A simple approach for surface hardening of polystyrene

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ABSTRACT

One strategy in prolonging the lifetime of polymer materials is to improve their surface mechanical properties. A simple and easy method to modify the polymer surface based on the preferential segregation of inorganic materials is applied to a glassy polymer. We clearly show that the polystyrene film with a few nm-thick hybrid surface layer with hydrolyzed tetraethoxysilane exhibits excellent wear resistance and anti-oxidant properties.

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1. Introduction

Nowadays, polymers are ubiquitous in our daily lives because of their flexibility, functionality, lightness in weight, low cost, and so on [1,2]. As such, their long term performance is required. One strategy in prolonging the lifetime of these materials is to improve their mechanical properties at the surface. Conventionally, hard coating processes such as vapor deposition, sputtering, plating, and spraying are used to serve this purpose [3–5]. Although these methods have a tremendous potential, they also possess the drawbacks of high fabrication cost due to the multi-step procedure associated in these strategies. Also, if the adhesion between the coating layer and the underlying matrix is not good enough, it will result in the delamination of the coating layer leading to the more serious problem of loss in the reliability of the material [3–5,7,8].

Recently, we have proposed a one-pot process to construct a nm-thick inorganic layer in the surface region of a typical rubbery polymer, polyisoprene [6]. Our method is based on the preferential segregation of hydrolyzed tetraethoxysilane (TEOS) fed into the system in tiny amounts. The modified surface exhibited several prominent characteristics such as surface hardness, antioxidant properties, transparency, and so forth. Then, it should be next studied whether our method is effective even on a glassy polymer. We first characterize the surface of polystyrene (PS) in which tiny amounts of hydrolyzed TEOS are fed, and then examine wear resistance and the anti-oxidant properties of the system.

2. Experimental

PS with a number-average molecular weight of 180k and a polydispersity index of 1.03 was synthesized by a living anionic polymerization. TEOS (Sigma–Aldrich Co.) was used as a surface modifier. To promote the hydrolysis of TEOS, ethanol (Wako Pure Chemical Industries, Ltd.), H_2O, and hydrochloric acid (HCl, Wako Pure Chemical Industries, Ltd.) were mixed with TEOS. The equimolar ratios of ethanol, H_2O, and TEOS were used. HCl was used as a catalyst at a fixed molar ratio of 0.05 relative to H_2O. The solution was stirred for 2 h at 333 K under an ambient atmosphere. A clear transparent solution was obtained under this condition. We would like to note that the sol–gel reaction in our study was carried out in acidic condition in the presence of HCl. In doing so, the resulting structure of TEOS tends to form slightly branched chain-like structure rather than silica nanoparticles [9,10]. The rate of the sol–gel reaction of TEOS was 74% (26% of the residual ethoxy groups which have not reacted with H_2O) as evaluated by nuclear magnetic resonance (^{1}H NMR). The mixture of PS and TEOS was prepared by blending a cyclohexanone solution of PS and hydrolyzed TEOS solution at a mixing weight ratio of PS and TEOS fixed to 95/5. PS films containing hydrolyzed TEOS (PS/TEOS) were spin-coated from the mixed solution onto hydrogen-passivated silicon wafers. The films were annealed for 24 h at 333 K under ambient atmosphere. In general, the sol–gel reaction is divided into two steps: hydrolysis of metal alkoxides to produce hydroxyl groups and polycondensation
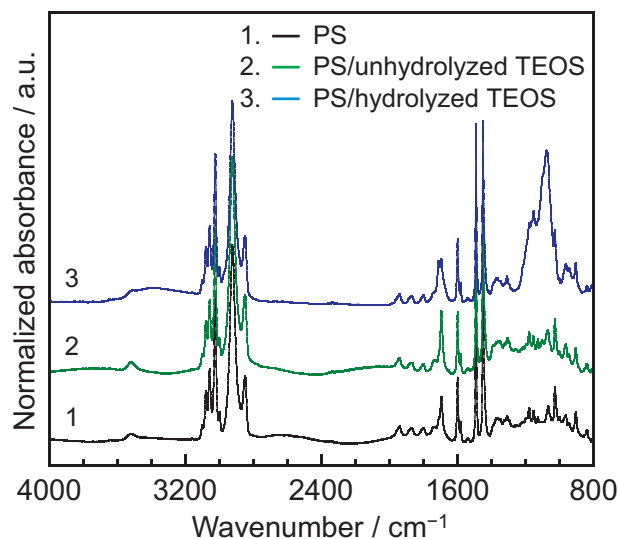
Fig. 1. FT-IR spectra for the PS film, PS film with unhydrolyzed TEOS, and PS film with hydrolyzed TEOS.

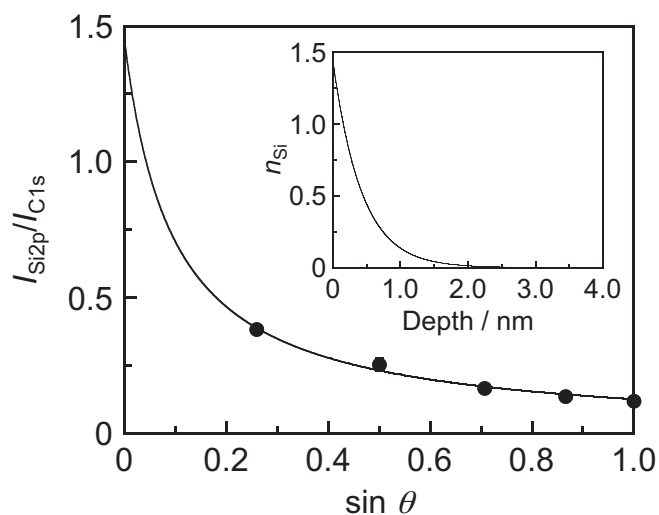**Fig. 2.** Sin θ dependence of the integral intensity ratio of Si_{2p} to C_{1s} ($I_{Si_{2p}}/I_{C_{1s}}$) for the PS/TEOS film. The solid plot denotes the best-fit curve. The inset shows the depth profile of the atomic ratio of silicon to carbon (n_{Si}).

