

# EVALUATION OF STRUCTURE DEVELOPMENT AND STRETCHABILITY DURING THE STRETCHING PROCESS FOR VARIOUS POLYPROPYLENES

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## Abstract

The structure development and stretchability of various kinds of polypropylenes(PP) during the stretching process of both MD stretching and TD stretching were evaluated by using in-situ observation such as light scattering, birefringence and small angle X-ray scattering. As samples of polypropylenes, molecular weight distribution and tacticity were changed. Furthermore very low tacticity polypropylene was added to the standard stretching PP or high tacticity PP.

It was found that three stretching regions existed during the uni-axial stretching process. In the first region, the stress increased with increasing stretching strain, but the spherulite was not broken up and birefringence did not increase very much. In the second region, the spherulite was broken up and birefringence increased with increasing strain ratio. In the third region, stretching stress increased gradually and birefringence reached the maximum value.

From the stress and strain curve, high tacticity polypropylene showed high stress and clear yield values at the initial stretching strain and had large spherulite size. Molecular weight distribution made no big difference at the yield value, but the stretching stress at the larger stretching ratio decreased with increasing molecular weight distribution. The polypropylene blended with very low tacticity polypropylene showed, like low tacticity polypropylene, low stretching stress at the yield value. In terms of the process conditions, the cooling conditions when producing the sheet sample before stretching influenced stretching stress in MD, but did not influence stretching stress in TD.

From the experimental results, the structure development of various polypropylenes during the stretching process could be evaluated, and then the polymer with good stretchability and film uniformity could be designed using only a small amount of sample in a short time.

## 1.Introduction

Polypropylene is one of the most popular resins and its film has been widely used for various applications. Many of the polypropylene films are produced by the successive biaxial process. In the polypropylene film production process, recently high-speed production and thinner films are desired, and it is very important to obtain a good relationship among molecular design, structure development and stretchability during film stretching. If this relationship has not been acquired, the stretching test must be done using a lot of time and samples.

The purpose of this study is to evaluate structure development and stretchability using an in-situ observation method with a small amount of resin during the polypropylene stretching process. This study used various samples of changing tacticity, molecular weight distribution and of blending very low isotacticity polypropylene. The superstructure of polypropylene during the uniaxial stretching was measured by online light scattering measuring and molecular orientation was measured by online-birefringence measuring. The degree of orientation of the lamella crystal was estimated by small-angle x-ray scattering.

This study was done in order to establish the evaluation technology for stretchability of polypropylene film. This analysis technology is useful for film production site.

## 2.Experimental

### 2.1 Materials

Polypropylenes produced by Primepolymer and Idemitsu Kosan Co.,Ltd. were used in this study. The characteristics of the samples are shown in Table 1.

Each sample was produced at the chill roll temperature 30°C by sheet extrusion and its thickness was 300µm. The standard sample was F-300SP. Other samples were high tacticity PP F-300SV, low tacticity F-300SP2, wide molecular weight F-300S, widest molecular weight distribution F300S2. Blend samples were prepared by blending standard F-300SP with very low tacticity LP200 or LMPP. LMPP is very low tacticity PP and low molecular weight. LP200 is low tacticity PP and the same molecular weight as the standard sample. HM1 and HM2 were LP200 5% and 10% blended in standard PP and LM1 and LM2 were LMPP 5% and 10% blended in standard PP.

## 2.2 Experimental Equipment

The opt-rheometer produced by Orc Manufacturing Co., Ltd. was used. The stretching experiment was done by using the uniaxial stretcher with the birefringence measurement system using the photoelasticmodular and the load cell measuring stretching force. The stress and strain data and the birefringence could be obtained at the same time. In addition, the light scattering data was also obtained by using high power He-Ne laser in order to evaluate the super structure development.

The sheet was cut in a rectangular shape 10mm×25mm and chucked by clips and then heated at 140 °C in the thermostatic oven for 5minutes. Then it was stretched at stretching ratio of 9 at the speed of 1700%/min. The Hv scattering pattern which reflects the scattering of polymer superstructure was evaluated using the equipment shown in Fig.1 and recorded by video camera during the stretching process. After stretching, each sample was measured by SAXS in order to study the crystalline structure development.

