Recoverable Surface Modification Using Dendritically Fluorocarbon-Functionalized Poly(methyl methacrylate)

Richard L. Thompson, Amilcar Pillay Narrainen, Stuart M. Eggleston, Imtiyaz A. Ansari, Lian R. Hutchings, Nigel Clarke

Department of Chemistry, Durham University, South Road, Durham, DH1 3LE, United Kingdom

ABSTRACT: Dendritically fluorocarbon-functionalized poly(methyl methacrylate) (PMMA) has been explored as a robust surface-modifying additive in PMMA blends. These functionalized materials, denoted $F_x PMMA_y$, where x is the number of $C_8 F_{17}$ fluorocarbon groups per dendron connected to a PMMA chain of y kg/mol, have been synthesized by living radical polymerization. These materials adsorb efficiently to the surfaces of their blends with unfunctionalized PMMA, resulting in increased hydrophobicity and lipophobicity. Contact-angle goniometry has indicated a substantial reduction in the surface energy toward polytetrafluoroethylene-like surface properties in the case of pure $F_4 PMMA_{8.6}$ and substantial, but incomplete fluorocarbon surface coverage at a lower $F_x PMMA_y$ concentration. The partial coverage has been confirmed by Rutherford backscattering and, together with the weak dependence of the surface modification on the $F_x PMMA_y$ structure, indicates incomplete equilibrium of the surface adsorption. The modified surfaces are quite durable with respect to abrasion under water but are progressively eroded when the double-wipe test is carried out with acetone. $F_x PMMA_y$, dispersed in the remaining film, acts as a reservoir of spare functional groups, from which the damaged surface may be replenished, leading to the recovery of the modified surface properties. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 623–628, 2007

Key words: absorption; blends; dendrimers; fluoropolymers; modification; surfaces

INTRODUCTION

The ongoing drive to develop new technologies and improve the performance of materials in existing applications has generated a huge range of strategies to provide bespoke bulk and surface characteristics. Common examples of this practice applied to polymer surfaces include the use of reactive plasmas or corona discharge and myriad coating methods.[1,2] The durability of a modified surface is an inevitable concern because this places limitations on the range of applications and product lifetime. Clearly, the strength of the bond between the modified surface and the bulk material is of critical importance to its durability. End-functionalized polymers (EFPs) have the innate appeal of a high degree of compatibility with other polymers comprising the same repeat unit. If EFPs can be used to modify the surface properties of a material, then it is expected that the polymer chain of the EFP, being compatible with the matrix, should act as an anchor to the functional group. This in turn should impart an enhanced degree of stability to the modified surface.

Recently, it has been shown that dendritic or multifunctional EFPs have greatly increased surface activity in comparison with their monofunctional counterparts.[3–5] Koberstein and coworkers[6,7] have shown that the optimal effectiveness of EFPs with low energy functional groups is attained with functional groups adjacent to one another on the same end of each polymer chain. Clearly, dendritic functionalization meets this criterion; therefore, the enhanced performance of dendritically multifunctionalized EFPs is not surprising. Before this development, monofunctional EFPs were of academic interest for their ability to promote adsorption to external surfaces[8,9] but of limited practical value because the proportion of the surface that is modified by a single group is generally small in comparison with the area occupied by the anchoring polymer chain.

An additional point of interest with EFP additives is that there may be an equilibrium between the EFP that is adsorbed at the surface of the material and that which is dispersed in the bulk. The EFP in the bulk of the polymer could be viewed as a reservoir of spare functional groups, from which the modified surface may be repaired, should the original functionalities somehow be lost. In this article, we explore the surface properties of dendritically fluorocarbon-functionalized

poly(methyl methacrylate) (PMMA) in blends with unfunctionalized PMMA. In particular, we are concerned with the influences of the additive concentration, molecular structure, and surface (mis)treatment and the potential for recovering the enhanced surface properties.

