

Microporous Polypropylene Sheets Containing CaCO₃ Filler

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SYNOPSIS

Biaxial stretching of polypropylene sheets containing CaCO₃ filler results in microporous sheets, that feel soft and dry. Their properties depend on filler content, particle size of the filler, and stretching degree etc. We have studied the dependency of some properties of the microporous polypropylene sheets on stretching degree. It is elucidated that mechanical properties are controllable by adjusting stretching degrees in machine and transverse directions. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Many investigators have studied microporous separators (membranes, sheets, and films) as key materials of separation technology. Separators are prepared by using various materials and methods. They are practically used in many ways.¹⁻⁵ We have found a unique method of preparing microporous polypropylene (PP) sheets by biaxially stretching PP sheets containing large amounts of the filler CaCO₃.⁶ The resultant sheets have some interesting properties: soft and dry to the touch, controllability of gas permeation, and permeability for water vapor but not for liquid water.⁷⁻¹⁰ Accordingly, these microporous PP sheets are practical. The registered name is Tokuso NF sheet®.

The properties of microporous PP sheets are controllable by adjusting filler content, particle size of filler, and stretching degree. In particular, mechanical properties, which are very important in practical uses, are significantly dependent on the stretching degree in machine direction (MD) and transverse direction (TD). Then it is elucidated that mechanical properties (tensile strength at yield and elongation to break) are controllable by adjusting stretching degrees in MD and TD. Accordingly, the resultant microporous PP sheets have well-balanced mechanical properties. This is an outstanding merit of the preparative method to make microporous PP sheets practical and widely applicable.

EXPERIMENTAL

Materials

PP was Y-117 (MFI, 1.7) from Tokuyama Soda Co., Ltd. CaCO₃ filler (average particle size, 3.2 μm) was of commercial grade. Poly(oxyethylene) oleate (hydrophile-lipophile balance, 10.8) and 2,6-di-*t*-butyl-4-methylphenol were of commercial grade and used as the surface-treating agent of CaCO₃ filler and antioxidant, respectively.

Preparation of Microporous PP Sheets

PP powder (32.0 wt %), CaCO₃ filler (65.8 wt %), poly(oxyethylene) oleate (2.2 wt %), and a small amount of 2,6-di-*t*-butyl-4-methylphenol were well mixed in advance and then extruded at 200–210°C and pelletized with the aid of an extruder of tandem type (Nakatani Machine Co., Ltd.). Subsequently, base sheets were molded at 210–220°C through a flat die attached to a uniaxial extruder (Iwamoto Manufacturing Co., Ltd.) and a pair of cooling rollers. The base sheets were stretched with the aid of a biaxial stretching machine (Iwamoto Manufacturing Co., Ltd.). First, the base sheets were stretched in MD, fixing the base sheets to keep their width constant. The stretching degree in MD (δ_{MD}) is defined as follows.

$$\delta_{MD} = (L/L_0) \times 100 \quad (1)$$

where L_0 is the length of the base sheet (cm) and L , the length of the sheet stretched in MD (cm).

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Subsequently, the sheets stretched in MD were stretched in TD. The area stretching degree (δ_S) is defined as follows.

$$\delta_S = (S/S_0) \times 100 \quad (2)$$

where S_0 is the area of the base sheet (cm^2) and S , area of biaxially stretched sheet (cm^2).

Measurement

Apparent Density and Volume Fraction of PP

Apparent density of microporous PP sheet (D , g/cm^3) is determined as follows

$$D = W/(t \times S) \quad (3)$$

where W is the weight of the microporous PP sheet (g) and t , the thickness of the microporous PP sheet (cm). (JIS K-6767). The microporous PP sheet consists of PP, CaCO_3 filler, and void. Hence, their volumes in the microporous PP sheet (100 g) are shown as ΔR , ΔF , and ΔV , respectively. Apparent density is also shown as follows

$$D = 100/(\Delta R + \Delta F + \Delta V). \quad (4)$$

Volume fraction of PP in the microporous PP sheet (ϕ_R) is shown as follows.

