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Polymer Vol. 36 No. 5, pp. 959–966, 1995
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0032-3861/95/$10.00+0.00

Elastic modulus of the crystalline regions of ethylene–vinyl alcohol copolymers

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(Received 9 June 1994; revised 25 August 1994)

The elastic modulus E_l of the crystalline regions in the direction parallel to the chain axis was measured by X-ray diffraction for a number of ethylene–vinyl alcohol (EVA) copolymers with various vinyl alcohol (VA) contents. Although the E_l values of polyethylene (235 GPa) and poly(vinyl alcohol) (250 GPa) are very high, these copolymers possessed much lower E_l values. The change in the E_l values of the copolymers with VA content could be expressed by a parabolic curve with a minimum value of 79 GPa (VA = 40.0 mol%). This tendency corresponded well to the change in the fibre identity period where the EVA copolymer (VA = 40.0 mol%) shows the most contracted skeletal. These results could be explained with a kinked-chain model where a contracted portion was introduced into the chain, with the latter bringing about the low E_l value for the EVA copolymer. The E_l value for the EVA copolymer (VA = 62.0 mol%) increased from 108 GPa at 25°C to 226 GPa at −150°C. The contracted portion was considered to be introduced into the chain by thermal vibrations, even at room temperature.

(Keywords: EVA copolymer; elastic modulus; X-ray diffraction)

INTRODUCTION

The elastic modulus of the crystalline regions of polymers is one of the most important mechanical properties of such materials. We have been measuring the elastic modulus E_l of the crystalline regions in the direction parallel to the chain axis for a large number of polymers by X-ray diffraction[1–5]. Examination of the data accumulated so far has led us to be successful in relating the E_l value, i.e. the extensivity of a polymer molecule, to the molecular conformation and the deformation mechanism in the crystal lattice. The values of E_l for polymers with a fully extended planar zigzag conformation, e.g. polyethylene (PE) and poly(vinyl alcohol) (PVA), were found to be 235[1,4] and 250 GPa[1,5], respectively. In these cases, the chains deform through bond stretching and bond angle bending, which have relatively high force constants. Along with their small cross-sectional areas, this is the reason why these polymers have the highest E_l values among the flexible polymers[3].

Ethylene–vinyl alcohol (EVA) copolymer, which is a random copolymer of ethylene and vinyl alcohol (VA), is a typical amphoteric polymer composed of hydrophobic and hydrophilic segments, and where the properties are expected to vary widely with the copolymer composition. The relationships between the chemical composition and both the crystal structure[6] and physical properties[7], have been extensively investigated for a series of EVA copolymers. It was found that the EVA copolymers are co-crystallizable over the entire range of copolymer compositions and can form isomorphic crystals. It has been said that the EVA copolymers also have an extended planar zigzag conformation of the chain in the crystalline regions, as observed for PE and PVA. Thus, high E_l values, over 200 GPa, should be expected for these copolymers. However, when the skeletal conformation is observed precisely, the peak position of the meridional reflection of, for example, an EVA copolymer with a VA content of 40.0 mol% (abbreviated as EVA (40.0 mol%)), locates at a higher angle than those of the PE and PVA homopolymers, as shown in *Figure 1*, which exceeds the experimental error. This indicates that the fibre identity period of the EVA copolymer is shorter than those of PE and PVA. Thus, the chain of the copolymer has a somewhat contracted conformation, rather than a fully extended planar zigzag conformation.

In this study, the E_l values of various EVA copolymers with a wide range of VA contents were measured by X-ray diffraction, and the relationships between the copolymer component, contraction of the chain, and the E_l values, were investigated.

EXPERIMENTAL

Samples

Eight kinds of EVA copolymers, with VA contents ranging from 0 to 100 mol%, were used in this study. The trade names, grades, manufacturer's details and the condition of preparation of each EVA copolymer are shown in *Table 1*. The copolymer entries marked with * (VA content) were prepared by saponifying the corresponding ethylene–vinyl acetate (EVAc) copolymers by methanolic KOH in benzene. The degree of saponification was more than 98% in all cases. Linear low-density

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Table 1 Sample details and methods of preparation of the series of ethylene–vinyl alcohol copolymers[a]

VA content (mol%)	0	6.1*	13.8*	40.0*	62.0	73.0	82.0*	100
Sample name	108F-2	Evaflex #560	Evaflex P-3307	Soalex DI	EP-H101A	EVOH	MZ-1345	NH-18
Manufacturer	Showa Denko KK	Mitsui Polychemicals, Inc.	Mitsui Polychemicals, Inc.	Nippon Synthetic Chem. Ind. Co., Ltd	Kuraray Co., Ltd	Nippon Synthetic Chem. Ind. Co., Ltd	Showa Highpolymers Ltd	Nippon Synthetic Chem. Ind. Co., Ltd
Method	Melt press	Melt press	Melt press	Melt press	Melt press	Melt press	Melt press	Cast
Temperature (°C)	170	130	160	200	200	235	235	r.t.
Draw temperature (°C)	r.t.	90	90	80	100	100	90	180
Draw ratio	5	7	8	4	11	8	5	7
Annealing temperature (°C)	97	90	90	100	110	120	150	180
Annealing time (h)	2	2	2	2	2	2	2	0.5

[a] Entries marked with * indicate that copolymer sample was prepared by saponification of corresponding EVAc copolymer (see text for details)

