

Surface modification of ethylene-vinyl alcohol (EVOH) copolymer films by the attachment of triethoxysilane functionality

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Summary

Triethoxysilane groups were covalently attached onto the surface of ethylene-vinyl alcohol (EVOH) copolymer film via a urethane linkage through reaction between the hydroxyl groups in EVOH and 3-isocyanatopropyltriethoxysilane in the presence of dibutyltin dilaurate as catalyst. This reaction was confirmed by ATR-IR and XPS analysis. XPS results also indicated that this reaction was not surface sensitive and the modified layer was at least 40 Å in depth. The modified film samples were further reacted with tetramethoxysilane (TMOS) for partial hydrolysis and condensation and XPS results showed a significant increase in the contents of oxygen and silicone on the surface which confirmed the above reaction.

Introduction

Ethylene-vinyl alcohol copolymers (EVOH) are hydrolyzed copolymers of vinyl acetate and ethylene. They are semicrystalline and their properties are dependent on the relative concentration of the comonomers. The vinyl alcohol component has exceptionally high gas barrier properties while the ethylene offers good moisture resistance, mechanical and thermal properties, and processibility (1,2). Because of their excellent gas barrier properties, they are commercial materials with applications mainly in food packaging. The increase in practical applications in food packaging has also brought about gradual expansion into other fields such as containers, pipes, and construction materials for surface applications. In order to improve the properties of this material and further exploit its utility in more fields in the future, it is necessary to prepare the copolymer surface with specific functional groups in defined locations. For example, a multilayer composite can be made by coating, laminating, or coextrusion. In these cases, poor adhesion between different layers can occur and result in poor properties. To overcome this problem, functional groups can be introduced on the surface through chemical reaction and serve as the bond

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between the non-adhering layers. This paper reports the surface modification of EVOH films by the attachment of triethoxysilane functionality and the application of a sol-gel coating of tetramethoxysilane (TMOS) on this surface.

Experimental

Materials

Isopropanol, tetrahydrofuran (THF), toluene, and dibutyltin dilaurate were purchased from the Aldrich Company. TMOS and 3-isocyanatopropyltriethoxysilane were obtained from Hüls America Company and used without additional purification. EVOH films were obtained from the Hoechst Celanese Company. The thickness of the film was 1 mil. The quoted ethylene content was 32 mol%. Figure 1 shows the DSC behavior for the EVOH copolymer used in this study. As clearly noted, a well defined melting point occurs at 184 °C. The T_g of 84 °C labeled in this figure has also been confirmed by dynamic mechanical spectroscopy (DMS). Prior to XPS (X-ray photoelectron spectra) studies, the film samples were extracted with refluxing isopropanol for 1 hour and dried at 100 °C under vacuum for 24 hours in order to dramatically reduce the amount of contaminants on the film surface. XPS experiments did demonstrate that this procedure can give samples consistently free of detectable contaminants. The shrinkage of EVOH films during solvent extraction was found negligible (less than 1 %).

Reaction Between Copolymer Film And Silane (Preparation Of EVOH-OC(O)NH(CH₂)₃Si(OEt)₃).

EVOH film samples were placed in a flask and purged with nitrogen for several minutes. Toluene (10 g), dibutyltin dilaurate (0.05 g), and 3-isocyanatopropyltriethoxysilane (10 g) were then added into the flask. The whole system was purged again with nitrogen. The reaction was allowed to proceed at 50 °C for about 20 hours. After the reaction, samples were washed with THF (3 x 15 ml), isopropanol (2 x 15 ml), and toluene (2 x 15 ml) and then dried for 24 hours under vacuum.

Partially Co-hydrolysis And Condensation Of TMOS And EVOH-OC(O)NH(CH₂)₃Si(OEt)₃.

TMOS, isopropanol, and 0.5 N aqueous HCl solution (with molar ratio TMOS/H₂O/isopropanol/HCl = 1/1.5/2/0.014) were mixed together in a flask under stirring. EVOH-OC(O)NH(CH₂)₃Si(OEt)₃ film samples were then put into this solution and the partial hydrolysis and condensation reactions were allowed to proceed at room temperature for 24 hours. The film samples were washed

with isopropanol (3 x 15 ml), water (3 x 15 ml), and toluene (3 x 15 ml), and dried for 24 hours under vacuum.