$$\phi_R = \Delta R/(\Delta R + \Delta F + \Delta V) \times 100. \quad (5)$$

Next, eq. (6) is derived from eqs. (4) and (5).

$$\phi_R = \Delta R \times (D/100) \times 100. \quad (6)$$

Here, ΔR is calculated as follows

$$\Delta R = (\text{weight fraction of PP in the sheet, 32\%}) / (\text{density of PP, } 0.91 \text{ g/cm}^3) = 35.2 \text{ cm}^3.$$

Therefore, ϕ_R is determined as follows

$$\phi_R = 35.2 \times (D/100) \times 100. \quad (7)$$

Peel Strength

The microporous PP sheets (thickness: about 200 μm ; width: 30 mm; length: 100 mm) are laminated with PP cloth by using chlorinated PP as an adhesive, as shown in Figure 1. Peel strength was determined by pulling the ends of the PP cloth with

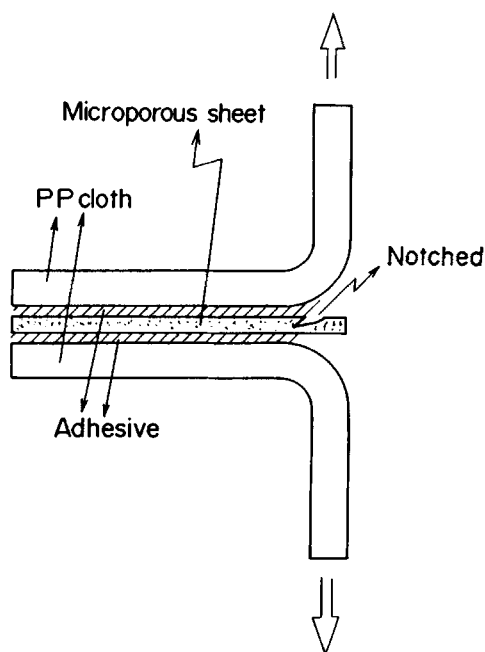


Figure 1 Specimen for measurement of peel strength.

the aid of an Autograph IS-2000 (Shimazu Seisakusho Co., Ltd.). The peeling rate was 200 mm/min.

Tensile Strength at Yield and Elongation to Break

The microporous PP sheets (length: 150 mm; width: 25 mm) were prepared and the length direction was just parallel to MD or TD. The measurement was carried out by using Autograph IS-2000 (Shimazu Seisakusho Co., Ltd.), when the conditions were as follows: temperature, 23°C; relative humidity, 50%; and pulling rate, 200 mm/min. Three measurements were done for each sample and the average values are shown. (JIS K-7127)

Electron Microscopy

The surface and cross section of the microporous PP sheets were observed with the aid of an electron microscope, Type JSM-T-220 (JEOL Ltd.). The inner section was prepared by peeling the outer part of the microporous PP sheet with the aid of an adhesive tape.

Crystallinity

Microporous PP sheets were treated with a mixed solution of methanol and an aqueous solution of HCl in order to remove CaCO_3 filler, rinsed with



(a)

50 μm 

(b)

50 μm

Figure 2 Scanning electron micrographs: cross section of microporous PP sheet. Stretching degree: (a) 250% in MD and 160% in TD; (b) 250% in MD and 400% in TD.

methanol, and dried. The crystallinity degrees of the resultant sheets were estimated: wide-angle X-ray diffraction was measured with nickel filtered Cu-K α radiation by using Rotaflex PU-200PL (Rigaku Denki Co., Ltd.).¹¹

RESULTS AND DISCUSSION

Microporous polymeric films are prepared by stretching crystalline polymeric films containing no filler under definite condition.^{4,5} The lamellar struc-

