Polymer Vol. 37 No. 24, pp. 5537–5539, 1996
Copyright © 1996 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/96/$15.00 + 0.00

S0032-3861(96)00479-X

Plasma copolymerization as a route to the fabrication of new surfaces with controlled amounts of specific chemical functionality

Alison J. Beck, Frank R. Jones and Robert D. Short*
Laboratory for Surface and Interface Analysis, Department of Engineering Materials, University of Sheffield, Mappin Street, Sheffield S1 3JD, UK

(Revised 15 April 1996)

The plasma copolymerization of allyl amine with 1,7-octadiene and of acrylic acid with hexane has been investigated. Plasma copolymerization is shown to be a promising route to the fabrication of new surfaces with controlled concentrations of specific surface functionalities; in this case, amine and carboxylic acid. Copyright © 1996 Elsevier Science Ltd.

(Keywords: plasma copolymerization; polymer surface; plasma polymer)

Introduction

Ultra-thin, pinhole-free films can be prepared from radiofrequency-induced, non-equilibrium plasmas of volatile organic compounds. The process is attractive as an exact control over film thickness can be exercised, film deposition is conformal (even on substrates of complicated geometry) and polymerization takes place in a 'clean' environment without the use of solvents. A number of potential applications for these films have been described in the literature[1–6]. The majority of reports describe films that are insoluble in common solvents, and it is reportedly difficult to prepare films of more than 1 μm thickness[1].

Traditionally, plasma polymers have been thought of as materials ideally suited for use as inert, protective coatings. However, recent work in a number of laboratories has shown that careful control of the deposition parameters allows the fabrication of films that feature a high degree of retention of the chemical functionality of the monomeric precursor. For example, we have found high levels of retention when employing low plasma power, termed 'mild plasma conditions'. This has been demonstrated by the use of X-ray photoelectron spectroscopy (X.p.s.) and secondary ion mass spectroscopy in the analyses of plasma polymers of various methacrylates[7,8], allyl alcohol[9], sulfones[10] and acrylic and methacrylic acids[11]. High levels of functional group retention can also be achieved by significantly reducing the substrate temperature[12].

Retention of monomer functionality offers the exciting possibility of exercising a very high degree of control over processes that depend on surface chemistry. Further significant benefits would accrue if an exact control over the concentration of a specific surface functionality could be achieved. In the plasma polymerization of allyl alcohol[9] it is reported that plasma polymers containing hydroxyl concentrations of up to 23 per 100 carbons can be prepared under mild conditions. An increase in the plasma power reduces this number, but it also introduces a wider range of oxygen–carbon functionalities. Plasma power also affects the film's physical properties, which can vary from low molecular weight oil to highly cross-linked powder. Therefore, plasma power is not an ideal variable for achieving the purpose of controlling functional group concentration. Another variable that affects the level of functional group retention is the monomer flow rate. However, this variable can also produce considerable changes in the deposit's physical properties. The choice of monomer offers some control. However, only a limited range of monomers are available for polymerization—those that have a significant vapour pressure at 10^{-2} mbar. The application of heat to the monomer widens this range, but then monomer stability becomes an issue. Hence, control, over a wide range of concentrations, cannot be simply achieved through the choice of monomer.

We have, therefore, approached the problem by plasma copolymerizing the 'functionalized' monomer with 'dilutent' hydrocarbon monomer. In this preliminary report, we describe the use of plasma copolymerization to exert an exact control over the concentration of surface functionality in plasma deposited films. We have studied two systems. First, we describe the plasma copolymerization of allyl amine with octadiene. We show that, by varying the monomer flow ratio of allyl amine/octadiene, thin-film materials with a range of amine surface concentrations are produced. Second, this approach is shown to be generally applicable, by repeating with acrylic acid and hexane.

Experimental

Plasma copolymerization. Allyl amine (*alam*), acrylic acid (*aa*), 1,7-octadiene (*oct*) and hexane (*hex*) were obtained from Aldrich Chemical Company Co., UK.

