Surface Modification of Polyethylene by Photochemical Grafting with 2-Hydroxyethylmethacrylate

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SYNOPSIS

The photochemical grafting of 2-hydroxyethylmethacrylate onto low-density polyethylene film is described. The grafting technique employed involved irradiating a solution of 2-hydroxyethylmethacrylate and benzophenone in acetone spread between films of poly(ethylene terephthalate) or glass and low-density polyethylene. After irradiation for 2 min, the contact angle of the polyethylene films with water fell from 97° to about 50°. The contact angle of the poly(ethylene terephthalate) substrate also fell during grafting. X-ray photoelectron spectroscopy was consistent with the presence of poly(2-hydroxethylmethacrylate) at the surface of the polyethylene. The effect of solvent on the photochemical grafting of 2-hydroxyethylmethacrylate onto low-density polyethylene is discussed. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The bulk and surface properties of polymers have been successfully exploited to produce materials that have a wide range of applications. Surface properties are important because the interaction of polymers with their environments occurs chiefly at their surfaces. The tailoring of these properties by surface modification has attracted considerable interest in recent years. One method that has been used to alter the surface properties of polymers is photochemical grafting. The technique involves the initiation of polymerization of vinyl monomers at sites generated on solid polymer surfaces. The grafting of polymer chains onto a polymer surface can alter the surface properties of the substrate without adversely affecting its bulk properties. This approach has been used to increase the hydrophilicity of materials such as polyethylene (PE),[1] polypropylene (PP),[2,3] and poly(ethylene terephthalate) (PET)[4,5] and to prepare membranes based upon poly(vinylchloride)[6] and poly(ethylene-co-tetrafluoroethylene).[7] Biocompatible materials have been prepared by the re-

action glycidyl methacrylate-grafted PE with poly(ethylene glycol) (PEG).[8]

PE itself has been photochemically grafted with a variety of hydrophilic vinylic monomers using solution and vapor phase techniques.[9-12] The resulting surface-modified polymer films exhibited improved wettability and printability. A method for a continuous process for the surface modification of high-density PE (HDPE) tape has been published recently.[13] Here, we report some results for the surface modification of low-density PE with poly(2-hydroxyethylmethacrylate) [poly(HEMA)].

EXPERIMENTAL

LDPE (75 μm thick, 54% crystallinity by differential scanning calorimetry) and PET were cleaned before and after grafting by immersion in boiling methanol for 45 min and distilled water at room temperature for 30 min and dried under vacuum. HEMA was distilled at reduced pressure in the presence of anhydrous CuCl (65–68°C, 12 mm Hg) and stored under nitrogen at −20°C. Benzophenone and acetone [high-performance liquid chromatography (HPLC) grade] were used as supplied. The ultraviolet lamp used was an Hanovia UVS 1000. Contact angles

(water, 2 μL) were measured using a Rame Hart NRL 100 Contact Angle Goniometer. X-ray photoelectron spectroscopy (XPS) was performed using a Kratos ES300 electron spectrometer. Samples were irradiated with $MgK_{\alpha1,2}$ X-rays at a pressure of 10^{-8} torr and an electron takeoff angle of $35°$. XPS spectra were fitted as described by Clark and Shuttleworth.[14] The binding energies of the electrons were referenced to carbon at 285 eV. Atomic ratios were computed from area ratios using the appropriate experimentally derived sensitivity factors for the instrument configuration. Attenuated total reflectance infrared (ATRIR) spectra were recorded using a Perkin-Elmer 1710 Fourier transform infrared (FTIR) equipped with a zinc selenide cell.

