(Received July 15, 1983)

EFFECT OF HYDROGEN BOND FORMATION ON PHYSICAL AGING OF ETHYLENE-VINYL ALCOHOL COPOLYMERS WITH ANNEALING BELOW T_g

By Hirohisa Yoshida, Hajime Kanbara^{*1}, Naoto Takemura^{*2}
and Yasuji Kobayashi^{*3}

(Department of Industrial Chemistry, Faculty of Technology,
Tokyo Metropolitan University, 2-1-1, Fukazawa, Setagaya-ku,
Tokyo 158 Japan)

Synopsis

The changes of the mechanical properties of poly(ethylene-co-vinyl alcohol) (EVA) with annealing below T_g were studied. EVA samples obtained by quenching from the molten state, having 11–17% of crystallinity, were annealed at ($T_g - 10^\circ\text{C}$) for 4–160 hrs. From the stress-strain curves of the original and the annealed samples, yield strain (ϵ_y), yield stress (σ_y) and Young's modulus (E) were obtained. The changes of ϵ_y with annealing depends on the VA content. σ_y and E of all samples increased with the annealing. The changes of E with annealing were discussed by assuming the first-order process. The higher the VA content, i.e., the richer the hydrogen bonding, the slower the rate of E change with annealing. This result agreed with the fact that the enthalpy relaxation was restricted by the hydrogen bond formation.

INTRODUCTION

When an amorphous and/or semi-crystalline polymer is annealed at temperatures below its glass transition temperature (T_g), the morphology^{1,2)}, thermodynamic quantities^{3,4)} and mechanical properties^{5,6)} changes. These changes of physical properties with annealing below T_g were thermal reversible phenomena, and were known as "Physical Aging". Occurrence of physical aging in the glassy state is a manifestation of the slow process of the approach of the glass to thermodynamic equilibrium.

Extensive studies on the effect of physical aging on creep behavior of a number of polymers and other organic glasses were carried out by Struik^{5,7)}. The effect of annealing on the physical properties of amorphous and semi-crystalline poly(ethylene terephthalate)^{8,9)} and on the stress relaxation

behavior of polycarbonate, polystyrene and their polyblends^{10,11)} were studied. Also, we reported the changes of mechanical properties and morphology of polystyrene with sub- T_g annealing¹²⁾.

In previous papers, we reported the effects of chemical structures¹³⁾, tacticity¹⁴⁾ and hydrogen bonding¹⁵⁾ on the rate of enthalpy relaxation of the glassy state of polymers with annealing below T_g . These studies show that the enthalpy relaxation proceeded as a result of a cooperative segmental motion of a few consecutive repeating units. Also, the hydrogen bond formation delayed the rate of enthalpy relaxation.

In this study, the effect of hydrogen bonding on the changes of mechanical properties with annealing below T_g was studied for the various content of ethylene-vinyl alcohol copolymers (EVA).

EXPERIMENTAL

Sample

Ethylene-vinyl acetate copolymers containing 22, 28.5, 43.2 and 65.5 mole percent vinyl acetate were saponified under the presence of alkali (one-half equivalent of NaOH/methanol solution) in

^{*1} Present address: Shikoku Chemical Co. Ltd., Marugame, Kagawa-ken

^{*2} Present address: Terumo Co. Ltd., Hatagaya, Shibuya-ku, Tokyo

^{*3} Present address: Meiji Gakuin Women's College, Nakaochiai, Shinjuku-ku, Tokyo

toluene solution at 60°C for 10 hrs. After that, the partially saponified copolymers were re-saponified in methanol solution at 60°C for 6 hrs. After the removal of alkali, the obtained EVA samples were purified by the reprecipitation. The vinyl acetate content was less than 0.1 mole percent in every EVA. From elemental analysis, the vinyl alcohol contents of the obtained copolymers were 25, 30, 42 and 68 mole percent.

EVA was pressed at 150°C (25-EVA), 160°C (30-EVA), 180°C (42-EVA) and 200°C (68-EVA) in a hot press and quenched in ice water. The thickness of films were about 0.3 mm. The specimens for tensile test (width 5 mm $\times$ length 100 mm) were cut out from the pressed film and dried for a week over phosphorus pentoxide in vacuo. After drying, the specimens were kept at temperature 10 degrees above the corresponding glass transition temperatures (T_g) for 5 minutes in order to eliminate the previous thermal history. After that, the samples were quenched to room temperature. The specimens thus prepared were used as the "original" sample.

