

Study on orientable EVOH

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Abstract

Nippon Gohsei has studied orientability of biaxially oriented multilayer film containing EVOH (Ethylene vinyl alcohol copolymer). This paper will review orientability of multilayer film containing EVOH and describe the required properties of EVOH that is suitable for oriented film. This paper also describes how this understanding has led to a newly designed EVOH for barrier oriented film applications.

Introduction

NIPPON GOHSEI developed Soarnol[®] EVOH more than 25 years ago. Our EVOH is manufactured at our Mizushima plant (JAPAN) and at our U.S. plant, NOLTEX L.L.C. (La Porte, TX), and will be manufactured at our U.K. plant, NIPPON GOHSEI UK (Hull, U.K.) beginning 2003 4Q. Novel EVOH grades and new applications are developed at our Central Research Laboratory (Osaka, JAPAN) and Processing-Technique Development Center (Okayama, JAPAN). Our overseas marketing and technical sites are SOARUS L.L.C. (Arlington Heights, IL), NOLTEX L.L.C and NIPPON GOHSEI EUROPE (Duesseldorf, GERMANY).

EVOH is widely used in packaging applications for foods and non-foods because it has excellent gas barrier property, flavor barrier and good solvent resistance. These excellent properties exist because EVOH has a hydroxyl group on a side chain. This strong intermolecular hydrogen bonding results in high crystallinity and less free volume in the amorphous region. This is the reason why EVOH has outstanding gas barrier property.

Generally, EVOH is seldom used as monolayer for packaging application. EVOH is usually used in multilayer films or sheets in order to avoid absorbing moisture and to obtain mechanical strength. The multilayer films and sheets are often fabricated into final product. However, due to strong intra-/intermolecular interaction by hydrogen bonding, EVOH does not have good stretchability compared to other general resins such as Polyolefins. The drawing temperature of commercialized oriented PA/EVOH/PA films are relatively high and the drawing ratio is around 10 times by area. On the other hand, the drawing ratio of oriented PP is around 50 times by area in order to improve mechanical properties. The demand of EVOH is strongly increasing in recent years especially in advanced nations, because of the trend to use environment friendly material that does not contain chlorine. For the replacement of PVDC coated OPP film, the requirement of improving orientability is increasing because standard EVOH such as Ethylene content 44mol% or 48mol%EVOH does not offer adequate drawing performance for oriented PP/EVOH/PP film.

In this paper, we will describe the concept used to design EVOH suitable for orientation and the result of our evaluation.

Difficulty orientation of EVOH

Because of the strong intra-/intermolecular interaction of hydrogen bonding, conventional EVOH does not have good stretchability. It can be explained by the study of orientation factor "F", measured by polarized IR spectroscopy. Orientation factor "F" is calculated by using the phenomenon that when molecules orient in extension direction, absorbance of parallel and perpendicular to the stretching direction is different. We measured the extension ratio dependency of orientation factor by the polarized infrared method. Orientation factor of ethylene and vinyl alcohol group were focused. Orientation factor, *F* was calculated using the following equations.

$$F = (I-D)/(I+2D), D = A_{\perp} / A_{//}$$

D : dichroic ratio

*A*_⊥ : absorbance of perpendicular to stretching direction

*A*_{//} : absorbance of parallel to stretching direction

Following spectral was used for calculation of orientation factor, *F*.

$F_{ethylene}: 2858\text{ cm}^{-1} \nu(\text{CH}_2)$, $F_{vinyl\ alcohol}: 1093\text{cm}^{-1} \nu(\text{CO})$

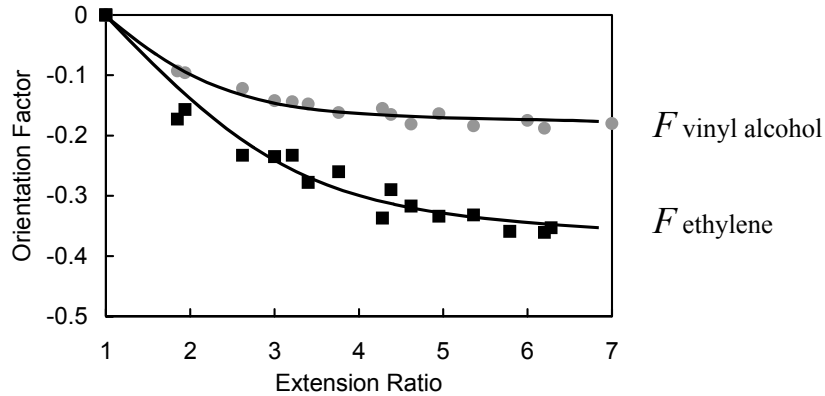


Fig. 1 orientation factor of vinyl alcohol and ethylene

The orientation factor of ethylene group shows dependence on extension ratio. . On the other hand, orientation factor of vinyl alcohol group is saturating at low extension ratio (approximately 3 times). This phenomenon says that the hydrogen bonding hinders the vinyl alcohol group being oriented, and shows EVOH is hard to orient.

Suitable EVOH for orientation

In order to design an orientable EVOH, we have to consider how a softer EVOH will orient. The following factors exert influence on the orientability of EVOH.

1. Ethylene content
2. Degree of crystallinity
3. Vicat softening point, Glass transition temperature (T_g)
4. Crystalline size

1. Ethylene content

It is well known that orientability of EVOH depends on its ethylene content. Higher ethylene content EVOH which has less hydrogen bonding has more orientability than lower ethylene content EVOH. Therefore high ethylene EVOH (Ethylene content 44mo% or 48mol%EVOH) is being used for multilayer oriented film applications. Fig. 2 shows S-S curve of conventional EVOH-38, 44, 48. Fig. 3 shows dynamic viscoelasticity of EVOH-38, 44 and 48. Both graph shows that higher ethylene content is softer than lower ethylene content. From our researchin orientation, it is known that yield stress is very important factor in orientation process. When yield stress is low, uniform orientation will be carried out.

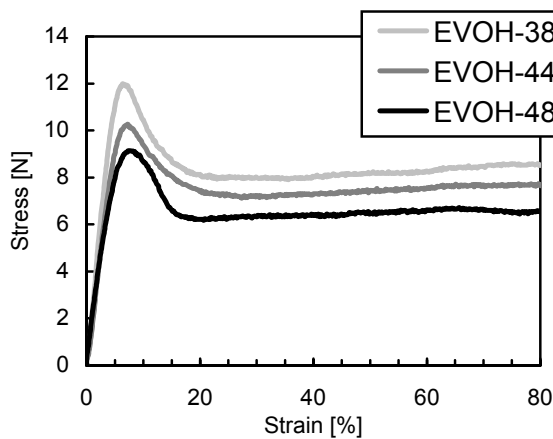


Fig. 2 S-S curve of EVOH-38, 44, 48

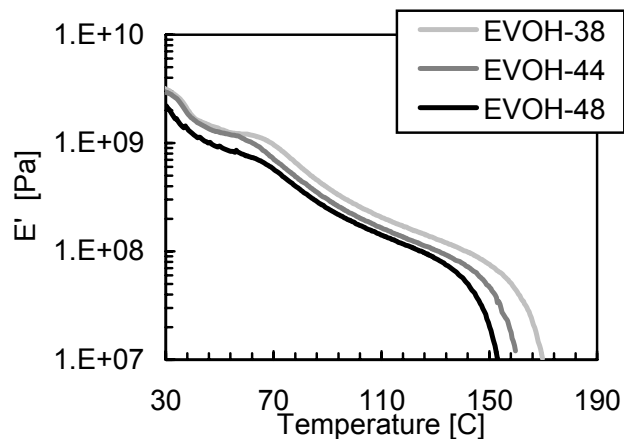


Fig.3 dynamic viscoelasticity of EVOH-38, 44,

2. Degree of crystallinity

It is quite common for every resin that the original sheet, which is for orientation, is quenched. And the sheet quenched to be controlled its crystallinity low shows better orientability. The same goes for EVOH, and the EVOH with low crystallinity shows better orientability. Figure 2 indicates S-S curves of normal EVOH and controlled EVOH. Since the controlled EVOH with lower crystallinity shows a lower yield point, we find this EVOH is easier to draw.