The allyl amine and octadiene were copolymerized at a fixed plasma power of 2.5 W and with a total flow rate of approximately 2.2 cm^3 min^{-1}. A polymerization time of 10 min was used. Plasma copolymers were deposited on to a clean aluminium substrate. A summary of the

---

* To whom correspondence should be addressed

Table 1 Summary of experimental conditions for plasma copolymerization of allylamine (*alam*) and 1,7-octadiene (*oct*)

F (*alam*) (cm^3 min^{-1})	F (*oct*) (cm^3 min^{-1})	Total F (measured) (cm^3 min^{-1})	$F_{alam}/(F_{alam} + F_{oct})$ (cm^3 min^{-1})
2.2	0.0	2.2	1.0
1.7	0.55	2.0	0.76
1.2	0.94	2.5	0.56
0.0	2.2	2.2	0.0

r.f. power = 2.5 W
Total flow rate *ca* 2.2 cm^3 min^{-1}
Plasma polymerization time = 10 min

Table 2 Summary of experimental conditions for plasma copolymerization of acrylic acid (*aa*) and hexane (*hex*)

F(*aa*) (cm^3 min^{-1})	F(*hex*) (cm^3 min^{-1})	Total F (measured) (cm^3 min^{-1})	$F_{aa}/(F_{aa} + F_{hex})$ (cm^3 min^{-1})
1.06	0.0	1.06	1.0
0.74	0.29	1.03	0.72
0.55	0.51	1.06	0.52
0.27	0.76	1.03	0.26
0.0	0.99	0.99	0.0

r.f. power = 0.5 W
Total flow rate *ca* 1 cm^3 min^{-1}
Plasma polymerization time = 10 min

Table 3 X.p.s. analysis of plasma copolymers (*alam/oct*) prepared at a total flow rate of *ca* 2 cm^3 min^{-1} and a r.f. power of 2.5 W. N 1s peak fit

	% of N 1s core level (binding energy[a])	
$F_{alam}/(F_{alam} + F_{oct})$ (cm^3 min^{-1})	Component 1 (NH_2)	Component 2 (see text)
1.0	85.2 (399.1)[b]	15.1 (400.1)[b]
0.76	84.3 (399.3)[c]	14.8 (400.5)[c]
0.56	76.7 (399.1)[d]	22.5 (400.5)[d]
0.0	—	—

[a] Binding energy after correction for charging of the sample during X.p.s.
[b] FWHM = 2.03 eV
[c] FWHM = 2.16 eV
[d] FWHM = 1.75 eV
(FWHM = full width half maximum)

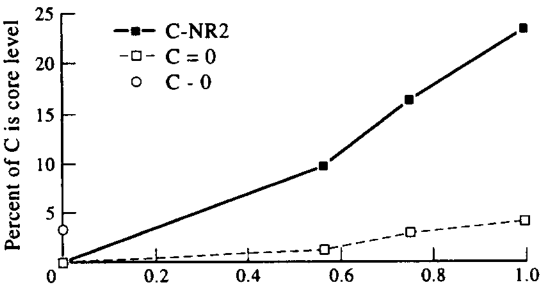

Figure 1 Changes in the peak fit of the C 1s core-line spectra of the plasma copolymers of *alam/oct* with changes in the monomer feed

experimental conditions used in the plasma copolymerizations is given in *Table 1*.

It is worth noting that if ideal gas behaviour is assumed, the ratio $F_{alam}/(F_{alam} + F_{oct})$, where F is the monomer flow rate, is also the mole fraction of allyl amine in the gas feed.

Acrylic acid and hexane were copolymerized using a total flow rate of 1 cm^3 min^{-1} and a power of 0.5 W. The remaining experimental conditions are summarized in *Table 2*.

In both experiments, the monomers were allowed to flow for 1 h after the plasma was extinguished in an attempt to minimize the uptake of oxygen by the plasma copolymers on exposure to the atmosphere.

The plasmas were sustained by a radiofrequency (13.56 MHz) signal generator inductively coupled to the plasma chamber. The reactor design is based on that reported elsewhere[11], although this particular reactor is not interfaced with a mass spectrometer.

