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Development of surface properties of ultra-highmolecular-weight polyethylene film using sidechain crystalline block copolymers

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Abstract: Ultra-high-molecular-weight polyethylene (UHMWPE) has been widely used in industry; however, the applications for UHMWPE are limited because of low hydrophilic and adhesive properties. Herein, we developed the surface properties of UHMWPE by using side-chain crystalline block copolymers (SCCBCs), which consist of a side-chain crystalline unit and a functional unit. This process only required immersing the UHMWPE film in the diluted SCCBC solution, which enabled the UHMWPE surface to be coated homogeneously. The results of the contact angle and tensile shear test showed that the surface of UHMWPE modified with SCCBC was improved in hydrophilicity and adhesive properties. In addition, high adhesion strength was measured on UHMWPE surfaces dipped in a SCCBC solution at high temperature with the UHMWPE film becoming elongated at all parts other than the adhesion contact area.

Keywords: adhesion; hydrophilicity; side-chain crystalline block copolymer; surface modification; ultra-high-molecular-weight polyethylene (UHMWPE).

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1 Introduction

Plastics have played an important role in industrial applications for many years. Global production of resins and fibers increased from 2 million tons in 1950 to 380 million tons in 2015 with an average compound annual growth rate of 8.4% [1]. Polyethylene (PE) accounts for 30% of the total plastic production in the world. Moreover, PE has been widely used in consumer products such as pipes and packaging materials because of its easy molding capabilities, low cost, and chemical resistance [2-4]. Various types of PE have been manufactured such as low-density PE (LDPE) [5], cross-linked PE [6], and high-density PE (HDPE) [7] to satisfy the high demand for a wide range of products in the market. Recently, ultra-high-molecularweight PE (UHMWPE) has been developed to improve the heat resistance and mechanical properties of PE [8]. UHMWPE is just one of a range of engineering plastics [9] such as polyoxymethylene [10], poly(butylene terephthalate) [11], and polyamide [12] that have been developed for various applications. UHMWPE has been widely used for artificial joints [13], ballistic protection [14], and rope [15] due to its excellent mechanical properties and biocompatibility. However, PE has low hydrophilicity and adhesion because PE consists of a very long alkane chain, which limits its usefulness.

Numerous processes have been developed to impart specific properties to PE. Some of these processes can be used for modification of PE by composite materials such as laminating multiple thin films and polymer blending with other kinds of material, which have been successful in improving hydrophilicity, adhesive properties, and mechanical strength of PE [16–19]. However, these methods generally require a high level of experimental technique to ensure successful and consistent results. On the other hand, surface modification has been developed as a simple process, which can modify the surface of PE easily with good repeatability [20]. It is difficult to use chemical treatments to modify the surface of PE due to its high chemical stability, so most surface modifications are performed by physical means such as plasma or corona treatment [21–23]. Although these methods have been

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successful in imparting dyeability, adhesion, and other properties by forming functional groups of hydroxy and carboxy groups accompanied by scission of the PE alkane chain at the surface, some drawbacks have been found. For example, surface modification using physical treatment requires special equipment such as a plasma generator, and the improvements in the PE properties were not always good enough. In addition, these methods were limited by the shape of substrates because for instance, plasma is not able to reach inside porous membranes. Moreover, chemical reactions of graft polymerization were necessary after surface modification in order to keep the modification effects for long time. For these reasons, the development of simple modification techniques for the addition of specific properties onto a PE surface has remained a challenging problem.

In our previous work, it was found that linear lowdensity polyethylene (LLDPE) surfaces could be easily modified by using side-chain crystalline block copolymers (SCCBC) which are a block copolymer consisting of both long alkane chains and functional units [24]. The surface modification mechanism is showed in Figure 1. At first, the side-chain crystalline unit of SCCBC was attracted to the LLDPE surface by van der Waals forces and adsorbed on the LLDPE surface by the formation of cocrystals because the long alkane chains of SCCBC and LLDPE have similar structures. As a result, the functional units of SCCBC covered the LLDPE surface, which imparted specific characteristics to the LLDPE. It was demonstrated that LLDPE, LDPE, and HDPE surfaces could show increased dispersibility, hydrophilicity, and adhesive properties using SCCBC [25-27]. In this study, the development of surface modification on UHMWPE surfaces using SCCBC to impart adhesive and hydrophilic properties is investigated. The process conditions such as the type of SCCBC, concentration and temperature of the solution, and the dipping time are varied in order to determine the optimal combination of condition. The characterization of the modified UHMWPE and the evaluation of

surface properties by tensile shear test and contact angle measurement are evaluated and it confirmed the success of the surface modification leading to the enhancement of surface properties of the UHMWPE.