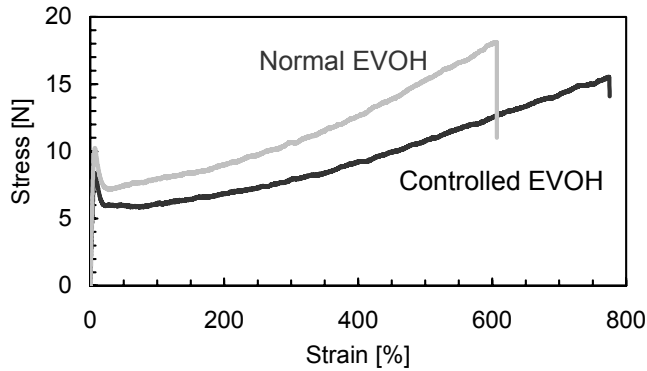


Fig. 4 comparison S-S curve of normal EVOH and controlled amorphous EVOH

3. Vicat softening point, Glass transition temperature (T_g)

Vicat softening point and T_g (Glass transition temperature) are factors that influence the process window for orientation. The lower these factors are, the better the orientability is.

4. Crystalline size

Small crystalline size has better orientability. This factor, however, is difficult to control due to very fast rate of crystallization for EVOH.

Modified EVOH

From the above considerations, we recognized that ethylene content and degree of crystallinity of EVOH are major factors in developing orientable EVOH. Higher ethylene content and lower degree of crystallinity are requirements. By controlling the ethylene content and the degree of crystallinity of EVOH, we designed new modified EVOH with softness that has better orientability. A series of evaluation results that used modified EVOH are shown below.

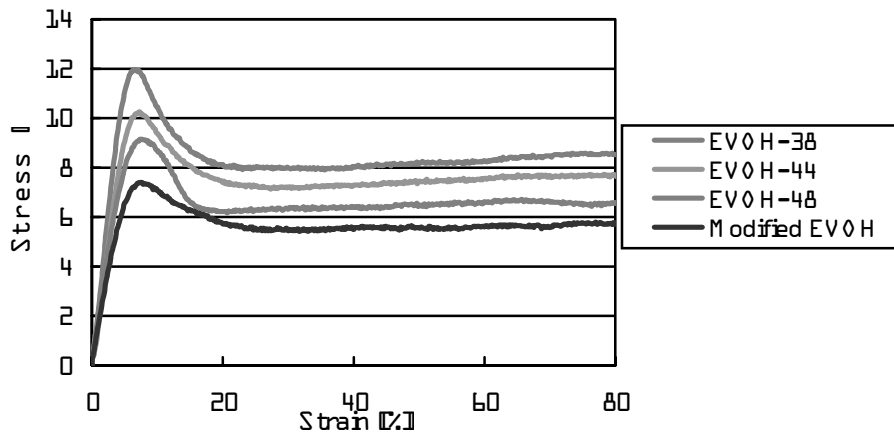


Fig. 5 S-S curve of EVOH-38, 44, 48 and modified EVOH

Fig. 5 shows Stress-Strain curve of modified EVOH. Measurement was carried out with monolayer film at the room temperature. Young's modulus and yield stress of modified EVOH is shown in Table 1. The graph shows modified

EVOH has lower yield stress than EVOH-48. This means the modified EVOH has better orientability than EVOH-48. The young's modulus of modified EVOH in table 1 also shows lower than another conventional EVOH. Therefore it can be estimated that the modified EVOH has outstanding orientability.

	EVOH-38	EVOH-44	EVOH-48	Modified EVOH
Young's modulus [MPa]	1360	1020	990	750
Yield stress [MPa]	64	55	50	43

Table 1 Young's modulus and yield stress

Vicat softening point of each EVOH is shown in Fig. 6. The measurement of vicat softening point was carried out according to the ISO standard No306. Modified EVOH shows significantly lower value than conventional EVOH.

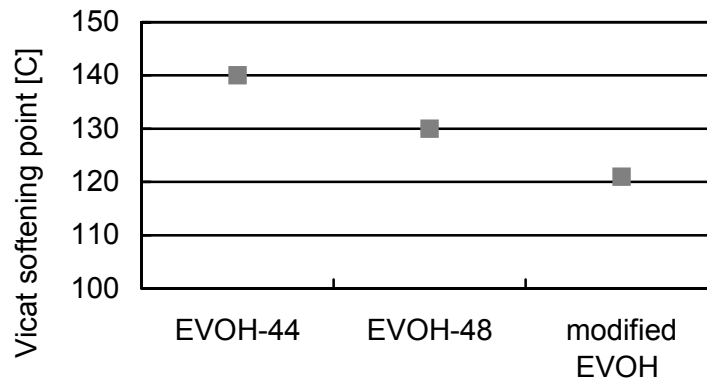


Fig. 6 Vicat softening point

Evaluation of modified EVOH

Film extrusion

Sample films for orientability test are extruded by 3-resins-5layers T-die. Film composition is following, LLDPE / tie / EVOH / tie / LLDPE = 65/25/25/25/65 μm , total thickness=195 μm

Film orientation test

Apparatus: biaxially orientation system

Method: simultaneous biaxially orientation

Draw speed: 300 mm/sec

Draw ratio and temperature: various

Specimen: 100mm x 100mm (drawn area is 80mm x 80mm)

Fig. 7 shows the orientability of modified EVOH comparing EVOH-44 and 48. The evaluation of orientability was carried out whether it can successfully draw at each draw temperature, or whether drawing was impossible. The area draw ratio that can be drawn was plotted in this graph. Y-axis in the graph means area draw ratio, draw ratio 9 means 3x3. At all draw temperatures, it turns out that modified EVOH has better orientability compared with conventional EVOH.

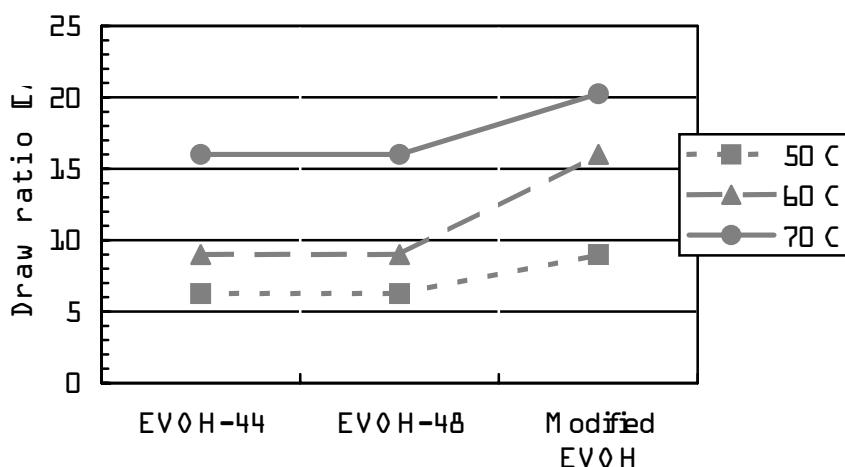


Fig. 7 the orientability of modified EVOH comparing EVOH-44 and 48

Table 2 shows Oxygen transmission rate (OTR) of oriented films and non-oriented films. The measurement was carried out at 20 degree C, 65%RH with 3x3 oriented films. OTR values are calculated to the value of 20um EVOH thickness. The modified EVOH maintains about the same OTR level as EVOH-48. OTR of oriented films with EVOH-44 and EVOH-48 are worse than OTR of non-oriented film. It is because film is not uniformly oriented, and it appears notably in EVOH-44.

