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Description	

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**Rheological response under non-isothermal stretching
for immiscible blends of isotactic polypropylene
and acrylate polymer**

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29 Synopsis

30 The addition of acrylate polymers with low molecular weight, such as poly(isobutyl
31 methacrylate) PIBM and poly(methyl methacrylate) PMMA, effectively enhances the force
32 required to stretch a molten polypropylene (PP) at the non-isothermal condition without the
33 enhancement of shear viscosity in the molten state. The mechanism of this phenomenon is
34 found to be attributed to prompt solidification of PIBM and PMMA droplets, which deform
35 greatly to the flow direction in the die land and near the die exit during the extrusion and
36 stretching processes. After the die exit, the deformed droplets show the glassification prior to
37 the crystallization of PP matrix because of the rapid cooling at stretching. Consequently, they
38 behave like rigid fibers in a molten PP, which provide the excess stress by large shear
39 deformation of the matrix between the dispersed glassy fibers during stretching.

40 I. INTRODUCTION

41 Since the pioneering work was carried out by Meissner [1], elongational viscosity has
42 been recognized as one of the most important rheological properties to decide the
43 processability at various processing operations, in which free surface of a polymer melt is
44 deformed. Along with the basic understanding by the theoretical approaches and the
45 advanced experimental set-ups for the measurements [2-7], various techniques to enhance the
46 elongational viscosity have been proposed.

47 One of the most well-known methods to enhance the elongational viscosity of a polymer
48 melt is the addition of high molecular weight fraction [8,9]. Another well-known method is to
49 incorporate long-chain branches by either in-reactor polymerization or postreactor operation.
50 Low-density polyethylene (LDPE) produced by a radical polymerization process is the most
51 well-known polymer having long-chain branches. The branch structure, which is decided by
52 the polymerization method and the reactor type, greatly affects the rheological response
53 under elongational flow [10,11]. In the last two decades, isotactic polypropylene (PP) having
54 long-chain branches has been also developed by copolymerization of propylene and
55 nonconjugated dienes by metallocene catalyst [12,13] and chemical reaction by peroxide
56 and/or radiation [14-22]. According to them, PP with long-chain branches provides marked
57 strain-hardening behavior in elongational viscosity, although the number of long-chain
58 branches is much fewer than that in LDPE. Moreover, because the localized deformation is
59 prohibited by the rapid increase in the stress by the deformation, they show good
60 processability at thermoforming and extrusion foaming [17,18,21,23]. The marked strain-
61 hardening in elongational viscosity is also responsible for the small level of neck-in at T-die
62 film processing including extrusion-coating. Such types of PP have been already
63 commercialized and known as HMS-PP (high-melt-strength PP) [14,24]. In contrast,
64 polymers containing long-chain branches show extrudate distortion even at a low out-put rate

65 owing to the unsteady contraction flow at the reservoir-to-die area, which can be improved by
66 the applied shear history, called shear modification [22,25-27].

67 In addition, mixing of rigid fibers with a large aspect ratio has been known to enhance
68 the elongational viscosity of a molten polymer without an increase in the strain-hardening
69 behavior, meaning that a composite shows high transient elongational viscosity in the whole
70 time/strain region [28-33]. During uniaxial elongational deformation with a constant volume,
71 excess localized shear deformation between neighboring fibers occurs, which is responsible
72 for the stress increase. Therefore, the enhancement of elongational viscosity is pronounced
73 especially for a dispersion containing long and thin fibers, which was theoretically derived by
74 Batchelor [34].

75 Not only rigid fibers but also flexible fine fibers have the capability to affect the
76 rheological response under elongational flow greatly for a polymer melt. The network
77 structure composed of flexible fibers in a polymer melt can be deformed to the flow direction
78 without losing the topological interaction between fibers because of their flexibility.
79 Consequently, the frictional force between fibers and bending force of a part of fibers provide
80 the excess stress, which is responsible for the strain-hardening in elongational viscosity [35-
81 38].

82 Since the drawdown force, *i.e.*, the force required to stretch a melt uniaxially, has a close
83 relationship with elongational viscosity, the drawdown force measurement is one good
84 approach to evaluate the rheological responses of a molten polymer under uniaxial
85 elongational flow [39-44]. Moreover, the processability is often predicted directly from the
86 drawdown force, because the measurement is performed at the non-isothermal condition as
87 similar to actual processing operations [3,18,40,44-46]. According to previous studies on the
88 rheological properties for an immiscible polymer blend with sea-island structure, in which the
89 dispersion has lower viscosity, the interfacial tension is known to barely affect the

90 elongational viscosity including the strain-hardening behavior [47-52]. To the best of our
91 knowledge, moreover, it has been never reported that the drawdown force for a polymer is
92 enhanced by an immiscible polymeric material with low molecular weight.