2 Materials and methods

2.1 Materials

The UHMWPE film was supplied by Yodogawa Hu-tech Co., Ltd., Osaka, Japan and was cut in the dimensions of $100.0 \times 25.0 \times 0.5$ (length × width × thickness in mm). The Aron Alpha 201 instant adhesive which included α-cyanoacrylate as the main ingredient was purchased from Toagosei Co., Ltd., Tokyo, Japan. Other ingredients (used without further purification) were acquired as follows: Blemmer® VA (behenvl acrylate) (BHA) from NOF Corp., Tokyo, Japan; 2-(tert-butylamino)ethylmethacrylate (TBAEMA) from Sigma-Aldrich Co., LLC., State of Missouri, USA; stearyl acrylate (STA) from Tokyo Chemical Industry Co., Ltd., Tokyo, Japan; di(ethylene glycol)ethyl ether acrylate (DEEA) from Sigma-Aldrich Co., LLC., State of Missouri, USA; BlocBuilder® MA from Arkema Inc., Paris, France; xylene from FUJIFILM Wako Pure Chemical Corp., Osaka, Japan; and butyl acetate from FUJIFILM Wako Pure Chemical Corp., Osaka, Japan.

2.2 Polymerization of SCCBC

Polymerization of SCCBC and surface modification was conducted as described previously [26, 27]. Two different kinds of SCCBC; BHA-TBAEMA, and STA-DEEA, were prepared in this study. For BHA-TBAEMA, a solution of BHA (5.0 g, 13.1 mmol) in butyl acetate (5.0 ml) and BlocBuilder® MA (0.38 g, 1.0 mmol) was added to a separable flask under nitrogen flow. The mixture was heated to 110°C and stirred for 24 h. A solution of TBAEMA (5.0 g, 27.0 mmol) in

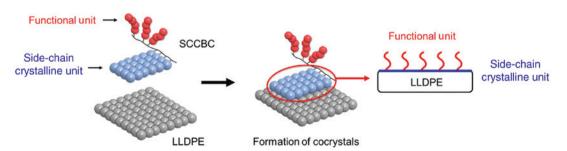


Figure 1: Schematic diagram of an adsorption mechanism of side-chain crystalline block copolymer (SCCBC) on linear low-density polyethylene (LLDPE) surface [24].

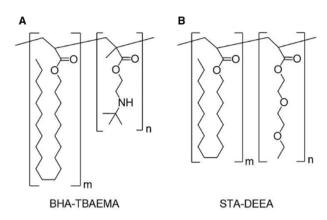


Figure 2: Chemical structure of SCCBC; (A) behenvl acrylate-2-(tert-butylamino)ethylmethacrylate (BHA-TBAEMA) and (B) stearyl acrylate- di(ethylene glycol)ethyl ether acrylate (STA-DEEA).

butyl acetate (5.0 ml) was deoxygenated with nitrogen for 20 min and then added to the separable flask and stirred at 110°C. After 24 h, the mixture was cooled rapidly in order to quench the polymerization. The reaction mixture was purified by re-precipitation using methanol. The mixture was then filtered and the residue evaporated under reduced pressure to afford BHA-TBAEMA as a pale-yellow solid. For STA-DEEA, the polymerization was prepared using the same procedure. The chemical structure and molecular weight of the polymerized SCCBC; BHA-TBAEMA and STA-DEEA are shown in Figure 2 and Table 1, respectively.

2.3 Surface modification of UHMWPE by SCCBC

A solution of SCCBC (BHA-TBAEMA or STA-DEEA, 40.0 mg, 0.1 wt%) in xylene (40.0 g) was heated to 60°C. Then, UHMWPE films were immersed in the SCCBC solution for 10 min and dried for 1 day in order to remove the solvent.

2.4 Characterization

X-ray diffraction (XRD) profiles were recorded by a LabX XRD-6100 (Shimadzu Corp., Japan). The Fourier transform

Table 1: Number-average molecular weight (M_p) , weight-average molecular weight (M...), and polydispersity index of polymerized side-chain crystalline block copolymer (SCCBC).