## 3. Results and Discussion

### 3.1 Stretchability of Various molecular Design PP

#### Tacticity

The stress and strain curve data of three different tacticity PP are shown in Fig.2. F-300SV has the largest yield value and then F-300SP has a medium value and F-300SP2 has the lowest yield value, which corresponds to tacticity. High tacticity is easy to crystallize and makes thicker crystalline. The model of lamella structure dependent on tacticity is shown in Fig. 3. Highest tacticity F-300SV has the thickest lamella and then F-300SP, F-300SP2 respectively. The yield value is very much dependent on crystallinity, which makes the stretchability worse. When comparing F-300SP2 with F-300SV, F-300SP2 shows a 30% lower yield value than F-300SV.

#### Molecular Weight Distribution

The stress-strain curves of three different molecular weight distribution samples F-300SP, F-300S and F-300S2 are shown in Fig. 4. Fig. 4 shows that wide molecular weight samples have lower stresses after the yield value. The effect of the low molecular weight portion may reduce the stress. When comparing F-300SP with F-300S and F-300S2, both F-300S and F-300S2 had 10% lower stress at the high stretching ratio.

#### Blend of low tacticity PP

The stress and strain curves for the blend of very low tacticity PP in the standard PP are shown in Fig. 5. The blending of very low tacticity PP decreases the yield value of stress and a higher blending ratio causes a reduction in the yield stress by more than 30%.

The blending of low tacticity PP in F-300SP may reduce the crystallization speed, which decreases crystallinity.

Furthermore, a small portion of blend melts during the stretching as very low tacticity PP has low melting point.

### 3.2 Superstructure and molecular orientation

#### Superstructure

The stress-strain curve of F-300SP is shown in Fig. 6. The points from a to j (true strain from 0.1 to 0.9) and point x (true strain 2.2) in Fig.6 show the stretching ratios of obtaining the light scattering and SAXS. Fig. 7 shows data of the light scattering and SAXS.

The scattering pattern of an un-stretched sample shows a clear clover pattern which demonstrates the existence of spherulites.

In the region at the beginning of stretching and elastic deformation namely b (true strain 0.1), there is not a big change. From the point c (true strain 0.2), the scattering pattern is changed and spherulites deform. As the stretching proceeds, the light scattering pattern deforms in the equator and the spherulites elongate elliptically in the stretching direction.

The clover shape of scattering pattern which is a sign of spherulites disappeared from point e (true strain 0.4) to point f (true strain 0.5), meaning the spherulites broke up.

SAXS pattern shows crystalline orientation occurs at point e (true strain 0.4). It can be found that the spherulites break up at the yield value and lamellas are oriented in the stretching direction. At the point of true strain 0.7, the SAXS pattern shows strong scattering in the meridian direction which means the oriented crystalline structure.

In the region of stress hardening, the clover pattern of the light scattering disappears and streak pattern in the equator direction and the high order structure is changed from the spherulites structure to the fibril structure.

From the light scattering data shown in Fig. 8, the average spherulite sizes are 5.8µm for F-300SV and 4.3µm for F-300SP. The blend sample shows very weak scattering intensity. The scattering pattern changes from point b, and the clover pattern is disappearing at point c. For this reason, as the blend sample begins to disappear the clover pattern at the lower strain than F-300SP, the blend sample is under lower strain to break up the spherulites than F-300SP. In a comparison of the blend SAXS pattern with F-300SP, the blend sample shows higher orientation than F-300SP which has a broad light scattering pattern. This result means that the low tacticity portion blend decreases crystallinity and makes the spherulites break up easily.

#### Molecular Orientation

The stress and strain curves of F-300SP (a), F-300SV (b), LM2 (c) and HM2 (d) are shown in Fig. 9. The birefringence of all the samples does not increase at the beginning of stretching and then increases rapidly after the yield value passes. And then, the birefringence increases gradually after the stress

reaches strain hardening. From these data, the superstructure pattern is divided into three regions, namely Region I where birefringence remains low, Region II where birefringence increases rapidly after the stress passes the yield value, and in Region III where birefringence increases gradually and stress hardening takes place.