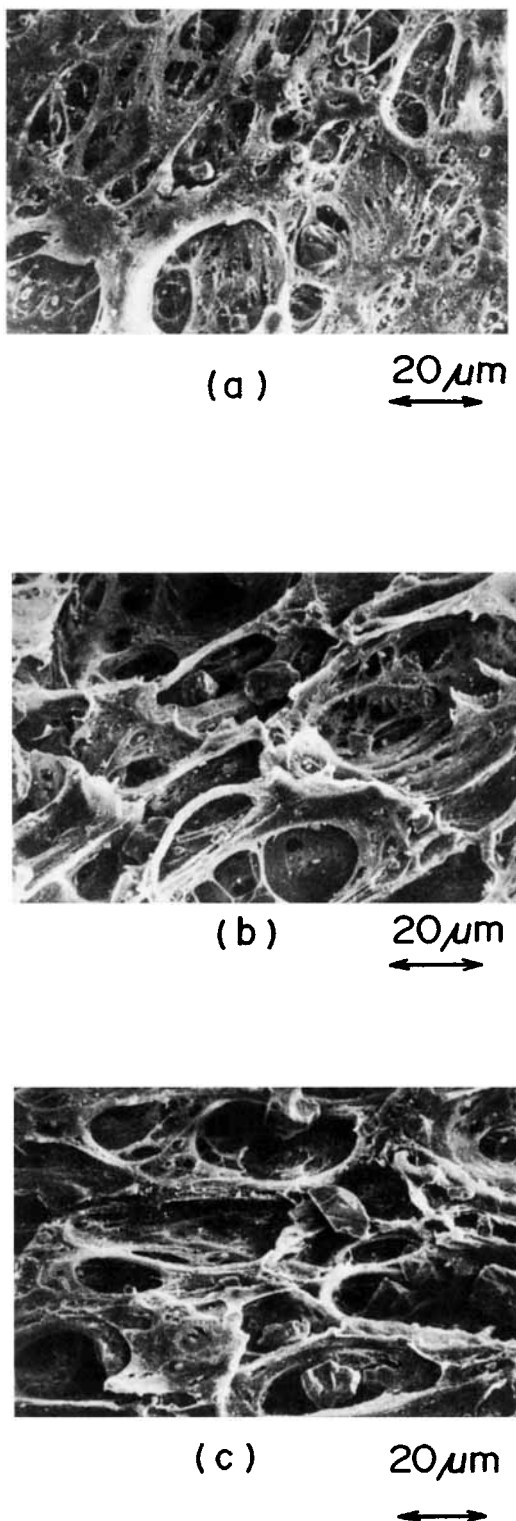


Figure 3 Scanning electron micrographs of microporous PP sheet: (a) surface; (b) inner section at the depth of $35\ \mu\text{m}$ from surface; and (c) inner section at the depth of $100\ \mu\text{m}$ from surface. Area stretching degree, 400%.

ture is deformed to produce an interconnecting network of slit-like voids during stretching up to 300%. On the other hand, microporous PP sheets are prepared by biaxially stretching PP sheets containing filler such as powdery CaCO_3 . The mechanism of porous structure formation is clearly different from using no filler.

1. The properties of the microporous PP sheets are controllable by adjusting filler content, particle size of filler, and stretching degree etc.⁷⁻¹⁰
2. Stretching degree in MD causes splitting of the continuous PP phase of the base sheets at the periphery of the filler particles. Minute voids are formed and then enlarged with increasing stretching degrees in MD and TD.^{8,12,13}
3. The microporous PP sheets have a layered structure: very thin and microporous PP phase forms multi-layered structure interconnected with very fine PP fibrils. Filler particles are dispersed inside of the micropores.⁷⁻¹⁰

Porous Structure

Figure 2 shows scanning electron micrographs of the cross sections of the microporous PP sheets. The continuous PP phase of the base sheet evidently changes to be more finely fibrous with increasing stretching degree. Also, the increase in area stretching degree makes the layered structure clearer. Figure 3 shows scanning electron micrographs of the surface and inner sections parallel to the surface. There are round pores with various sizes, in which there are filler particles. The pattern of the surface is a little different from the others. It is explicable as follows: molded polymeric sheet has a skin layer in general, whose structure is different from that of inner part; so the stretching behavior of the skin layer should be different from that of the inner part of the sheet.