Surface analysis. X-ray photoelectron spectra of the plasma copolymers were acquired on a VG Clam 2, using Mg K_α X-rays to excite a spectrum. The X-ray source was operated at 100 W. A take-off angle of 30° wrt the sample surface was used. The pass energy of the spectrometer was 20 eV for narrow scans, and this determined the energy resolution of the spectrometer (Ag $3d_{5/2}$ FWHM of *ca* 1.2 eV). Peak fitting was carried out using Scienta software. The peak fits of spectra obtained on this instrument have been compared with those obtained with data acquired on the ESCA 300 (Scienta) and are in good agreement[8]. X.p.s. analysis was performed immediately after sample preparation. Peak fitting of the core-level spectra was performed using a least-squares routine which, in an iterative manner, achieved optimization of each parameter defining the several component peaks contained within the experimental spectral envelope. The chemical shifts employed in the peak fits were based on those reported in the literature[13].

Results and discussion

Allyl amine/octadiene. The X-ray photoelectron core-line spectra (N 1s, O 1s and C 1s) were run of the plasma copolymers. After appropriate charge correction (to hydrocarbon at 285 eV), the N 1s core-line was peak fitted using two components, and the results of this are given in *Table 3*.

The binding energies of these components can be used to identify the types of chemical environments present within the chemical deposits. The major component of the peak fit (at *ca* 399.1) is consistent with the binding energy reported for NH_2. A smaller component, 15–20% of the intensity of the major component, has been fitted at about 400 eV. This represents N in a more electropositive environment; however, this binding energy is too low for N–O. The most likely environment is that of amide.

The C 1s core-line spectra were fitted using three components corresponding to (1) *C*–H, (2) *C*–NH_2 and *C*–O, and (3) *C*=O chemical environments. The change in the relative contribution of these to the C 1s core-line with variation in the allyl amine/octadiene feed is displayed graphically in *Figure 1*. It is assumed that the major contribution to (2) is *C*–NH_2, based on the low oxygen content of these films (< 4%).

From this figure it can be appreciated that the amount of NH_2 measured in the plasma copolymers is dependent on the mole fraction of allyl amine in the feed. Small amounts of carbon–oxygen functionality were also detected. Since the original monomers did not contain

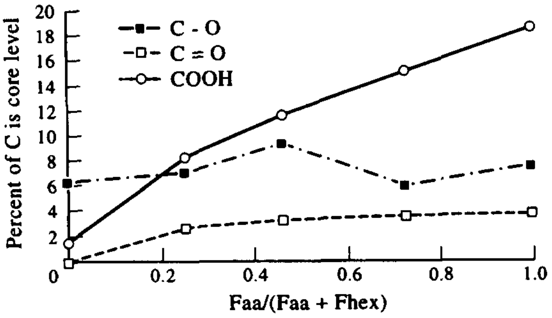

Figure 2 Changes in the peak fit of the C 1s core-line spectra of the plasma copolymers of *aa*/*hex* with changes in the monomer feed

oxygen, it is most likely that these arose from reaction of the copolymers with atmospheric oxygen.

Acrylic acid/*hexane*. The C 1s core-line spectra obtained from plasma copolymers of acrylic acid with hexane were peak fitted using four components, corresponding to *C*–H, *C*–O, *C*=O and O–*C*=O. In *Figure 2*, the changes in the relative contributions of the latter three have been plotted against the monomer feed ratio.

The interpretation of the data presented in *Figure 2* is complicated by the uptake of oxygen from the atmosphere. This effect is most clearly seen in the 'pure' hexane plasma polymer, where over 8% of the carbon is associated with oxygen. However, from the figure it is also evident that the amount of O–*C*=O in the plasma copolymers increases with an increase in the amount of acrylic acid in the monomer feed, and that the relationship is approximately linear. By X.p.s. it is not possible to distinguish carboxylic acid from ester; however, based on the i.r. spectroscopy of some of these plasma polymers, to be reported elsewhere, we believe that most of the O – *C*=O component is indeed carboxylic acid[14]. In this forthcoming report we show that these plasma polymers readily form a salt complex when immersed in a dilute aqueous solution of $NaHCO_3$—which is only possible for acids.