A diagram of the grafting apparatus is shown in Figure 1. The apparatus consists of two glass tubes. The smaller tube has cooling water inlet and outlet tubes. A larger tube that has a purge gas inlet, a 1 × 7.5-mm slit, and a quartz or Pyrex window is placed over the smaller tube. The films to be grafted are placed in the space between the two tubes via the slit and exposed to ultraviolet radiation for the required time. The grafting technique involved applying a nitrogen-purged (10 min) solution of HEMA ($2M$) and benzophenone ($0.2M$) in acetone or pure HEMA to the PET substrate and placing a film of LDPE on top of the solution. The films were then flattened to remove gas bubbles and irradiated with ultraviolet light through the quartz or Pyrex window so that the dry side of the HDPE film was facing the ultraviolet lamp. Irradiation was carried out in air or nitrogen. After irradiation, the films were peeled apart and washed. Blank experiments (time = 0) were performed by irradiating polymer

films through the quartz filter in a nitrogen environment for 10 min.

RESULTS AND DISCUSSION

The photochemical grafting of vinylic compounds onto polymer surfaces can be achieved using a sensitizer such as benzophenone. Irradiation of benzophenone at $\lambda_{max} = 345$ nm efficiently gives the triplet excited state via intersystem crossing from the initially formed singlet state. Benzophenone triplets are effective in abstracting hydrogen atoms from polymer surfaces to leave macroradicals that can initiate graft polymerization.[1,13]

Photochemical grafting experiments were carried out using both Pyrex and quartz filters in air and nitrogen environments. Pyrex absorbs radiation below about 300 nm and should decrease the amount of homopolymer formed during irradiation because vinyl homopolymerization can be readily initiated by short wavelength ultraviolet. LDPE is effectively transparent to ultraviolet above 200 nm and should allow the graft polymerization of HEMA to occur on one side of the LDPE film. The blank (time = 0) experiments resulted in a material that exhibited a contact angle with water of $97°$ and an XPS atomic O/C ratio of 0.04.

Grafting in a Nitrogen Environment

The variation of contact angle with time for LDPE grafted through Pyrex and quartz filters are shown in Figure 2. The error bars reflect the standard deviations of the contact angle measurements. The
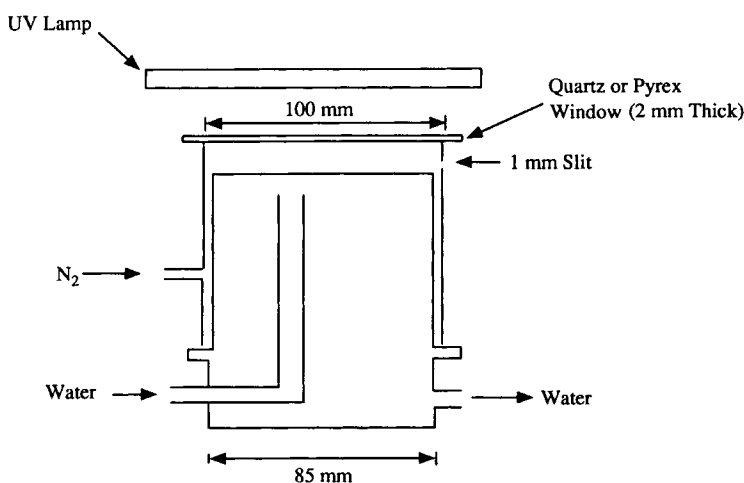