Effect of Stretching Degree to Mechanical Properties

Figure 4 shows the effect of area stretching degree to apparent density and volume fraction of PP in the resultant microporous PP sheet. The larger the area stretching degree, the smaller both the apparent density and the volume fraction of PP. This means

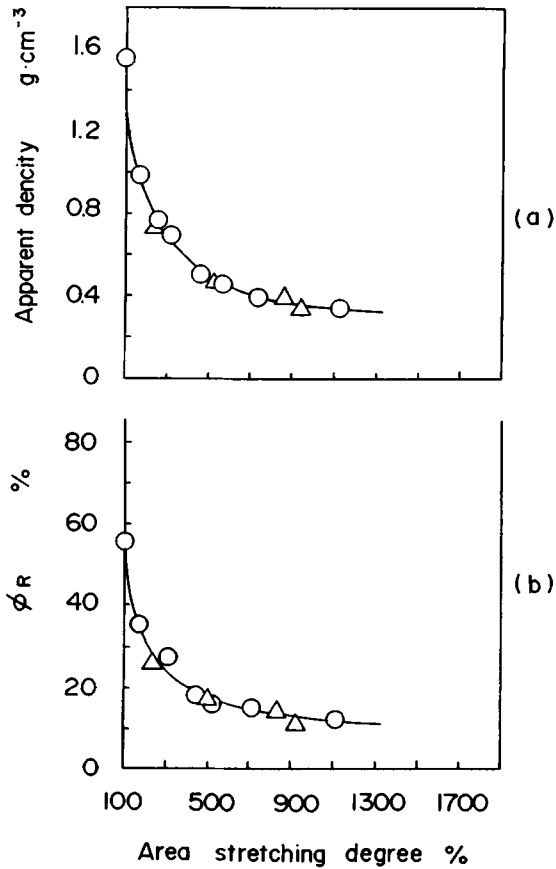


Figure 4 Effect of area stretching degree to (a) apparent density and (b) ϕ_R of microporous PP sheet. Stretching degrees were equal both in MD and TD. Stretching: MD, at 110°C; TD, \circ at 120°C and Δ at 140°C.

that the increase of vacancy in the microporous PP sheet occurs with increasing the area stretching degree. Figure 5 shows the dependency of peel strength on area stretching degree. The peel strength evidently decreases with increasing area stretching degree. This is reasonable because the increase of the area stretching degree results in the more developed layered structure.⁹

Figure 6 shows the dependency of tensile strength at yield (TS) and elongation to break (E_b) on stretching degree in MD. With increasing the stretching degree in MD, TS in MD increases and TS in TD gradually decreases, and also E_b in MD decreases to a definite value and E_b in TD once increases and then decreases. Stretching in MD causes splitting of PP phase at periphery of filler particles,^{9,12} as shown in Figure 7, and the increase of stretching degree in MD results in enlargement of the voids along MD. Furthermore, stretching in MD engenders orientation of resultant PP fibrils and PP molecular chain along MD. Increase of the stretch-

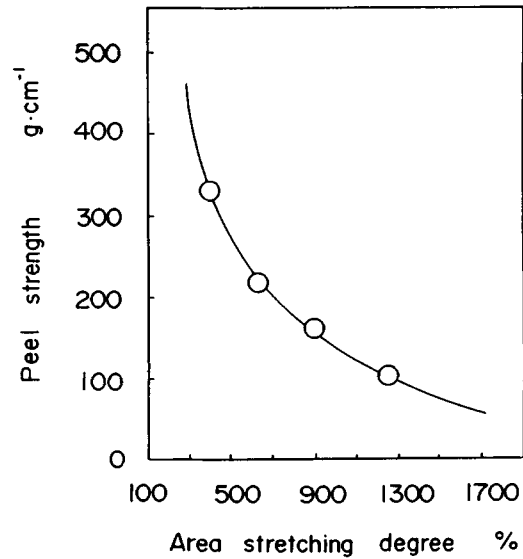


Figure 5 Dependency of peel strength on area stretching degree. Stretching degree in MD is equal to that in TD. Stretching temperature, 110°C.