	OTR [cc.20um/m2.day.atm]		
	Modified EVOH	EVOH-48	EVOH-44
Oriented film	4.0	3.5	2.2
Non-oriented film	4.2	3.4	1.5

Table 2 oxygen transmission rate (OTR) of oriented films and non-oriented films

Conclusions

Nippon Gohsei has studied orientability of biaxially oriented multilayer film containing EVOH. We recognized that ethylene content and degree of crystallinity of EVOH are major factors in developing orientable EVOH. We investigated “modified EVOH” with low yield stress, low young’s modulus and low vicat softening point. “Modified EVOH” shows high orientability and maintains similar OTR level as 48mol% ethylene content EVOH.

References

1. Correlation Study between Oxygen Permeability and Free Volume of EVOH, *Macromolecules*, [34], 6153 (2001)
2. Shinta Miyazumi et al., Stretchable EVOH and its properties, *SP2001, 17th Annual world congress*, (2001)
3. Kobunshi no kotaikouzou2, kyouritsu-shuppan, page 331, (1984)
4. Soarnol technical note

Study on Orientable EVOH

TAPPI 9th European PLACE conference
14th May 2003, Roma

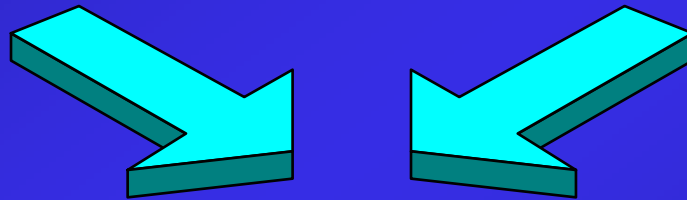
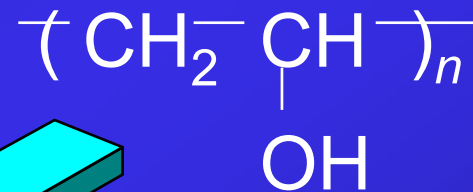
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NIPPON GOHSEI EUROPE GmbH

Structure of Ethylene-Vinyl alcohol copolymer (EVOH)

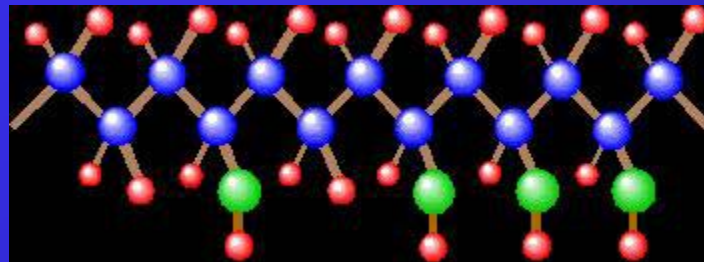
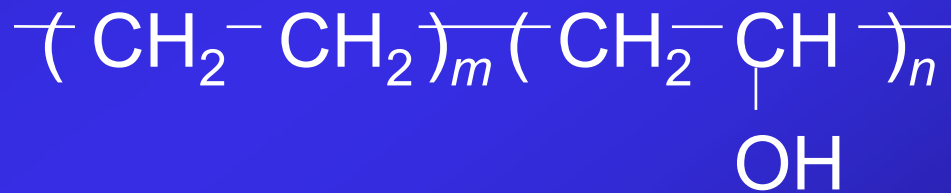
PE(Polyethylene)



PVOH(Polyvinyl alcohol)