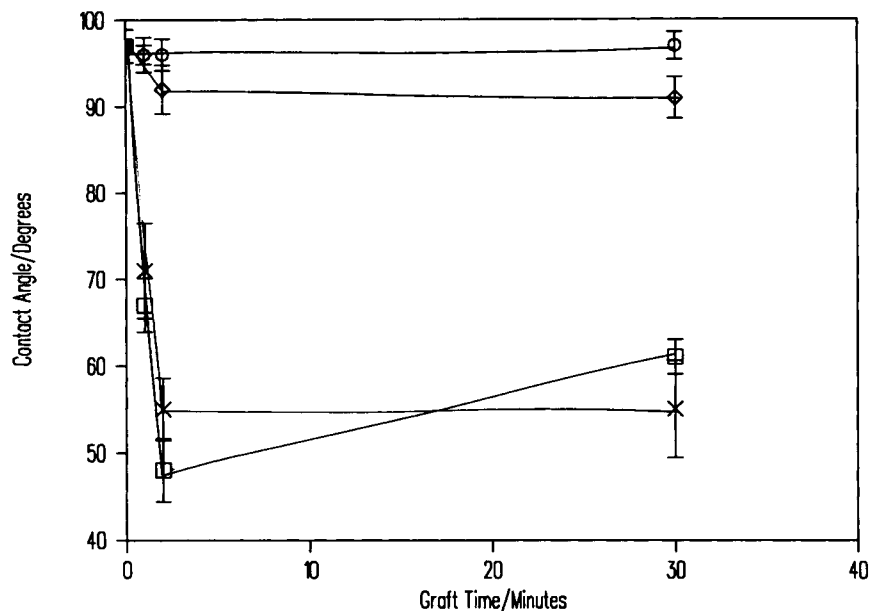**Figure 1** Diagram of the grafting apparatus.

Figure 2   Variation of contact angle with graft time for grafting of HEMA onto LDPE:
Nitrogen environment. Pyrex filter: (O – O) lamp-facing side; (X – X) opposite side. Quartz
filter: (< > – < >) lamp-facing side; ([ ] – [ ]) opposite side.

contact angle decreases rapidly and after 2 min
reaches a value of about 50° for both filters. This is
comparable to results reported for the solution phase
grafting of acrylic acid onto low-density PE (LDPE)
at 60°C.[15] The contact angle of the lamp facing side
of the LDPE is unchanged when a Pyrex filter is
used but decreases by 5–6° when a quartz filter is
employed. This small but reproducible effect is pos-
sibly a consequence of photochemically induced in-
teraction between chromophores that are present in
low concentrations in the LDPE film surface (chain
ends and defects) and absorb below 300 nm and
traces of moisture and dioxygen.

After grafting for 30 min, a film was visible on
the LDPE surfaces when either a quartz or Pyrex
filter was used. ATRIR spectra of the grafted sides
of the films were identical to that of poly(HEMA).
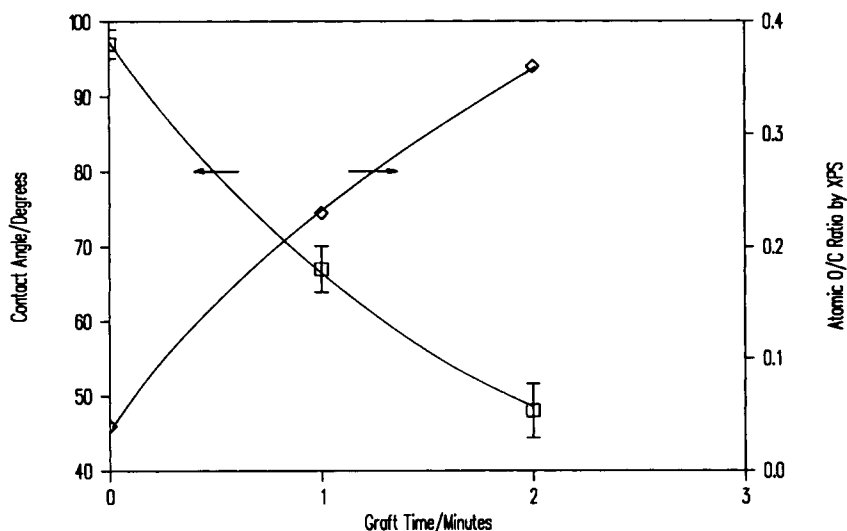The LDPE films that had been grafted for 30 min