SCCBC type	M _n (g/mol)	M _w (g/mol)	PDI
BHA-TBAEMA	5600	6300	1.12
STA-DEEA	8600	5500	1.57

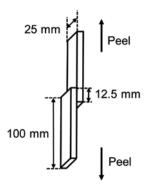


Figure 3: Ultra-high-molecular-weight polyethylene (UHMWPE) sample dimensions for the tensile shear test.

infrared (FTIR) spectra were obtained with a Spectrum Two (PerkinElmer Inc., USA). Adhesion strengths were evaluated by tensile shear tests using an EZ-LX compact table-top tester (Shimadzu Corp., Japan). Two films of modified UHMWPE were fixed by an instant glue with a contact area measuring 12.5×25 mm. The tensile shear tests were performed after curing the glued films at room temperature for 1 day after applying the adhesive. Five samples of each were tested and averaged for evaluation of the adhesive strength test. The schematic of UHMWPE films after applying the adhesive is shown in Figure 3. The water contact angle was measured by the DropMaster DM-301 (Kyowa Interface Science Co., Ltd., Japan) in order to evaluate the hydrophilicity of the UHMWPE films. The measurement of contact angle was averaged from five samples.

3 Results and discussion

3.1 Verification of surface modification

Figure 4 shows XRD profiles of UHMWPE and SCCBCs. Two intensive crystalline peaks of UHMWPE were detected at 22° and 25°, which corresponded to the (110) and (200) plane, respectively [28, 29]. SCCBCs of both BHA-TBAEMA and STA-DEEA also showed a diffraction peak at 22°, which was approximately the same position as the (110) plane of UHMWPE. This result suggests that the sidechain crystalline unit of both SCCBCs (BHA or STA) were aligned epitaxially and formed cocrystals on the UHMWPE surface because of the same crystal plane at (110). As a result, SCCBCs adhered to the UHMWPE, which effectively inherited specific properties from the functional unit of the each SCCBC (TBAEMA or DEEA).

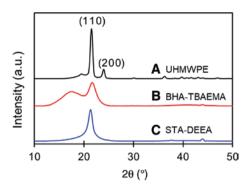


Figure 4: X-ray diffraction profiles; (A) nonmodified UHMWPE, (B) BHA-TBAEMA, and (C) STA-DEEA.

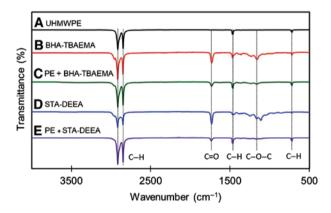


Figure 5: Fourier transform infrared spectra; (A) nonmodified UHMWPE, (B) BHA-TBAEMA, (C) UHMWPE modified by BHA-TBAEMA, (D) STA-DEEA, and (E) UHMWPE modified by STA-DEEA.

Figure 5 shows FT-IR spectra of nonmodified UHMWPE, two kinds of SCCBCs (BHA-TBAEMA, and STA-DEEA), and UHMWPE modified by both SCCBCs. Nonmodified UHMWPE (Figure 5A) shows the typical alkane peak (C-H) at 2915, 2848, 1473, 1463, 731, and 719 cm⁻¹ [30, 31]. New peaks appeared in both modified UHMWPE films derived from both SCCBCs (STA-DEEA and BHA-TBAEMA) that corresponded to the C=O of ester group stretching at 1733 cm⁻¹, and the C-O-C asymmetric stretching at 1160 cm⁻¹. These results confirmed that UHMWPE was successfully modified by SCCBCs (BHA-TBAEMA and STA-DEEA).

3.2 Evaluation of adhesive properties of UHMWPE modified by BHA-TBAEMA

The adhesive strength of UHMWPE modified by BHA-TBAEMA for different preparation conditions was evaluated by tensile shear tests and are shown in Figure 6. Nonmodified UHMWPE film was easily peeled off with an adhesive strength of 0.16 N/mm². Figure 6A shows the effects of solution temperature on the adhesive strength of the modified UHMWPE. It was found that the adhesion strength increased to 0.43 N/mm² for UHMWPE modified at 20°C. In addition, the adhesive strength improved to 0.73 N/mm² for UHMWPE films that were modified by BHATBAEMA solution at 80°C and 100°C. At 120°C, the adhesion strength of the modified UHMWPE film decreased to 0.64 N/mm² because of the deformation of the UHMWPE surface. However, at 120°C the adhesive strength improved on UHMWPE films when the dipping time was decreased from 5 min to 1 min.

The effect of dipping time and BHA-TBAEMA concentration at 80°C were investigated and summarized in Figure 6B,C, respectively. It was found that all UHMWPE film modified by BHA-TBAEMA exhibited a strong and consistent adhesive strength for a range of dipping times from of 0.17 min to 30 min (Figure 6B). When UHMWPE film was modified by different concentrations of BHA-TBAEMA solution (Figure 6C), the adhesive strength was measured as 0.48 N/mm² at both 0.01 and 1.00 wt%. However, for concentrations of 0.05, 0.10, and 0.50 wt% the modified UHMWPE film showed an adhesive strength of 0.73 N/mm². From these results, it can be deduced that the maximum adhesive strength of UHMWPE modified by BHA-TBAEMA solution was achieved at 0.1 wt%, 80°C, and dipping for 5 min.