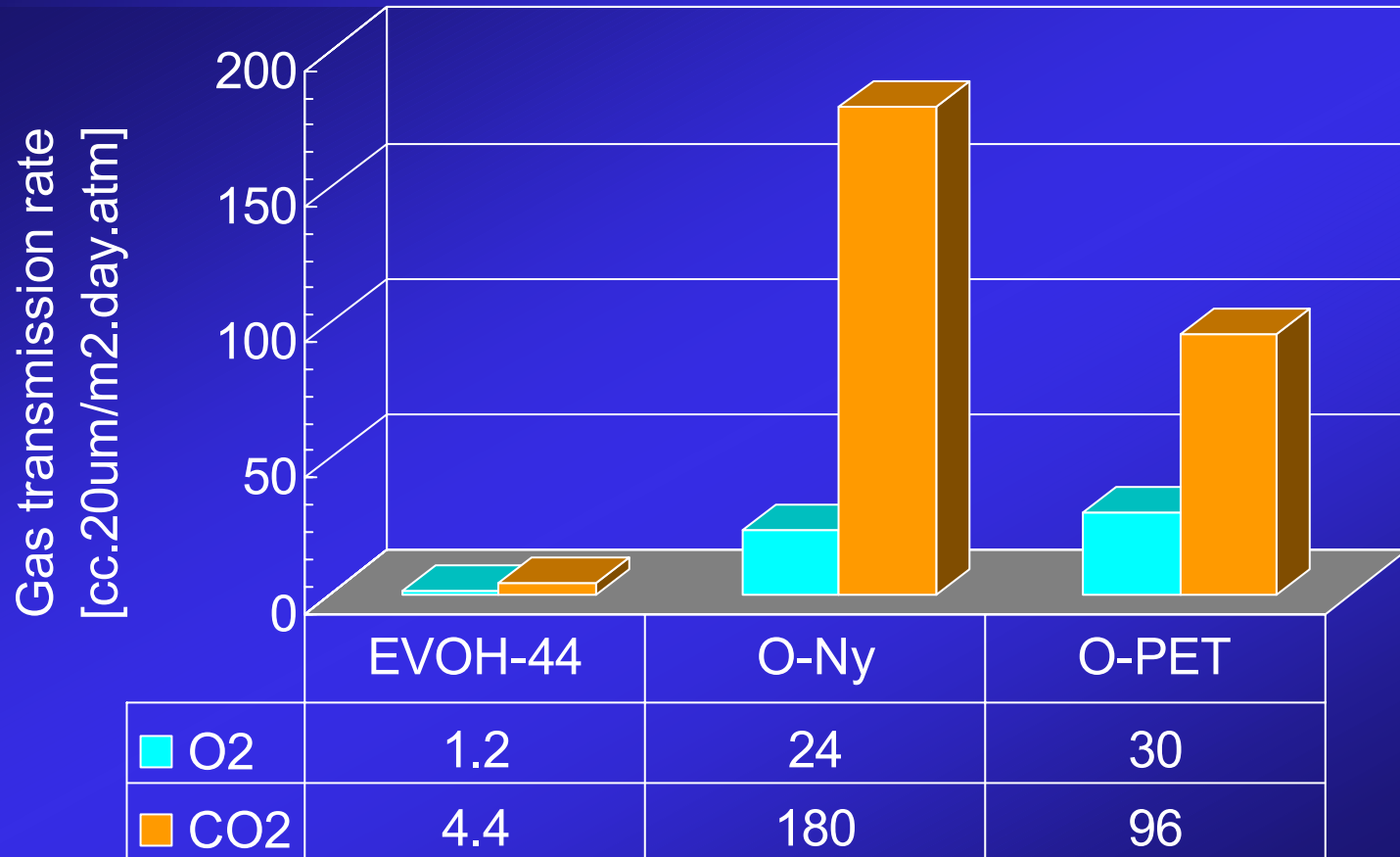


EVOH



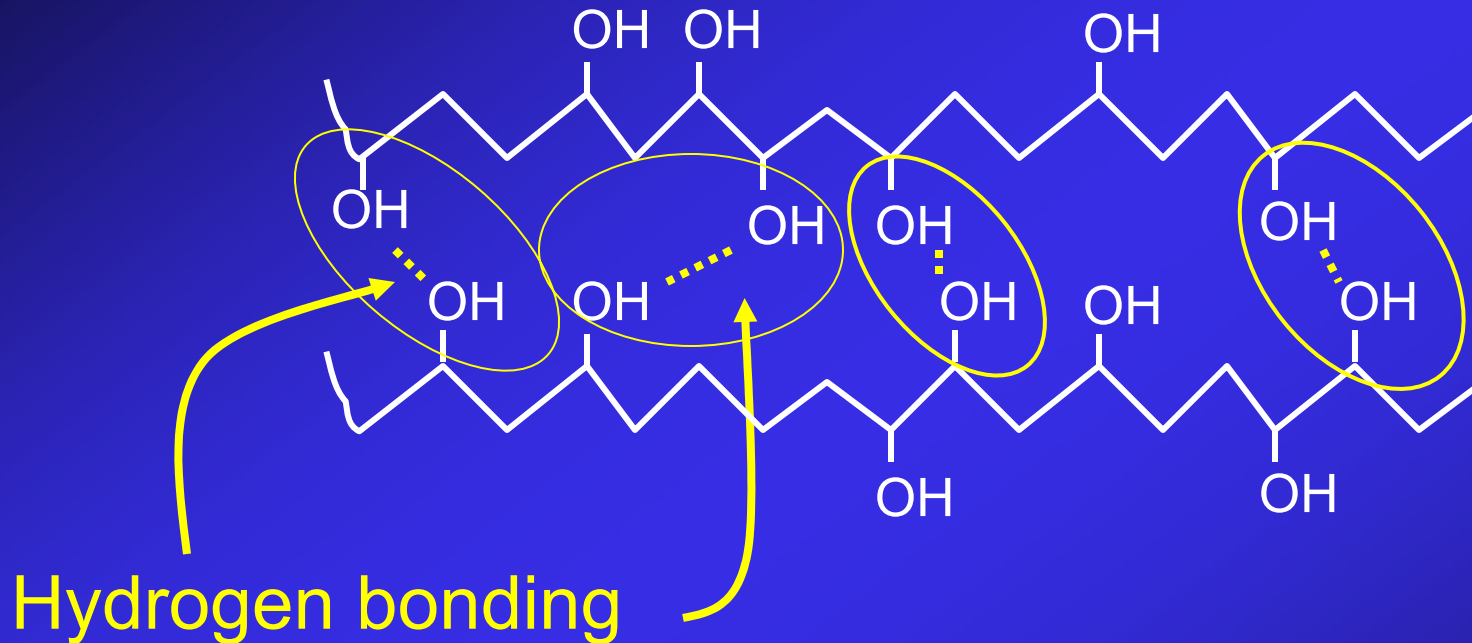
...
C
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HO
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EVOH has excellent gas barrier



@ 20C, dry

Why does EVOH have excellent gas barrier property?



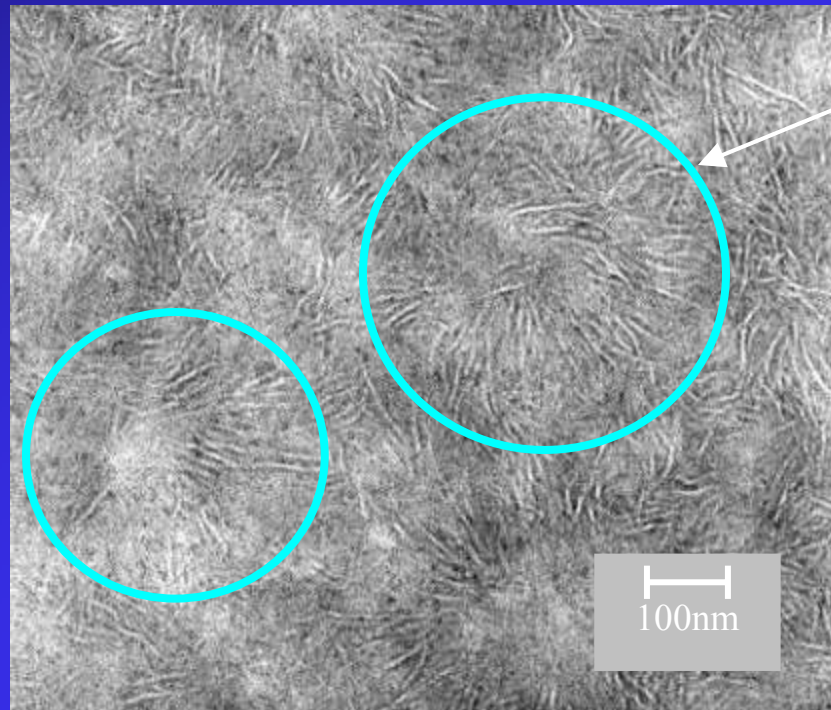
- ***High crystallinity***
- ***Less free volume***



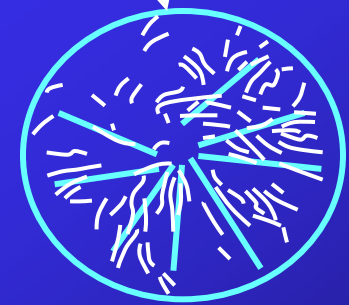
Excellent gas barrier

Spherulite of EVOH by TEM

x50,000



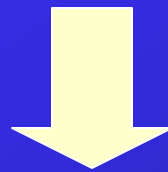
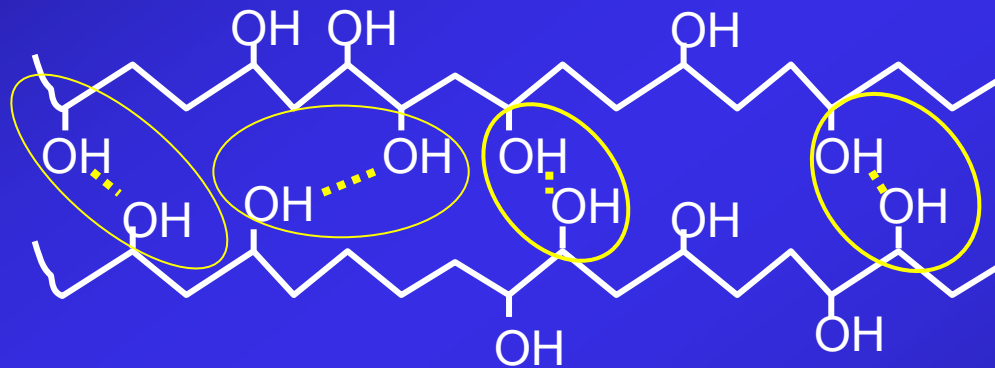
spherulite