93 Here, a new method to enhance the drawdown force of PP at capillary extrusion is
94 proposed; the addition of acrylate polymers with low molecular weight such as poly(isobutyl
95 methacrylate) PIBM and poly(methyl methacrylate) PMMA. Since it is firstly reported that
96 an immiscible linear polymer with low shear viscosity in the molten state can be used as a
97 rheological modifier to enhance the drawdown force, this method would possess strong
98 impact on industry.

99

100 **II. EXPERIMENTAL**

101 **A. Materials and sample preparation**

102 Two types of commercially available propylene homopolymer (PP) having different
103 molecular weight (Japan Polypropylene, Japan), denoted as PP-H ($M_n = 4.5 \times 10^4$, $M_w = 2.6 \times$
104 10^5 , and $M_w/M_n=5.8$) and PP-M ($M_n = 4.3 \times 10^4$, $M_w = 2.1 \times 10^5$, and $M_w/M_n=4.9$), were
105 employed in this study. Melt flow rates (MFR) of PP-H and PP-M are 5 and 10 g/10 min,
106 respectively. In addition, a random polymer of polypropylene having 3 wt.% of ethylene
107 content with 10 g/10 min of MFR (Prime Polymer, Japan), denoted as PP-random, was also
108 used. Poly(isobutyl methacrylate) PIBM and poly(methyl methacrylate) PMMA, kindly
109 provided by Mitsubishi Rayon Co., Ltd., Japan, were used as the rheological modifiers. Both
110 PIBM and PMMA are fully amorphous with linear structure. The number- and weight-
111 average molecular weights are as follows: $M_n = 1.6 \times 10^4$, $M_w = 2.9 \times 10^4$, and $M_w/M_n = 1.8$
112 for PIBM and $M_n = 1.8 \times 10^4$, $M_w = 3.1 \times 10^4$, and $M_w/M_n = 1.7$ for PMMA, as a polystyrene
113 standard.

114 The sample was prepared by melt-mixing of PP with 5 wt.% of either PIBM or PMMA
115 using an internal batch mixer (Labo-Plastmill, Toyoseiki, Japan) with a blade rotational speed
116 of 30 rpm at 200 °C for 3 minutes with the presence of 5,000 ppm of thermal stabilizers, such
117 as tris(2,4-di-tert-butylphenyl)phosphate (Irgafos168, Ciba, Switzerland) and pentaerythritol
118 tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate) (Irganox1010, Ciba, Switzerland).
119 Then the mixed sample was compressed into a flat sheet at 230 °C for 3 minutes using a
120 compression-molding machine (IMC-180C, Imoto, Japan) and subsequently quenched in the
121 cooling unit. Some of the compressed sheets were cut into small pieces to evaluate the
122 rheological properties by a capillary rheometer.

123

124 **B. Measurements**

125 A dynamic mechanical analyzer (E4000, UBM, Japan) was used to investigate the
126 temperature dependence of oscillatory tensile moduli such as storage modulus E' and loss
127 modulus E'' . The measurement was performed in the temperature range between -80 and 170
128 °C at a heating rate of 2 °C/min. The applied frequency was 10 Hz. The measurements were
129 performed twice without changing the sample to confirm that the samples are thermally
130 stable.

131 A cone-and-plate rheometer (AR2000, TA Instruments, USA) was used to evaluate the
132 frequency dependence of oscillatory shear moduli such as storage modulus G' and loss
133 modulus G'' . The measurements were performed at various temperatures such as 190, 210,
134 230 and 250 °C. The angle of a cone was 4° and the diameter was 25 mm. Furthermore, the
135 rheometer was used to evaluate the steady-state shear stress and primary normal stress
136 difference at 190 °C. To confirm the accuracy of the data, the measurements were performed
137 twice without changing the sample.

138 The growth curves of uniaxial elongational viscosity were obtained by the rotational
139 rheometer equipped with a universal testing platform (SER2-G, Xpansion Instruments, USA)
140 at 190 °C. Rectangular samples with 10 mm wide, 15 mm long, and 0.5 mm thick were used.