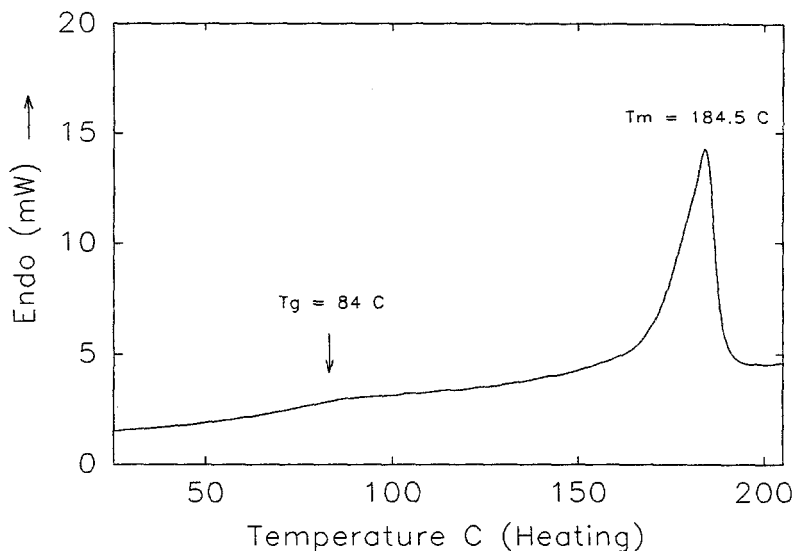


Figure 1. DSC behavior of EVOH film.

Surface Characterization.

XPS were recorded by using a Kratos XSAM800 spectrometer with Mg K α excitation (260 W). Spectra were obtained using an analyzer positioned at 75 $^{\circ}$ or 15 $^{\circ}$ from the film surface. Atomic compositions were determined by using the instrument's computer and programmed sensitivity factors: C_{1s}, 389.945; O_{1s}, 667.441; N_{1s}, 552.978; Si_{2p}, 457.914. Attenuated total reflectance infrared (ATR-IR) spectra were recorded under nitrogen by using a Bio-Rad FTS-40A FTIR spectrometer and a germanium internal reflection element at a 45 $^{\circ}$ angle.

Results and Discussion

Reaction Between Copolymer Film And Silane.

Since hydroxyl groups react with isocyanate groups at high temperature or in the presence of catalyst, the first question addressed was whether the hydroxyl groups on or near the surface of the EVOH film would also react with the isocyanate groups of the 3-isocyanatopropyltriethoxysilane moieties. The swelling experiment showed that EVOH film cannot be swollen by isopropanol,

THF, toluene, or 3-isocyanatopropyltriethoxysilane. Therefore, EVOH copolymer films were placed in the toluene solution of 3-isocyanatopropyltriethoxysilane and the reaction was carried out as described in the experimental section. It was found from XPS and ATR-IR measurements that the hydroxyl groups on the surface of EVOH films did react with 3-isocyanatopropyltriethoxysilane. Figure 2 shows a generalized scheme of this reaction. There is no by-product in this reaction, with urethane linkages being the sole product. The ATR-IR spectra in Figure 3 clearly shows the loss of the broad O-H band at 3335 cm^{-1} , which indicates that reaction has occurred between the hydroxyl groups and isocyanate groups. Also, the appearance of carbonyl band at 1695 cm^{-1} and a coupled N-H/C-N deformation band at 1528 cm^{-1} occurs which indicates the formation of urethane linkages. These results were further confirmed by use of XPS as displayed in Figure 4 and through use of the atomic composition data in Table 1. The data in Table 1 show that the atomic composition on the surface observed by XPS agreed well with the atomic