The stresses show big difference among various samples, but birefringence show only slight differences. Low tacticity PP has the same level of birefringence as high tacticity PP at the same stretching ratio and obtains the same molecular orientation at the low stretching stress, which means less possibility of breakage during the stretching .

### **3.3 Relationship between Stress and Birefringence**

The relationship between stress and birefringence during the stretching process is shown in Fig. 10. All the samples show that the stress increases, but the birefringence does not increase during the beginning of stretching. And then, the birefringence suddenly increases after passing the yield value of stress and then gradually increases. At the beginning of the stretching, as the spherulites do not break up, molecular orientation does not proceed and birefringence does not increase much. The stress increases and reaches the yield value. After the yield value, the spherulites break up and lamellas rotate to the stretching direction, so the birefringence rapidly increases. The oriented lamella is shifted to a fibril structure and molecular chains are elongated in the stretching direction.

As F-300SV has large spherulites and high crystallinity, the yield value which is the stress of breaking up the spherulites is large.

### **3.4 Superstructure change during stretching process**

From the results of in-situ data, the stress-strain curve can be divided into three regions. In region I , as the light scattering pattern shows the clover pattern, the spherulites exist and are only deformed by the stretching stress. The crystalline structure does not change much and birefringence also changes a little.

In region II , after the stress reaches the yield value, the scattering pattern of the clover shape is gradually disappearing, which means the spherulites break up, and SAXS pattern shows that the lamellas rotates in the stretching direction and are oriented.

In region III, the lamellas are divided into small parts and are shifted into fibril structures. As the lamellas already rotate in region II , the stress increases and birefringence increases gradually.

Fig. 11 shows the stress-strain curve, birefringence, the light scattering and SAXS of F-300SP.

The superstructure development during the stretching process is modeled in Fig. 12.

### **3.5 Stretchability in TD of Various Molecular Design PP**

The experiment of TD stretching took place in the same way as the MD stretching by using the opt-

rometer produced by Orc Manufacturing Co., Ltd. after the roll stretching in MD with a stretching ratio of 5.

The influence of tacticity on the stress-strain curve is shown in Fig.13. High tacticity PP F-300SV shows very high yield stress and also high stretching stress at high strain ratio in TD. This trend is much larger in MD stretching than in TD stretching.

Fig.14 shows the yield value of stretching stress in TD is clearer and higher than that of MD. Furthermore, PP which has a wider molecular weight distribution shows lower stretching stress at the high stretching ratio.

The effect of low tacticity blend on the stress-strain curve is very clear. Adding low tacticity PP to standard PP F-300SP reduces the yield value of stress and stretching stress at the high stretching ratio. Fig.15-a shows the entire result and Fig.15-b emphasizes the yield value of stretching stress at the first stage.

Fig.16 shows the influence of the chill roll temperature producing the pre-stretched sheet on stretching stress. Fig.16-a is the data of stretching stress in MD and Fig.16-b is the data of stretching stress in TD. The chill roll temperature influences the stretching stress in MD, but does not influence the stretching stress in TD.

Fig.17 shows that the birefringence suddenly increases and then reach the constant value. The stretching stress in TD does not show any induction period.

## **4. Conclusion**

The in-situ observation such as stress-strain, light scattering, birefringence and SAXS enabled us to evaluate the structure development during the uniaxial stretching.

As a result, the stretchability, the thickness uniformity and stress development could be evaluated for high speed stretching or thin stretching film forming.

Table 2 shows the influence of polymer design on stretchability. Low tacticity influences spherulite size and lamella thickness and decreases yield value. To reduce the yield value improves thickness uniformity and prevents film break. Wide molecular weight distribution decreases stretching stress at high stretching ratio. Stress control at high stretching ratio prevents film break. Blending of very low tacticity portion decreases crystallinity and both yield value and final stress. Reduction of yield value and stress at the high stretching strain prevents film break and gives uniform thickness.