EXPERIMENTAL

Materials and methods

Unfunctionalized PMMA [weight-average molecular weight (M_w) = 49.0 kg/mol, weight-average molecular weight/number-average molecular weight (M_w/M_n) = 1.02] was prepared with standard living anionic polymerization techniques. Dendritically fluorocarbon-functionalized PMMAs were prepared via living radical polymerization from a fluorocarbon-functionalized dendritic initiator. Here we use the notation F_xPMMA_y, where x denotes the number of C_8F_{17} functional groups per dendritic initiator and y is the weight-average molecular weight of the PMMA chain (kg/mol). F_2PMMA_{40} (M_w = 39.6 kg/mol, M_w/M_n = 1.36) was prepared from a fluorocarbon-functionalized benzyl bromide initiator with CuCl. Although this method was successful for producing high-molecular-weight F_xPMMA_y, it was found that better control over the target molecular weight and polydispersity could be achieved with the corresponding bromoester initiator and CuBr.

The structures of the fluorocarbon-functionalized bromoester initiators are shown in Figure 1, and a typical polymerization was carried as follows: Cu(I)Br (0.25 mmol) and the initiator (0.25 mmol) were placed together with a magnetic stirrer bar in an oven-dried Schlenk tube. The tube was fitted with a rubber septum and pump-filled with nitrogen three times. Degassed N-(n-propyl)-2-pyridylmethanimine (0.50 mmol), methyl methacrylate (25.0 mmol), and toluene (66% v/v) were transferred to the Schlenk tube via a syringe. The solution was further degassed by three freeze–pump–thaw cycles. The tube was then lowered in a thermostatically controlled oil bath at 90°C, and the polymerization was carried out under nitrogen for 5–9 h. Purification was achieved as follows: the solution was allowed to cool, diluted in toluene, and passed through a column of aluminum oxide. The collected solution was concentrated, and the polymer precipitated in hexane. The polymer was dried under a vacuum for 2 days. Two materials synthesized in this way were $F_2PMMA_{8.6}$ (M_w = 8.6 kg/mol, M_w/M_n = 1.28) and $F_4PMMA_{8.2}$ (M_w = 8.2 kg/mol, M_w/M_n = 1.13). In this report, all molecular weight data were obtained by size exclusion chromatography and are given with respect to polystyrene standards.

Sample preparation

Blended films of F_xPMMA_y and unfunctionalized PMMA were prepared by codissolution in toluene fol-
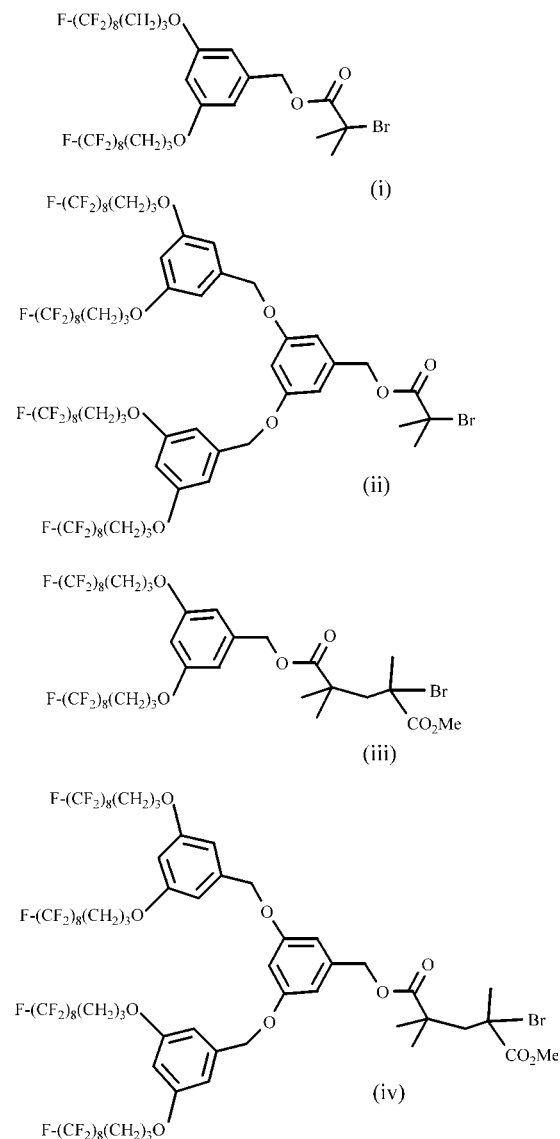
Figure 1 Structures of (i) the dendritic initiator for F_2PMMA_y, (ii) the dendritic initiator for F_4PMMA_y, (iii) F_2PMMA_y, and (iv) F_4PMMA_y.

lowed by spin coating onto silicon wafers. The film thickness was characterized by ellipsometry and optical reflectometry with a Sentech SE500 combined ellipsometer/reflectometer (Berlin, Germany). A native oxide layer of approximately 2.3 nm was present on the silicon wafers, and PMMA films were found to be highly stable with respect to annealing on this surface. The films were allowed to relax toward their equilibrium configuration by annealing above the glass-transition temperature. Before the analysis, all the specimens were annealed under a vacuum for 1 h at 150°C.