Figure 3   Variation of contact angle and XPS O/C ratio with graft time for the grafting
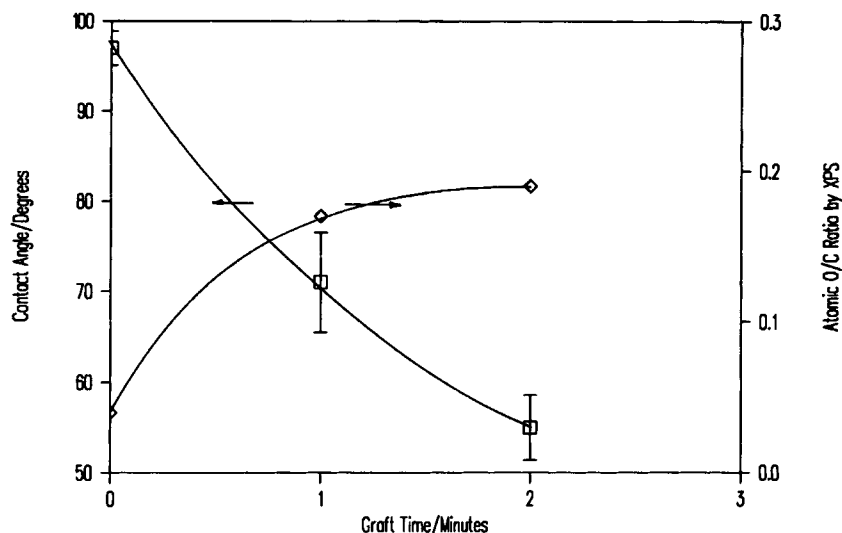of HEMA onto LDPE: Quartz filter, nitrogen environment.

Figure 4 Variation of contact angle and XPS O/C ratio with graft time for the grafting of HEMA onto LDPE: Pyrex filter, nitrogen environment.

were qualitatively more rigid than untreated films. However, the grafting system that employed a quartz filter produced a film that swelled and began to peel during washing whereas the system that used a Pyrex filter produced a stable product with a smooth, clear layer of poly(HEMA) on the surface of the LDPE. A possible explanation for this observation is the presence of substantial quantities of ungrafted homopolymer when the quartz filter is used; such material would be both fully swellable and detachable from the substrate.

The variation of contact angle and the O/C atomic ratios derived from the XPS spectra with short graft times using Pyrex and quartz filters are shown in Figures 3 and 4. The XPS data show that the ratio of oxygen to carbon in the surface increased with increasing graft time with a value of 0.19 and 0.36 being observed after 2 min for Pyrex and quartz filters, respectively. The theoretical value for poly(HEMA) is 0.5. Grafting for 30 min resulted in XPS atomic O/C ratios of 0.36 and 0.31 for Pyrex and quartz filters, respectively, which can be interpreted in two ways. The XPS technique samples a layer about 30–50 Å thick under our experimental conditions. It is clear from the O/C ratio that we are not sampling pure homopolymer of HEMA. The actual ratios of carbon environments in the deconvoluted C_{1s} envelope[14] for a sample grafted through a Pyrex filter for 30 min were 4 : 1 : 2 : 1 for peaks at 285.0 eV (saturated aliphatic C), 285.7 eV $(C-C=O)$, 286.8 eV $(C-O)$, and 288.9 eV $(C=O)$, respectively. Pure poly(HEMA) displays a 2 : 1 : 2 : 1 ratio for the same set of XPS shifts.

The extra aliphatic carbon signal must either arise from exposed LDPE, which would mean that the LDPE surface was not completely covered, or from surface hydrocarbon contamination on the poly(HEMA), which could arise from mobile hydrocarbon materials present on the LDPE sample (mold release agents, pump oil, etc). ATRIR resolved this question because the spectrum of the grafted surface was identical to that of pure poly(HEMA). Because the ATRIR technique samples a film of ca. 0.6 μm thickness (at the carbonyl

Table I Variation of Contact Angle with Graft Time for the Grafting of HEMA onto LDPE: No Acetone, Nitrogen Environment