EVOH shows high crystallinity

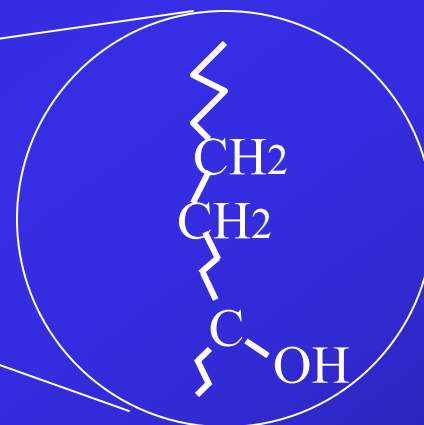
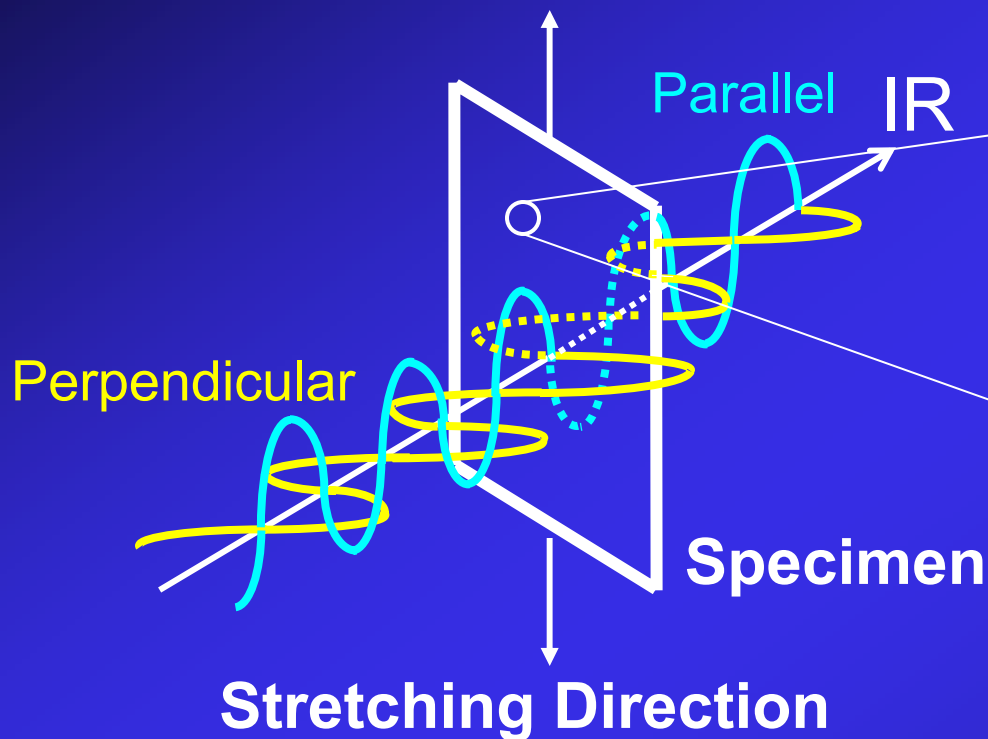
But...

due to high intra- / intermolecular
hydrogen bonding



EVOH is difficult to orientate!

Polarized Infrared Spectroscopy



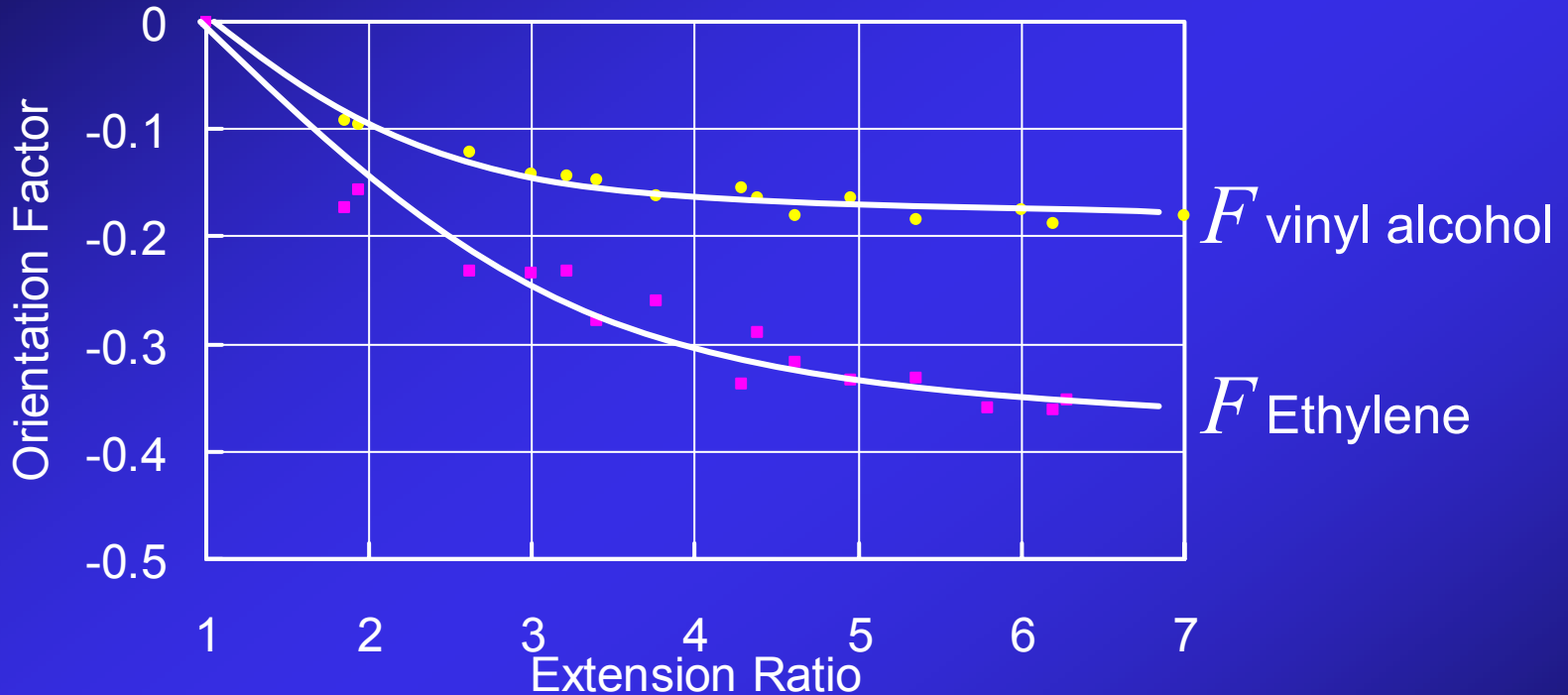
Orientation Factor

$$F = \frac{1 - D}{1 + 2D} \quad (1)$$

F : Orientation Factor

D : Dichroic Ratio

Orientation factor, F



F vinylalcohol is saturating at low extension ratio, because hydrogen bonding is preventing extension.



EVOH is difficult to orientate!