141 The drawdown force, defined as the force required to stretch a polymer melt uniaxially,
142 was measured using a capillary rheometer (140 SAS-2002, Yasuda Seiki Seisakusyo, Japan)
143 equipped with dies having L/D ratios of 10/1 and 40/1. An entrance angle of the dies was
144 180°. A set of rotating wheels and a tension detector were attached to the capillary rheometer
145 in order to evaluate the drawdown force at a constant draw ratio, *i.e.*, the ratio of the average
146 flow velocity at the die exit to that at the rotating wheels. The draw ratio, *i.e.*, 2.4, was chosen
147 to evaluate the value precisely. The apparatus was shown in our previous paper [45]. The
148 applied shear rate and temperature in the die and reservoir were controlled at 124 s⁻¹ and 190
149 °C, respectively. The distance between the die exit and the tension detector was 235 mm.
150 Flow curve was investigated at various shear rates by the capillary rheometer at 190 °C using
151 a die with an L/D of 10/1. In the case of the flow curve measurements, the diameter of an
152 extruded strand was evaluated online without stretching a strand by means of a laser detector
153 fixed 50 mm below the die.

154 Thermal properties were evaluated by a differential scanning calorimeter (DSC 820,
155 Mettler-Toledo, USA). The sample was heated from 25 to 190 °C with a heating rate of 30
156 °C/min. Then, it was cooled down to 25 °C with various cooling rates, *i.e.*, 1, 3, 10, 30, 100
157 and 300 °C/min. We used a small amount of the sample, *i.e.*, approximately 2 mg, to avoid
158 the effect of the thermal conductivity and heat capacity at the high cooling rate.

159 An X-ray diffractometer (R-Axis IIC, Rigaku, Japan) was employed to investigate the
160 molecular orientation of the extruded samples. The strands extruded from the dies with
161 various lengths, *i.e.*, 10 and 40 mm, at a draw ratio of 4 were irradiated using a graphite
162 monochromatized CuK α radiation beam focused via a 0.3 mm pinhole collimator with a flat

163 $20 \times 20 \text{ cm}^2$ imaging plate (IP) detector of $1,900 \times 1,900$ pixels. The sample was exposed to
164 the X-ray beam perpendicular to the strand axis in the through view direction for 7 min.

165 Morphology of the dispersed phase in PP matrix was observed using a scanning electron
166 microscope (SEM) (S400, Hitachi, Japan). The fractured surface in liquid nitrogen of a
167 compressed film was used for the SEM observation after sputter-coating. Moreover, the
168 deformation of the dispersed acrylate polymers in an extrudate was characterized by SEM.
169 The strand extruded from the die with an L/D ratio of 40/1 or 10/1 without stretching was cut
170 in the cross-section (end-view) and along the flow direction (side-view) using a razor blade.
171 Then, the cut sample was soaked into acetone for overnight to dissolve the acrylate polymer.
172 After sputter-coating of the dried sample, the cut surface was observed by SEM. Deformation
173 of the dispersed phase was further confirmed by the measurement of lateral expansion of a
174 strand after dipping into a silicone oil bath at $170 \text{ }^\circ\text{C}$ for 10 seconds.

175

176 **III. RESULTS AND DISCUSSION**

177 Fig. 1 shows the temperature dependence of oscillatory tensile moduli at 10 Hz with the
178 SEM image of the fractured surface for a compressed film of PP-H/PIBM (95/5). In the
179 figure, the E'' curves of the pure components, *i.e.*, PP-H and PIBM, are plotted together in the
180 figure by the open symbols, which are shifted in the vertical direction to see the peaks clearly.
181 The peak temperatures in the E'' curves ascribed to the glass-to-rubber transition for
182 individual pure polymers, *i.e.*, β -relaxation for PP-H and α -relaxation for PIBM, are 10 and
183 $62 \text{ }^\circ\text{C}$ for PP-H and PIBM, respectively. As seen in the figure, there are double peaks in the
184 E'' curve for the blend, which correspond with the individual peaks of the pure components,
185 *i.e.*, PP-H and PIBM. This result demonstrates that PP-H and PIBM are immiscible, as
186 demonstrated by the SEM picture. The diameter of the dispersed PIBM droplets is found to

187 be 0.5-3 μm . A similar result is obtained for the PP-H/PMMA blend. The diameter of PMMA
 188 droplets is 2-10 μm .

189 [FIG. 1]

190 Fig. 2 exemplifies the master curves of frequency dependence of oscillatory shear moduli
 191 for PP-H/PIBM (95/5), PP-H and PIBM at the reference temperature of 190 $^{\circ}\text{C}$. The time-
 192 temperature superposition principle is applicable to all samples including the blends with
 193 acrylate polymers. Both moduli of PP-H/PIBM (95/5) are almost the same with those of the
 194 neat PP-H even though the blend shows phase-separated structure. Since the amount of the
 195 dispersed phase is only 5 wt.%, the contribution of interfacial tension to the moduli is
 196 negligible. The zero-shear viscosities η_0 at 190 $^{\circ}\text{C}$ obtained from the master curves are
 197 shown in Table I. As seen in the table, the viscosities of both PIBM and PMMA are much
 198 lower than those of PP samples at the extrusion temperature.