Annealing

Samples were sealed in a glass tube which were filled with dry nitrogen gas, and were annealed at 33°C (25-EVA), 40°C (30-EVA), 48°C (42-EVA) and 55°C (68-EVA). Before annealing, the previous thermal history of samples were cancelled by the same way described above. After that, the samples were quenched to the annealing temperature, and were annealed. Immediately after annealing, the samples were used for the tensile test.

Apparatus

The thermal analysis of samples were carried out by use of a DuPont differential scanning calorimeter DSC 990 at the heating rate of 10°C/min. Before measuring T_g , samples were heated to temperature 10 degrees above the corresponding T_g 's in order to eliminate the previous thermal history, and quenched to -30°C. T_g was estimated from the intersection between the initial base line and the sloping portion of the line as the base line shifts during the transition.

The tensile test was carried out by use of a conventional tensile tester, which covered the rate of deformation from 1.7×10^{-4} to 2.8×10^{-2} m/sec. The numbers of measurements tested per each specimen were eleven. The stress-strain curves

gave Young's modulus (E), tensile stress at yield (σ_y), and extension to yield (ϵ_y). The tensile test were carried out at $23 \pm 1^\circ\text{C}$. The substantial dimensions for the test were 5 mm in wide and 60 mm in length.

X-ray diffractograms of the samples were obtained with a Rigaku Denki Model RU-3 diffractometer provided with a proportional counter.

RESULTS AND DISCUSSION

The DSC curves of EVA samples were shown in Fig. 1. Not only the glass transition but also the small melting peak were observed for every sample. Generally, the glass transition temperature (T_g) of polymers depends on the annealing^{4,9}. As EVA have the low T_g 's near room temperature, the aging occurred and T_g changed while samples were handled at room temperature. For amorphous polymers such as polystyrene and/or poly(methyl methacrylate), the previous thermal history can be eliminated by heating to temperature 30°C above T_g . After such a treatment, the amorphous polymer shows T_g which is independent on the thermal history. For EVA, however, the crystallization occurred in the temperature range between $T_g + 20^\circ\text{C}$ and the melting temperature (T_m). In this study, EVA samples were held at $T_g + 10^\circ\text{C}$ for 5 minutes and quenched to room temperature, in order to eliminate the previous thermal history without any crystallization. The increase of crystallinity with this treatment was negligible for every sample.

Fig. 1 DSC curves of ethylene-vinyl alcohol copolymers (EVA). Numbers in figure show vinyl alcohol content (mol%). Heating rate is 10°C/min.

T_g and T_m of the original samples were listed in Table 1, and the values show good agreements with the previous papers^{16,17}). According to Matsumoto et al.¹⁶), T_g of EVA increased suddenly above 15 mole% of vinyl alcohol content because of the increase of hydrogen bond formation. As EVA is the typical random copolymer¹⁷), the hydrogen bond should distribute randomly. Also, the annealing temperature (T_a) was shown in Table 1.

Table 1 Thermal analysis results of samples.

Sample	VA content (mol %)	T_g ^{*1} (°C)	T_m ^{*2} (°C)	T_a ^{*3} (°C)
25-EVA	25	43	109	33
30-EVA	30	50	118	40
42-EVA	42	58	146	48
68-EVA	68	65	178	55

^{*1} Glass transition temperature obtained at 10°C/min.

^{*2} Melting temperature obtained at 10°C/min.

^{*3} Annealing temperature ($T_g - 10^\circ\text{C}$)

Fig. 2 X-ray diffractograms of original EVA. Direction of incident X-ray beam is perpendicular to film surfaces. Numbers in figure show vinyl alcohol content (mol%).

The X-ray diffractograms of the samples were shown in Fig. 2. The direction of the incident X-ray beam was perpendicular to the film surfaces. Every sample show low crystallinity. Usually, it is difficult to obtain the exact value of crystallinity. In this study, the degree of crystallinity was estimated by the assumption of additivity of the heat of fusion based on mole fraction of copolymers. From the heat of fusion, the degree of crystallinity of every sample were about 11–17% by the use of the heat of fusion for polyethylene

Fig. 3 Stress-strain curves of original and annealed 25-EVA (25 mol% vinyl alcohol). Annealing temperature is 33°C and numbers in figure show annealing time (hrs). Samples are deformed at 23°C at rate of 1.7×10^{-4} m/sec.