ing degree makes the orientation more developed. This means that the resultant sheets are rather easily splittable along MD. These results are considered

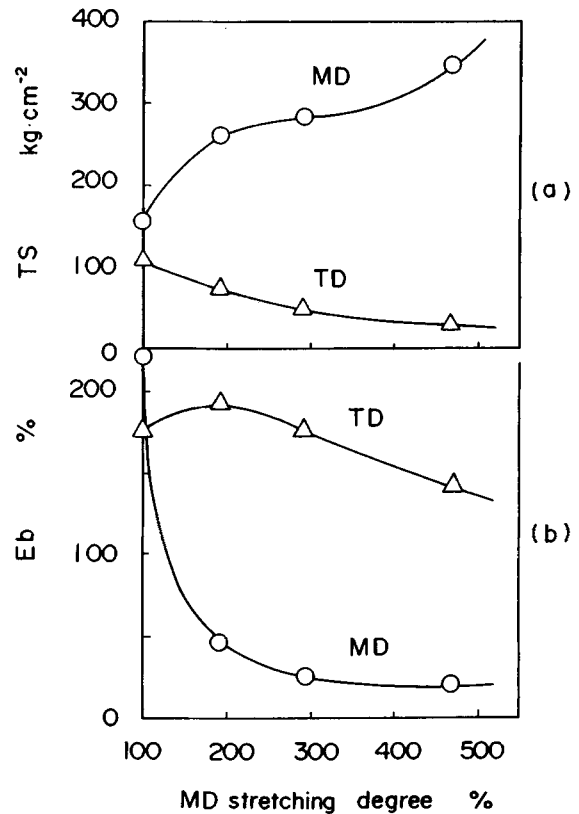


Figure 6 Dependency of TS and E_b on stretching degree in MD. Stretching temperature, 120°C.

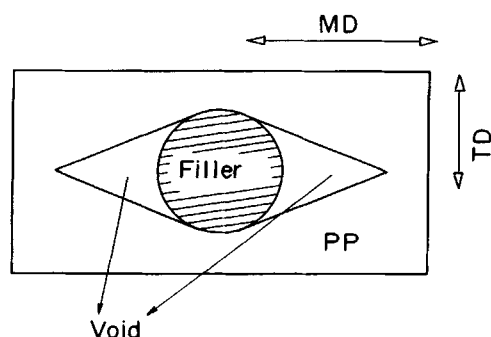


Figure 7 Model of void formation by stretching in MD.

to be caused by the change in orientation degree by the stretching.

Figure 8 shows the effect of area stretching degree to TS and E_b , when stretching degrees are equal in MD and TD. Not only TS but E_b in MD and TD decreases with increasing area stretching degree, because of the decrease of volume fraction of PP. These results show that the resultant sheets have rather imbalanced TS and E_b between MD and TD. Here, we determined TS of PP itself (TS') by using eq. (8), as shown in Figure 9.