Contact-angle analysis

The hydrophobicity and lipophobicity were determined by contact-angle analysis using high purity deionized water and dodecane as contact liquids. An

average of at least three measurements carried out on sessile drops was taken, and the results were generally consistent within $\pm 2°$.

Double-wipe test

The durability of the surface properties was tested by a double-wipe test. Samples were wiped back and forth with a cotton bud, which had been soaked in water or acetone first. The samples were allowed to dry at room temperature before contact-angle measurements were repeated to assess the durability of the surfaces with respect to abrasion under water and acetone.

Ion-beam analysis

The near-surface concentration of fluorocarbon was determined by Rutherford backscattering with a National Electrostatics Corp. (Middleton, WI) 5SDH Pelletron ion-beam accelerator. PMMA is well known to degrade rapidly in ion beams;[10,11] therefore, the following precautions were taken to minimize beam damage to each sample: The incident beam current was restricted to 4 nA to minimize sample heating, and the sample and mount were cooled with liquid nitrogen to less than $-50°C$. A 2-mm-diameter beam was used at an incidence of $85°$ to the sample normal. The total beam charge delivered to any single spot was 0.5 µC, and the summation of data over 12 spots was used to obtain statistically significant data.

RESULTS

Results for the contact angle versus the concentration of the F_xPMMA_y additive are shown in Figure 2. A relatively large increase in the contact angle was found with an increasing additive concentration up to approximately 10%. Further increasing the F_xPMMA_y concentration gave rise to a very slight increase in the hydrophobicity. Not only do the dendritic additives cause surfaces to become significantly more hydrophobic, but as the methyl methacrylate groups at the surface are replaced by fluorocarbon, there is a marked increase in lipophobicity. Dodecane spreads on bare PMMA, giving an effective contact angle of $0°$. However, with as little as 1% $F_4PMMA_{8.2}$, dodecane contact angles of stable sessile drops could be measured. The EFPs contain only a small proportion of fluorocarbon ($\sim 2\%$ by mass in the case of F_2PMMA_{40}), so the surface modification of the blends is very efficient in terms of the amount of fluorocarbon used to achieve the surface properties.

The contact-angle data appeared to show little dependence on the number of C_8F_{17} groups per polymer chain. If anything, the F_2PMMA chain appears to have a greater influence on the polymer film surface than the F_4PMMA chain of a similar molecular weight. This result is somewhat surprising because previously we have found that increasing the number of fluorocar-
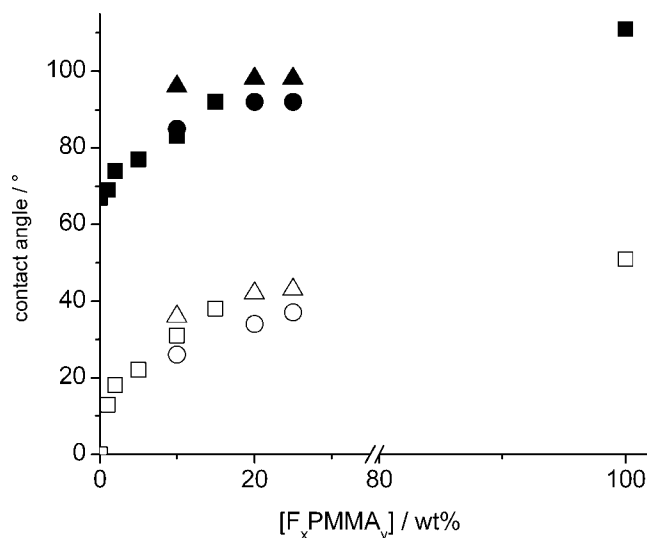
Figure 2 Water and dodecane contact angles versus the concentration of ($\blacksquare,\square$) $F_4PMMA_{8.2}$, ($\blacktriangle,\triangle$) $F_2PMMA_{8.6}$, and ($\bullet,\circ$) F_2PMMA_{40} in blends with unfunctionalized PMMA. The data for water are indicated by solid symbols, and the data for dodecane are indicated by open symbols.

bon groups per polymer chain significantly increases the extent of surface adsorption and contact angle.[3] Increasing the F_2PMMA chain length from 8.6 to 40 kg/mol reduces the measured contact angle at any given concentration. This is the expected result because the relatively large PMMA chain will reduce the maximum packing density (fluorocarbon per unit of area) that can be attained.

