Surface Free Energy Analysis of Poly(vinyl alcohol) Films Having Various Molecular Parameters

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ABSTRACT: The molecular parameters of poly(vinyl alcohol) have enormous effects on its physical and chemical properties. Therefore, the surface characteristics of poly(vinyl alcohol) films are also determined by the molecular parameters. In this study, the dependence of the surface free energy on the molecular weight, degree of saponification, and stereoregularity of poly(vinyl alcohol) films has been evaluated with contact-angle measurements. The surface free energy of poly(vinyl alcohol) films increases with decreases in the syndiotactic dyad content, molecular weight, and degree of saponification. The polar component of the surface energy is not affected by the deviation of the molecular weight and degree of saponification very much. However, it decreases with increases in the syndiotactic dyad content and ranges from 11.64 to 4.35 dyn/cm. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 424–428, 2007

Key words: PVA film; surface free energy

INTRODUCTION

Poly(vinyl alcohol) (PVA) has been used in various applications, including binders and adhesives, warp sizers, fibers, films, and embolic materials.[1,2] This is possible because of the various characteristics of PVA, such as high solvent resistance, high tensile and compressive strength, high tensile modulus, good abrasion resistance, superior oxygen barrier properties, water solubility, and biocompatibility. The physical properties of PVA are highly correlated with the three major molecular parameters of PVA: the molecular weight, the degree of saponification (DS), and the stereoregularity.[3–5] These molecular parameters of PVA have an especially large effect on the surface characteristics of PVA films. In other words, control of the surface properties of PVA films is possible through the variation of the molecular parameters.

Generally, commercialized PVA has been limited to atactic poly(vinyl alcohol) (a-PVA) with a low or medium molecular weight. Until now, the surface characteristics of PVA films have been mainly controlled by DS. It is well known that PVA has maximum water solubility with a DS value of about 88%, and it gradually decreases with increasing DS.[1] However, until now, research on the surface free energy and hydrophilicity of PVA films according to the stereoregularity has been rare. Chen and Ruckenstein[6] studied the effect of high-molecular-weight a-PVA with a number-average degree of polymerization (P_n) of 2600 and a DS value of 99%, coated on poly(methyl methacrylate), on the reduction in the interfacial energy. Nguyen[7] measured the contact angles of PVA-coated polyester films to obtain the equilibrium surface energy components of the films immersed in water and exposed to air. He used a-PVA with a P_n value of 500–2500 and a DS value of 87.0–98.9%; it was prepared through the polymerization of vinyl acetate (VAc) followed by saponification. Studies on the surface characteristics of a-PVA-based blend films with poly(3-hydroxybutyric acid) and chitosan were also performed by Ikejima et al.[8] and Koyano et al.,[9] respectively. Pemberton and Jaeger[10] prepared polyorganophosphazene-grafted PVA to modify the surface characteristics of PVA films, and Nishino et al.[11] fluorinated PVA to impart low surface free energy to it. However, all these results are for a-PVA with restricted molecular parameters.

In this article, the effects of molecular parameters (the molecular weight, DS, and stereoregularity) on the surface free energy of PVA films is evaluated. To prepare syndiotactic poly(vinyl alcohol) (s-PVA) with a syndiotactic dyad (S-dyad) content of 62%, vinyl

pivalate (VPi) with bulky side groups, which could generate steric hindrance, was polymerized and saponified.

EXPERIMENTAL

Materials

VAc (Shin-Etsu Co., Tokyo, Japan) and VPi (Aldrich Co., St. Louis, MO) were washed with an aqueous solution of $NaHSO_3$ and water, dried over anhydrous $CaCl_2$, and then distilled under the reduced pressure of nitrogen. The initiator 2,2′-azobis(2,4-dimethylvaleronitrile) (Wako Co., Osaka, Japan) was recrystallized in methanol. Other extrapure-grade reagents were used without further purification. PVAs of various molecular parameters were prepared through the polymerization of VAc and VPi followed by saponification. The molecular parameters of PVA used in this work were varied, as shown in Table I.