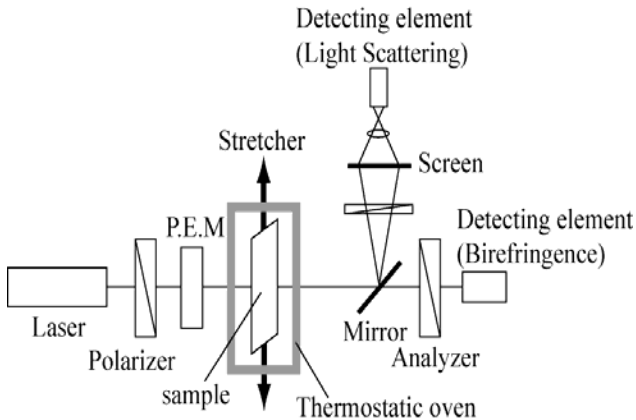
The stretchability and structure development can be predicted using only a small amount of sample.

## **References**

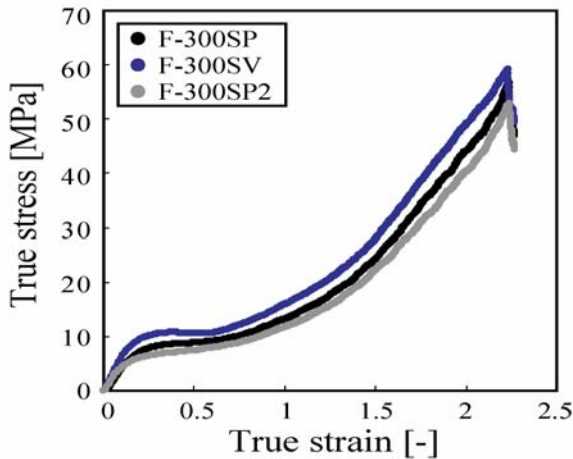
1. Y.Koiike, M. Cakmak, *Polymer*, 2003,44, 4249-4260
2. For proceedings: T.Kanai in PPS-2007 Regional Europe Proceedings CD,

**Table I Molecular characteristics of PP sample**

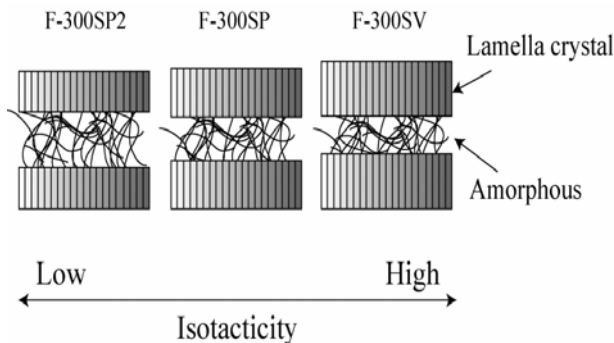
sample	F-300SV	F-300SP	F-300SP2	F-300S	F-300S2	LP200	LMPP
MFR [g/10min]	3.2	30	3.0	2.7	3.2	1.9	1000
Mn × 10 <sup>-4</sup>	8.22	81	7.7	7.0	6.6	19.3	1.7
Mw × 10 <sup>-4</sup>	31.8	377	38.9	38.1	36.9	43	3.1
Mw/Mn	3.87	47	5.0	55	56	2.2	1.8
mmmm/NMR [%]	97.7	90.0	89.0	90.5	89.7	45.0	45.0
Tm [K]	439	434	434	435	435	343	343



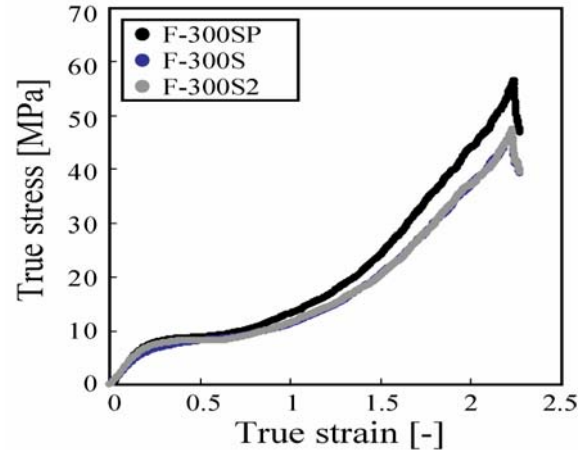
**Fig.1 Schematic diagram of experiment apparatus**