The influence of abrasion on modified surfaces with acetone and water is shown in Figure 3. Although this is a rather crude test, it does show that the modified PMMA surface has an appreciable level of resistance to mechanical abrasion even though the functionality responsible for the modification is no more than a molecular layer thick. Clearly, the surface is much more susceptible to attack by a solvent such as acetone than it is to water. After 16 double wipes, the measured contact angles were less than or approximately equal to those measured for pure PMMA; therefore, the sample surfaces must be almost devoid of fluorocarbon functionality. These samples were then annealed under a vacuum for $150°C$ for 1 h, and this process was sufficient to restore much of the original increase in the hydrophobicity. Eventually, with subsequent wiping and re-annealing cycles, the ability to restore the modified surface properties was diminished, and there was a systematic shift in all contact angles toward lower values.

The fluorocarbon content of the near-surface region was determined with Rutherford backscattering. Figure 4 shows typical data for a blended film surface. The magnitude of the small peak at a recoil energy of approximately 775 keV is proportional to the surface concentration of fluorocarbon, and this was determined with the SIMNRA fitting routine and Rutherford
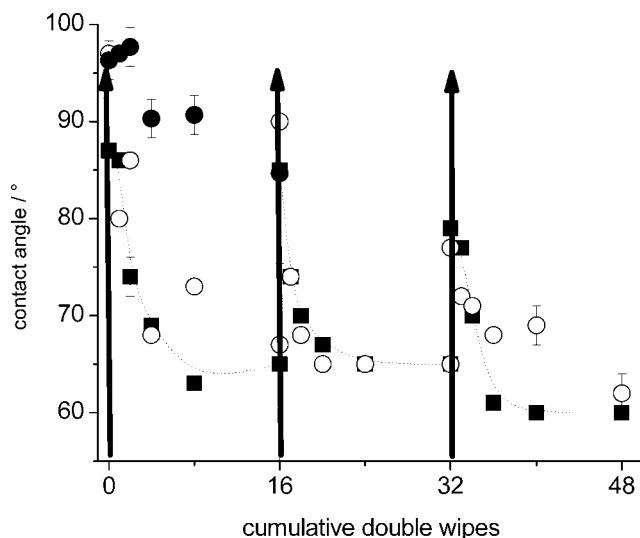
Figure 3 Influence of abrasion on 20% blends of (○) $F_2PMMA_{8.6}$ and (■) F_2PMMA_{40} in PMMA. The vertical arrows indicate the stages at which the surface is annealed for 1 h at 150°C. The influence of double wipes with water instead of acetone is shown for (●) $F_2PMMA_{8.6}$. The dotted lines are guides for the eye.

scattering cross sections.[12] The fluorocarbon content of the surface layer was determined to be 0.56 ± 0.11 mg/ m² of C_8F_{17}.

DISCUSSION

The trend of increasing surface coverage with increasing F_xPMMA_y concentration toward a plateau value is consistent with the expected behavior, although it is notable that significant changes in the contact angle as a result of EFP adsorption are normally limited to very low (subentanglement) molecular weight polymers. Here we demonstrate that large increases in the hydrophobicity are achievable with an EFP that exceeds the entanglement molecular weight. In the quest for durable modified surfaces, this is a significant step forward.