Preparation of the films

PVAs of various molecular parameters were dissolved in dimethyl sulfoxide at a polymer concentration of 2.5 g/dL. This solution was poured into a stainless steel dish and dried *in vacuo* at 40°C for several days to prepare PVA films of similar thicknesses (ca. 70 µm) and with a degree of crystallinity of 20–25%.

Contact-angle measurements

PVA films ($10 \times 10 \times 0.007$ mm³) were placed inside a glass test cell measuring $55 \times 20 \times 20$ mm³. The hydrocarbon, cyclohexane (c-hexane) or iso-octane (i-octane), was added to the cell by 10 mL of the hydrocarbon being poured into the cell. The whole test cell was then placed inside the chamber of a goniometer (Erma). A small drop of water was carefully placed on the upside of the film with a microsyringe. Then, the contact angle was measured instantaneously at room temperature within 10 s. The surface free energy components of the films were determined from contact-angle measurements with c-hexane and
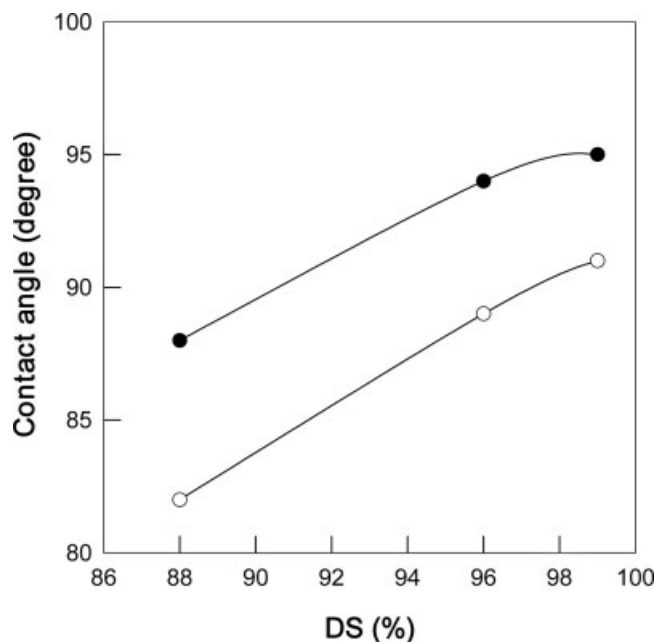

Figure 1 Water contact angles of PVAs with various DS values. The measurements were carried out in (●) c-hexane and (○) i-octane. The P_n value and S-dyad content of PVA were maintained at 2000 and 52%, respectively.

i-octane. The contact angle was measured through the water phase. A smaller contact angle indicated that the surface was more hydrophilic. Contact-angle measurements were taken on both sides of a drop, and at least 10 drops were delivered to the surface.
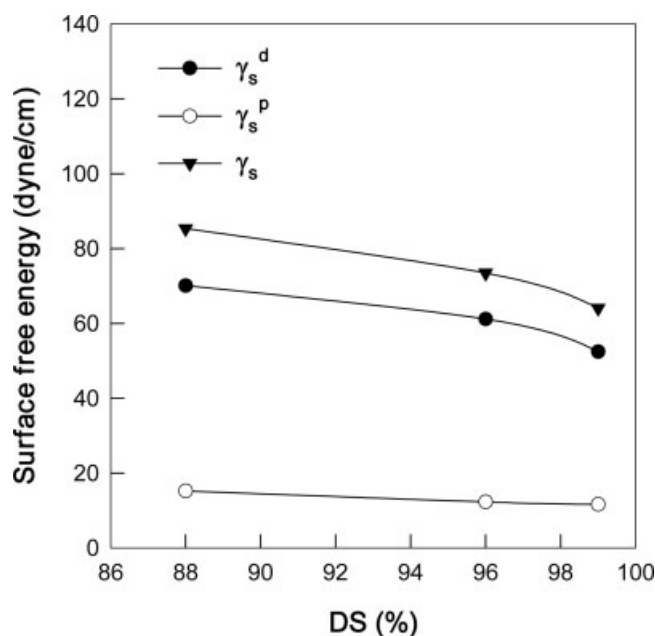

Figure 2 Effect of DS on the surface free energy of PVAs having a P_n value and an S-dyad content of 2000 and 52%, respectively.

