

Development of polyolefin materials with biocompatible surface using supercritical carbon dioxide

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To utilize polyolefins for biomaterials, biocompatible group was introduced onto polyolefins. In general, however, it is difficult to introduce biocompatible groups directly onto the hydrophobic surface of polyolefins. In this study, we paid attention to poly(vinyl acetate) (PVAc) of which the side group can be readily converted to the hydrophilic group. PVAc was immobilized onto polyethylene (PE) by *in situ* radical polymerization of vinyl acetate monomer using supercritical carbon dioxide as a solvent of monomer and swelling agent of polymer. The acetyl group on the surface of the prepared PE/PVAc blend was converted to the hydroxyl group by hydrolysis. The hydroxyl group on the surface of PE was reacted with 2-chloro-2-oxo-1,3,2-dioxaphospholane followed by adding trimethylamine, to form the phosphorylcholine (PC) group as a biocompatible surface of PE. The products were characterized by attenuated total reflection fourier transform infrared spectroscopy (ATR-FTIR), contact angle measurement, and X-ray photoelectron spectroscopy (XPS). ATR-FTIR and XPS measurement revealed that PC group was introduced onto the surface of PE. The contact angle decreased with the increase in polarity of functional group on the surface of PE. Thus, we could introduce the hydroxyl group on the surface of PE effectively. Various functional groups containing PC group can be also introduced on the surface of polyolefins based on this method.

Key words: phosphorylcholine, polyolefin, supercritical carbon dioxide, surface modification

1. INTRODUCTION

Polyolefins such as polypropylene (PP) and polyethylene (PE) etc. are conventional polymer materials due to low cost and versatile properties. They have specific characteristics such as chemical and water resistance, flexibility, non-toxicity, processability, low density, transparency, permeability, electrical insulation, and mechanical properties [1]. One of application fields of polyolefin is the biomaterial. The demand for the polyolefin increases because polyolefin is a raw material for single-use medical devices. The reason for the increase of demand is that the polyolefin is excellent in the mechanical properties, the economy, and molding [2]. But, the biocompatibility has not been considered in polyolefin. It is known that the surface of polyolefin has been poor in the biocompatibility. For example, when it contacts blood, thrombus is formed on the polyolefin very easily [3].

If the biocompatibility of PE can be improved without loss of its excellent feature, modified-PE would be used much more for biomaterials. Therefore, the aim of this work is to introduce the phosphorylcholine (PC) group having an excellent biocompatibility onto the polyolefin surface. Because, PC group has control over nonspecific adsorption of protein, adhesion and activation of cells and living tissues [4-6]. It is difficult to introduce PC group having polar element into the polyolefin of the non-polarity polymer [2].

In recent years, there has been a great deal of interest in using supercritical carbon dioxide (scCO₂) as a

solvent and/or a swelling agent for polymer processing [7]. scCO₂ has been widely used in the fields of polymer sciences such as synthesis of different kinds of polymers [8-11], preparing fibers[12-14], generation of fine particles[15-18], preparing polymer composites [19-21], incorporation of additives into polymers[22, 23], and producing foam materials [24-26]. It can dissolve small organic molecules, and can swell most polymers. scCO₂ has near-zero surface tension and large diffusion coefficient. Therefore, it can be used to impregnate different organic molecules into polymer matrix. When monomer and initiator were impregnated into the polymer substrate and subsequently polymerized, a new polymer blend can be prepared [19, 20]. Miscibility is realized only the surface by controlling the mass gain rate.

Using the scCO₂, we succeeded to obtain miscible blends of isotactic polypropylene (iPP) or syndiotactic polystyrene (sPS) with poly(methyl methacrylate) (PMMA) even though the two polymers are incompatible in conventional methods [27-29]. The solubility of the molecule having polar group such as PC or hydroxyl group, to the scCO₂ is very low. Therefore, it is difficult to impregnate the PC monomer directly.

In this study, we paid attention on poly(vinyl acetate) (PVAc) of which the side group can be readily converted to the hydroxyl group. PVAc was immobilized onto PE by *in situ* radical polymerization of the vinyl acetate monomer using scCO₂ as a solvent of monomer and swelling agent of polymer. The acetyl group was

converted to the hydroxyl group by hydrolysis on the surface of the obtained PE/PVAc blend. PE with the biocompatible surface was prepared by adding the PC group to the hydroxyl group. The products were characterized by attenuated total reflection fourier transform infrared spectroscopy (ATR-FTIR), contact angle measurement, and X-ray photoelectron spectroscopy (XPS).