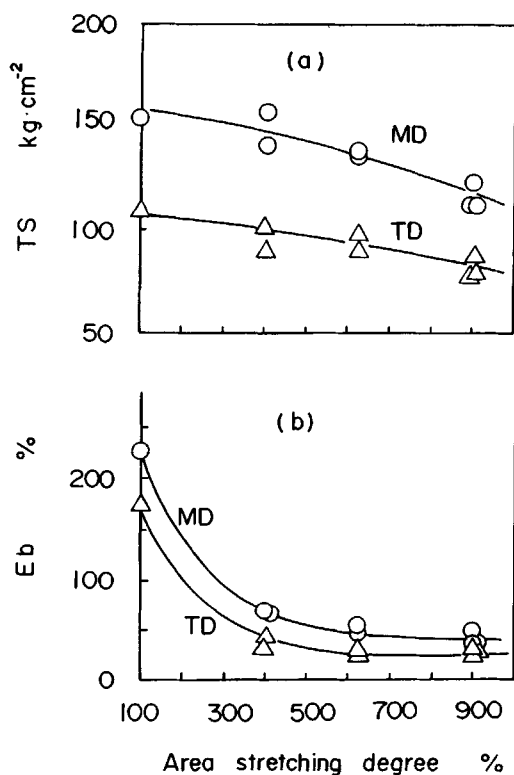


Figure 8 Effect of area stretching degree to TS and E_b . Stretching degrees are equal both in MD and TD. Stretching temperature: MD, 110°C and TD, 120°C.

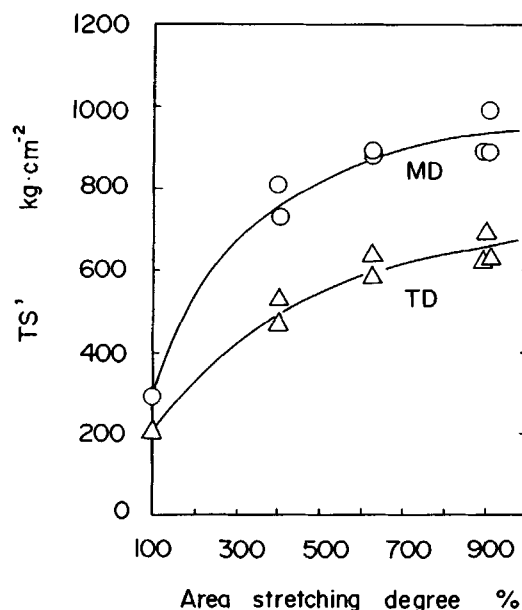


Figure 9 Tensile strength of PP itself (TS') in micro-porous PP sheet. Calculated from the data shown in Figures 4 and 8 by using eq. (8).

$$TS' = (TS/\phi_R) \times 100. \quad (8)$$

TS' in both MD and TD increases with increasing area stretching degree, when the stretching degrees are equal in MD and TD. As shown in Figures 8 and 9, TS and TS' in MD are larger than those in TD in all the range of area stretching degree. These results are explained as follows. The PP molecular chain is orientated to some extent in MD during the extrusion process to mold base sheet. Therefore, when the base sheets are biaxially stretched with the same stretching degrees in MD and TD, the orientation degree of PP molecular chain along MD in the resultant microporous PP sheets should be larger than that along TD. Furthermore, it is well known that TS in the stretching direction increases with increasing stretching degree.¹³

Figure 10 shows the dependency of TS and E_b on the stretching degree in TD, when the stretching degree in MD is constant (200%). With increasing the stretching degree, TS decreases in MD and contrarily increases in TD. Also, E_b gradually increases in MD and decreases in TD with increasing the stretching degree. With increasing stretching degree in TD, the orientation degree of PP fibrils and PP molecular chain becomes smaller in MD and larger in TD. Here, stretching degree is related not only to orientation degree but to TS. The obtained results are very interesting and important. Namely, these results clearly show that the mechanical properties (TS and E_b) can be controlled by adjusting stretch-

ing degrees in MD and TD. This is a very important point from the practical application viewpoint.

Effect of Stretching Degree onto Crystallinity of PP

As shown in Figure 9, TS' in MD and TD increases with the increasing area stretching degree. Then the change in crystallinity of PP was investigated in relation to stretching degrees, as shown in Figure 11. The increase of stretching degree in MD causes the increase of crystallinity at first and then the crystallinity attains a definite value; and the subsequent stretching in TD does not substantially affect the crystallinity. The crystallinity value after stretching of 200% in MD is approximately the same as the value after stretching in TD, independent of the stretching degree. On the other hand, crystallinity of biaxially stretched PP films containing no filler is 50–60%, similar to the values shown in Figure 11.¹⁴ Therefore, the stretching behavior of the PP phase itself is considered to be similar to that of the PP films containing no filler.