Key properties for orientable EVOH

- **Ethylene content**

Higher is better

- **Degree of crystallinity**

Lower is better

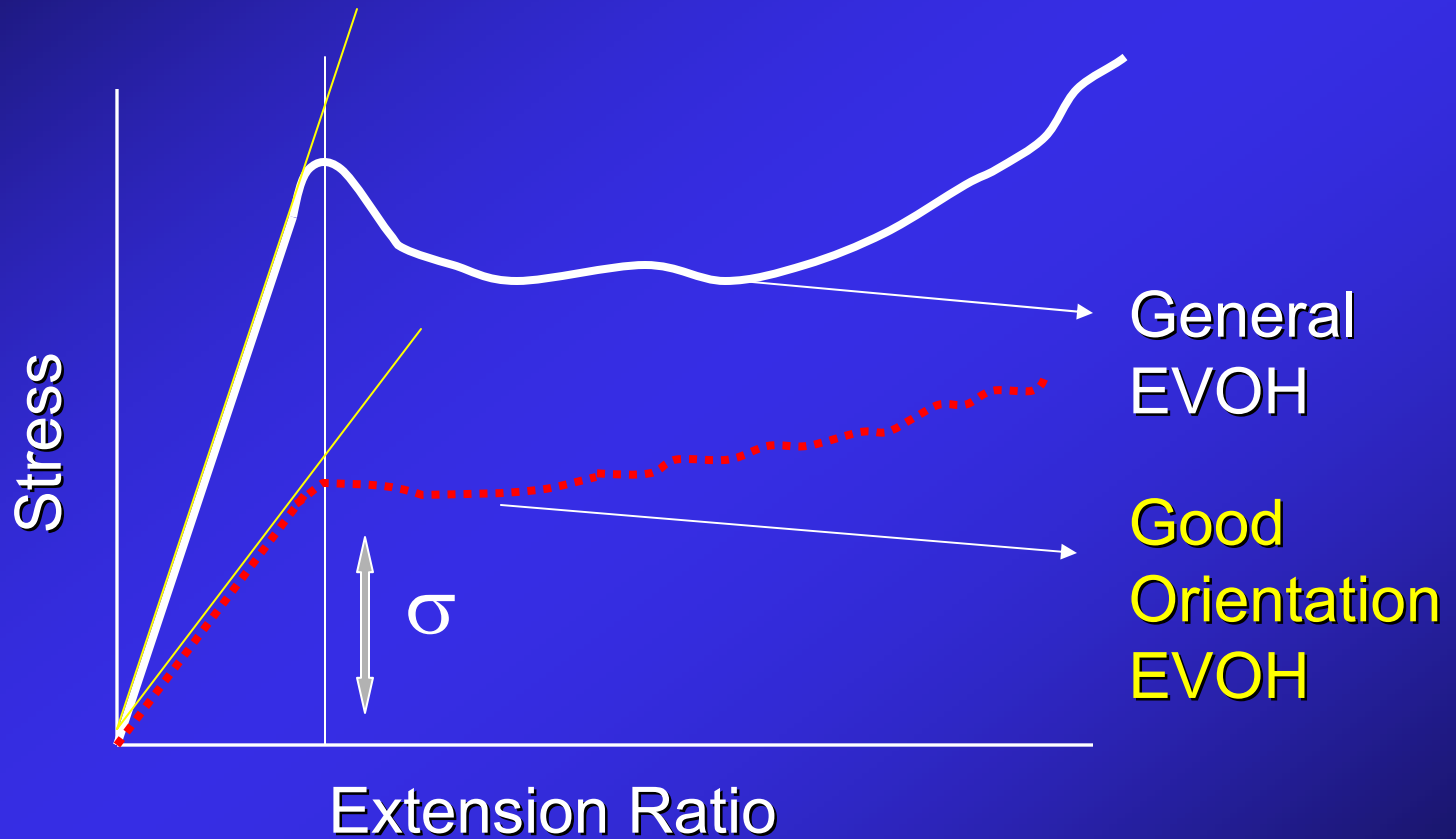
- **Tg , Vicat softening point**

Lower Tg and Vicat softening point is better

- **Crystalline size**

Smaller is better, but size is difficult to control

Extensional Mechanism of Orientable EVOH



Lower yield stress (σ)
Lower Young's modulus

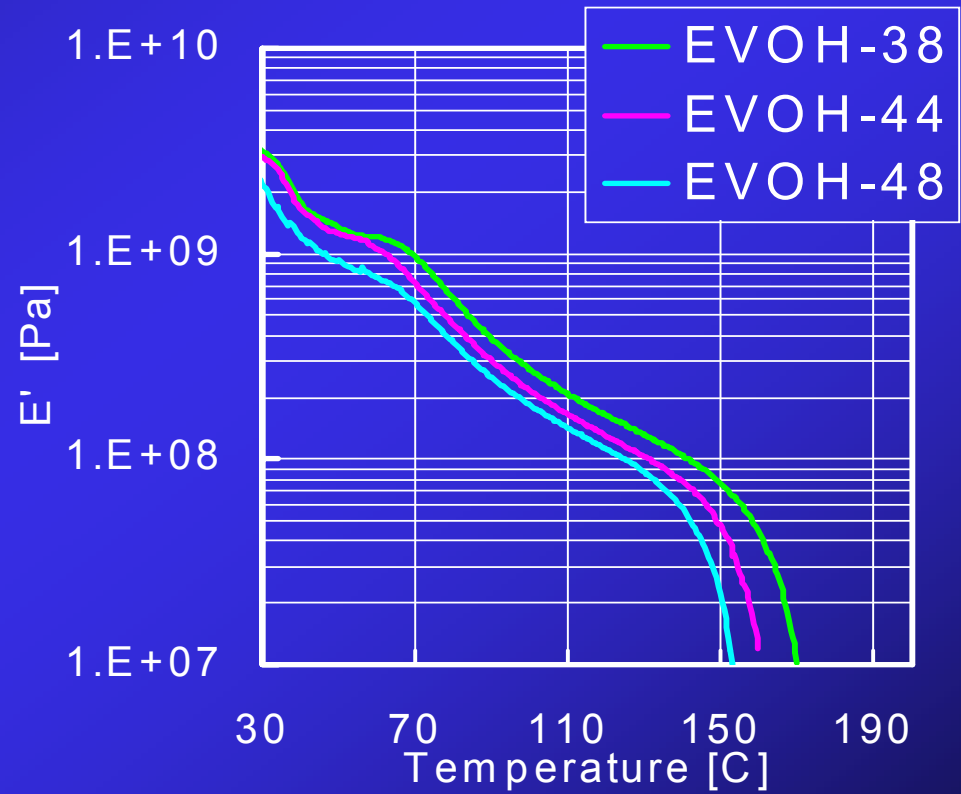
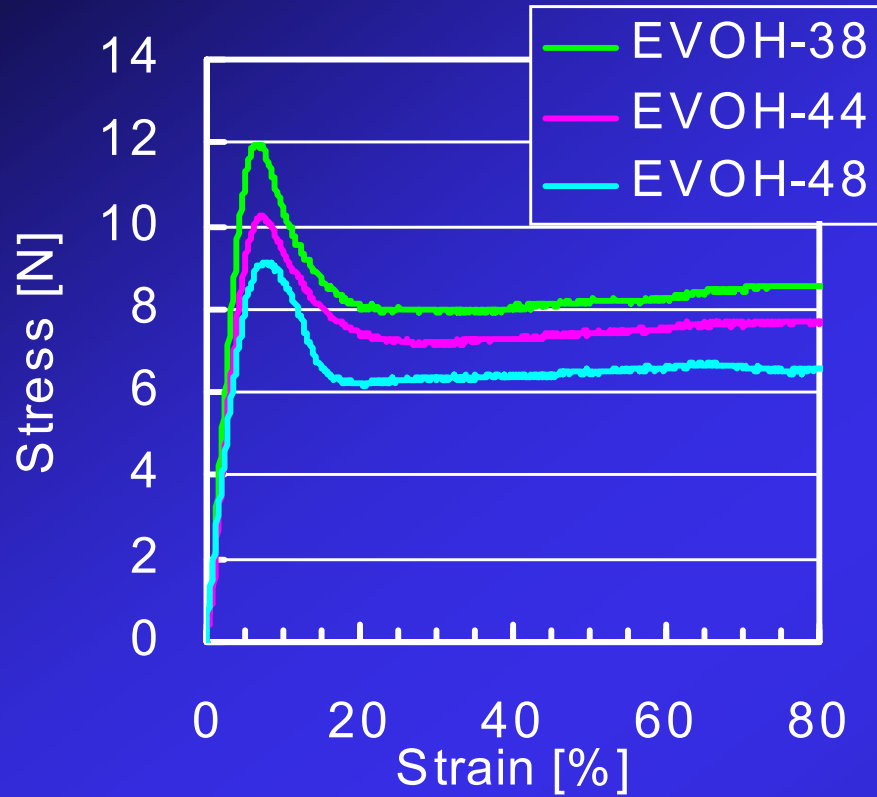