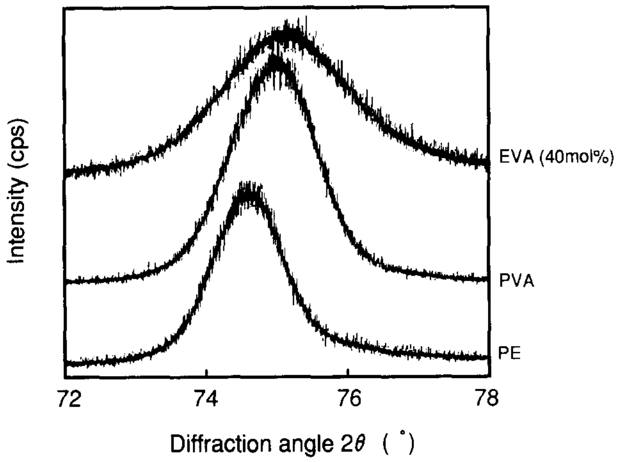

Figure 1 Diffraction profiles for the meridional reflections of polyethylene, poly(vinyl alcohol) and an ethylene–vinyl alcohol copolymer with a vinyl alcohol content of 40 mol%

PE (17.7 ethyl branches per 1000 main-chain methylene units) was employed as EVA (0 mol%), for the reason that the EVA copolymer was derived from the corresponding EVAc copolymer, which was prepared by high pressure radical copolymerization of ethylene and vinyl acetate. EVA copolymer films, except for PVA, were prepared by melt pressing at 8 MPa for 10 min, followed by quenching in ice–water. A rectangular EVA copolymer film was drawn at the preset temperature and then annealed for 2 h at constant length. PVA film was cast from 10 wt% aqueous solution at room temperature, and then drawn and annealed under the conditions shown in *Table 1*. All of the films were dried under vacuum for 2 days prior to the experiments.

Sample characterization

The densities of the specimens were obtained by a flotation method (benzene–carbon tetrachloride system for the EVA copolymers; toluene–chlorobenzene system for PE) at 30°C.

The melting point T_m and the heat of fusion ΔH of each EVA copolymer sample were measured using a differential scanning calorimeter (Daini Seikosha, SSC-560S) at a heating rate of $10^\circ C\,min^{-1}$, with a sample weight of ~ 10 mg. The T_m and ΔH values were determined as the peak temperature and the area of the whole melting endotherm, respectively. Indium was used as a standard sample.

The stress–strain curves for the specimens were measured by using a tensile tester (Shimadzu, Autograph SD-100) at 25°C, from which the macroscopic specimen moduli were measured from the initial slopes. The initial length of all of the specimens was 20 mm, and the extension rate was $2\,mm\,min^{-1}$. At the same time, the tensile strength and the elongation at break were also measured.

The meridional reflection shown in *Figure 1* are usually referred to as the 002 reflection for PE and the 020 reflection for PVA. Thus, in order to avoid confusion, we here cited the fibre identity period, which was determined from twice the lattice spacing of each meridional reflection. Lithium fluoride was used as the standard sample.

The degree of crystallite orientation π was defined by the following relationship:

$$\pi = (180 - H^0)/180 \qquad (1)$$

where H^0 is the half-width of the intensity distribution curve for the meridional reflection of each sample along the Debye–Scherrer ring.

To obtain the crystallite size D along the chain axis, the observed integral width for the meridional reflection was corrected for both the instrumental and CuKα doublet broadening (Jones' method). Then D was calculated using Scherrer's equation, as follows:

$$D = \lambda/\beta \cos\theta \qquad (2)$$

where β is the pure integral width of the meridional reflection, θ is the Bragg angle of the reflection, and λ is the X-ray wavelength.

Small-angle X-ray scattering was measured with a small-angle X-ray diffractometer (Rigaku Denki, with slit collimation; sample–counter distance = 300 mm). After background reduction, the long-period along the chain axis was measured by adopting the Bragg equation to the first peak position of the scattering profile.

Elastic modulus E_l *of the crystalline regions*

The lattice extension under a constant load was measured by means of an X-ray diffractometer (Rigaku Denki RAD-B System) equipped with both a stretching device and a load cell. The strain ε in the crystalline regions was estimated by use of the following relationship:

$$\varepsilon = \Delta d / d_0 \qquad (3)$$

where d_0 denotes the initial lattice spacing, and Δd is the change in lattice spacing induced by a constant stress. The experimental error in measuring the peak shift was generally evaluated to be less than $\pm 0.01°$ for a 2θ angle.

The stress σ in the crystalline regions was assumed to be equal to the stress applied to the sample. This assumption of a homogeneous stress distribution has been proven experimentally for PE[4], PVA[2], cellulose[2], poly(*p*-phenylene terephthalamide)[8], and poly(ethylene terephthalate)[9], plus various other polymers.

The elastic modulus E_l was calculated as follows:

$$E_l = \sigma / \varepsilon \qquad (4)$$

E_l at low temperatures was measured by using a cooling (liquid N_2) cell with a temperature controller (± 1°C).

Detailed descriptions of all of these measurements have been given in earlier papers.

