Polymer Bulletin 27, 441–445 (1992)

Polymer Bulletin

The surface modification of poly(ether-imide) by photochemical grafting

Stephen Edge[1], W. James Feast[1,]*, Witold F. Pacynko[2], Linda Preston[1], and Susan Walker[1]

[1]Interdisciplinary Research Centre in Polymer Science and Technology, University of Durham, Durham, UK

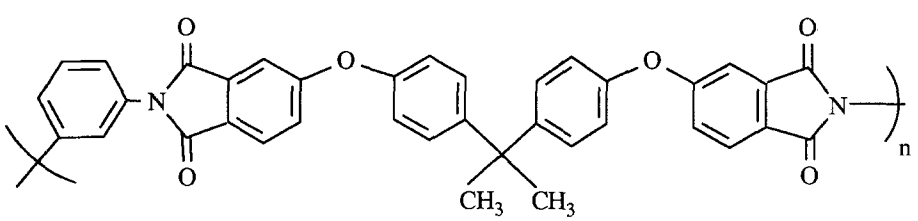
[2]British Petroleum International plc, Sunbury-on-Thames, Middlesex, UK

SUMMARY

The surface modification of poly(ether-imide) by the photochemical vapour phase grafting of poly(2-hydroxyethylmethacrylate) is described. After grafting for four hours the contact angle of the film surface was 62° compared to a value of 80° for an untreated sample. XPS confirmed the presence of 2-hydroxyethylmethacrylate in the polymer surface.

INTRODUCTION

The surface modification of polymers has attracted considerable interest in recent years. One method which has been used to alter the surface properties of polymers is grafting. This technique involves the initiation of polymerisation of vinyl monomers at sites generated on solid polymer surfaces using chemical[1,2] or radiative techniques[3,4]. The grafting of polymer chains onto polymer surfaces can alter the surface properties of the substrate without adversely affecting the bulk properties. In particular this approach has been used to increase the hydrophilicity of materials such as polyethylene[5], polypropylene[6] and poly(ethylene-terphthalate)[7]. Grafting has also been used to prepare membranes based on poly(vinylchloride)[8] and poly(ethylene-tetrafluoroethylene)[9]. In this paper we describe the photochemical grafting of 2-hydroxyethylmethacrylate (HEMA) onto a poly(ether-imide), "Ultem".



Ultem

Ultem is a material which exhibits excellent mechanical properties and has potential applications in the electronics and adhesive industries and in membrane technology. We had an interest in increasing the hydrophilicity of the surface of the material. The grafting of a vinylic monomer such as HEMA onto Ultem should produce a material with increased surface wettability.

EXPERIMENTAL

Reagents and Apparatus:

Acetone (Aldrich, HPLC grade), dichloromethane (Aldrich, HPLC grade) and

*To whom offprint requests should be sent

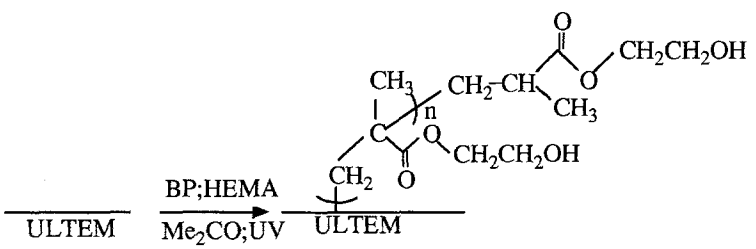
benzophenone (Aldrich) were used as supplied. HEMA (Aldrich) was distilled under reduced pressure in the presence of CuCl (65-68°C, 12mm Hg) and stored under nitrogen at -20°C. Ultem films (thickness 30-50μm) were prepared by casting a solution of Ultem (20% w/w in dichloromethane) using a 200μm blade. Ultem films were washed with MeOH (60°C, 10 mins.) and distilled water (room temperature, 30 mins.) and dried under vacuum before and after grafting. The ultraviolet lamp used was a Hanovia UVS 1000. Contact angles (water, 2μl) were measured using a Rame Hart NRL 100 Contact Angle Goniometer. X-Ray photoelectron spectroscopy (XPS) was performed on a Kratos ES300 electron spectrometer. Samples were irradiated with $Mg_{\alpha 1,2}$ X-rays at a pressure of 10^{-8} torr and an electron take off angle of 35^0. XPS spectra were fitted as described by Clark and Shuttleworth[10]. The binding energies of the electrons were referenced to carbon at 285eV. Atomic ratios were computed from area ratios using the appropriate experimentally derived sensitivity factors for the instrument configuration.