2. EXPERIMENT

Materials

The liner-low-density polyethylene (PE) sheet was prepared by hot-pressing a commercial pellet (Mitsui Chemical, Inc) at 170°C. This sheet was cut into the size of 20×20×0.5mm, extracted with methanol for 24h in a Soxhlet-extractor, and dried *in vacuo* at room temperature. Vinyl acetate (VAc), methanol, acetone, and sodium hydrate (NaOH) were purchased from Kanto Chemical Co. and used without further purification. Tetrahydrofuran (THF) and trimethylamine (TMA) were purchased from Kanto Chemical Co. and used after distillation. 2-Chloro-2-oxo-1,3,2-dioxaphospholane (COP) was synthesized and purified by the previously reported method [6]. 2,2'-Azobisisobutyronitrile (AIBN) were purchased from Kanto Chemical Co. and used after recrystallization in methanol. Carbon dioxide (CO₂) with purify of 99.5% was provided by Tomoe Shokai Co. and used as received.

Preparation of PE-PVAc blend using supercritical carbon dioxide

An apparatus for preparation of PE/PVAc blend consisted of a 50ml stainless steel vessel, a magnetic stirrer, a constant temperature air bath (Model SCF-Sro, JASCO), a thermo couple and a pressure gauge. The pressure gauge was composed of a transducer (Model PTX1400, Druck Japan Co.) and an indicator, with precision of ±0.2%FS in the pressure range of 0 – 40 MPa. PE sheet was suspended in the vessel by means of wire mesh. No part of PE sheet was contact with the monomer solution and with the wall of the vessel. PE sheet, VAc and AIBN were placed in the vessel, and sealed. Air in the vessel was replaced by CO₂ in atmospheric pressure. After the system had reached thermal equilibrium (35°C), the vessel was pressurized to 6.0MPa CO₂ by a CO₂ delivery pump (Model SCF-Get, JASCO) and heated to a reaction temperature (80 °C) for about 25 min. After the reaction was completed, the vessel was cooled to 10 °C before depressurisation. The PE-PVAc blend sheet was dried *in vacuo* at room temperature after extracted with acetone for 5 h to remove unreacted reagents and homopolymer by using a Soxhlet-extractor. The mass gain was calculated by the following equation:

$$\text{Mass gain (\%)} = \frac{W_t - W_0}{W_0} \times 100 \quad (1)$$

where W_0 is the initial weight of PE sheet and W_t is the weight of PE-PVAc blend sheet after dry.

Hydrolysis of acetyl group on the surface of PE-PVAc blend sheet

PE-PVAc blend sheet was refluxed in 30ml of a 0.2M NaOH/methanol solution for 3h. PE-OH sheet was obtained after washing with methanol and water, and dried *in vacuo* at room temperature.

Addition of PC group onto PE-OH sheet

PE-OH sheet was soaked in water overnight, and then freeze-dried. After PE-OH sheet had been soaked in COP for 2h at room temperature, the sheet was washed five times by distilled THF. The sheet and distilled THF (25ml) were put in a flask, and then it was cooled to -30°C. Excess amount of dry TMA was added in the flask. This flask was then closed, and maintained at room temperature for 24h. After the sheet was washed with methanol and dried, PE-PC sheet was obtained.

Characterization

The measurement of ATR-FTIR of the surface of product sheets (PE, PE-PVAc, PE-OH and PE-PC) was carried out with a FTIR spectrophotometer (Perkin-Elmer Spedtrum One) with universal ATR sampling accessory.

The surface of product sheets was analyzed using highly sensitive XPS (AXISHSi, Shimadzu/KRATOS). The releasing angle of the photoelectron for each atom was fixed at 90°.

The static contact angle of water on the products sheets was measured using the sessile drop method at room temperature (21°C) using a contact angle goniometer (Erma G-1). The static contact angle measurement was repeated at least 5 times, and the mean value was shown as data.

3. RESULTS AND DISCUSSION

Preparation of PE-PVAc blend sheet using supercritical carbon dioxide

The PE-PVAc blend preparation was performed at 80°C and for different time periods. Fig.1 illustrates the effect of reaction time on the percentage of mass gain. It is evident that the percentage of mass gain increases initially and reaches a plateau in 5h. After some time, all the initiator and monomer are consumed, thus no further change in mass gain rate was observed with increasing reaction time.

