Spontaneous enrichment of phosphorylcholine groups on polyolefin surface with perfluoroalkylated lipids additives

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Introduction: There has been a great deal of interest in the phosphorylcholine surfaces in both research and technology due to the possibilities of many potential biomedical applications.[1]

Surface modification via surface enrichment of one component of a multicomponent system, the driving force for surface modification in such a system, is largely thermodynamic where the component with the lowest critical surface tension rises to the air/polymer interface, thereby lowering the interfacial free energy.

Consequently, fluorochemicals and fluoropolymers have often been studied as surface-modifying molecules for various applications. We report here a new feature for highly wettable polyethylene films prepared by spontaneous surface-enrichment of perfluoroalkylated phosphorylcholine (PC) additives via a simple heat-press technique.

Methods: Perfluoroalkyl phosphorylcholines (n=6,8,10) were synthesized by an improved process of 2-methacryloxyethyl phosphorylcholine (MPC) synthesis.[2] The chemical structure of perfluoroalkylated PCs is shown in Figure 1. Hexadecyl phosphorylcholine (C_{16}PC) was also synthesized as previously reported.[3]

The composite polyethylene films were processed by a heat-press technique. Typically, the low-density polyethylene (LDPE) micro particles (0.5 g) and 2-(perfluorodecyl)ethyl phosphorylcholine (CF_{10}PC, 0.05 g, 6.86 x 10^{-5} mol) were mixed and thoroughly ground in a mortar. The mixed powder was then placed between two stainless steel plates and pressed at 120°C at a pressure of about 5 MPa for 3 min. To determine the appropriate CF_{10}PC composition, we prepared films with different blend ratios [CF_{10}PC/PE=1/10 (0.05 g, 6.86 x 10^{-5} mol/0.5 g); 1/25 (0.02 g, 2.74 x 10^{-5} mol/0.5 g); 1/50 (0.01 g, 1.37 x 10^{-5} mol/0.5 g); and 1/100 (0.005 g, 6.86 x 10^{-6} mol/0.5 g) by weight]. Other PC compounds were mixed with PE particles with molar compositions similar to that of CF_{10}PC.

X-ray photoelectron spectroscopy (XPS) was performed on a Scienta ESCA-200 spectrometer with AlKα. The dynamic water contact angles for the samples were recorded using a First Ten Angstroms FT-125 goniometer and Gilmont syringes. The advancing (θ_A) and receding (θ_R) contact angle was measured with addition to and withdrawal from the drop, respectively.

Results and Discussion: Figure 2 shows the surface enrichment of the PC additives on the composite films. On every composite film, the surface P/C ratio was higher than that of the bulk ratio. While the P/C ratio was not changed remarkably with the bulk composition of C_{16}PC, the ratio was increased with an increase in the composition of perfluoroalkylated phosphorylcholine. In particular, the phosphorus concentration of the CF_8PC/PE film was significantly higher than those of other composite films with low molar CF_8PC (1.37 x 10^{-5} mol).

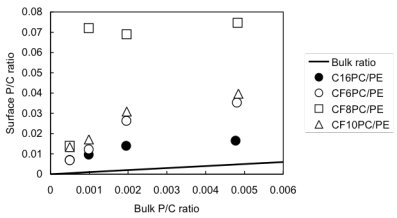

Figure 2 Surface vs. bulk P/C ratio of composite films

Water contact angle data for the PE film was θ_A/θ_R =97°/81°. The contact angles were decreased with an increase in the composition of PC additives. On the C_{16}PC/PE surface, the contact angles reached θ_A/θ_R =43°/15° when the composition of C_{16}PC was 6.86 x 10^{-5} mo1. At this concentration, the surface coverage of C_{16}PC was ~15% calculated from XPS data and was lower than that of fluoroalkylated PCs. The water contact angles of the C_{16}PC/PE film were then relatively high.

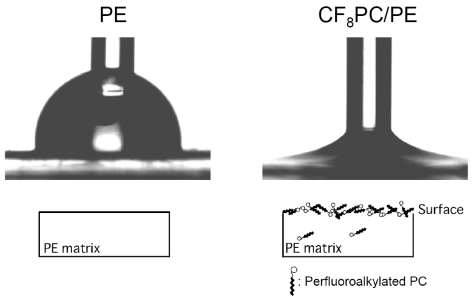

Figure 3 Water drops on PE and CF8PC/PE films

The surface contact angles (θ_A/θ_R) of CF_8PC/PE were dramatically decreased at 28°/8° with 2.74 x 10^{-5} mol CF_8PC and 17°/<5° with 6.86 x 10^{-5} mol CF_8PC. The effects of CF_6PC and CF_{10}PC on improving surface wettability were less than CF_8PC because of their low surface coverage. Photographs of typical water drops on PE and CF_8PC/PE are shown in Figure 3. While a water drop on PE film has a round shape, the shape spread out completely on CF_8PC/PE film with 2.74x10^{-5} mol of CF_8PC. Surface activity and mobility of CF_8PC may be the optimum for the enrichment of polyethylene film surfaces. Perfluoroalkylated PCs are potential compounds to improve wettability of polyethylene film. The high wettability can be obtained without any chemical and physical treatment. Furthermore, no solvent was needed.

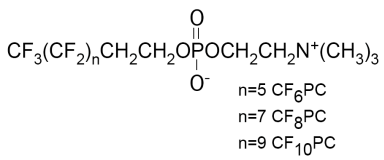

Figure 1 Chemical structure of fluoroalkylated PCs

References: [1] Iwasaki Y et al., *Anal Bioanal Chem* 2005, 381, 534. [2] Ishihara K et al., *Polym J* 1990, 22, 355. [3] Kang EC et al., *Bull Chem Soc Jpn* 2005, 78, 1558.