RESULTS AND DISCUSSION

Characteristics of the EVA copolymers

Figure 2 shows the X-ray fibre photographs of a series of drawn and annealed EVA copolymers. The diffraction patterns of PE and PVA were sharp and clear, but those of the copolymers were diffuse and the equatorial reflections of the samples with a VA content of ~40.0 mol% were not separated. These suggest that the copolymer molecules in the crystalline regions are much more disordered than those of PE and PVA, and that some of them are packed in pseudo-hexagonal cells[6].

Table 2 shows various characteristics of each EVA copolymer sample. The VA content in the crystal lattice was reported to be approximately consistent with that in the bulk[10], and so therefore we used the bulk VA content as a parameter in this study. The density increased nearly linearly with the VA content, accompanied by the introduction of hydroxyl groups. On the other hand, T_m showed the minimum value for EVA (13.8 mol%). The

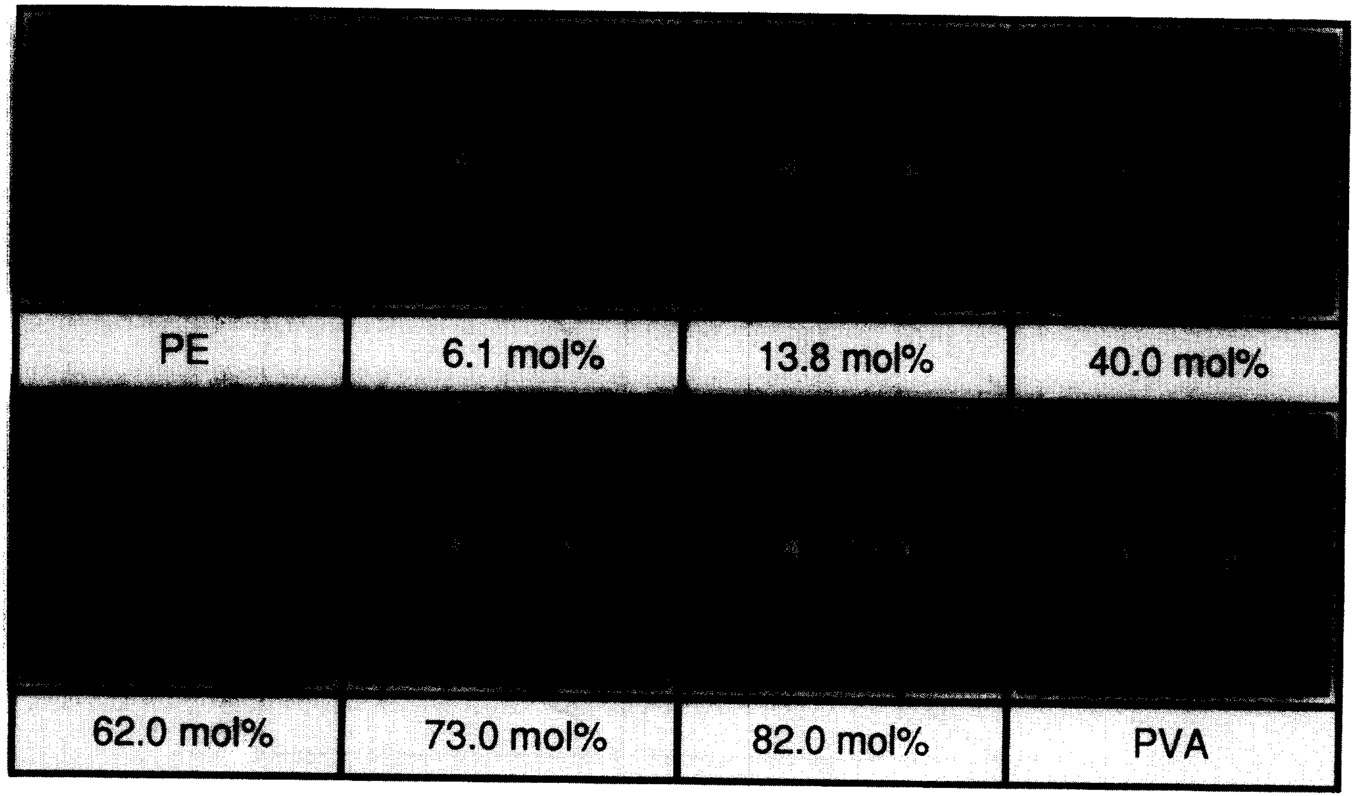

Figure 2 X-ray fibre photographs of polyethylene, poly(vinyl alcohol) and the series of ethylene–vinyl alcohol copolymers

Table 2 Characteristics of the series of ethylene–vinyl alcohol copolymers

VA content (mol%)	0	6.1	13.8	40.0	62.0	73.0	82.0	100
Density (g cm^{-3})	0.919	0.945	0.978	1.076	1.162	1.200	1.227	1.302
Melting point (°C)	123	110	107	141	174	188	205	225
Heat of fusion (cal g^{-1})	22.5	26.9	19.7	9.84	17.3	17.2	19.8	17.0
Elastic modulus (GPa)	0.4	1.3	2.6	1.3	8.0	7.1	4.6	12.6
Tensile strength (MPa)	101	113	180	58	483	358	199	472
Elongation at break (%)	17.1	17.9	14.4	23.9	10.1	6.96	24.1	10.6
Degree of orientation	0.94	0.98	0.97	0.93	0.96	0.96	0.93	0.97
Crystallite size (Å)	106	109	92	51	83	72	53	90
Long period (Å)	183	177	156	118	143	110	113	161
VA content in crystal (mol%)	0	4.4	10.8	48.2	69.7	79.6	86.5	100