The *C*–O and *C*=O components arise from fragmentation and rearrangement of the acrylic acid in the plasma and post-plasma reactions with the atmosphere. Appreciable amounts of *C*–O were found in deposits even when there was no acrylic acid in the monomer feed, indicating that post-plasma reactions are probably the major contributor to this signal. From *Figure 2*, the *C*=O component is seen to be more sensitive to the addition of acrylic acid to the monomer feed.

In both systems, allyl amine with octadiene and acrylic acid with hexane, there is a clear relationship between the amount of functionalized monomer in the feed and the concentration of surface functionality obtained. These plasma copolymers have been used as thin surface coatings on carbon fibres to control the interfacial bonding between fibre and resin. A direct relationship between interfacial shear strength and the concentration of functionality, amine or carboxylic acid, respectively, has been observed. These data are reported in full elsewhere[15].

A more complete account of the above study is in preparation[16]. Therein, we expand on the reported data, as well as examine the influence of three different hydrocarbon 'dilutent' monomers in the plasma copolymerization of acrylic acid.

Conclusions

The plasma copolymerization of allyl amine with octadiene and acrylic acid with hexane has been investigated. It is shown that plasma copolymerization facilitates surface molecular engineering—where films with controlled concentrations of a specific chemical functionality may be produced. This is achieved simply by varying the mole fractions of the reactants in the monomer feed.

Allyl amine may be used to provide thin surface coatings with controlled amounts of amine. No significant amounts of other chemical functionalities were obtained in the plasma copolymerization with octadiene. In this system there was little post-plasma uptake of oxygen.

The data are complicated in the plasma copolymerization of acrylic acid with hexane by reaction of the plasma copolymers with atmospheric oxygen. Why these plasma copolymers pick up more oxygen, post-plasma, than their allyl amine/octadiene counterparts is still under investigation. However, it is clear that there is still a direct relationship between the amount of carboxylic acid in the plasma copolymers and the amount of acrylic acid in the monomer feed.

Acknowledgements

We gratefully acknowledge the support of the Defence Research Agency (Project DRA-FRN1c/337). Published with the permission of the controller of Her Britannic Majesty's Stationery Office.

References

1 Morita, S. and Hattori, S. in 'Plasma Deposition, Treatment, and Etching of Polymers' (Ed. R. d'Agostino), Academic Press, London, 1990, Ch. 6
2 Chilkoti, A., Ratner, B. D. and Briggs, D. *Anal. Chem.* 1991, **63**, 1612
3 Gombotz, W. and Hoffman, A. *J. Appl. Polym. Sci.* 1989, **37**, 91
4 Inagaki, N. and Matsunga, M. *Polym. Bull.* 1986, **13**, 349
5 Sanchez Urrutia, M., Schreiber, H. P. and Wertheimer, M. R. *J. Appl. Polym. Sci., Polym. Symp.* 1988, **42**, 305
6 Munro, H. S., Ward, R. J., Davies, M. C. and Short, R. D. *Polymer* 1993, **34**, 2250
7 Ward, A. J. and Short, R. D. *Polymer* 1993, **34**, 4179
8 Ward, A. J. and Short, R. D. *Polymer* 1995, **26**, 18, 3439
9 Ameen, A. P., Short, R. D. and Ward, R. D. *Polymer* 1994, **35**, 4382
10 Ward, A. J. and Short, R. D. *Surf. Interface Anal.* 1994, **22**, 477
11 O'Toole, L., Beck, A. J., Ameen, A. P., Jones, F. R. and Short, R. D. *J. Chem. Soc., Faraday Trans.* 1995, **91**, 21, 3907
12 Lopez, G. P., Chilkoti, A., Briggs, D. and Ratner, B. D. *J. Polym. Sci., Part A: Polym. Chem.* 1992, **30**, 2427
13 Beamson, G. and Briggs, D. 'High Resolution XPS of Organic Polymers, The Scienta ESCA300 Database', John Wiley, Chichester, UK, 1992
14 O'Toole, L., Beck, A. J. and Short, R. D. *Macromolecules* (in press)
15 Kettle, A., Jones, F. R., Beck, A. J., O'Toole, L. and Short, R. D. *J. Comp. Sci. Technol.* submitted
16 Beck, A. J., Jones, F. R. and Short, R. D. (in preparation)