts in the surface region of the film. However, these results do not fall in line with the contact angle measurements, which show a relatively hydrophobic grafted surface. Most likely, in spite of the surface-selective nature of ATR, it has certain penetration within the surface and interacts with the grafts located therein.

The SEM results on the films are presented in Figure 4. The virgin film is smooth on the surface but the grafting leads to the nonhomogeneous structures. The nonhomogeneity was observed to be dependent on the nature of the grafting medium. Among the Mohr's salt, methanol, and acetone as additives, the surface nonhomogeneity is the most prominent with acetone in the acetone-water grafting medium and the Mohr's salt provides the smoothest surface. The grafting is known to follow the "grafting front" mechanism by progressive diffusion of monomer through the grafted layers.¹⁷ As long as the graft propagation proceeds in a homogeneous medium within the film, the surface remains smooth. This is the reason that the Mohr's salt caused little nonhomogeneity on the surface, given that the grafted chains remain solubilized in the water-swollen grafted layer. The behavior in solvent-added grafting seems to be associated with the non-solvent nature of both the methanol and acetone for the polyacrylamide moiety. Both nonsolvents diffuse into the medium-swollen PE surface and precipitate out the polyacrylamide chains. Under such circumstances, polyacrylamide chains agglomerate and form independent domains within the PE matrix. The hydrophilicity of the grafted PAAm domains further helps in phase separation within the hydrophobic PE matrix. This is reflected in the surface nonhomogeneity in solvent-assisted grafting reaction. It is interesting to see that the presence of acetone leads to a high level of nonhomogeneity in the form of globules compared to that of methanol [Fig. 4(c) and (d)]. This may be because of the solubility parameter of acetone (9.9) being close to PE (7.7) compared to that of methanol (14.5).²³ Therefore, by virtue of the high concentration of acetone over that of methanol-assisted grafting and the solubility parameter being closer to that of PE, the acetone concentration within the film may be higher and might be responsible for the higher level of phase separation and nonhomogeneity.

CONCLUSIONS

The surface morphology and behavior of the grafted polyethylene (PE) films prepared by radiation grafting of acrylamide strongly depend on the reaction medium. The additives such as Mohr's salt, methanol, and acetone influence the surface morphology in dif-

ferent ways. The additives such as Mohr's salt does not cause any significant change on the surface. However, the addition of solvents such as acetone and methanol to the grafting medium leads to the nonhomogeneity on the surface. It seems that such behavior is associated with the nonsolvent nature of both acetone and methanol toward polyacrylamide grafts, which are precipitated out within the hydrophobic PE matrix. Acetone has the strongest influence over the development of nonhomogeneity on the film surface. The contact angle of PE films also did not show any significant decrease in any of the grafted films. These observations suggest that the inhibitory action of all three additives leads to film surfaces devoid of any significant amount of polyacrylamide grafts. The grafted chains remain confined more or less to the bulk of the PE matrix. These studies suggest that the physicochemical nature of the surface and bulk of the grafted films may be easily controlled by careful selection of the reaction medium.

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