crystal structure of this copolymer has been reported to be classified (by the VA content) into three regions[6]. EVA copolymer with a VA content less than 12.3 mol% exhibits a crystal structure analogous to that of orthorhombic PE, while a monoclinic system, isomorphous to PVA, is observed for copolymer with a VA content greater than 60.0 mol%. In the intermediate regions, with VA contents from 13 to 60 mol%, the copolymer shows the pseudo-hexagonal system. Thus, the decrease in T_m in going from PE to EVA (13.8 mol%) is considered to be related to the observations that the orthorhombic system was disordered by the incorporation of hydroxyl groups and that the packing of the chain becomes loosened by migrating to the pseudo-hexagonal system. The increase in T_m for EVA copolymers with a VA content larger than 40.0 mol% is due to the formation of intermolecular hydrogen bonds. This tendency corresponds to the change in the elastic modulus of the crystalline regions of the copolymer in the direction perpendicular to the chain axis, which is governed by the intermolecular cohesive energy[11].

The specimen moduli ranged from 0.4 to 12.6 GPa, which were much lower than the E_l value shown later in this report. Thus, the deformation of the EVA copolymer is highly controlled by that of the amorphous region. The specimen modulus, the tensile strength, the elongation at break, the degree of crystallite orientation, the crystallite size, and the long period, depended on the conditions of the sample preparation, rather than the VA contents, with a particular effect on the draw ratio.

Elastic modulus E_l *of the crystalline regions of the EVA copolymers*

Figure 3 shows the stress (σ)-strain (ε) curves for the meridional reflections of the copolymers with various VA contents at 25°C. All the σ–ε curves could be expressed by a straight line passing through zero, and the lattice extensions were always reversible. The slope changed with the VA content, i.e. it increased with increasing VA content and reached the maximum value at EVA (40.0 mol%), followed by a gradual decrease. These results imply that the E_l values changed with the VA contents.

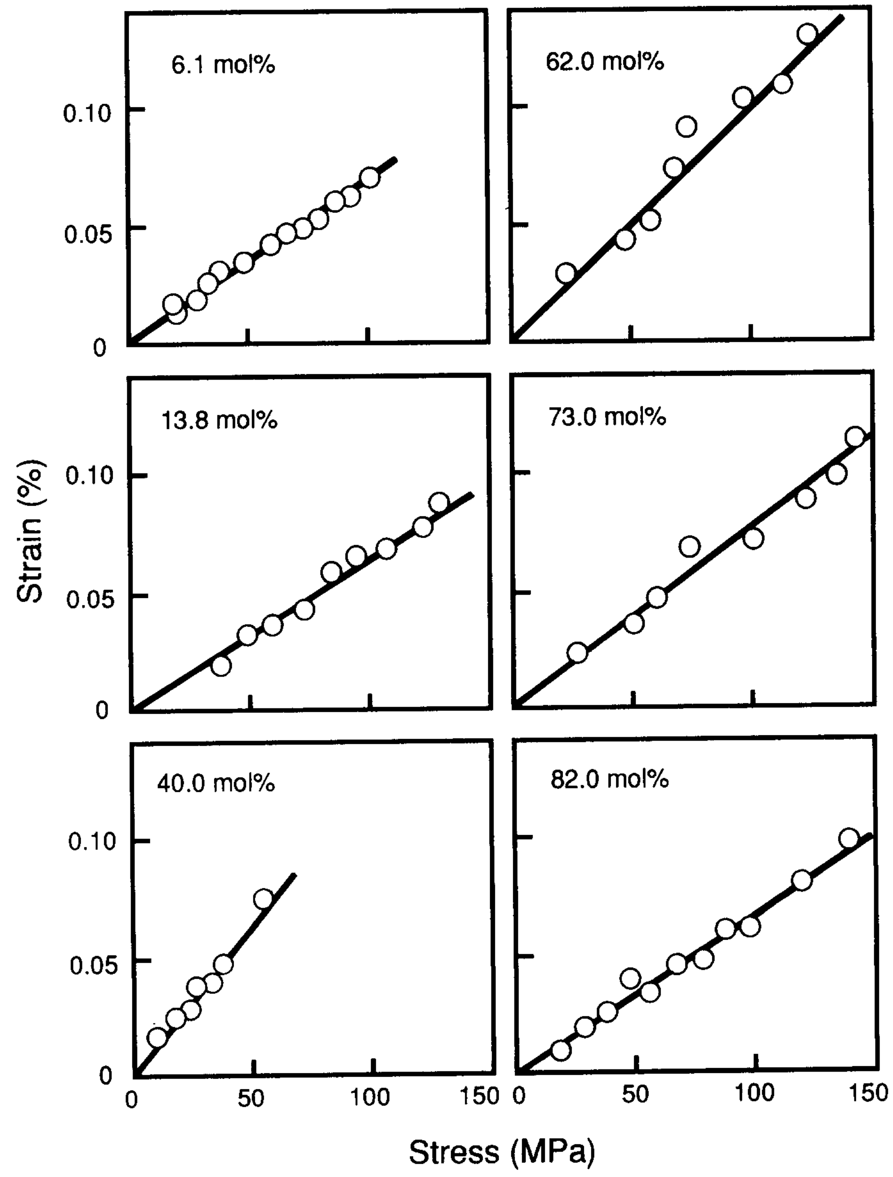

Figure 3 Stress–strain curves for the meridional reflections of the series of ethylene–vinyl alcohol copolymers at 25°C