Photografting:

The sample (4cm x 8cm) was placed on a stand in the sealed photografting cabinet along with a solution of benzophenone (0.2M) and HEMA (2M) in acetone which had been purged with nitrogen for 10 minutes. This solution was shielded from UV with aluminium foil. The cabinet was then purged with dry oxygen free nitrogen for 45 minutes and heated to 80°C using a thermostated waterbath. The system was allowed to equilibriate for 30 minutes and irradiated through a quartz plate for the required time.

RESULTS AND DISCUSSION

In its triplet state benzophenone is an efficient abstractor of hydrogen from the substrate. In this case radicals are created in the polymer surface which react with HEMA to produce poly(HEMA) chains (see Scheme 1).



Scheme 1 The Grafting of Ultem with Poly(HEMA).

Ultem films were grafted for 1,2,3 and 4 hours. The contact angle of water on the surface of the films was measured as a function of graft time. The results are shown in Figure 1. It can be seen that the contact angle decreases with increasing grafting time falling to a value of about 65°. As a reference Ultem films were maintained in an acetone saturated nitrogen atmosphere and irradiated through a quartz window. There was no detectable change in the contact angle or XPS spectra. Taken together these results indicate that the surface of the Ultem is rapidly covered with poly(HEMA). The low standard deviation of the contact angle measurements indicates that the poly(HEMA) is homogeneously spread over the surface of the substrate. However these values are higher than the contact angle of 45° for poly(HEMA) which was prepared using a similar

technique. XPS was employed in order to investigate the grafting of HEMA on to Ultem. The results are shown in Table 1.

Figure 1. The Variation of Contact Angle With Grafting Time.

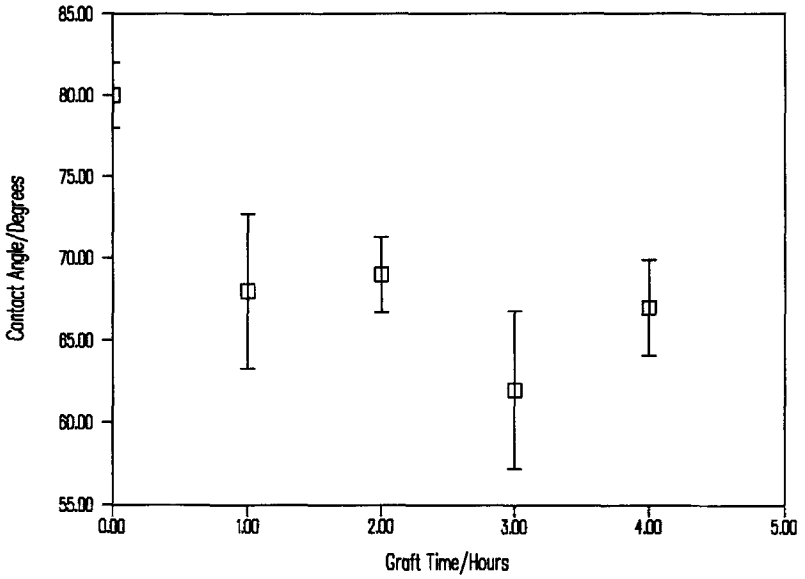


Table 1. XPS Results for Ultem Grafted With Poly(HEMA).

Graft Time / Hours	Atomic Ratio		
	O_{1s}/C_{1s}	N_{1s}/C_{1s}	Si_{2p}/C_{1s}
0 (Theory)	0.16 (0.16)	0.05 (0.05)	0.04 (0.00)
1	0.17	0.02	0.06
3	0.25	0.03	0.02

XPS shows the presence of the four elements C, O, N and Si at the surface of all the samples. The presence of Si is probably due to the contamination of the apparatus with silicone grease. Prior to grafting, the surface of the substrate is seen to have a structure close to that expected. On treatment with the grafting material the amount of nitrogen decreases as would be expected. There is little difference between the one and three hour