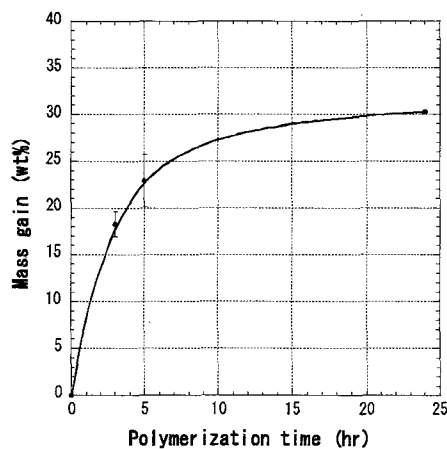


Fig.1 Effect of polymerization time on the mass gain of PVAc into PE.

All reactions were conducted under the following conditions; P = 6.00 MPa, T = 35 °C, polymerization temp. = 80 °C, The concentration of VAc with 1.2 wt% AIBN added is 1.00 mol/L.

ATR-FTIR spectroscopy measurements

Fig.2 shows the ATR-FTIR spectra of original PE sheet, PE-PVAc sheet, PE-OH sheet and PE-PC sheet.

It can be seen that the spectra of original PE sheet and PE treated by $scCO_2$ are almost identical. This means that $scCO_2$ dose not affect on the chemical structure of PE in the course of swelling [30]. The ATR-FTIR spectrum of PE-PVAc sheet shows stretching bonds at 1725 cm^{-1} for C=O groups (Fig.2(b)). It was confirmed that PVAc was immobilized on the PE sheet.

PE-OH sheet was prepared using hydrolysis of acetyl group on the surface of PE/PVAc sheet. The spectrum of PE-OH sheet shows stretching bonds at 3500 cm^{-1} for -OH group (Fig.2(c)). The absorption of the acetyl group of PVAc disappeared, and the absorption of the hydroxyl group could be observed. It was found that the acetyl group on the surface of PE-PVAc sheet was hydrolyzed.

After addition of PC group onto the surface of PE-OH sheet, new absorptions at $1200 \sim 1350\text{ cm}^{-1}$ (-P=O, C-N) and $960 \sim 1150\text{ cm}^{-1}$ (P-O-R, -N⁺R₃, R is alkyl group) were confirmed (Fig.2(d)). The hydroxyl group on the surface of PE was reacted with COP(chloride) followed by adding TMA, to form PC group. This method can be also applicable to introduce various functional groups using other chloride.

XPS measurements

Fig.3 shows the XPS spectra of original PE, PE-PVAc, PE-OH and PE-PC. In the original PE sheet, a strong intensity at 285 eV was observed. This is attributed to carbon atoms in the methylene chain. A small peak at 535 eV was also observed. This peak is attributed to oxygen atoms and may come from oxidation or contamination of the PE sheet.

After immobilization of PVAc into PE sheet, XPS

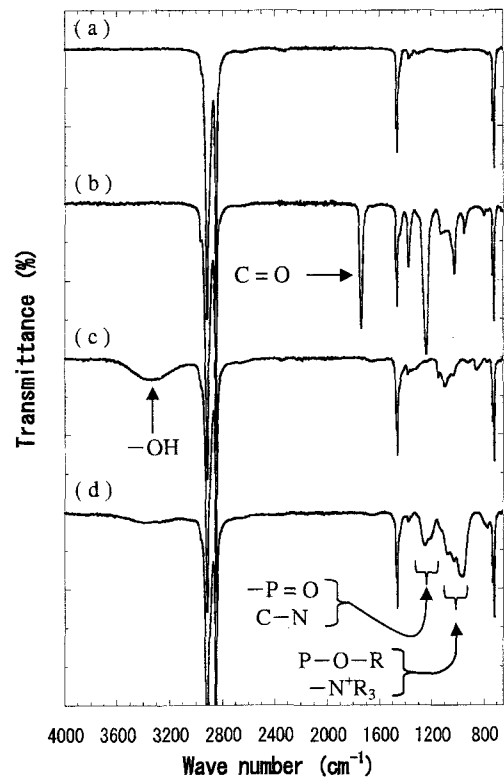


Fig.2 ATR-FTIR spectra of (a) PE, (b) PE-PVAc(mass gain 19.8wt%), (c) PE-OH(hydrolysis of (b)) and (d) PE-PC(addition of PC group to (c)).