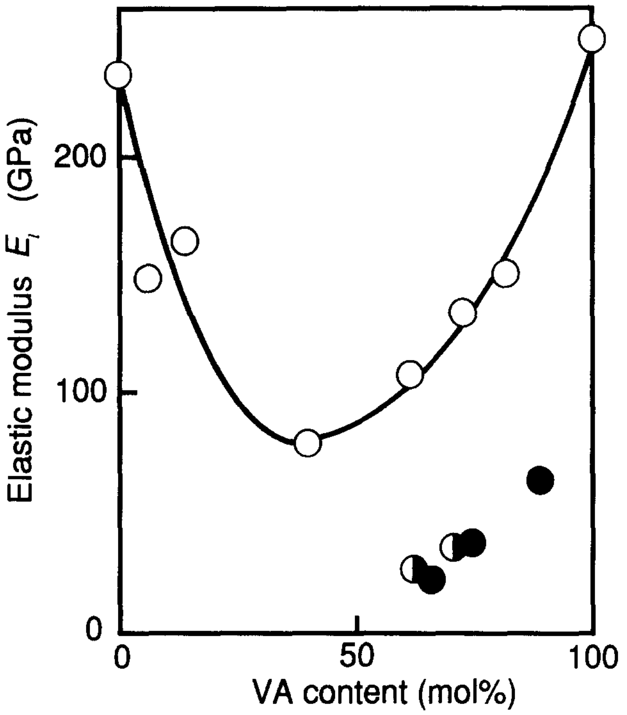

Figure 4 Relationship between the elastic modulus E_l and the vinyl alcohol content of the series of ethylene–vinyl alcohol copolymers; filled[12] and half-filled[13] circles represent values of the macroscopic specimen moduli reported in the literature

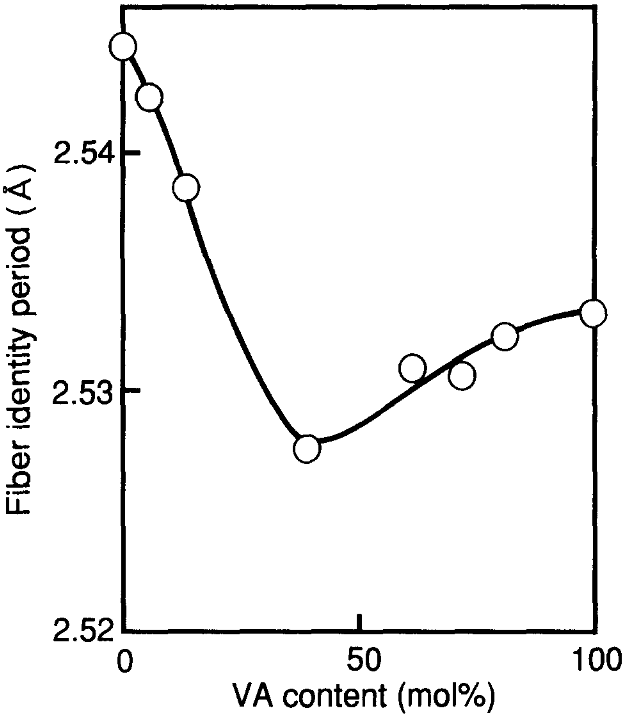

Figure 5 Relationship between the fibre identity period and the vinyl alcohol content of the series of ethylene–vinyl alcohol copolymers