Fig. 4 Stress-strain curves of original and annealed 68-EVA (68 mol% vinyl alcohol). Annealing temperature is 55°C and numbers in figure show annealing time (hrs). Samples are deformed at 23°C at rate of 1.7×10^{-4} m/sec.

(7.87 kJ/mol) and poly(vinyl alcohol) (6.87 kJ/mol)¹⁸. The X-ray diffraction did not change with annealing below T_g for every sample. With the increase of vinyl alcohol contents, the degree of crystallinity increased slightly.

The typical changes of stress-strain curves with annealing below T_g were shown in Fig. 3 (25-EVA) and Fig. 4 (68-EVA). 25-EVA and 68-EVA were annealed at 33°C and 55°C, respectively. Numbers in the figures show the annealing time (hr). The rate of deformation was 1.7×10^{-4} m/sec. The higher strength of 68-EVA should come from the hydrogen bonding.

For the stress-strain curves of 25-EVA, the yield point was not observed clearly. However, necking appears in both samples. For 25-EVA, the yield stress and Young's modulus, which was obtained from the initial slope of stress-strain curve, increased with annealing. On the other hand, the yield strain increased and the yield behavior become clear with the annealing on the stress-strain

curve of 68-EVA. However, Young's modulus of 68-EVA scarcely increased with annealing. The stress-strain curves of 30-EVA and 42-EVA are similar to those of 25-EVA and 68-EVA, respectively.

The changes of mechanical quantities with sub- T_g annealing were shown in Fig. 5 (25-EVA), Fig. 6 (30-EVA), Fig. 7 (42-EVA) and Fig. 8 (68-EVA). In Figs. 5–8, open and close circles show the values at the deformation rate of 1.7×10^{-4} and 1.7×10^{-3} m/sec, respectively.

As the yield point of 25-EVA was not clear as shown in Fig. 3, it was difficult to determine the yield point. We determined the yield point of 25-EVA as the point where the stress-strain curve deviated from the initial linear slope. For 25-EVA, ϵ_y decreased and σ_y and E increased with the annealing as shown in Fig. 5. According to Petrie¹⁹, the ductile properties of amorphous poly(ethylene terephthalate) and atactic polystyrene changed to the brittle ones with annealing below

Fig. 5 Dependences of yield strain (ϵ_y), yield stress (σ_y) and Young's modulus (E) on annealing time for 25-EVA. Annealing temperature is 33°C. Samples are deformed at 23°C at rate of 1.7×10^{-4} (○) and 1.7×10^{-3} (●) m/sec.

Fig. 6 Dependences of yield strain (ϵ_y), yield stress (σ_y) and Young's modulus (E) on annealing time for 30-EVA. Annealing temperature is 40°C. Samples are deformed at 23°C at rate of 1.7×10^{-4} (○) and 1.7×10^{-3} (●) m/sec.

Fig. 7 Dependences of yield strain (ϵ_y), yield stress (σ_y) and Young's modulus (E) on annealing time for 42-EVA. Annealing temperature is 48°C. Samples are deformed at 23°C at rate of 1.7×10^{-4} (○) and 1.7×10^{-3} (●) m/sec.

Fig. 8 Dependences of yield strain (ϵ_y), yield stress (σ_y) and Young's modulus (E) on annealing time for 68-EVA. Annealing temperature is 55°C. Samples are deformed at 23°C at rate of 1.7×10^{-4} (○) and 1.7×10^{-3} (●) m/sec.

T_g .

The stress-strain curve of the original 30-EVA was similar to that of 25-EVA, and the yield point was not clear. For the annealed sample of 30-EVA, however, the yield point appeared. With an increase of annealing time, ϵ_y decreased and σ_y and E increased slightly as shown in Fig. 6. For 42-EVA in Fig. 7, the yield point appeared on the stress-strain curve, and ϵ_y scarcely changed with annealing but σ_y and E increased slightly. For 68-EVA, ϵ_y , σ_y and E increased with annealing as shown in Fig. 8.