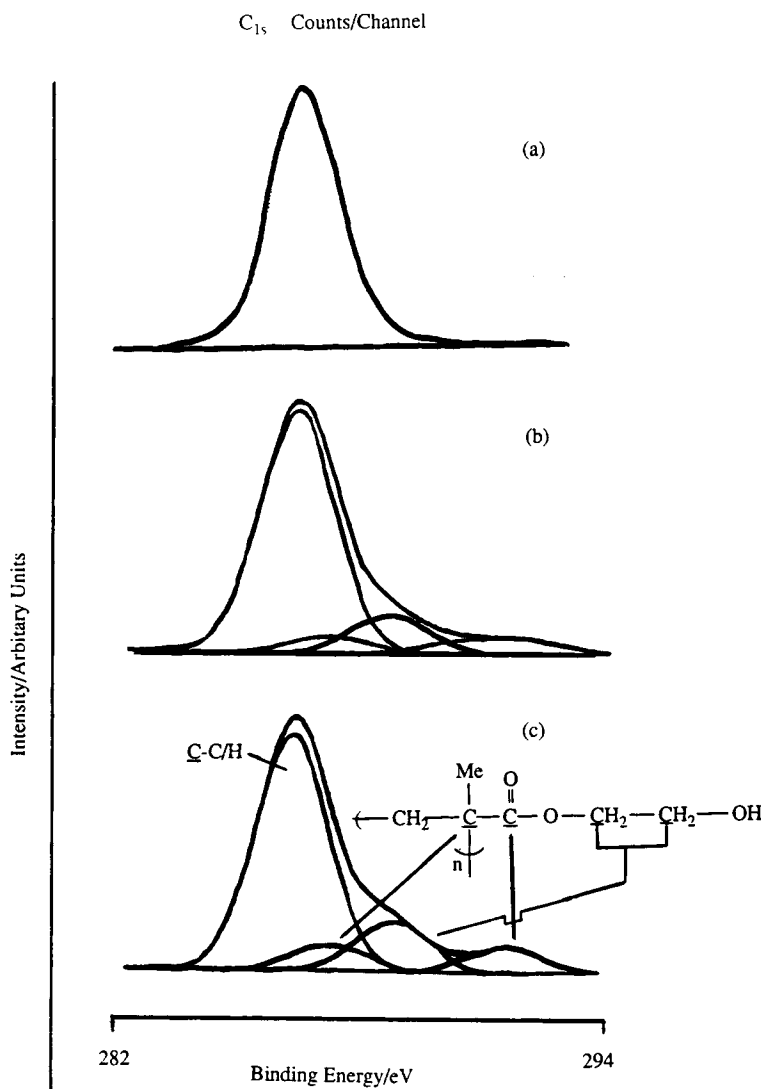| Filter | Graft Time (min) | Grafting Solution | |
		HEMA Contact Angle (°)	HEMA/ PH_2CO Contact Angle (°)
Pyrex	0	97 (1.9)	97 (1.9)
	1	97 (0.8)	85 (4.3)
	2	96 (2.0)	98 (2.6)
	30	95 (1.6)	53 (2.7)
Quartz	0	97 (1.9)	97 (1.9)
	1	75 (1.7)	a
	2	54 (2.7)	a
	30	a	79 (9.1)[b]

[a] Film adhered to mylar.
[b] Film was creased.

Figure 5 XPS C_{1s} spectra of LDPE grafted with HEMA. (a) Untreated; (b) 1-min graft; (c) 2-min graft.

absorption frequency), we must have a film of at least this thickness covering the LDPE and the inconsistencies in the XPS analysis must be due to surface contamination. The C_{1s} spectra of LDPE grafted with HEMA using a Pyrex filter for 1 and 2 min are shown in Figure 5. It can be seen that the spectra are consistent with the presence of poly(HEMA) at the surface of the LDPE. Peaks appear at 288.9 eV, assigned to $O - C = O$; at 285.7 eV, assigned to $C - C = O$; and at 286.8 eV, assigned to $C - O$. The relative atomic ratios of these peaks (1:1:2) are consistent with the presence of a grafted poly(HEMA) layer but clearly at this early stage there is even more aliphatic carbon (285 eV) visible.