The contact angle (θ) is related to the polar and dispersive components of the surface energy:[13,14]

$$\cos \theta = \frac{2\sqrt{\gamma_s^d \gamma_l^d}}{\gamma_l} + \frac{2\sqrt{\gamma_s^p \gamma_l^p}}{\gamma_l} - 1 \qquad (1)$$

where γ_l^p, γ_l^d, and γ_l are the polar, dispersive, and total surface energies of the probe liquid and γ_s^p and γ_s^d are the polar and dispersive components of the solid surface energy, respectively. The results obtained by the simultaneous solution of eq. (1) for two liquids yield dispersive components of the solid surface energy that are dominated by the contact angle measured with the nonpolar liquid and a polar component that is most

sensitive to the polar liquid. Using this approach, we estimate that the dispersive and polar components of a pure $F_4PMMA_{8.2}$ surface are 16.8 ± 0.6 and 0.4 ± 0.15 mJ/m². Clearly, this represents a very large reduction in the surface energy in comparison with the solid surface energy of PMMA ($\gamma_s \sim 42.1$ mJ/m²)[15] and is slightly less than literature values for polytetrafluoroethylene (PTFE) obtained in a similar way.[14] Lower surface energies than those of PTFE are possible in this system because the surface energy of CF_3 groups (which are present in our materials at much higher levels than in PTFE) is lower than that of CF_2 groups. The lack of any influence of the number of fluorocarbon groups per PMMA chain on contact angles could indicate that the adsorption of these materials reaches a kinetically stable state, at which point further adsorption is extremely slow. We note that the hindered approach to equilibrium is well established for reactive EFPs, forming brushlike layers at solid surfaces[16] and polymer–polymer interfaces.[17,18] If the system were genuinely close to equilibrium, then the absence of increasing hydrophobicity with increasing fluorocarbon content per functional group could indicate that the surfaces of the F_2PMMA blends were close to being saturated with fluorocarbon. In this case, there would be little benefit in using F_4PMMA except at very low additive concentrations. Because the synthetic effort required to produce dendritically functionalized polymers increases with the dendron generation number, it is important to distinguish these possible mechanisms by the determination of the fluorocarbon content of the blend surface.

A simple estimate of the fractional fluorocarbon surface coverage, ϕ_s, is possible from the contact-angle data with water.[19] The inherent assumption is that the
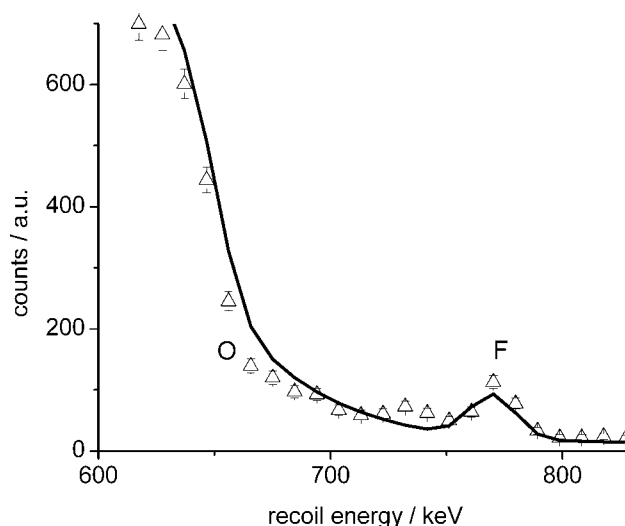

Figure 4 RBS data and fit for 25% $F_2PMMA_{8.6}$ in a PMMA blend. The elemental markers indicate the maximum recoil energies of 1.8 MeV $^4He^+$ from O and F.

surface energies of the blend components at the surface add according to their relative surface coverage, such that

$$\phi_s = \frac{\cos\theta - \cos\theta_{PMMA}}{\cos\theta_{FC} - \cos\theta_{PMMA}} \qquad (2)$$

where θ_{PMMA} is our measured value for the water contact angle on unmodified PMMA and θ_{FC} is the contact angle on a pure fluorocarbon surface. Literature values for the contact angle of water on PTFE vary from around 110 to 115°, and our measured value for pure $F_4PMMA_{8.2}$ is 111°. Using this latter value for θ_{FC} yields $\phi_s \sim 0.67$ for the blend containing 25% $F_2PMMA_{8.6}$ in PMMA. Rutherford Back Scattering (RBS) analysis of the same blended film gave a value of approximately 0.56 mg/m^2 of C_8F_{17}, which is equivalent to 0.4 $F_2PMMA_{8.6}$ chain ends adsorbed per square nanometer. Maximum surface coverage would be obtained if the C_8F_{17} chains were oriented horizontally, in which case the calculated effective area per C_8F_{17} is approximately 0.7 nm^2. Because our measurement of the surface excess indicates approximately 1.25 nm^2 per adsorbed C_8F_{17} unit, we obtain $\phi_s = 0.56 \pm 0.11$. This value is somewhat smaller than, but consistent with, the previous result inferred from contact-angle goniometry. We should therefore conclude that in the intermediate concentration range, a substantial proportion of the polymer surface is covered by fluorocarbon, but ϕ_s is significantly less than unity in all of the blended films. This observation, coupled with the absence of a significant influence in increasing the number of C_8F_{17} groups per polymer chain, strongly suggests that the approach to equilibrium is incomplete within the annealing regime used.