As shown in Figs. 5–8, the changes of ϵ_y with annealing depend on the VA content. ϵ_y of 25-EVA decreased more than that of 30-EVA with sub- T_g annealing. On the other hand, ϵ_y of 42-EVA scarcely changed, and ϵ_y of 68-EVA increased slightly with annealing. This phenomena may come from the difference of yield behavior among samples. As shown in Fig. 3 and 4, the yield point was scarcely observed on the stress-strain curves

of 25 and 30-EVA. On the other hand, the stress-strain curves of 42 and 68-EVA showed the yield point clearly. Despite all samples are deformed at temperature below T_g , there may be difference of yield mechanism among samples.

According to Petrie¹⁹⁾, the changes of modulus are parallel to the extent of enthalpy relaxation that occurred during the annealing as a result of the nonequilibrium nature of the glassy state, i.e., the modulus increased with time and approached a limiting value that increased with decreasing temperature. In a previous paper¹⁵⁾, Young's modulus of atactic polystyrene also increased with annealing. Therefore, Young's modulus E calculated from the initial slope of the stress-strain curve will reflect the annealing effect. From Figs. 5–7, E increased with annealing and approached a limiting value. However, E of 68-EVA increases slightly within the experimental time scale, and it might further increase.

In order to analyze the physical aging process

kinetically, the changes of E with annealing were noted. The changes of E was assumed as a first-order reaction, just as in the cases of thermosetting plastics²⁰⁾ and the hydrogen bond formation²¹⁾

Generally, the kinetic process can be described as;

$$\frac{dx}{dt} = k(a-x)^n \quad (1)$$

where, a , x and n are the initial concentration, the quantity reacted at time t and the reaction order, respectively. When the initial condition is that $x=0$ at $t=0$, the integrated equation gives the first-order process;

$$\ln\left(\frac{a}{a-x}\right) = kt \quad (2)$$

where, k is the rate constant. If there is a linear relation between x and physical property (M) changes, we obtain equations as follows;

$$a - x = M_{\infty} - M_t \quad (3)$$

$$a = M_{\infty} - M_0 \quad (4)$$

$$x = M_t - M_0 \quad (5)$$

When applying the external forces to the materials, the rearrangement of molecules will occur to relax the stress. The increase in Young's modulus is due to the increased time required for molecular rearrangements. As free volume and molecular mobility of the glasses decrease with annealing below T_g ^{5,9)}, molecular responses against the external forces become slower. Therefore, a and x are assumed the molecular mobility at time 0 and t , respectively, and M is assumed Young's modulus. Although the values of E have not always saturated within the experimental time, M_{∞} and M_0 are regarded the values of E for the samples annealed for 160 hrs and the original one, respectively. When equations (3)–(5) are substituted in equation (2), we obtained equation (6) for E change with annealing.

$$\ln\left(\frac{E_{160} - E_0}{E_{160} - E_t}\right) = kt \quad (6)$$

Thus, when $\ln[(E_{160} - E_0)/(E_{160} - E_t)]$ was plotted against the annealing time, a linear relation was obtained for the initial stage as shown in Fig. 9. For 25-EVA and 30-EVA, the plot for a long time

Fig. 9 Plots of $\ln(E_{160} - E_0)/(E_{160} - E_t)$ vs annealing time. Numbers in figure show vinyl alcohol content (mol%).

annealing deviated from the linear relation. It was thought that the initial stage could not be detected within the experimental time scale, since the rate of E changes of these samples with annealing was too fast. Such a change of E with sub- T_g annealing may be not necessarily the same for the cases of thermosetting plastics²⁰⁾ and the hydrogen bond formation²¹⁾ which could be assumed as a first-order process. In previous papers^{22,23)} the relaxation time increased with annealing time in the enthalpy relaxation process with annealing. If the changes of E shown in Fig. 9 is consistent with the changes of thermodynamic quantities such as enthalpy and volume with annealing, the deviation of 25-EVA and 30-EVA in the long annealing time may be explained by use of the concept of the time dependence of the relaxation time in the enthalpy relaxation process. Also, the rate of molecular mobility changes would vary with the free volume fraction due to the feed back effect as indicated by Struik⁵⁾.

From the slope of each straight line, the values for k in Fig. 9 were estimated. It is suggested that the rate of E change with annealing becomes slower with the increase of VA content, i.e., the increase of the number of hydrogen bonding. This result agreed with the fact that the enthalpy relaxation process was restricted by the hydrogen bond formation¹⁴⁾. Therefore, the changes of E

with annealing may be correlated to the relaxation of thermodynamic quantities, such as free volume and enthalpy.