199 [FIG. 2]

200

201 Table I Zero-shear viscosity at 190 $^{\circ}\text{C}$ of the materials

Samples	η_0 at 190 $^{\circ}\text{C}$
PP-H	9,850
PP-M	3,930
PP-random	4,930
PIBM	45
PMMA	280
PP-H/PIBM (95/5)	9,300
PP-H/PMMA (95/5)	9,500

202

203 Fig. 3 shows the shear stress and primary normal stress difference at the steady-state
 204 shear flow, evaluated by the cone-and-plate rheometer at 190 $^{\circ}\text{C}$. As seen in the figure, both
 205 shear stress and normal stress difference for the blend are slightly lower than those of pure
 206 PP-H, although the difference is not so obvious. The slight decrease in the shear viscosity is

207 reasonable because of the low shear viscosity of PIBM at 190 °C (Table 1). Furthermore, the
 208 result corresponds with the oscillatory data.

209 [FIG. 3]

210 The flow curves at 190 °C for PP-H and PP-H/PIBM (95/5) are also evaluated by the
 211 capillary rheometer, as shown in Fig. 4. As similar to the result in Fig. 3, the shear viscosity
 212 of the blend is slightly lower than that of the neat PP-H at low shear rates. This is reasonable
 213 because PIBM has significantly lower shear viscosity than PP-H. Moreover, it is almost the
 214 same at high shear rates. The extrudate swell is also evaluated at this measurement (without
 215 stretching). It is found that there is no difference in the swell ratio. These results indicate that
 216 blending PIBM hardly affects the rheological responses of PP-H under shear flow at 190 °C.

217 [FIG. 4]

218 Fig. 5 shows the transient elongational viscosity as a function of time at various Hencky
 219 strain rates for PP-H/PIBM (95/5) at 190 °C. The solid line in the figure represents three
 220 times of the growth curve of shear viscosity in the linear region, *i.e.*, $3\eta^+$, which was
 221 calculated by the following equation proposed by Osaki *et al.* [53].

$$222 \quad \eta^+(t) = t \left[G''(\omega) + 1.12G'(\omega/2) - 0.200G'(\omega) \right]_{\omega=1/t} \quad (1)$$

223 The upturn departure of elongational viscosity from the predicted values is not clearly
 224 detected for the blend, as similar to the neat PP-H (data not shown). In other words, the
 225 addition of the acrylate polymers does not provide strain-hardening behavior in the
 226 elongational viscosity.

227 It is concluded from Figs. 2-5 that the rheological responses of PP-H are barely affected
 228 by the addition of PIBM at least at 190 °C, which corresponds with previous reports [47-52].

229 [FIG. 5]

230 The drawdown force evaluated using two types of dies is shown in Fig. 6. It should be
 231 noted that the blend with an acrylate polymer exhibits a high value of the drawdown force,

232 which is more pronounced for the blend with PIBM. The enhancement is obvious when using
233 the long die. This is a surprising result because the acrylate polymers with linear structure
234 show much lower shear viscosity than PP, which will be discussed later.

235 [FIG. 6]

236 The enhancement of the drawdown force for crystalline polymers such as PP and HDPE
237 is pronounced when using a long die as discussed in our previous works [45,46]. Because a
238 flow history in a long die reduces the number of entanglement couplings with marked
239 molecular orientation due to the prolonged exposure to high shear stress in a laminar flow in
240 the die land, the crystallization takes place rapidly as the melt leaves the die, resulting in the
241 steep increase in the elongational stress and thus, the drawdown force. Such phenomenon is
242 pronounced for a system with long relaxation time. This behavior was confirmed by 2D X-
243 ray diffraction (2D-XRD) patterns. Since the same phenomenon, *i.e.*, enhancement of the
244 drawdown force, is detected for the present blends, the orientation of PP chains is examined.
245 Fig. 7 shows the 2D-XRD patterns for the strand of PP-H and the blend extruded from the die
246 with an L/D of 40/1. The strong peaks in equator, ascribed to the (040) plane of α -form
247 monoclinic crystals, demonstrate that PP chains orient to the flow direction for both PP-H
248 and the blend. Furthermore, the (110) plane of β -form crystals is detected near the (040) of α -
249 form, which also shows the orientation in the flow direction. Moreover, it should be noted
250 that the azimuthal intensity distribution becomes narrow for the strand of the blend,
251 suggesting the high level of molecular orientation. The same XRD pattern was obtained for
252 the blend with PMMA (but not present here).

