Hydrophobic acrylic hard coating by surface segregation of hyper-branched polymers

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ABSTRACT

The ability of hyperbranched polymers (HBPs) to preferentially segregate to the surface of its matrix owing to its unique structure makes it a good candidate as a surface modifier. One particular challenge in its application as an efficient surface modifier, however, is its possible elimination from the surface due to the lack of attachments between a HBP (modifier) and its host material (polymer matrix). Here, we present a novel approach to efficiently prevent the removal of HBPs from the surface of its host material by directly reacting a HBP containing fluoroalkyl segments (F-HBP) to a multi-functional acrylate monomer prior to curing. We also have characterized surface structure and wettability of the acrylic hard coating material by X-ray photoelectron spectroscopic and contact angle measurements, respectively. The results show that since F-HBP was segregated at the surface, the surface became hydrophobic and more stable. Thus, we claim that our approach results in the formation of a water-repellent acrylic hard coating material.

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1. Introduction

Plastic films bearing a hard outer layer are integral parts of many electronics today. They are found in display panels in televisions, personal computers and mobile phones. The surface of these films is usually modified by a hard coating imparting improved and/or new characteristics that have rendered various applicabilities for these materials in a wide variety of applications. One particular process involves the use of multi-functional acrylates [1]. To prepare the hard coating layer, the most commonly employed technique is the use of a gravure coating method where the film to be coated is passed through a solution containing the hard coating agents composed of the acrylates and a photocatalyst dissolved in an organic solvent. The film is then dried to remove any residual organic solvent. The film is cured by ultraviolet (UV) irradiation afterwards. The curing reaction of the adhered acrylates leads to the formation of a three-dimensional network, imparting hardness and scratch resistance properties to the film [2,3]. A hard coat layer with a thickness ranging from 1 to 10 μm can be obtained [4].

The hard coat layer in such materials is sensitive to physical contact (*e.g.* when touched, fingerprints are left behind limiting

visibility and displayability of graphics). This is because water from the sweat facilitates leaving of imprints during the use of these products. Such issue is particularly relevant with the advent of touch panel displays in today's electronics. One possible solution is the development of a water-repellent surface from such a hard coating process.

Hyperbranched polymers (HBPs) have been widely studied as a novel pathway to enhance synthetic polymer functions [5–7]. They have a significantly larger number of end groups per a molecule compared to linear polymers. Thus, the number density of functional groups in each molecule can be easily increased by introducing them to the end groups. Such has been used in various fields such as biosensing [8], electric devices [9] and so on. Also, the chain dimension of a HBP is relatively smaller than that of a linear polymer with a comparable molecular weight. When a HBP is mixed with a linear polymer matrix, it is preferentially segregated to the surface. This phenomenon can be explained in terms of less conformational entropic penalty and/or translational entropic gain for HBP, present at the surface in addition to the surface localization of chain end groups [10,11]. All these attributes make HBPs a good candidate as a highly functionalized surface modifier for film materials [12]. For example, the surface covered with polyoxometalates was prepared by mixing HBP to a matrix polymer [13]. The dewetting behavior of polymer was also regulated by the presence of HBP [14]. As a surface modifier, one particular drawback of using a HBP, however, is the lack of attachments between the HBP
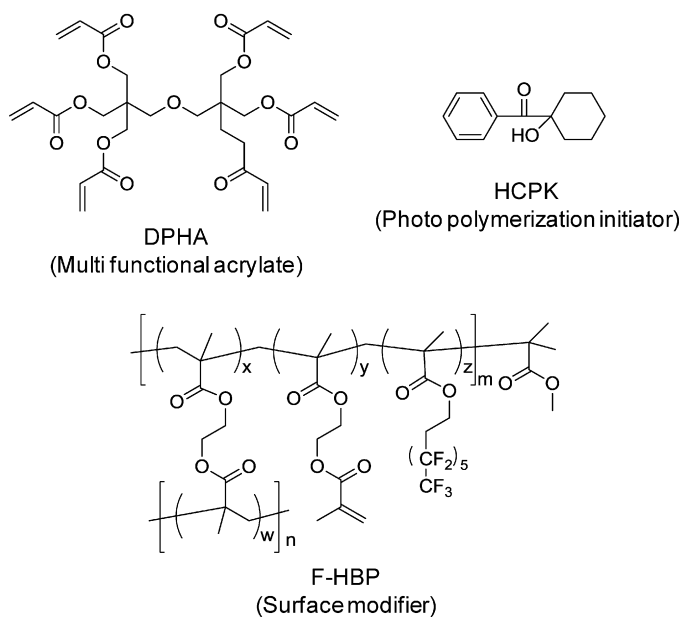

Fig. 1. Chemical structure of DPHA, HCPK and F-HBP.

modifier and its polymer matrix which makes it susceptible for removal from the surface.

In this study, we show the formation of a water-repellent acrylic hard coating material based on a HBP modifier. To efficiently prevent the removal of the HBP modifier from the surface of its host material, we directly reacted a HBP containing fluoroalkyl segments (F-HBP) to a multi-functional acrylate monomer prior to curing.

2. Experimental

2.1. Sample and film preparation

A multifunctional acrylate, dipentaerythritol hex-aacrylate (DPHA), was purchased from Toagosei Co. Ltd. 1-Hydroxycyclohexyl phenyl ketone (HCPK) (BASF Japan Ltd.) was used as the photo polymerization initiator. Solvents like methyl isobutyl ketone (MIBK) and toluene (Kanto Chemical Industry Co. Ltd.) and polymethyl methacrylate (PMMA) (Wako Pure Industry Co. Ltd.) were used as received.