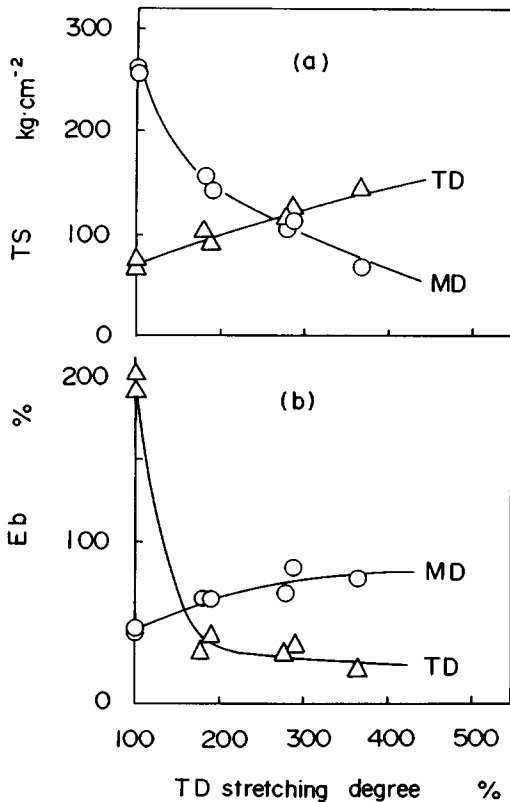


Figure 10 Relations among TS, E_b , and stretching degree in TD. Stretching degree in MD, 200% at 110°C. Stretching temperature in TD, 140°C.

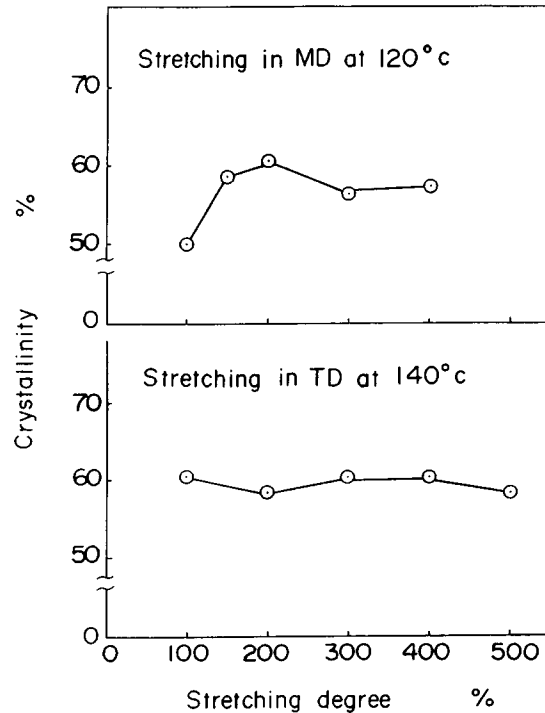


Figure 11 Effect of stretching degree to crystallinity of PP. Stretching in TD was done after stretching of 200% in MD.

CONCLUSION

Microporous polypropylene sheets are prepared by biaxially stretching polypropylene sheets containing CaCO₃ filler. The effect of stretching degrees are investigated in relation to some properties of the microporous sheets as follows.

1. Apparent density, volume fraction of PP, and peel strength of microporous polypropylene sheets decrease with stretching degrees.
2. Tensile strength at yield and elongation to break are controllable by adjusting stretching degrees in machine and transverse directions. This is very important for practical application.
3. Crystallinity of polypropylene in microporous sheets is about 50–60%, similar to the value of stretched polypropylene films containing no filler.

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