Orientable EVOH

Key properties for orientable EVOH

- **Ethylene content**
Higher is better
- Degree of crystallinity
Lower is better
- Tg , Vicat softning point
Lower Tg and Vicat softing point is better
- Crystalline size
Smaller is better, but size is difficult to control

Ethylene content dependency



High ethylene content EVOH has lower yield stress

Key properties for orientable EVOH

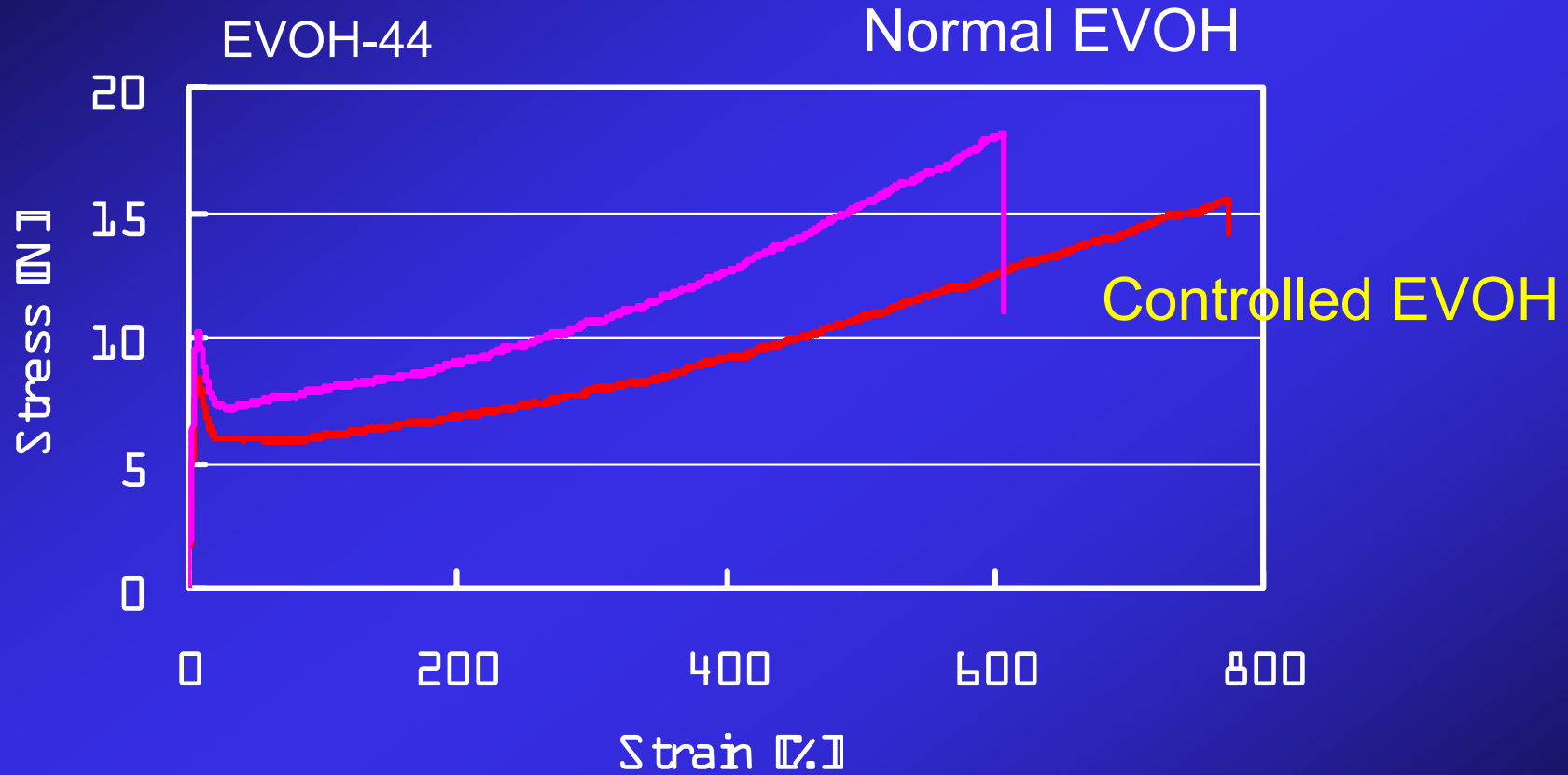
- Ethylene content
Higher is better

- **Degree of crystallinity**
Lower is better

└───→ **Amorphous control technique**

- Tg , Vicat softning point
Lower Tg and Vicat softing point is better
- Crystalline size
Smaller is better but difficult to control the size

Controlled amorphous EVOH



Low crystallinity EVOH has lower yield point and better elongation.

In order to obtain better orientation with EVOH, ...

□ **Ethylene Content**

Higher ethylene

□ **Degree of Crystallinity**

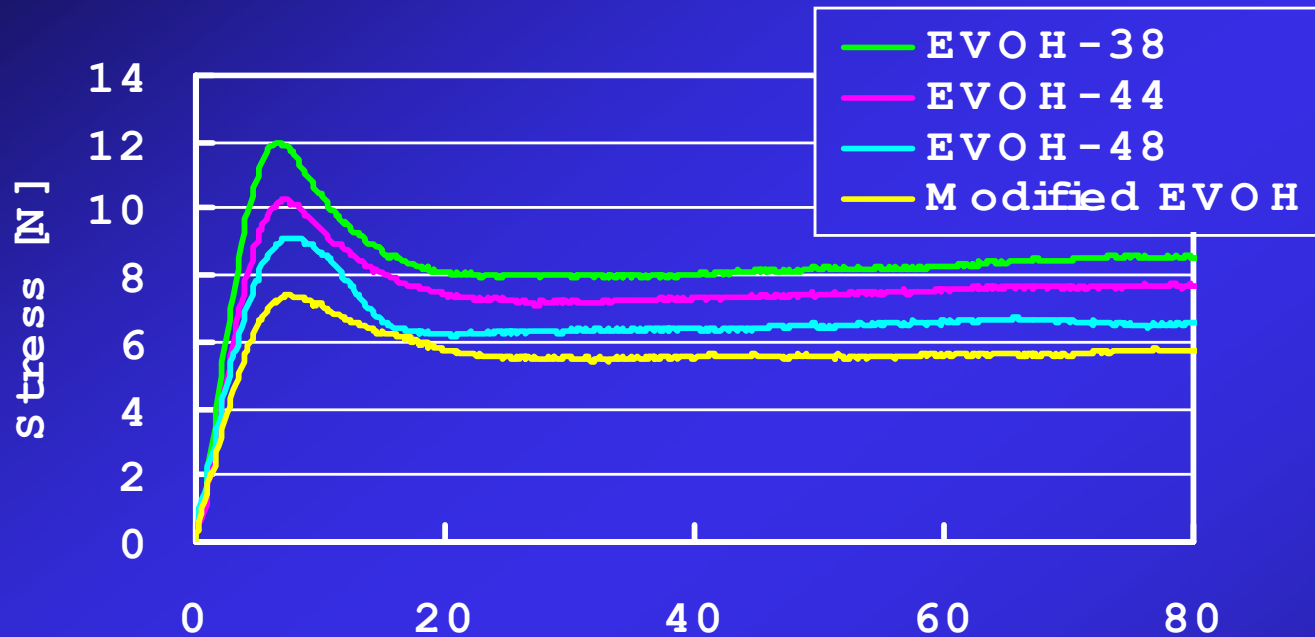
Lower degree of crystallinity

In order to meet above requirement.....