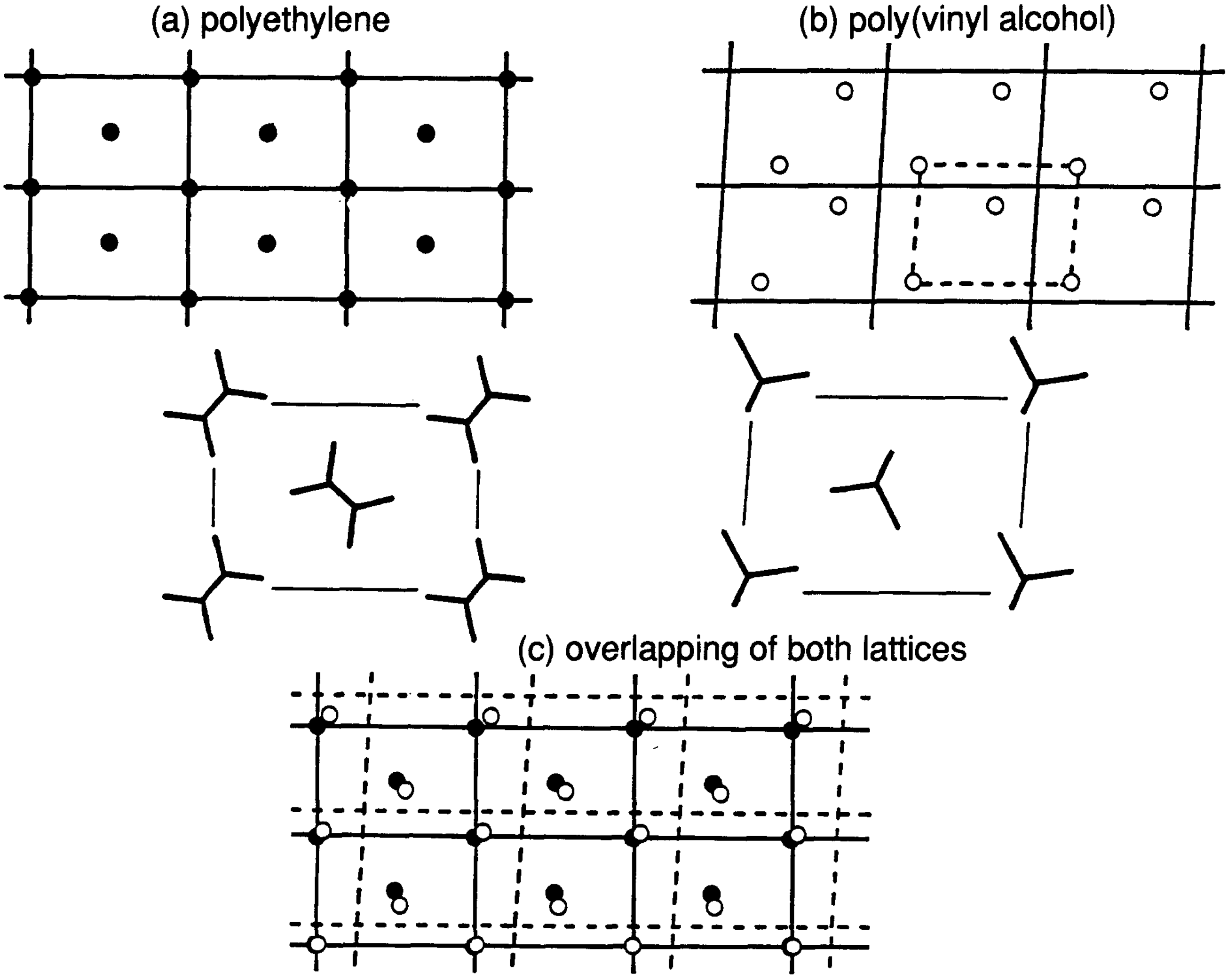

Figure 6 (a) The c-axis projection of the unit cell of orthorhombic polyethylene[14], (b) the b-axis projection of the unit cell of monoclinic poly(vinyl alcohol)[15], and (c) the geometric relationship between them, seen by overlapping both lattices

Figure 4 shows the relationship between the elastic modulus E_l, calculated from the slopes of the σ–ε curves in *Figure 3*, and the VA contents. The E_l values of the EVA copolymers were not the same as those of PE or PVA, but could be expressed by a parabolic curve with a minimum value of 79 GPa at EVA (40.0 mol%). This indicates that the chain molecules of the copolymer are three times easier to elongate to their chain directions than those of PE and PVA. In this figure filled circles[12] and half-filled circles[13] represent the maximum macroscopic modulus values for EVA copolymers reported in the literature aimed at achieving high-modulus polymers. Absolute values are quite different from the crystal modulus, with the tendency being for the former to resemble each other. Thus, one reason for the low macroscopic modulus of EVA copolymers is considered to be the low E_l values.

Figure 5 shows the relationship between the fibre identity period and the VA contents of the series of EVA copolymers. The fibre identity periods of the copolymers could also be expressed by a parabolic curve which had its minimum value at EVA (40.0 mol%). Here, the change shown in *Figure 5* exceeded the experimental error of ±0.01° at angle 2θ (corresponding to 0.0003 Å). The change in the fibre identity period with VA content appeared to correspond to that of the E_l value. This confirmed that the copolymer chain molecule does not have a fully extended planar zigzag conformation, but has a somewhat contracted conformation, in comparison with those of PE and PVA. In these contracted chains, internal rotation around the single bond of the chain can contribute to the deformation mechanism of the chain. Therefore, this is considered to be the reason for the low E_l values of the EVA copolymers.

Figure 6a shows the c-axis projection of the unit cell of orthorhombic PE ($a = 7.42$, $b = 4.95$, c (fibre axis) $= 2.545$ Å)[14]. The filled circles indicate the positions of the centres of the chains. The detailed chain packing is also shown in *Figure 6a*. On the other hand, *Figure 6b* shows the b-axis projection of the unit cell of monoclinic PVA ($a = 7.83$, b (fibre axis) $= 2.533$, $c = 5.53$ Å, $\beta = 87°$)[15]. The open circles indicate the positions of the centres of the chains. Here, the unit cell of PVA proposed by Sakurada *et al.*[15] was transformed parallel to its axes (as shown with a broken line), in order to have the centres of the chains located at the four corners of the cell. *Figure 6c* shows the geometric relationship between the orthorhombic PE and the monoclinic PVA, seen by

