Polymer Bulletin 47, 99–104 (2001)

Polymer Bulletin

Hydrophilicity and surface energy of polyethylene modified by radiation grafting of acrylamide

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Received: 12 March 2001/Revised version: 26 June 2001/Accepted: 27 June 2001

Summary

LDPE films were modified via direct γ-radiation grafting of acrylamide (AAm) from its 30% aqueous solution. Equilibrium swelling of the grafted samples in water, and a water/PAAm molar ratio in the swelled films were determined as a function of PAAm content. Contact angles formed by sessile drops of water or diiodomethane on the starting and modified LDPE were measured with following calculation of a surface energy in these samples. A gradual filling of LDPE surface with PAAm as well as changes in hydrophilic-hydrophobic properties of the composition during the grafting process was discussed. It has been found an essential increase in surface energy of the modified LDPE up to ~15% of the grafted PAAm content with a further stabilization of the energy value.

Introduction

There is a considerable practical interest in modification of polymers via radiation graft polymerization for preparation of materials which find various applications. Progress in obtaining of biocompatible grafted polymers, which are used to recostruct structure and functions of damaged tissues and organs (artificial vessels, skin etc), was generalized in some reviews and monographs (1-9). It should be noted that interaction of the polymer surface with a living tissue is a complicated and disputable question. But it has been shown an essential importance of hydrophilicity of the modified polymer surface to increase its biocompatibility; besides, a hypothesis about role of the hydrophilic-hydrophobic balance of a polymer surface for its better biocompatibility was proposed (1,10). Apparently, surface energy of the modified polymeric layers can affect on efficiency and selectivity of their interaction with components of the surrouding living tissues. Radiation grafting of acrylamide (AAm) or its derivatives onto polymers was used in attempts to improve their biocompatibility.

Radiation grafting of AAm onto low density polyethylene (LDPE) by the direct method, in which a polymer was irradiated in close contact with a monomer, was reported earlier (11-16). It has been found that optimal AAm concentration in aqueous solutions was within 20-40 wt %. Mohr's salt (ammonium ferrous sulphate) was added often as the effective inhibitor to minimize this monomer homopolymerization during irradiation, and its suitable concentration was found to be 2-3 wt%. Under these conditions and relatively low doses of irradiation (up to 10 kGy), the grafting process was not complicated by an essential AAm homopolymerization, and the crosslinked PAAm was not formed. It is known that efficient radiation crosslinking of PAAm requires essentially higher doses (17). Molecular weight of the PAAm formed during the grafting process was estimated as $\sim 10^5$ (14). Besides, it has been shown that grafted layers were located on the LDPE surface at a low PAAm content but they penetrated inside this polymer with increase in the grafting degree, and yield of the LDPE-g-PAAm insoluble gel fraction depended on the PAAm distrubution inside the modified polymer (13).

Hydrophilicity of the modified LDPE caused by the AAm grafting was studied (11, 15, 16) but effect of a chemical heterogeneity of the polymer surface at low values of grafting on its hydrophilic-hydrophobic properties was not analysed.

A method of determination of polymers surface energy by measuring of contact angles of liquids placed on polymers was developed and used earlier (18-23), but it seems to be no data on this energy for polymers modified via the AAm grafting.

This work presents the results of a study on hydrophilicity and surface energy of LDPE radiation-grafted with PAAm.

Experimental

LDPE films of thickness 100 µm (PEMEX, Mexico) were washed in benzene and methanol and dried under vacuum. AAm, purity 99% (Merck, Germany) was used without further purification.

LDPE strips were placed in glass ampoules which contained 30 wt% aqueous solution of AAm in the presence of Mohr's salt (2 wt%). The reaction mixture was deaerated under vacuum by repeated freezing and thawing method, ampoules were sealed and irradiated with a ^{60}Co γ-source (Gammabeam 651 PT, Nordion International Inc.) at a dose rate of 0.7 kGy/h and doses from 1 to 15 kGy. The grafted films were washed with hot water for 24 h to extract the residual monomer and the PAAm homopolymer that could be formed and occluded in the films. The grafting yield was determined gravimetrically as a weight percent of grafted PAAm in the modified LDPE.