A HBP-containing fluoroalkyl segments (F-HBP) used as a water-repellent surface modifier with a number-average molecular weight (M_n) of 6.2 K and polydispersity index (PDI) of 2.6 was synthesized following the method reported elsewhere [15]. Fig. 1 shows the chemical structure of DPHA, HCPK and F-HBP. The formulation solutions were prepared by mixing DPHA, HCPK, F-HBP and MIBK. The fraction of HCPK was fixed at 5 wt% DPHA. To examine the effect of varying amounts of F-HBP on the surface properties of the films, the fraction of F-HBP in the mixture was varied from 0 to 1.0 wt%. Then, DPHA containing F-HBP was spin-coated onto a polycarbonate substrate. The wet films were annealed at 373 K for 10 min, and then were exposed to UV with a pressure mercury lamp (20 mW cm^{-2} at 365 nm) for 5 s. The UV level was calculated to be equal to 100 mJ cm^{-2}. For comparison, F-HBP/PMMA blend films with a F-HBP fraction of 0.5 wt% were also prepared.

2.2. Characterizations

The rate of the photocrosslinking reaction in the films was evaluated by using attenuated-total-reflection infrared spectroscopy (ATR-IR, Nicolet 6700 IR spectrometer, Thermo Fisher Scientific Inc.). The chemical composition at the film surface was examined by

X-ray photoelectron spectroscopy (XPS, PHI Quantera SXM, Ulvac-Phi, Inc.) using monochromatic Al Kα source operated at 15 kV and 1.7 mA. The C_{1s} peak was calibrated to a binding energy of 285.0 eV for the neutral carbon to correct the charging energy shifts. The analytical depth of XPS is given by $3\lambda \cdot \sin\theta$, where λ and θ are the inelastic mean-free path of photoelectrons in the solid state and the emission angle, respectively. The static contact angle of water on the films (droplet volume was 1 μL) was measured by a DM501 (Kyowa Interface Science Co. Ltd.). The surface morphology of the film surface was observed by an atomic force microscope (AFM, Veeco Instruments Dimension 3100).

3. Results and discussion

First of all, the effect of UV irradiation level on the curing reaction of DPHA was examined. Fig. 2(a) shows the ATR-IR spectra for DPHA with F-HBP. Since the concentration of the carbonyl groups is unchanged during the reaction, the peak associated with the vinyl groups in the IR spectra was normalized against the stretching vibrations of the carbonyl groups. The stretching vibrations of the vinyl groups and the carbonyl groups of DPHA were observed at 1635 and 1730 cm^{-1}, respectively. The absorbance arising from the vinyl groups, namely at 1635 cm^{-1}, decreased with increasing UV irradiation time. The extent of the curing reaction was simply evaluated on the basis of the consumption ratio (CR) of DPHA as shown by the following relation:

$$CR = \left\{ \frac{A_o - A_t}{A_o} \right\} \times 100 \qquad (1)$$

where A_o and A_t are the absorbance at 1635 cm^{-1} before and after UV irradiation, respectively. Using this relation, we here show in Fig. 2(b) the extent of the curing reaction as a function of the amount of UV exposure. The CR value increased with increasing UV irradiation time and until it plateaus around 80 mJ cm^{-2}. However, it did not go beyond 35%. This can be explained in terms of the length of the spacer group among the acrylate units in the DPHA. It has been widely accepted that the rate of the propagation reaction in multi-acrylate monomers decreased with decreasing length of the spacer groups among the acrylate units, resulting in a low CR value [16]. This has been attributed to steric hindrance effect which becomes more significant when the spacer group becomes shorter.

Then, the surface composition of the DPHA film including the F-HBP was examined by XPS. Fig. 3 shows the $\sin\theta$ dependence of F_{1s} to C_{1s} (I_{F1s}/I_{C1s}) for the DPHA film containing 0.5 wt% F-HBP treated under UV irradiation at 100 mJ cm^{-2}. Smaller $\sin\theta$ corresponds to shallower analytical depth. The molar fraction of fluorine and carbon in F-HBP was determined by ^{1}H NMR measurement [17]. The bulk concentration of 0.5 wt% F-HBP can be simply converted then to the atomic ratio of fluorine to carbon of 1.4×10^{-3}%, which is much smaller than the corresponding surface value, as shown in Fig. 3. In addition, the I_{F1s}/I_{C1s} value increased with decreasing $\sin\theta$. Thus, it can be claimed that F-HBP is segregated at the surface of the DPHA film, leading to the hydrophobic surface.

Taking into account that a smaller amount of the additive fed into the polymers would be better for our purpose, the relation between the amount of F-HBP and the I_{F1s}/I_{C1s} was next examined. Fig. 4 shows the I_{F1s}/I_{C1s} value acquired at $\theta = 45°$ against the fraction of F-HBP in the DPHA film. The UV level for the curing reaction was 100 mJ cm^{-2}. For comparison, the bulk ratio of F/C is also shown. It is again clear that F-HBP is segregated at the surface in the DPHA film. The I_{F1s}/I_{C1s} increased with increasing amount of F-HBP fed into the DPHA. The surface segregation of F-HBP was achieved even at 0.5 wt% only. In most systems, the fractional amount of a surface modifier fed into the system is 1 wt% or more with respect to the matrix [18,19].