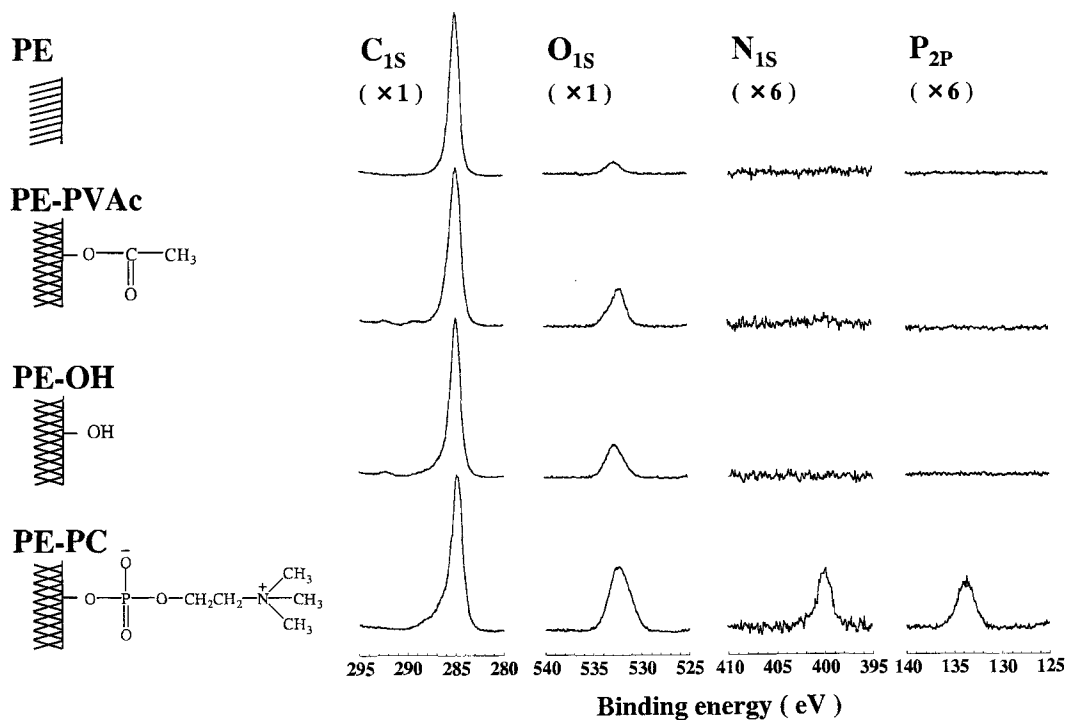


Fig.3 XPS charts of PE, PE-PVAc (mass gain 19.8wt%), PE-OH and PE-PC. Intensities of each atom was normalized by that of C_{1s} at 285eV.

peaks became broad in the carbon atom region and the new peak was observed in the oxygen atom region. This broad peak was attributed to acetyl group in the carbon atom region and new peaks of the oxygen atom region was attributed to carbonyl group (C=O) of acetyl group.

In the case of the hydrolysis of the PE-PVAc sheet, the shape of the peak on the oxygen region transformed. The transformation of the peak was caused that acetyl group was converted to hydroxyl group.

After addition of PC group, the XPS dramatically changed. In the carbon atom region, XPS peaks became broad. This broad peak was attributed to the ether bond (C-O-C) and carbonyl group (C=O). In the oxygen atom region, the increase in peak intensity is caused by the increase in amounts of oxygen. The nitrogen peak was observed at 401 eV. In addition, phosphorus peak was observed at 134eV, and was attributed to the PC group.

Contact angle measurements

The water contact angles on original PE, PE-PVAc sheet, PE-OH sheet and PE-PC sheet were $96\pm 3^\circ$, $88\pm 3^\circ$, $62\pm 5^\circ$ and 78° , respectively. The contact angle on the PE-PC sheet varied greatly. This fact may be thought that the inhomogeneous surface was formed. Formation of the inhomogeneous surface was caused by the low reaction rate due to Solid-liquid reaction and the low molecular mobility of the hydroxyl group on PE. Thus, the contact angle decreased with the increase in polarity of functional group on the surface of PE.

4.CONCLUSION

PVAc onto polyethylene(PE) was immobilized by *in situ* radical polymerization of the vinyl acetate monomer using supercritical carbon dioxide as a solvent of monomer and swelling agent of polymer.

ATR-FTIR spectra of PE-PVAc and PE-OH sheets indicate that PVAc was immobilized onto PE, and the acetyl group on the surface of the prepared PE/PVAc blend sheet was converted to the hydroxyl group by hydrolysis.

ATR-FTIR and XPS spectra of PE-PC sheet indicate that PC group was introduced onto the surface of PE sheet.

The contact angle decreased with the increased in polarity of functional group on the surface of PE. It was considered that the surface of PE-PC sheet was an inhomogeneous surface due to a dispersion of the water contact angle.

We could introduce the hydroxyl groups on the surface of PE effectively. These hydroxyl groups could be substituted by other functional groups. So, various functional groups including PC group could be introduced on the surface of polyolefins based on this method.

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