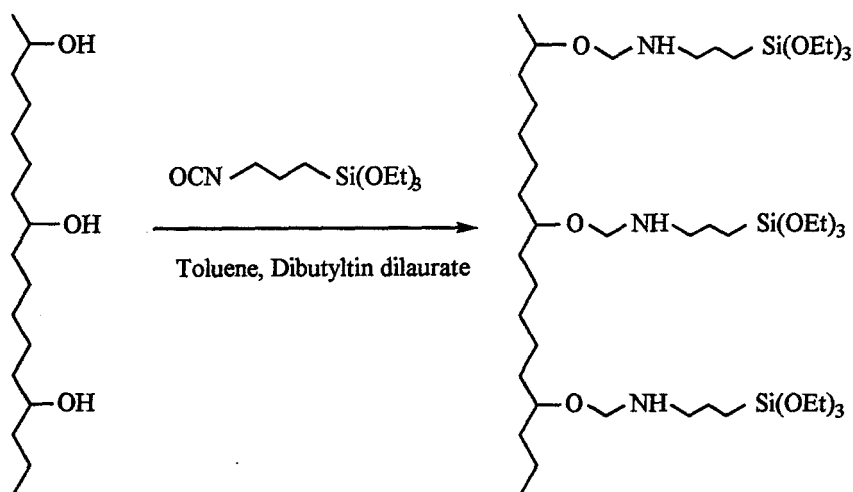


Figure 2. Reaction scheme for the surface modification of EVOH films.

composition calculated based on the empirical formula and the above chemical reaction mechanism. The atomic composition observed at the take off angles of 75° (40 Å) and 15° (10 Å) clearly indicated that the entire outer 40 Å of surface had undergone reaction at the conditions utilized. It has been confirmed

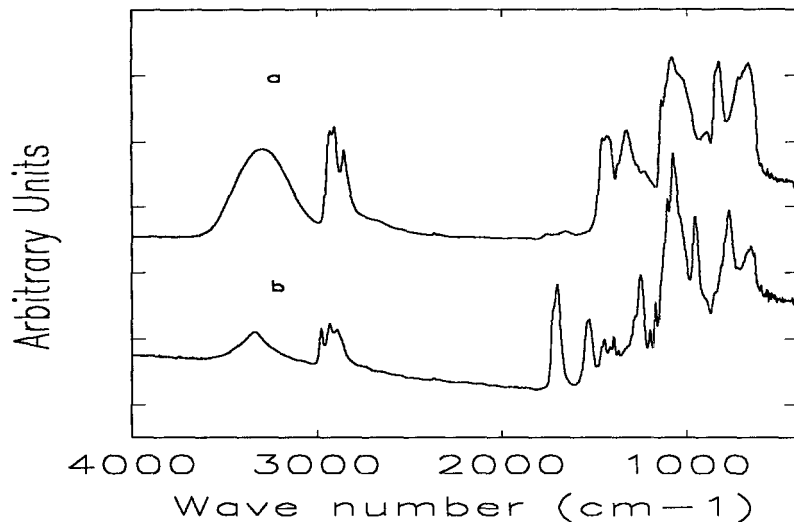


Figure 3. ATR-IR spectra of EVOH film surface. (a) before surface modification, (b) after surface modification (EVOH-OC(O)NH(CH₂)₃Si(OEt)₃).

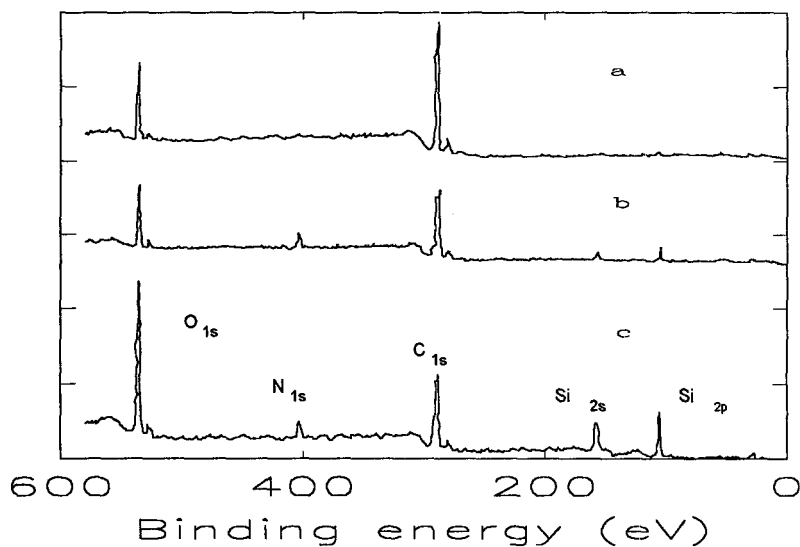


Figure 4. XPS spectra of EVOH film surface. (a) before surface modification, (b) after surface modification with silane (EVOH-OC(O)NH(CH₂)₃Si(OEt)₃), (c) after partial hydrolysis and condensation of EVOH-OC(O)NH(CH₂)₃Si(OEt)₃ with TMOS.

that this reaction is not a very surface sensitive reaction and the depth of reaction should be much larger than 40 Å (3,4). Figure 5 shows the high resolution C_{1s} spectrum of the modified surface. As noted, this spectrum has been fit with three peaks. The high binding energy peak was assigned to the carbonyl carbons, the middle binding energy peak to the carbons bound to N and O, and the low binding energy peak to the remaining carbons.