TABLE I
Molecular Parameters of PVA

DS (%)	P_n	S-dyad content (%)
88	2,000	52
96	2,000	52
99	2,000	52
99	2,000	57
99	900	62
99	2,000	62
99	6,000	62
99	10,000	62

TABLE II
Surface Free Energy Data for Water and Hydrocarbons

	Water	c-Hexane	i-Octane
γ^d (dyn/cm)	21.8	25.2	18.9
γ^p (dyn/cm)	51.0	0.0	0.0
γ (dyn/cm)	72.8	25.2	18.9

RESULTS AND DISCUSSION

This work was intended to precisely identify the effects of the molecular parameters of PVA on the surface characteristics of its films. Figure 1 shows the effect of DS on the contact angle of PVA films measured in c-hexane and i-octane environments. The S-dyad content and P_n of PVA were maintained at 52% and 2000, respectively. It is well known that the hydrophilicity of PVA increases with increasing DS, reaches a maximum at a DS value of about 88%, and decreases afterward. In this work, the minimum DS value for PVA was 88%, so a reduction of the hydrophilicity of the PVA film with an increase in DS was assumed. This assumption was in good agreement with the contact-angle measurements shown in Figure 1; the contact angle increased from an acute angle to an obtuse one with increasing DS. The surface free energy changes of PVA films according to the DS are also shown in Figure 2. Interfacial forces were deter-

mined according to Tamai et al.'s method[12] as follows with the data shown in Table II:

$$\gamma_H - 2\sqrt{\gamma_S^d \gamma_H} = \gamma_W - 2\sqrt{\gamma_S^d \gamma_W^d} - I_{SW} + \gamma_{HW}\cos\theta \quad (1)$$

$$\gamma_{HW} = \gamma_H + \gamma_W - 2\sqrt{\gamma_H^d \gamma_W^d} \quad (2)$$

where γ is the force component and I is the energy due to the stabilization by the nondispersion force; subscripts W, H, and S refer to the water, hydrocarbon, and solid, respectively; superscript d indicates the dispersion component; and θ is the measured contact angle. Equation (2) is the Fowkes method.

Polymer molecules on the surface have a great degree of freedom for rearrangement and can reorient in response to their local environments to increase their interaction with the surfaces and minimize the total free energy of the system, especially in aqueous environments. In aqueous environments, there is a polar–polar interaction between the water molecules and the polar groups of the polymer. On the basis of these results, we thought that the increased number of polar hydroxyl groups at the film surface increased the freedom of rearrangement for minimizing the total free energy of the system.