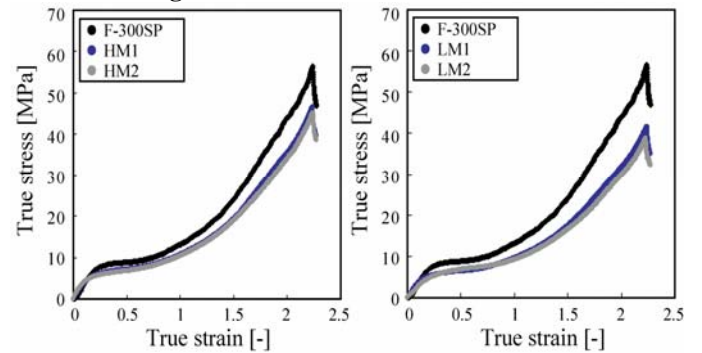
**Fig. 2 Comparison of the stress strain curve by different isotacticity**



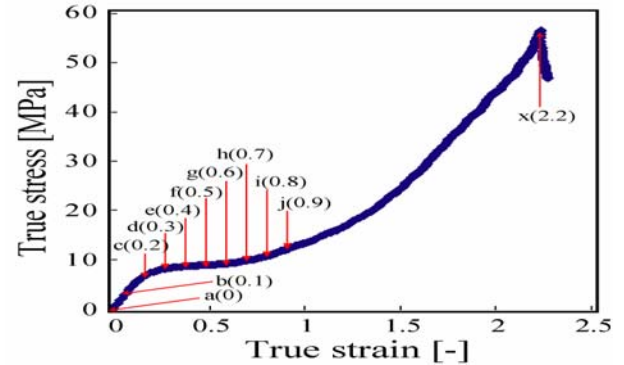
**Fig. 3 Change of the structure by tacticity**



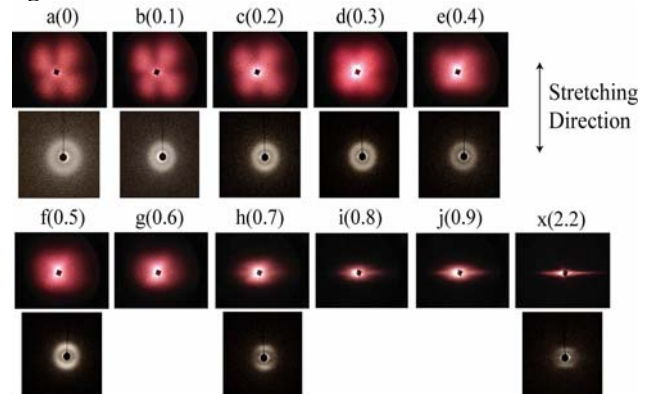
**Fig. 4 Comparison of the stress strain curve by molecular weight distribution**



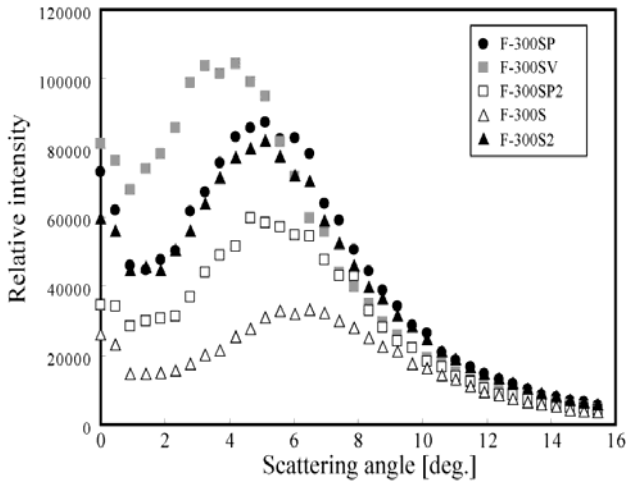
**Fig. 5 Comparison of the stress strain curve of blend sample**