REFERENCES

- 1) G. S. Y. Yeh and P. H. Geil; *J. Macromol. Sci.-Phys.*, **B1**, 235 (1967)
- 2) W. Frank, H. Godder and H. A. Stuart; *Polymer Letter*, **5**, 711 (1967)
- 3) A. J. Kovacs; *J. Polym. Sci.*, **30**, 131 (1958)
- 4) H. Suga and S. Seki; *J. Non-Crystalline Solids*, **16**, 171 (1974)
- 5) L. C. E. Struik; "Physical Aging in Amorphous Polymers and Other Materials", Elsevier, Amsterdam (1978)
- 6) K. Neki and P. H. Geil; *J. Macromol. Sci.-Phys.*, **B8**, 295 (1973)
- 7) L. C. E. Struik; *Polym. Eng. Sci.*, **17**, 165 (1977)
- 8) R. M. Mininni, R. S. Moore, J. R. Flick and S. E. B. Petrie; *J. Macromol. Sci.-Phys.*, **B8**, 343 (1973)
- 9) M. R. Tant and G. L. Wilkes; *J. Appl. Polym. Sci.*, **26**, 2813 (1981)
- 10) S. Matsuoka, C. J. Aloisio and H. E. Bair; *J. Appl. Phys.*, **44**, 4265 (1973)
- 11) H. Matsuoka and H. E. Bair; *ibid*, **48**, 4058 (1977)
- 12) H. Yoshida and Y. Kobayashi; *Polymer*, in press (1983)
- 13) H. Yoshida and Y. Kobayashi; *J. Macromol. Sci.-Phys.*, **B21**, 565 (1982)
- 14) H. Yoshida, K. Nakamura and Y. Kobayashi; *Polymer J.*, **14**, 855 (1982)
- 15) H. Yoshida and Y. Kobayashi; *ibid*, **14**, 925 (1982)
- 16) T. Matsumoto and K. Nakamae; *Koubunshi Kagaku*, **28**, 610 (1971)
- 17) H. Yoshida and Y. Kobayashi; *Sen-i Gakkaishi*, **33**, T-479 (1977)
- 18) J. Brandrup and E. H. Immergut, "Polymer Handbook", III-5, J. Wiley & Sons, New York
- 19) S. E. B. Petrie; *J. Macromol. Sci.-Phys.*, **B12**, 225 (1976)
- 20) D. H. Kaelble and E. H. Cirlin; *J. Polym. Sci.*, **C35**, 79 (1971)
- 21) S. Yano, H. Hatakeyama and T. Hatakeyama; *J. Appl. Polym. Sci.*, **20**, 3221 (1976)
- 22) H. Yoshida and Y. Kobayashi; *Sen-i Gakkaishi*, **37**, T-458 (1981)
- 23) H. Yoshida and Y. Kobayashi; *ibid*, **39**, T-146 (1983)

ガラス転移温度以下の熱処理によるエチレンー ビニルアルコール共重合体の機械的性質の変化 過程におよぼす水素結合の効果

東京都立大学工学部 吉田博久, 神原 肇,
竹村直人, 小林靖二

ビニルアルコール成分のモル分率が 25, 30, 42, 68% のエチレンービニルアルコール共重合体 (EVA) を用いて, T_g 以下の温度での熱処理が試料の力学的性質におよぼす影響を検討した。熔融状態から急冷によって得られた結晶化度 11~17% の EVA 試料を, 各々の T_g より 10°C 低い温度で 4~160 時間熱処理した。未熱処理試料と熱処理試料の引っ張り試験から得られた応力-歪曲線より, 降伏伸び (ϵ_y), 降伏応力 (σ_y), ヤング率 (E) を計算した。 ϵ_y の熱処理による変化は VA 組成によって異

なる挙動を示した。 σ_y と E はすべての試料について熱処理時間にもなって増加した。 T_g 以下の熱処理による E の増加過程を, 一次の動力学的過程として解析した。熱処理による E の変化速度は VA 組成が高くなる程, すなわち水素結合の数が多くなる程, 遅くなる。これは T_g 以下の熱処理によってエンタルピーや体積などの熱力学量の緩和過程が水素結合によって阻害される結果と良い一致を示した。