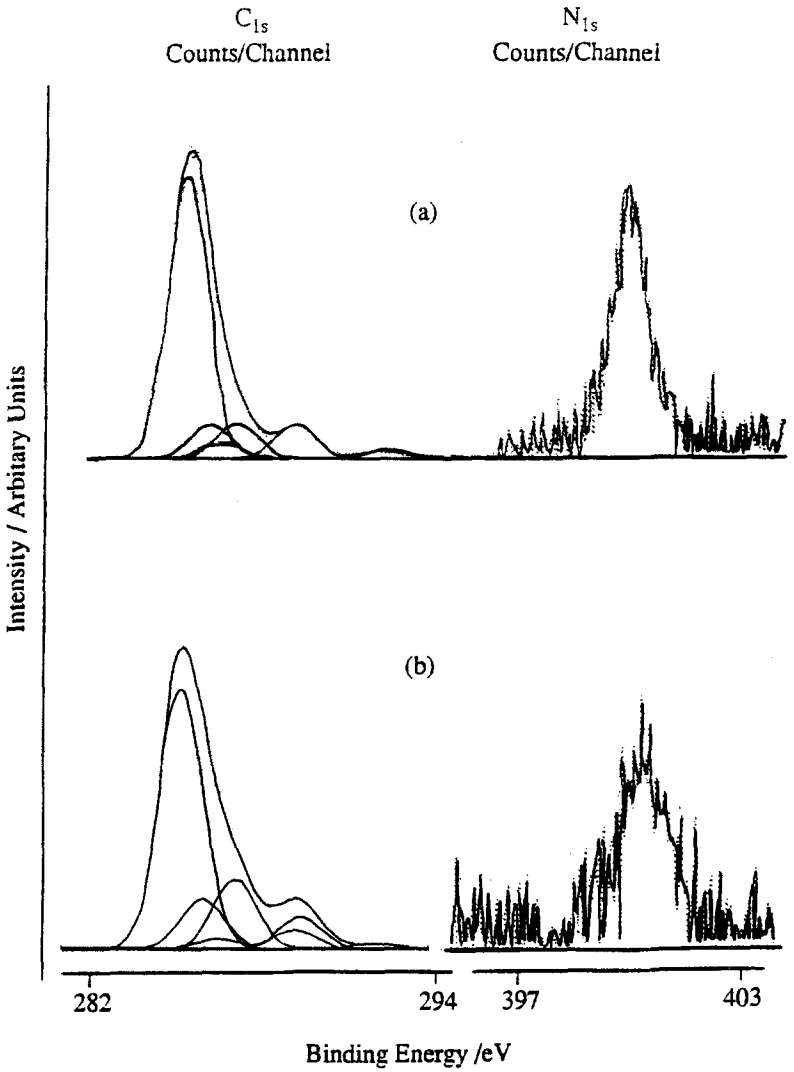


Figure 2 XPS Spectra of HEMA Grafted onto Ultem
(a) Before Grafting and (b) After Grafting for 3 hours.

treatment and in both cases the layer of the grafted material is less than the sampling depth of the XPS experiment (approximately 30 Å). The XPS spectra before and after grafting are shown in Figure 2. The results for the peak fitting of the data are shown in Table 2.

Table 2. Peak Fitting Analysis of XPS Data.

Peak Centre /eV		285.00	285.70	286.20	286.80	288.70	288.95	291.30
Assignment		C-C/H	C-C=O N/O	C-N	C-O	C=O N	C=O O	π–π^*
Area	Untreated	1875	220	111	234	224	-	58
	Treated (3 Hours)	1636	317	58	445	113	204	39

It can be seen that the results are consistent with the formation of poly(HEMA) on the surface of the polyimide. There is a decrease in the peaks corresponding to C-N and O=C-N which indicates that the substrate is being covered with a material which contains no nitrogen. The appearance of a peak which can be assigned to O=C-O is due to the ester linkage in poly(HEMA).

CONCLUSION

The vapour phase photochemical grafting of HEMA onto Ultem produces a material with increased surface wettability. XPS indicates that there is a thin layer of HEMA on the surface of treated Ultem.

ACKNOWLEDGEMENT

We thank British Petroleum International plc, Sunbury-on-Thames for financial support.

REFERENCES

1. R. K. Samal, S. Dash, and A. K. Sahu, *J. Appl. Polym. Sci.*, **41**, 195-203 (1990).
2. A. Tripathy, A., Mishra, M. S. Lenka and P. L. Nayak, *J. Appl. Polym. Sci.*, **26**, 2109-2111 (1981).
3. I. K. Metha, S. Kumar, G. S. Chauhan and B. N. Misra, *J. Appl. Polym. Sci.*, **41**, 1171-1180 (1990).
4. K. Allmer, A. Hult and B. Ranby, *J. Polym. Sci. Polym. Chem. Ed.*, **26**, 2099-2111 (1988).
5. H. Kubota and Y. Hata, *J. Appl. Polym. Sci.*, **41**, 689-695 (1990).
6. Z. P. Yao and B. Ranby, *J. Appl. Polym. Sci.*, **41**, 1469-1478 (1990).
7. E. Uchida, Y. Uyama, H. Iwata and Y. Ikada, *J. Polym. Sci. Polym. Chem. Ed.*, **28**, 2837-2844 (1990).
8. F. Vigo and C. Uliana, *J. Appl. Polym. Sci.*, **38**, 1197-1209 (1989).
9. T. Momose, T. Kitazumi, I. Ishigaki and J. Okamoto, *J. Appl. Polym. Sci.*, **39**, 1221-1230 (1990).
10. D. T. Clark and D. Shuttleworth, *J. Polym. Sci.* **16**, 1093 (1978).

Accepted October 28, 1991 C