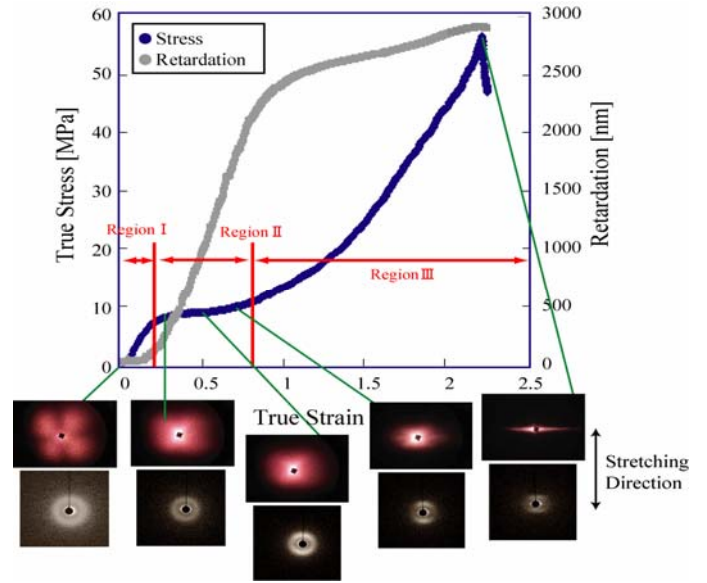
**Fig. 6 stress strain curve with strain data**



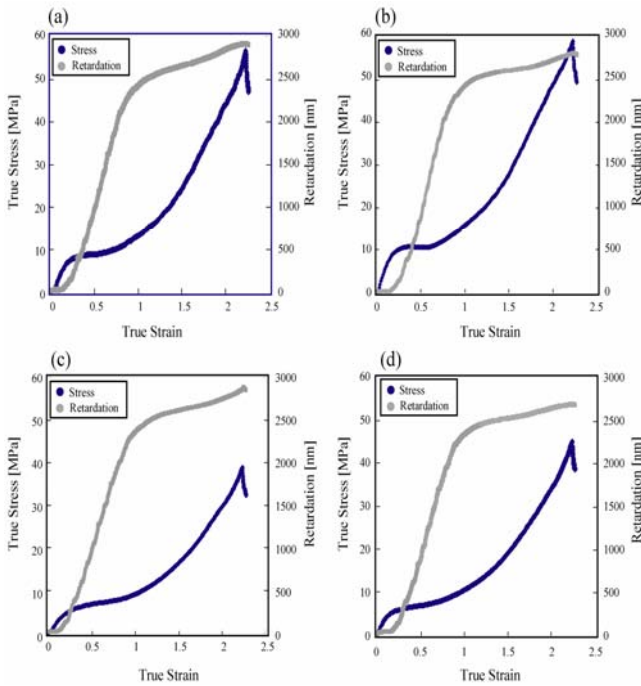
**Fig. 7 Light scattering and small-angle X-ray scattering pattern of F-300SP sample (Upper: Light Scattering, Lower: SAXS)**



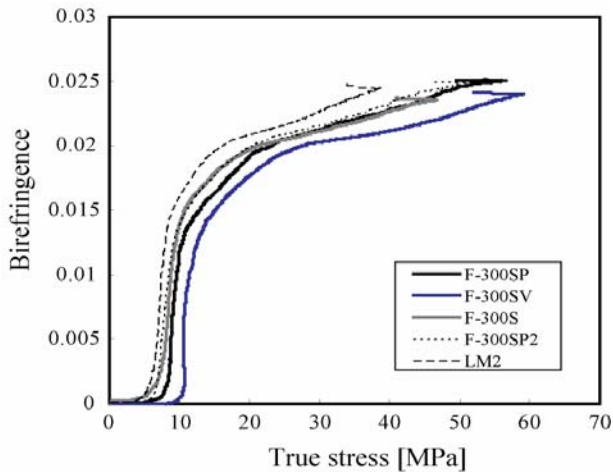
**Fig. 8** Relative intensity of light scattering