Swelling of the substrate by a solvent is thought

to be an important step during photochemical grafting. In this work, the grafting of HEMA onto LDPE in the absence of acetone was investigated. The results are summarized in Table I. Using a Pyrex filter, it is clear that the grafting of HEMA only occurs when benzophenone is present but there is no requirement for an additional solvent. There was no indication of poly(HEMA) formation when pure HEMA was used with a Pyrex filter even after grafting for 30 min. This is expected because HEMA exhibits a λ_{max} of 230 nm and the Pyrex filter effectively prevents any initiation of homopolymerization. When a quartz filter was used in the absence of benzophenone, the contact angle decreased rapidly even after thorough washing. It is possible that grafting
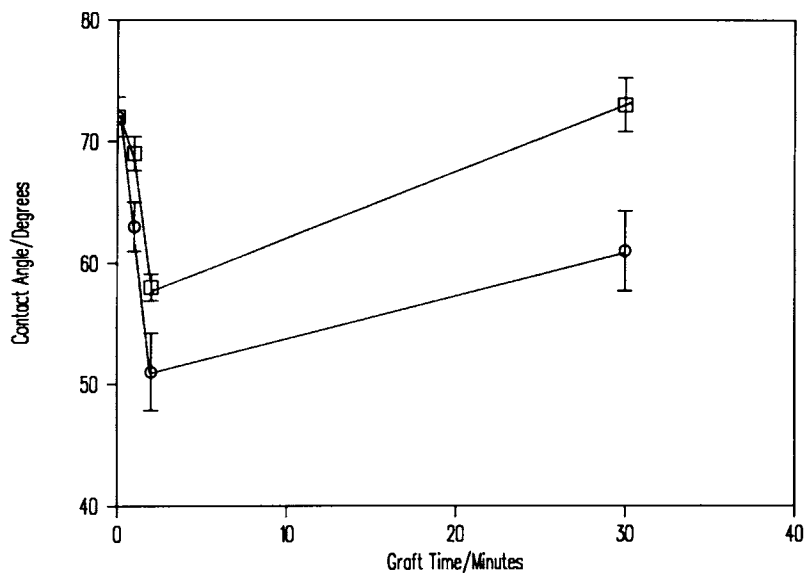
Figure 6 Variation of contact angle with graft time of the PET substrate: Quartz filter. (O – O) lamp-facing side; ([ ] – [ ]) opposite side.

occurred, but, despite the resistance of this layer to removal by washing, we cannot rule out the possibility of a strongly adhering (partially entangled) surface layer of homopoly(HEMA). When benzophenone was present, the LDPE and PET films could not be separated. If acetone as diluent was added, the LDPE tended not to adhere to the PET substrate.

The variation of contact angle with graft time for the PET substrates used during the grafting of HEMA onto LDPE are shown in Figures 6 and 7. It can be seen that the contact angles of both the lamp-facing side and the opposite side decrease after short irradiation times and then increase. The change in contact angle of the side of the films opposite the lamp may be due to photoinitiated mod-
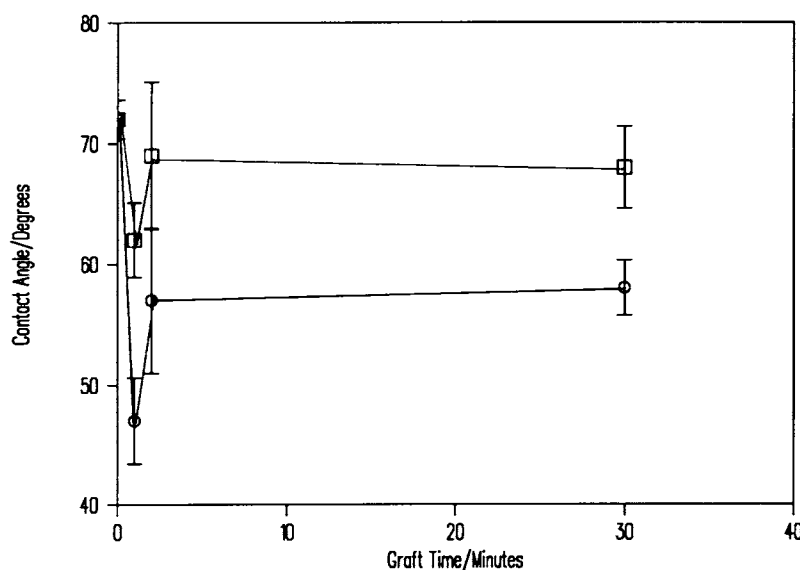