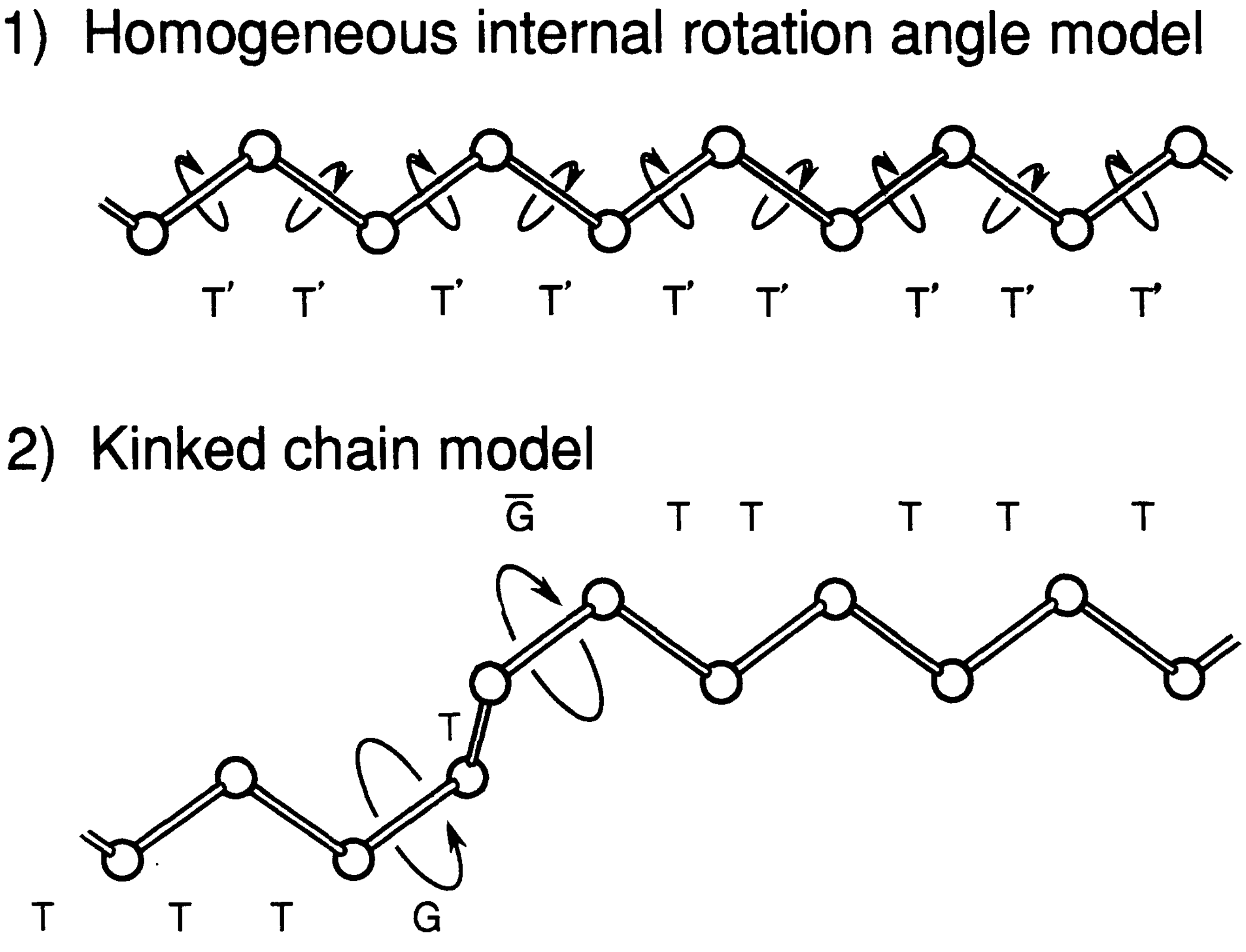

Figure 7 Schematic representations of (1) the homogeneous internal rotation angle model, and (2) the kinked chain model

overlapping both lattices. The lattice of PVA could be superposed on that of PE, and the centre of the chain did not need to be moved very much from the initial equilibrium position. Analogous results were also obtained with the unit cell of PVA proposed by Bunn[16]. This may be the reason for the isomorphic crystallization of the EVA copolymers over the entire range of VA contents. However, when packing both molecules into one unit cell, the centre chain must be rotated by about 65° (for the model of Sakurada *et al.*) from PE to PVA (95° for Bunn's model). It was reported that the crystal lattice of the EVA copolymer expands to the '*a*'-axis in order to relax the steric hindrance of the hydroxyl groups and reach the pseudo-hexagonal system. At the same time, the chains of the EVA copolymer apparently become cylindrical in form. Furthermore, this rotation is considered to cause the contraction and the disorder of the chain.

We will next consider two models in order to investigate the low E_l values of the EVA copolymers. *Figure 7* shows their schematic representations. One is a homogeneous internal rotation angle model, in which the chain molecule contracts by homogeneous internal rotation around the main-chain C–C bond. When the internal rotation angle τ for an all-*trans* conformation is defined as 180°, τ is 156.8° for EVA (40.0 mol%), calculated from the fibre identity period[8]. For the calculation of the E_l value, we used the method of Tashiro *et al.*[19]. The other model is a kinked chain model where two *gauche* conformations are introduced into the otherwise all-*trans* chain as the sequence, ···TTTGT$\bar{\text{G}}$TTT···, as shown in *Figure 7*. In this model, the chain molecule is contracted only in this portion. If the contraction of the EVA copolymer chain is caused entirely by the formation of these kinks, for example, they amount to 1.50 mol% for EVA (40.0 mol%). The mechanical series model between the kinked portion and the all-*trans* portion gives the whole E_l as follows:

$$1/E=(1-X)/E_0+X/E_{\text{kink}} \qquad (5)$$

where X is the amount of kink introduced, and E_0 and E_{kink} are the moduli of the EVA copolymer, for the fully extended structure and the kinked portion, respectively.