Methods for increasing the durability of modified surfaces and regenerating the properties of damaged surfaces are of obvious technological interest. Our results show that durable, recoverable hydrophobic and lipophobic surfaces are possible with these materials. The durability of these modified surfaces with respect to acetone double wipes appears to be similar for $F_2PMMA_{8.6}$ and F_2PMMA_{40}. All the materials that we have studied are above the entanglement molecular weight for PMMA ($M_e \sim 4.8$ kg/mol),[11] so it is clear that a larger molecular weight range must be studied to establish the role of the polymer chain length in surface durability. An attempt was made to examine the durability of blend surfaces using unreacted fluorocarbon-functionalized initiators, that is, F_2PMMA_0. After annealing under a vacuum, these films had surface properties indistinguishable from those of unfunctionalized PMMA, and this was ascribed to the loss of F_2PMMA_0 by evaporation. Although the precise relationship between the EFP-modified surface durability and polymer molecular weight lies beyond the scope of this work, we can at
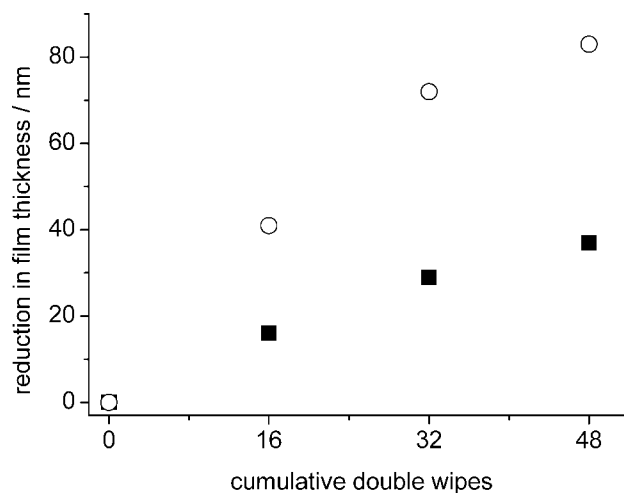
Figure 5 Reduction in the film thickness versus acetone double wipes for 10% blends in PMMA of ($\bigcirc$) $F_2PMMA_{8.6}$ and ($\blacksquare$) F_2PMMA_{40}.

least be sure the PMMA chain has rendered the surface-modifying agent involatile.

The incomplete regeneration of surface properties arises from two factors: First, the films become slightly roughened by the wiping process, which will tend to reduce contact angles below 90°.[1] This is clearly evident for the surfaces after 32 and 48 double wipes and explains why the measured contact angles fall below the value expected for unfunctionalized PMMA. Second, the blended films that were examined were quite thin, and therefore the adsorbed layer of the functionalized polymer accounts for a nontrivial fraction of the total amount in the film. At the beginning of the experiment, the F_2PMMA_{40} and $F_2PMMA_{8.6}$ films were 208 and 146 nm thick, respectively. A surface excess concentration of 0.4 chains/nm^2 corresponds to a surface excess of 4.8 nm. In the 146-nm-thick film of 20% $F_2PMMA_{8.6}$, this surface excess layer accounts for almost one-sixth of the total amount of the functionalized polymer in the film. Consequently, the action of stripping off the surface layer leads to a significant reduction in the overall concentration of the functional polymer remaining. In other words, the reservoir from which the film surface may be replenished is finite and proportional to the film or coating thickness.

The reduction in the film thickness resulting from the acetone double-wipe test is shown in Figure 5. Interestingly, the ability of the film to resist wear in the presence of acetone is significantly greater for the blend containing the higher molecular weight additive, suggesting that film surfaces that are enriched with the lower molecular weight polymer are more susceptible to abrasion. By the end of the experiment, the blend containing 20% $F_2PMMA_{8.6}$ had been reduced by approximately 60% of its original thickness, whereas the reduction of the film thickness for the 20% F_2PMMA_{40} blend was only 15%.