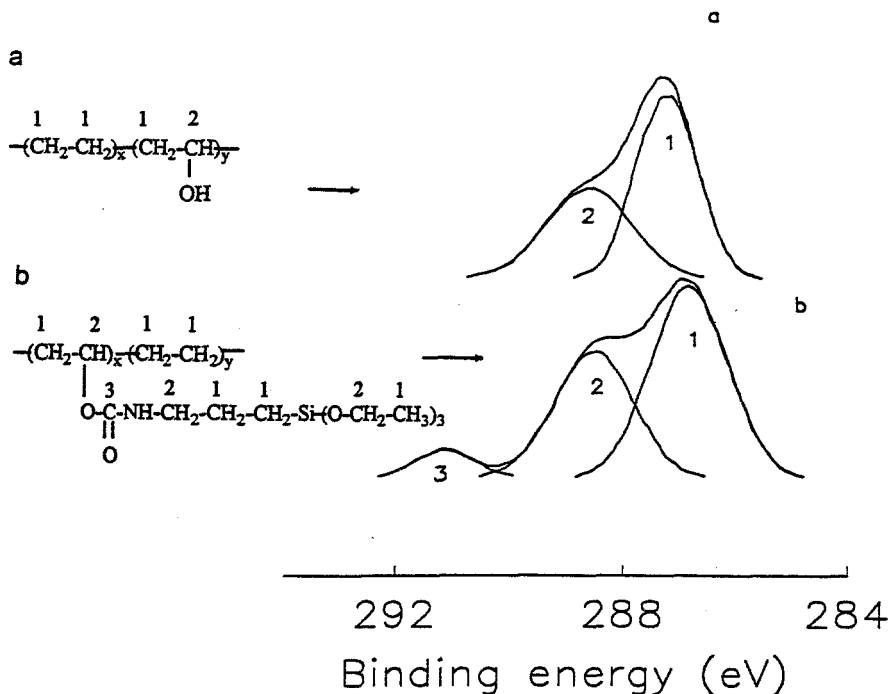


Figure 5. C_{1s} region of XPS spectrum of EVOH-OC(O)NH(CH₂)₃Si(OEt)₃ : (a) before and (b) after surface modification.

Reaction Between TMOS And EVOH-OC(O)NH(CH₂)₃Si(OEt)₃.

Since the silanol functionality can be introduced onto the surface of EVOH films through a urethane linkage, the applications of EVOH films can be expanded into some new areas which they could not be used before, particularly those which require an adhesive bond between EVOH and other substrates such as metal, another polymer, inorganic glass etc. For example, this method has been used to improve the adhesion between polypropylene and inorganic glass (5,6). By exploiting the nature of sol-gel chemistry, we have attempted to expose the sol-gel reactant TMOS to the surface of EVOH film. Through this approach a cross-linked siloxane surface can be formed through a further sol-gel reaction. In

this way, a silica coating layer chemically bonded to the EVOH film can be formed. It was found that in the presence of water, HCl, and isopropanol, the silanol functionality did react with tetramethoxysilane through partial hydrolysis and co-condensation. The XPS spectrum (Figure 4) and the data in Table 1 indicate that there was a significant increase in the content of Si at the surface.

Conclusions

Triethoxysilane groups were covalently attached to EVOH copolymer film surface via a urethane linkage through the reaction between the hydroxyl groups in EVOH and 3-isocyanatopropyltriethoxysilane in the presence of a dibutyltin dilaurate catalyst. This reaction was confirmed by ATR-IR and XPS analysis. XPS results also indicated that this reaction was not surface sensitive and the modified layer was at least 40 Å in depth. The modified film samples were further reacted with TMOS for partial hydrolysis and condensation and XPS results showed a significant increase in the contents of oxygen and silicone on the surface which confirmed the above reaction.

Acknowledgments

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