Figure 8 shows the calculated E_l values as a function of the VA content of the series of EVA copolymers. The homogeneous internal rotation angle model (broken line) could not entirely explain the change of the E_l value with the VA content, while the kinked chain model could do so (as shown by the envelope in *Figure 8*), by assuming E_{kink} to be between 1 and approximately 3 GPa; the calculated curve with $E_{\text{kink}}=1.9$ GPa (shown as a bold line), in particular, reproduced the experimental results quite well. Accordingly, the low E_l value and contracted fibre identity period for the EVA copolymers could only be explained by assuming that local internal rotation at the kinked portion has been introduced into the chain. We have already investigated the temperature dependence of the E_l value for a number of polymers[3]. Through these studies, a small contraction of the chain was found to bring about a great decrease in the E_l value above a particular temperature. This characteristic temperature is in accordance with the temperature range over which the thermal contraction of the polymer chain in the crystalline regions is more enhanced. The kinked chain model has been successful in explaining the temperature dependence of the E_l values for polymers with a planar zigzag conformation, such as atactic PVA[5], PE[16], polytetrahydrofuran[20] and others. In these cases, the small amount of the contracted portion was excited through thermal vibrations of the chain. In order to investigate whether the kinked chain in the EVA copolymers was introduced as a structural disorder or by thermal vibration, we next measured the E_l values at low temperatures, where thermal vibrations are restricted.

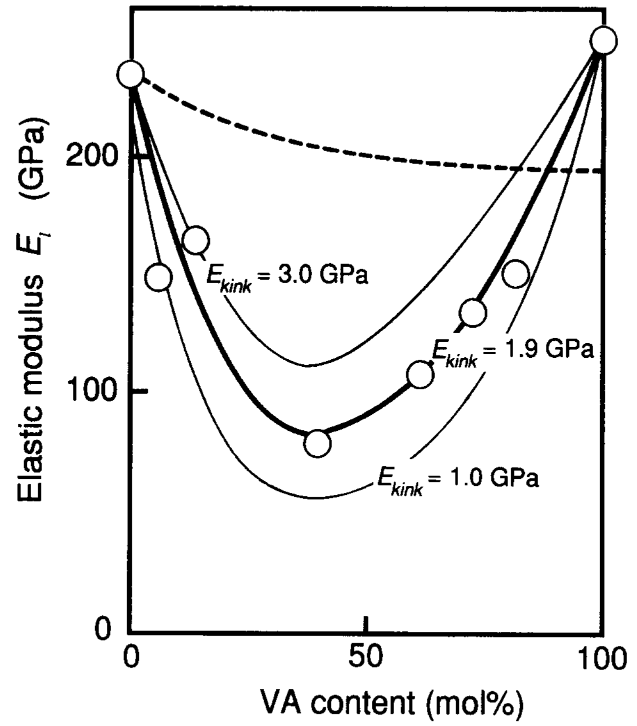

Figure 8 Relationship between the calculated elastic modulus E_l and the vinyl alcohol content of the series of ethylene–vinyl alcohol copolymers: (——) calculated with the kinked chain model; (- - -) calculated with the homogeneous internal rotation angle model

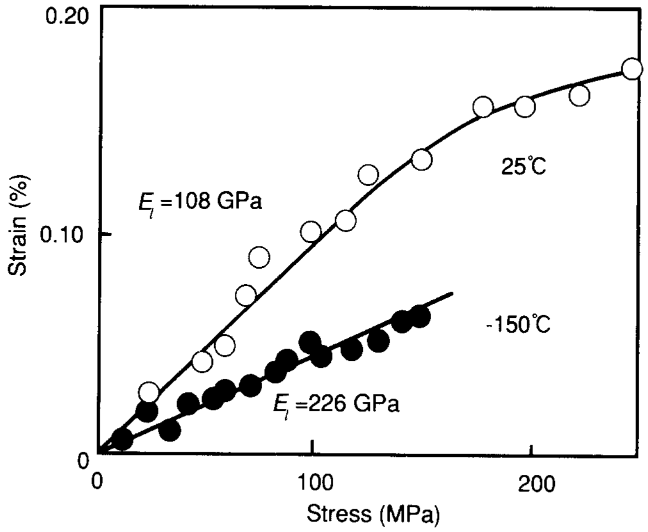

Figure 9 Stress–strain curves for the meridional reflection of an ethylene–vinyl alcohol copolymer with a vinyl alcohol content of 62.0 mol%: (○) at 25°C; (●) at −150°C

Elastic modulus E_l *of the EVA copolymers at low temperatures*

Figure 9 shows the σ–ε curves for the meridional reflection of EVA (62.0 mol%), both at 25°C (○) and

$-150°C$ (●). The initial slope decreased at low temperatures; the E_l value increased from 108 GPa at 25°C to 226 GPa at $-150°C$. At the same time, the fibre identity period increased from 2.531 Å at 25°C to 2.535 Å at $-150°C$, which shows that the copolymer chain molecules were elongated at low temperatures. In other words, the chain molecules of the EVA copolymer were contracted even at room temperature, with the decrease in the E_l value for the copolymer considered to be due to the incorporation of a small amount of a contracted portion, such as a kink excited by thermal vibrations.

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