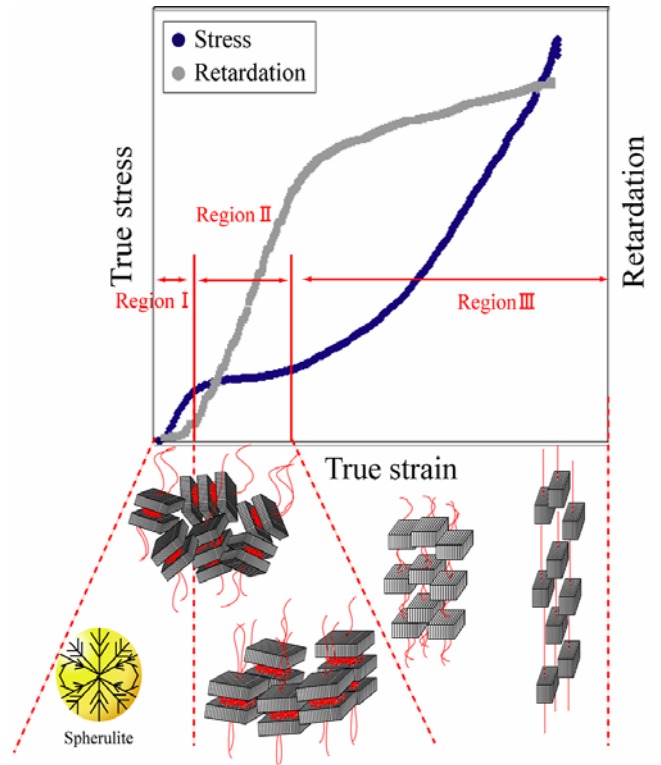
**Fig. 11** Structure development of F-300SP sample