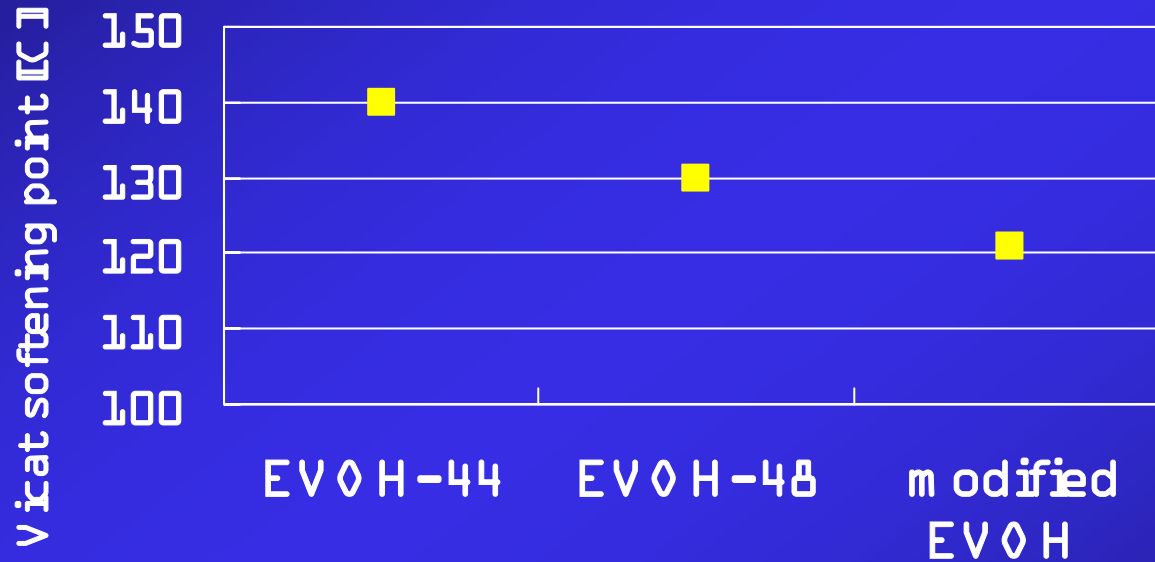
“Modified EVOH”

S-S curve of "Modified EVOH"



	EVOH-38	EVOH-44	EVOH-48	modified EVOH
Young's modulus [MPa]	1360	1020	990	750
Yield stress [MPa]	64	55	50	43

Vicat softening point of “Modified EVOH”



“Modified EVOH” gave low vicat softening point compared to conventional EVOH.

Evaluation of “Modified EVOH”

Multilayer film sample

LLDPE/tie/EVOH/tie/LLDPE = 65/25/25/25/65
total: 195 μ m

Orientation test

Biaxially Orientation System

Method: Simultaneous drawing

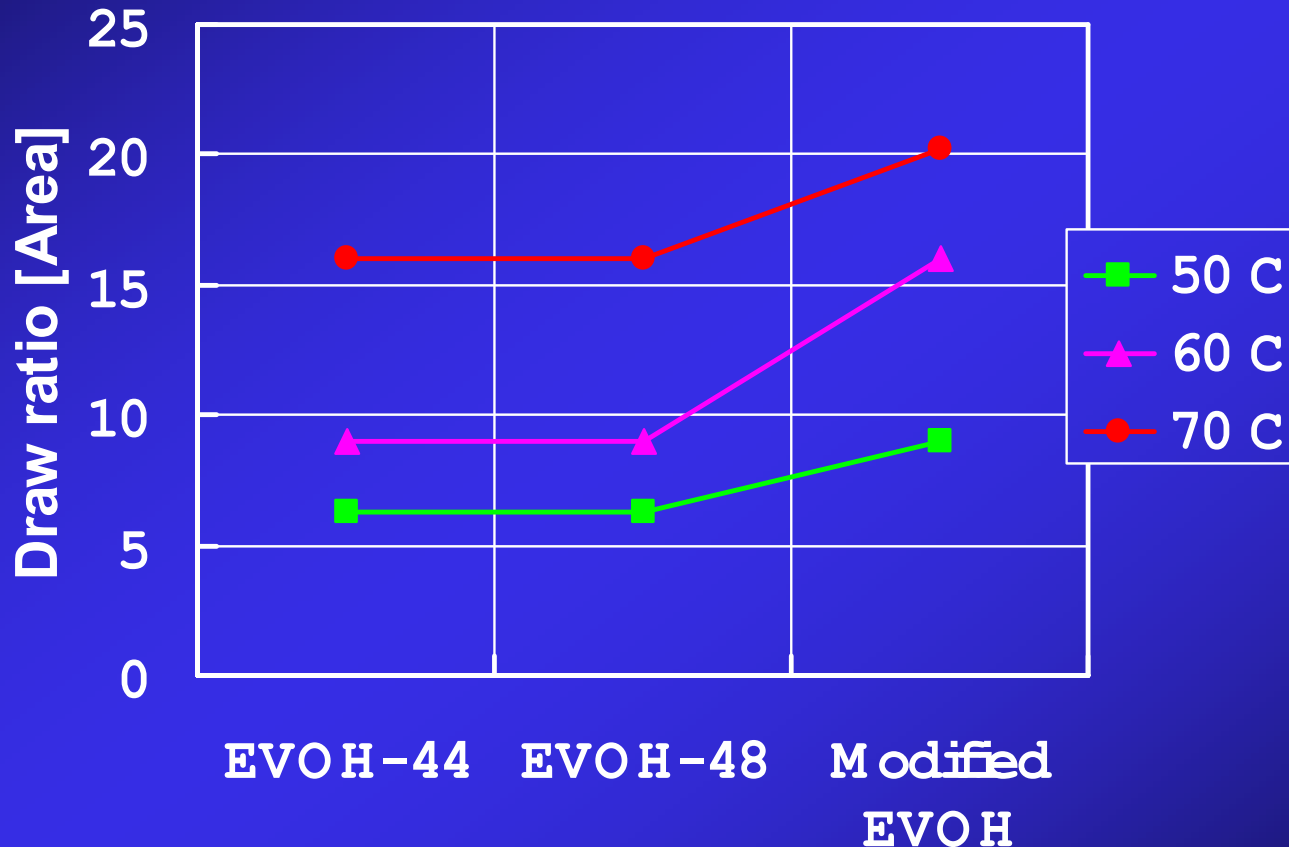
Drawing speed: 300 mm/sec

Sample

modified EVOH, EVOH-44, EVOH-48

Orientability of “Modified EVOH”

LLDPE/Adh/EVOH/Adh/LLDPE=60/25/25/25/60=195um



Modified EVOH gives good performance.

OTR data @ 20C, 65%RH

Sample: 3x3 oriented film

*Unit: cc.20um/m2.day.atm

	Modified EVOH	H4815	AT4403
Oriented film	4.0	3.5	2.2
Non-oriented film	4.2	3.4	1.5

with OXTRAN2/20

The modified EVOH gave about the same OTR value as 48 mol% conventional EVOH.

Summary

Nippon Gohsei has investigated “Modified EVOH” with.....

Low yield stress

Low young's modulus

Low vicat softening point

“Modified EVOH” shows high orientability and maintains about the same OTR as 48mol% EVOH.