Figures 3 and 4 show the effects of P_n of PVA on the contact angle and surface free energy of the film, respectively. The DS and S-dyad content of the specimens were controlled to 99 and 62%, respectively. The contact angles increased gradually (in other words, the hydrophilicity decreased) with an increase in the
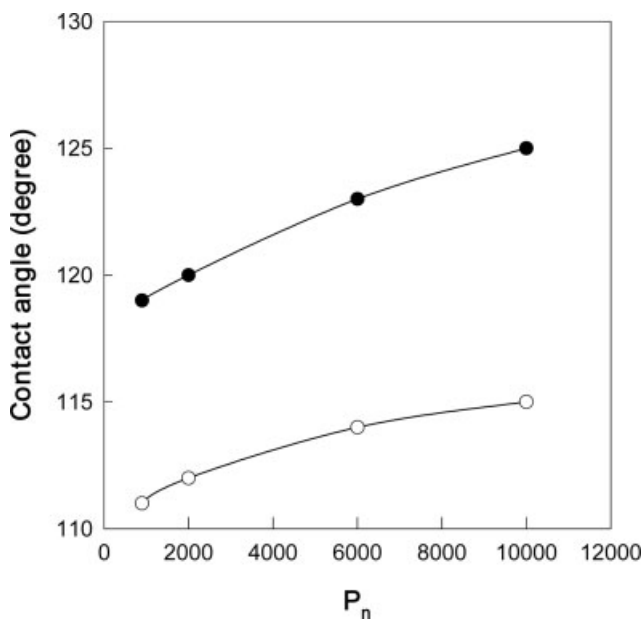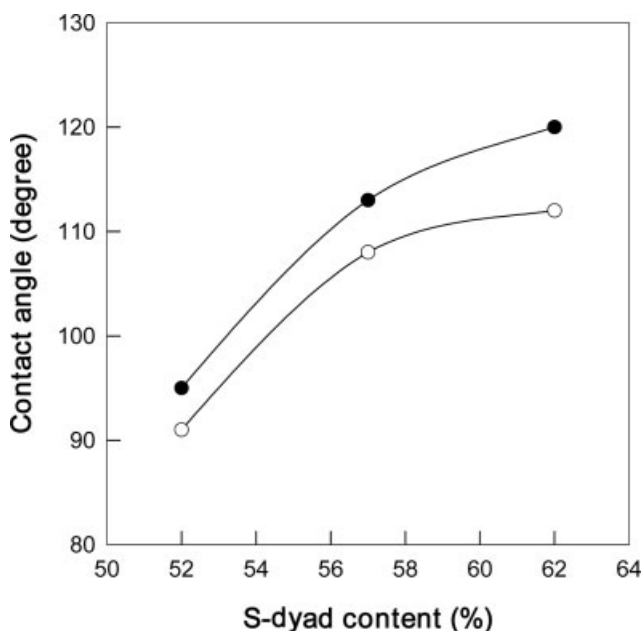

Figure 3 Water contact angles of PVAs with various molecular weights. The measurements were carried out in (●) c-hexane and (○) i-octane. The DS and S-dyad content of PVA were maintained at 99 and 62%, respectively.
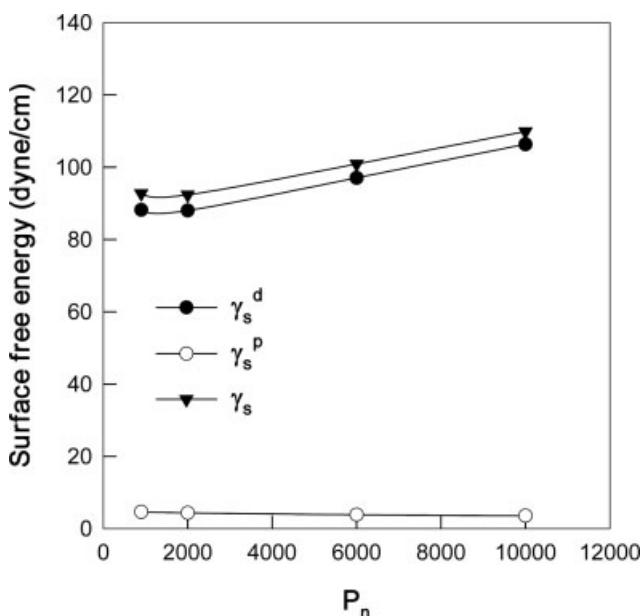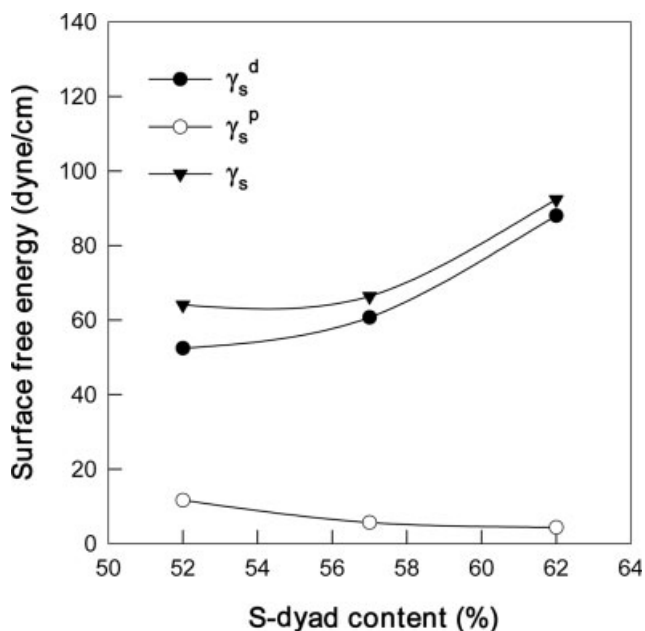