CONCLUSIONS

We have prepared a range of dendritically fluorocarbon-functionalized PMMA materials by living radical polymerization. These materials, when blended with unfunctionalized PMMA and cast as films, adsorb to the surface, causing significant increases in the hydrophobicity and lipophobicity. A large reduction in the surface energy toward PTFE-like surfaces could be inferred from contact-angle goniometry using polar and nonpolar fluids. For all the materials investigated, a broad plateau in the surface modification attained at additive concentrations of 10 wt % and above was observed. Contact-angle analysis and Rutherford backscattering analysis indicated that the surface fluorocarbon coverage in this region was of the order of 60%. Curiously, little influence on the molecular structure was observed with increasing fluorocarbon functionality per PMMA chain, and only a modest reduction in the surface modification with increasing PMMA chain length was found. It appears most likely that the approach to equilibrium is incomplete within the annealing period of 1 h at 150°C, so greater efficiency of surface modification may be attainable with increased annealing times or temperatures. The modified surfaces exhibited considerable durability with respect to wiping with water but were gradually eroded when wiped with acetone, and this resulted in PMMA-like surface properties. Re-annealing the samples was sufficient to restore much of the original level of surface modification, although this is ultimately limited by the quantity of functionalized PMMA available in the film and the surface roughness increase caused by abrasion.

References

1. Garbassi, F.; Morra, M.; Occhiello, E. Polymer Surfaces: From Physics to Technology; Wiley: New York, 1994.
2. Encyclopedia of Polymer Science and Engineering; Mark, H. F.; Bikales, N. M.; Overberger, C. G.; Menges, G., Eds.; Wiley: New York, 1985.
3. Narrainen, A. P.; Hutchings, L. R.; Ansari, I. A.; Clarke, N.; Thompson, R. L. Soft Matter 2006, 2, 126.
4. Li, H.; Zhang, Y. M.; Zhang, H.; Xue, M. Z.; Liu, Y. G. J Polym Sci Part A: Polym Chem 2006, 44, 3853.
5. Hutchings, L. R.; Narrainen, A. P.; Eggleston, S. M.; Clarke, N.; Thompson, R. L. Polymer 2006, 47, 8116.
6. Koberstein, J. T. J Polym Sci Part B: Polym Phys 2004, 42, 2942.
7. O'Rourke-Muisener, P. A. V.; Koberstein, J. T.; Kumar, S. Macromolecules 2003, 36, 771.
8. Elman, J. F.; Johs, B. D.; Long, T. E.; Koberstein, J. T. Macromolecules 1994, 27, 5341.
9. Hopkinson, I.; Kiff, F. T.; Richards, R. W.; Bucknall, D. G.; Clough, A. S. Polymer 1997, 38, 87.
10. Hutchings, L. R.; Richards, R. W.; Thompson, R. L.; Clough, A. S.; Langridge, S. J Polym Sci Part B: Polym Phys 2001, 39, 2351.
11. Shearmur, T. E.; Clough, A. S.; Drew, D. W.; van der Grinten, M. G. D.; Jones, R. A. L. Polymer 1998, 39, 2155.
12. Mayer, M. Technical Report, Simnra Users Guide; Max-Planck-Institut für Plasmaphysik, Garching, Germany, 1997.
13. Owens, D. K.; Wendt, R. C. J Appl Polym Sci 1969, 13, 1741.
14. Clint, J. H.; Wicks, A. C. Int J Adhes Adhes 2001, 21, 267.
15. van de Grampel, R. D.; Ming, W.; Gildenpfennig, A.; van Gennip, W. J. H.; Laven, J.; Niemantsverdriet, J. W.; Brongersma, H. H.; de With, G.; van der Linde, R. Langmuir 2004, 20, 6344.
16. Clarke, C. J.; Jones, R. A. L.; Clough, A. S. Polymer 1996, 37, 3813.
17. O'Shaughnessy, B.; Vavylonis, D. Europhys Lett 1999, 45, 638.
18. Coote, M. L.; Gordon, D. H.; Hutchings, L. R.; Richards, R. W.; Dalgliesh, R. M. Polymer 2003, 44, 7689.
19. Schaub, T. F.; Kellogg, G. J.; Mayes, A. M.; Kulasekere, R.; Ankner, J. F.; Kaiser, H. Macromolecules 1996, 29, 3982.