For the hydrophilicity to be characterized, the samples were immersed in distilled water at room temperature until equilibrium swelling was reached. Then samples were taken out and the excess of water deposited on the film surface was removed quickly with blotting paper, and samples were weighed. The swelling degree was calculated by the equation:

$$\text{swelling (\%)} = (W - W_0)\,100/W_0$$

where W and W_o are the weights of swollen and dry samples, respectively.

For the contact angles determination, sessile drops of distilled water or diiodomethane were placed on surfaces of the starting and modified LDPE films. Contact angles (θ) of the drops were measured with a Ramé-Hart Contact Angle Goniometer (model 100). The θ values were measured immediately after the drops placing on the polymer surface.

Results and discussion

LDPE films did not swell in aqueous solution of AAm. Fig. 1 shows effective grafting of this monomer onto LDPE under mild irradiation conditions. The grafting process was accompanied by a weak AAm homopolymerization at doses of 5 kGy and more, but formation of the crosslinked PAAm gel was not observed.

Equilibrium swelling of the grafted samples in water was reached from 3 to 10 min with increase in the grafted PAAm content. Starting LDPE hardly swells at all, but the modified polymer absorbed water in considerable amounts, and a linear dependence of swelling values on grafting ones was observed (Fig.2). Short time of the samples swelling as well as practically constant water/PAAm molar ratio (α) in the swelled films indicate a location of grafted chains in the surface layer of LDPE that promotes better contact of water with PAAm macromolecules.

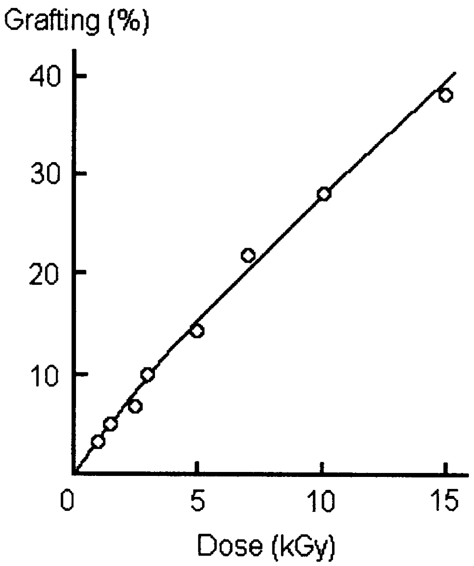

Fig.1. Grafting of AAm onto LDPE from aqueous solution of monomer. AAm and Mohr's salt conc.=30 and 2 wt%. Dose rate = 0.7 kGy/h

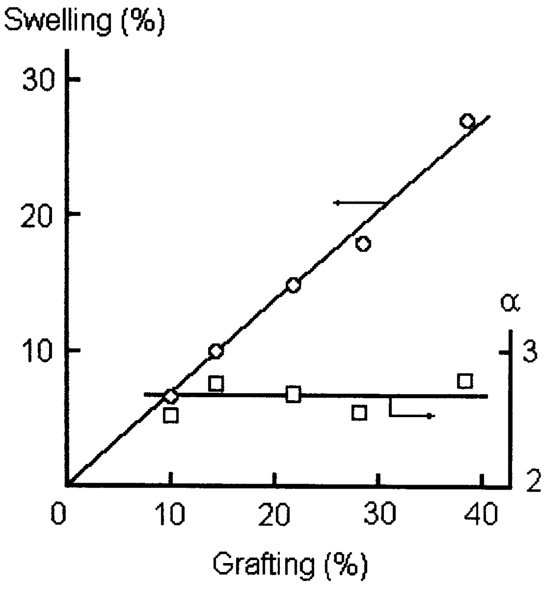

Fig.2. Equilibrium swelling of the modified LDPE in water, and water/PAAm molar ratio (α) as a functions of the grafting value.

Fig.3 testifies essential influence of LDPE modification via AAm grafting on θ changes for the testing liquids used. The θ decreased with an increase in PAAm content, and reached limiting values at ~15% of the grafting. The maximum reduction in θ, relatively to the starting LDPE, was equal to 25-26^0 and 8-9^0 for water and diiodomethane, respectively.