**Fig. 9** Stress strain curve and retardation change (a) F-300SP, (b) F-300SV, (c) LM2, (d) HM2



**Fig. 10** Birefringence vs. true stress



**Fig. 12** Schematic diagram of the superstructure development for stretching process

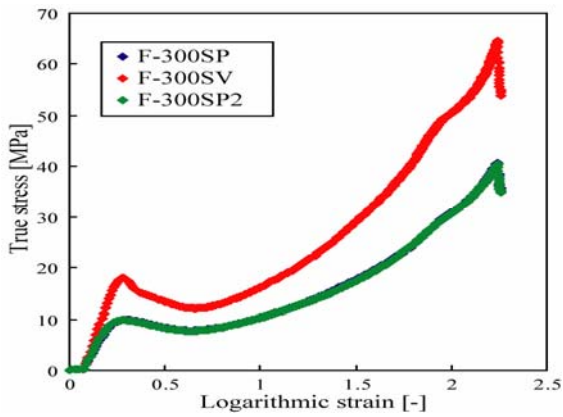


Fig.13 Influence of tacticity on stress-strain curve

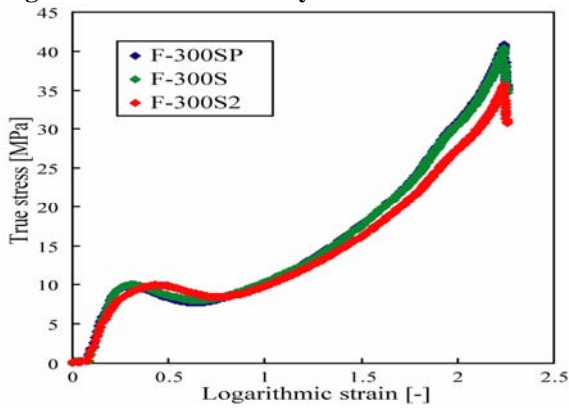


Fig.14 Influence of molecular weight distribution on stress-strain curve

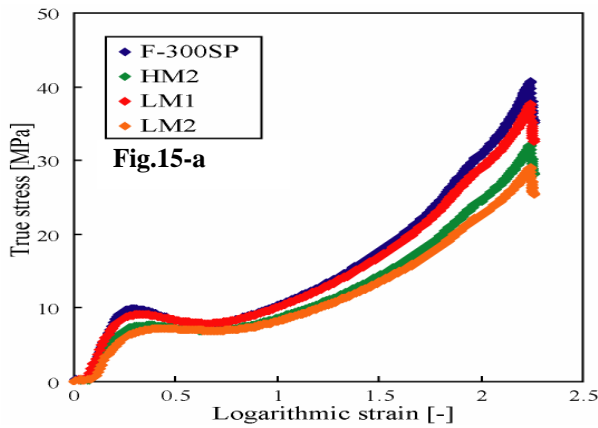


Fig.15-a

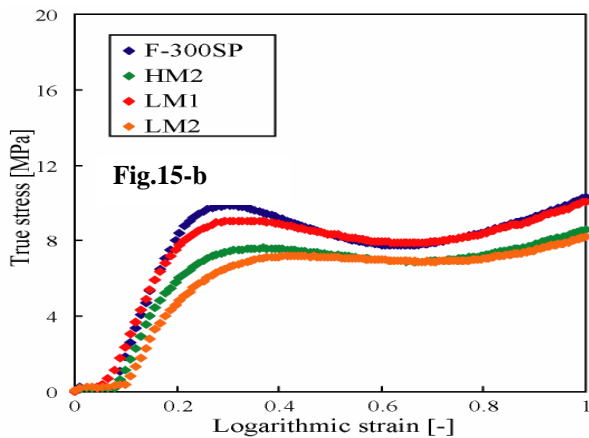


Fig.15-b

Fig.15 Influence of low tacticity PP blends on stress-strain curve

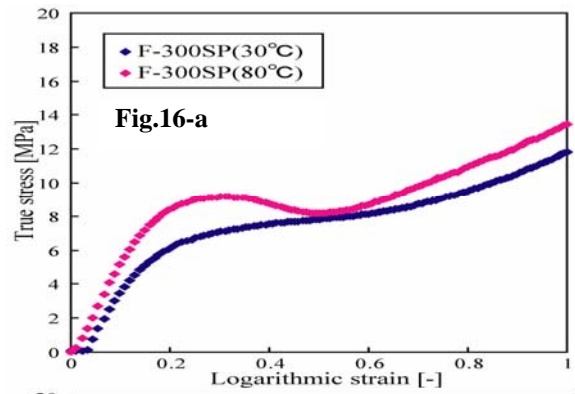


Fig.16-a

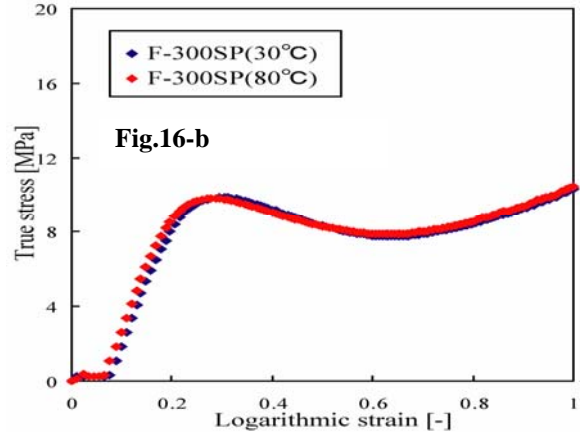


Fig.16-b

Fig.16 Influence of chill roll temperature on stress-strain curve a: Stretching in MD, b: Stretching in TD

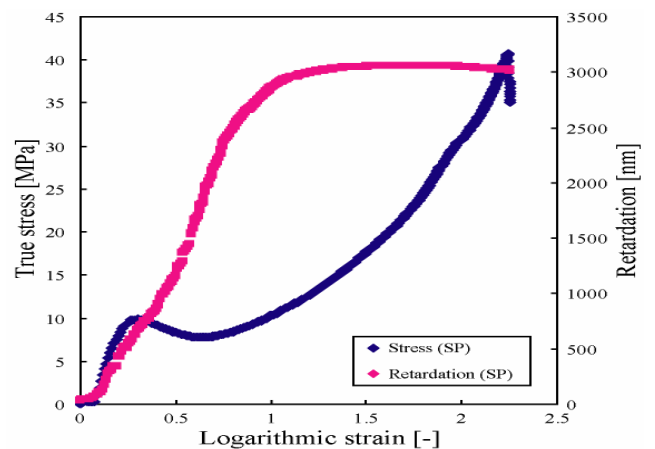


Fig.17 Stress and retardation vs. strain

Table2 Influence of Polymer Design on Stretchability