Figure 4 Effect of P_n on the surface free energy of PVAs with a DS value and an S-dyad content of 99 and 62%, respectively.

molecular weight. This result coincided to some extent with the effects of the molecular weight on the solubility of PVA: the lower the molecular weight was, the higher the water solubility was.[1] The polar component of the surface free energy was maintained at a constant value. From this result, it could be deduced that the polar–polar interaction between the water molecules and the hydroxyl groups of PVA did not change with the molecular weight of PVA. The total surface free energy increased with an increase in the molecular weight, and this was attributed to the increase in the dispersion component.

The contact angles and surface free energies of PVA films with various S-dyad contents are shown in Figures 5 and 6, respectively. All the PVA specimens had similar P_n and DS values of 2000 and >99%, respectively, and, as a result, the contact angles were obtuse for all samples. The hydrophilicity of the films decreased with an increase in the S-dyad content. This result is in good agreement with our previously reported results[3–5] showing enhanced water resistance of s-PVA. The surface free energy of PVA films, however, increased with an increase in the S-dyad content, and this was attributed to the increase in the strength of the intramolecular and intermolecular hydrogen bonds and resulting restricted molecular motions at the film surface. This could be also deduced from the decrease in the polar component of the surface free energy; the polar–polar interaction between the water molecules and the hydroxyl groups of PVA might be reduced because the hydroxyl groups of s-PVA

Figure 6 Effect of the syndiotacticity on the surface free energy of PVAs having DS and P_n values of 99% and 2000, respectively.

tended to interact with other hydroxyl groups, not with water molecules. This could be proved by the *in situ* fibrillation process of s-PVA reported by Lyoo and coworkers;[3,4] during the *in situ* fibrillation of s-PVA, a PVA gel with tetrahydrofuran, methanol, and water contracted and was separated by strong hydrogen bonding. Furthermore, PVA specimens with S-dyad contents over 56% can be prepared through *in situ* fibrillation. This might be explained by hydrogen bonding sufficiently strong to reduce the polar–polar interaction.

CONCLUSIONS

We have shown that the surface free energy of PVA films can be varied through the control of the molecular parameters of PVA. The surface free energy of PVA films decreased with increasing DS and decreasing molecular weight and S-dyad content. There were no significant changes in the polar component of the surface free energy with increases in the DS and molecular weight of PVA. From these results, it could be concluded that the DS and molecular weight of PVA did not affect the rearrangement of hydroxyl groups and polar–polar interaction with water molecules at the surface of the PVA films. In contrast, the polar component of the surface free energy decreased largely with an increase in the S-dyad content of PVA. This was attributed to the strengthened intramolecular and intermolecular hydrogen bonds of PVA due to the enlarged stereoregularity, which was based on the reported results about the destruction of the gel dur-

Figure 5 Water contact angles of PVAs with various syndiotacticities. The measurements were carried out in (●) c-hexane and (○) i-octane. The DS and P_n of PVA were maintained at 99% and 2000, respectively.

ing the *in situ* fibrillation of PVA by water and solvent collapse.

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