of the hydroxyl groups and residual alkoxyl groups [9–12]. Thermal annealing after film preparation should promote the latter step. However, when a higher temperature was adopted for this purpose, the surface roughness of the film increased due to the formation of cracks. Thus, an annealing condition at 333 K for 24 h, which could accelerate the polycondensation reaction without damaging the film, was chosen.

To confirm the resulting structure of TEOS fed into the system, Fourier-transform infrared (FT-IR) measurements were carried out. FT-IR spectra were obtained by a FT-IR620 (JASCO International Co., Ltd.) spectrometer under vacuum at a resolution of 2 cm^{-1}. The integration number of scans was 64. The chemical composition at the surface of the PS/TEOS film was also examined by X-ray photoelectron spectroscopy (XPS, PHI 5800 ESCA system, Physical Electronics, Inc.). The analytical depth of XPS from the outermost surface is given by $3\lambda \cdot \sin\theta$, where λ and θ are the inelastic mean-free path and take-off-angle for the photoelectrons, respectively [13]. Thus, changing θ enables us to gain direct access to the depth profile of the silicon composition, originating from the incorporated TEOS in the vicinity of the film surface. A scratch test by an atomic force microscope (AFM, E-sweep with an SPI3800 controller, SII Nano Technology Inc.) was performed to evaluate the wear resistance of the film [14,15]. Cantilever with a spring constant of 0.21 N m^{-1} having a tip of radius equal to 6.6 nm was used. The anti-oxidant properties of the film were evaluated on the basis of the surface composition changes after the treatment with O$_2$ plasma, which was generated using a plasma cleaner (PDC-32G, Harrick Plasma) at an applied power of 18 W. Plasma irradiation was conducted at room temperature under a pressure of 107 Pa for 10 s. The chemical composition at the surface of the films before and after the treatment was also examined by XPS.

3. Results and discussion

Fig. 1 shows the FT-IR spectra for a pristine PS film, a PS film with unhydrolyzed TEOS, and a PS film with hydrolyzed TEOS that was reacted under conditions mentioned in the experimental section. The FT-IR spectrum of the PS film containing unhydrolyzed TEOS was quite similar to that of the pristine PS film. This means that the hydrolysis reaction hardly occurred in the glassy polymer film. On the other hand, additional peaks were clearly observed in the Si—O—Si stretching region (1000–1200 cm^{-1}) [9,16] for the PS film

with hydrolyzed TEOS. Thus, this seems to suggest the presence of Si—O—Si bonds due to the hydrolyzed TEOS fed into the film. Hereafter, the PS film with hydrolyzed TEOS is simply referred to as the PS/TEOS film.

Fig. 2 shows the relation between $\sin\theta$ and the integral intensity ratio of Si_{2p} to C_{1s} ($I_{Si_{2p}}/I_{C_{1s}}$) for the PS/TEOS film. Black circles denote experimental data. Smaller $\sin\theta$ value corresponds to shallower analytical depth. The $I_{Si_{2p}}/I_{C_{1s}}$ value increased with decreasing $\sin\theta$. Since silicon exists only in TEOS, this result makes it clear that the TEOS was preferentially segregated at the surface of the PS/TEOS film. To extract the relationship between the real depth and the atomic ratio of silicon to carbon (n_{Si}), we applied a mean-field approximation, in which the surface enrichment of a component exponentially decays with increasing depth, in Fig. 2 as follows [17,18]:

$$n_{Si}(z) = n_{Si,\infty} + (n_{Si,0} - n_{Si,\infty})\exp\left(-\frac{z}{\xi}\right) \qquad (1)$$

where z and ξ are the distance from the outermost surface and the decay length showing how the surface composition reaches its bulk value, respectively. The $n_{Si,0}$ and $n_{Si,\infty}$ are the surface and bulk composition of silicon, respectively. The inset in Fig. 2 shows the depth profile of n_{Si} to reach the best-fitting curve. After Figs. 1 and 2, thus, it can be claimed that a few nm-thick hybrid layer with TEOS was constructed at the surface of the PS film. When two chemical species are mixed, the surface will be generally covered with the component having the lower surface energy [18–20]. Although the hydrolyzed TEOS possessed a higher surface energy than PS, it was enriched at the surface, as shown in Fig. 2. Thus, it can be inferred that the surface segregation of hydrolyzed TEOS is more of an entropy-driven than enthalpy-driven process. [21,22]. In general, the resulting structure through the sol–gel reactions is strongly affected by the reaction conditions such as the amount of H$_2$O added, temperature, the nature of the catalyst, etc. [9–12]. In the current study, TEOS was in part reacted before mixing it with PS solution to control the extent of sol–gel reaction of TEOS. This process was quite sensitive to the extent of the surface segregation for TEOS. For example, when TEOS was hydrolyzed under the presence of a large amount of H$_2$O over TEOS, the hydrolyzed TEOS was not effectively partitioned to the film surface of PS. This is simply because in this case, the network structure was mainly formed