Figure 7 shows photo images of UHMWPE films after the tensile shear test. It was found that nonmodified UHMWPE films were easily peeled off at the adhesion area (Figure 7A). On the other hand, UHMWPE modified by BHA-TBAEMA at 0.1 wt%, 80°C, and 5 min of dipping time showed elongation in all areas other than the adhesive contact area. This result supported the high adhesive strength of UHMWPE film observed after modification with BHA-TBAEMA.

3.3 Evaluation of hydrophilicity of UHMWPE modified by STA-DEEA

Hydrophilicity of UHMWPE was found to be improved by modification with STA-DEEA. Figure 8 shows water droplets on UHMWPE films. It was found that nonmodified UHMWPE film shows hydrophobicity with 94° of water contact angle (Figure 8A). In contrast, the hydrophilicity was detected on UHMWPE modified with STA-DEEA (Figure 8B) with 59° of water contact angle. Hence, hydrophilicity was successfully imparted to UHMWPE surface by modification with STA-DEEA.

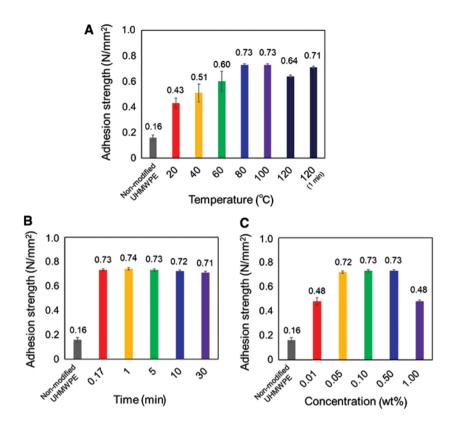


Figure 6: Adhesion strength of UHMWPE modified by BHA-TBAEMA with different preparation conditions; (A) dipped in a xylene solution adding 0.1 wt% BHA-TBAEMA at different temperatures for 5 min, (B) dipped in a xylene solution adding 0.1 wt% BHA-TBAEMA at 80°C for different times, and (C) dipped in a xylene solution at 80°C with different BHA-TBAEMA concentrations for 5 min.

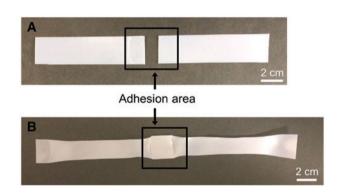


Figure 7: Images of samples after the tensile shear test; (A) nonmodified UHMWPE and (B) UHMWPE modified by BHA-TBAEMA.

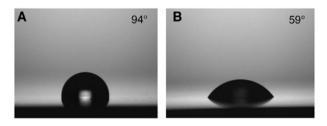


Figure 8: Images of water droplets on UHMWPE films; (A) nonmodified UHMWPE and (B) UHMWPE modified by STA-DEEA.

4 Conclusion

The adhesive properties and hydrophilicity of UHMWPE were improved significantly by a facile surface modification with SCCBC. Two kinds of SCCBC; BHA-TBAEMA and STA-DEEA were synthesized and prepared as diluted solutions prior to dipping by the UHMWPE film. The surface modification of UHMWPE by SCCBC; BHA-TBAEMA or STA-DEEA was successful, which was confirmed by the changes of chemical structure of UHMWPE due to the functional unit of the SCCBC (TBAEMA or DEEA). Moreover, the cocrystals between the side-chain crystalline unit of the SCCBC (BHA or STA) and the crystalline part of UHMWPE confirmed the successful surface modification by the dipping method. BHA-TBAEMA solution concentration, temperature, and dipping time were varied in order to determine the optimal combination of parameters. The highest adhesive strength of UHMWPE modified with BHA-TBAEMA (0.73 N/mm2) was obtained from 0.1 wt% of BHA-TBAEMA solution at 80°C for a dipping time of 5 min. Moreover, hydrophilicity was also improved on UHMWPE modified with STA-DEEA. The water contact angle of modified UHMWPE was around 59°, which showed the hydrophilic properties on the surface.

These results imply that surface modification of UHMWPE by using SCCBC can impart additional and improve properties on UHMWPE surface such as dye ability, biocompatibility, and conductivity by selecting a suitable functional group and degree of polymerization of SCCBC and using the optimal conditions for the preparation and use of the SCCBC solution. This method was expected to be a practical and alternative method for surface modification of PE surface.

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