Apparently, a reduction in contact angles for both liquids with an increase in grafting value up to ~15% is caused by a gradual filling of the LDPE surface with particles of the grafted PAAm. At first, this particles are formed as a separate microdrops on the polymer surface, and then they increase in size with the grafting value. After ~15% of grafting, a wetability of the surface did not change practically due to formation of a continuous layer of PAAm on the LDPE surface.

The surface energy (γ_S) of the starting and grafted LDPE was determined as the sum of its dispersion (γ_S^d) and polar (γ_S^p) components, which were calculated by equation (17):

$$1 + \cos\theta = 2(\gamma_S^d\,\gamma_L^d)^{0.5} / \gamma_L + 2(\gamma_S^p\,\gamma_L^p)^{0.5} / \gamma_L,$$

where γ_L^d and γ_L^p are dispersion and polar components of surface energy (γ_L) of the liquids used. The next values of γ_L^d, γ_L^p and γ_L (mN/m) were used for calculations (17): 21.8, 51.0 and 72.8 (water), and 49.5, 1.3 and 50.8 (diiodomethane).

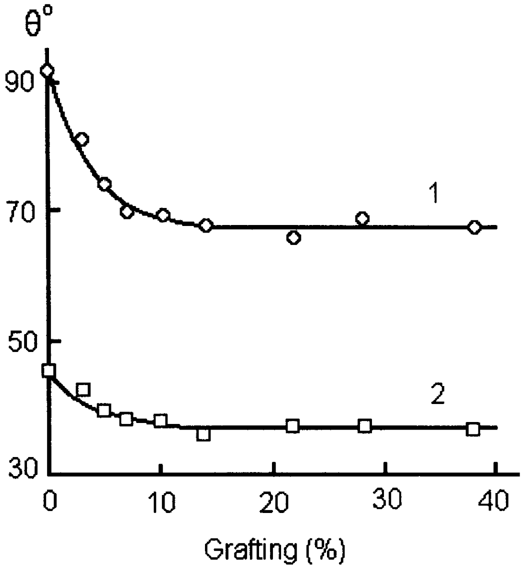

Fig.3. Dependence of contact angles for water (1) and diiodomethane (2) on the grafting value.

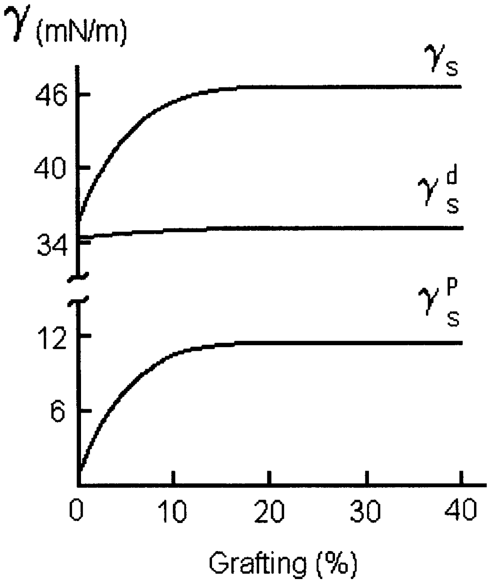

Fig.4. Dependence of surface energy (γ_S), their polar (γ_S^p) and dispersion (γ_S^d) components on the grafting value.

Fig.4 shows a gradual increase in surface energy of the modified LDPE with the grafted polyAAm content up to ~15%, and increment in γ_S was caused practically by increase in its polar component. If estimate a change in polarity of the polymer with a parameter $p = \gamma_S^p / \gamma_S$, this one increased from 0.05 for the starting LDPE to the maximum value of 0.25 for the modified polymer.

Conclusion

Radiation grafting of AAm from its aqueous solution onto LDPE resulted in gradual filling of this polymer surface with the grafted PAAm, and this process was accompanied by changes in hydrophilic-hydrophobic properties and surface energy of the modified polymer. Maximum value of this energy (46.5 mN/m) was reached at ~15% of the polyAAm content, and this increase, as compared with the starting LDPE (36.0 mN/m), was caused by polar component of the energy.

Acknowledgement

Author thanks Dr. Guillermina Burillo (Instituto de Ciencias Nucleares - UNAM) for helpful discussion of this work.

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