Figure 7 Variation of contact angle with graft time of the PET substrate: Pyrex filter. (O – O) lamp-facing side; ([ ] – [ ]) opposite side.

Table II   Variation of Contact Angle and XPS O/C Ratio with Graft Time for the Grafting of HEMA onto LDPE: Air Environment

| Filter | Graft Time (min) | Contact Angle (°) | | XPS O/C Ratio |
		Lamp Side	Opposite Side	Opposite Side
Pyrex	0	97 (1.9)	97 (1.9)	0.04
	1	93 (2.3)	94 (2.9)	0.08
	2	96 (1.0)	85 (5.2)	0.11
	30	a	a	a
Quartz	0	97 (1.9)	97 (1.9)	0.04
	1	91 (1.1)	88 (3.2)	0.08
	2	92 (3.6)[b]	73 (3.7)[b]	0.25

[a] Film adhered to PET.
[b] HDPE had begun to peel off the PET substrate.

ification at the PET surface as a consequence of migration of HEMA.

When glass is used as a substrate for the grafting of HEMA onto LDPE, a behavior similar to that noted with PET was observed. After irradiation through a quartz window for 2 min, the contact angle of the grafted side of the film fell from 97° (SD 1.9) to 47° (SD 6.1). Analysis using XPS gave an O/C atomic ratio of 0.29. The deconvoluted C_{1s} peak contained peaks that could be assigned to functional groups present in HEMA at 289.1 eV ($C=O$), 286.8 eV ($C-O$), and 285.7 eV ($C-C=O$). Grafting for 30 min caused the LDPE to adhere to the substrate.

Grafting in an Air Environment

The results for grafting in an air environment using PET as the substrate are given in Table II. It can be seen that the rate of decrease in contact angle when grafting in air is far slower than when the process is carried out under nitrogen. This is probably due to quenching of photochemical and/or radical processes. An increase in the XPS-derived O/C atomic ratio from 0.04 to 0.11 with a corresponding contact angle decrease from 97 to 85° is observed when using a Pyrex filter, indicative of grafting. Irradiation for 30 min using a Pyrex filter in air causes the films to adhere. The films could be partially separated and a smooth surface layer was present on the LDPE, similar to that observed when grafting in a nitrogen atmosphere. Grafting in air using a quartz window resulted in peeling of the LDPE films from the substrate after irradiating for

2 min, probably due to homopolymerization and excessive heating. The large O/C atomic ratio (0.25) obtained when grafting for 2 min through a quartz window is consistent with the presence of homopolymer.

CONCLUSIONS

The photoinitiated grafting of HEMA onto LDPE can be achieved using a solution phase method producing a material with increased wettability. The use of acetone as solvent helps prevent the LDPE film from adhering to the PET substrate. The presence of HEMA at the surface of the grafted LDPE was confirmed by XPS measurements. The use of a Pyrex filter allows the formation of stable poly(HEMA) grafts at long irradiation time whereas a quartz filter results in the formation of grafted poly(HEMA) that contains entangled homopolymer. Grafting in air using a Pyrex filter is possible but occurs at a decreased rate, probably because of partial inhibition of the initiation process.

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