253 [FIG. 7]

254 As the great enhancement of the drawdown force is observed for the blends with the
255 acrylate polymers, further experiments were performed to clarify the mechanism. Since the
256 marked molecular orientation of PP is detected for the blends, the nucleating ability of the

257 acrylate polymers was, then, studied by the DSC cooling curve as shown in Fig. 8. It is found
258 that the crystallization temperatures T_c 's of the blends are almost the same as that of the neat
259 PP-H. This result indicates that the acrylate polymers have no nucleating ability at the
260 crystallization of PP-H.

261 [FIG. 8]

262 Furthermore, the solidification behavior was studied at various cooling rates, because the
263 drawdown force is measured at the rapid cooling condition. It has been well known that the
264 cooling rate has strong impact on the T_c and glass transition temperature T_g of a polymer [54-
265 58]. In general, both T_c and T_g decrease with increasing the cooling rate. Fig. 9 shows the
266 effect of cooling rate on T_c of PP-H and T_g 's of PIBM and PMMA, evaluated by DSC. As
267 seen in the figure, T_c of PP-H is significantly sensitive to the cooling rate, because it
268 drastically decreases with the cooling rate. The T_c values, including those obtained at the high
269 cooling rates, well correspond with those reported previously, suggesting that the
270 measurements were performed correctly [58,59]. In the case of PIBM and PMMA, in
271 contrast, T_g 's are found to be less sensitive to the cooling rate. Further, T_g of PMMA is
272 located at a higher temperature than T_c of PP-H at a high cooling rate, *e.g.*, 300 °C/min,
273 indicating that the solidification, *i.e.*, glassification, of PMMA takes place prior to the
274 crystallization of PP-H at this condition. The actual cooling rate near the die exit at the
275 capillary extrusion with melt stretching is considerably high. At the present experiment using
276 PP-H, the freeze line was detected around at 10 mm below the die exit, suggesting that the
277 cooling rate is higher than 100 °C/s, *i.e.*, > 6,000 °C/min. As a result, the steep increase in the
278 viscosity of the acrylate polymers due to the glassification cannot be ignored. In fact, it has
279 been reported that T_c of PP is around 60 °C in this range of the cooling rate [58-60].
280 Regarding the cooling rate at the non-isothermal melt spinning, Joo *et al.* [61] calculated to
281 be about 50,000 °C/min by the numerical analysis, in which a similar condition to the present

282 study was assumed. Although the effect of the flow field on the crystallization behavior has
283 to be taken into consideration, it is obvious that the acrylate polymer acts as high viscous or
284 glassy dispersions in a molten PP at the non-isothermal stretching.

285 [FIG. 9]

286 Although the acrylate polymers do not show the nucleating ability for the crystallization
287 of PP-H, they strongly affect the drawdown force. Since PIBM and PMMA possess low shear
288 viscosity at the extrusion condition, they exist as dispersed liquid droplets in the PP matrix in
289 the die. Therefore, the deformation of droplets in a matrix has to be considered to understand
290 this interesting rheological behavior. In general, the size of droplets is determined by
291 interfacial tension, viscosity ratio, and mixing conditions including stress, type of flow, and
292 distributive performance. When the viscosity of droplets is much lower than that of a matrix
293 with a relatively small interfacial tension, droplets deform into fibrous shape by the
294 hydrodynamic force [62-66].

295 As shown in Fig. 10, both PIBM and PMMA deform to the flow direction, which is
296 pronounced in the strand after passing through the long die. Considering that the strands in
297 the figure were collected without stretching after the die exit, the result demonstrates that the
298 deformation of droplets occurs, at least, in the die land by the applied shear stress for a long
299 residence time in a laminar flow. Furthermore, the volume of a PIBM droplet is smaller than
300 that of PMMA on average. Since the viscosity ratio between the matrix and dispersion for the
301 PP/PIBM blend is larger than that for the PP/PMMA blend, this is presumably attributed to
302 the lower interfacial tension between PP and PIBM. The weak cohesive energy due to low
303 molecular weight may be also responsible for the fine dispersion of PIBM. Consequently, the
304 deformed PIBM has higher aspect ratio, whereas PMMA droplets deform into ellipsoidal
305 shape with low aspect ratio. Then, the deformed droplets will behave like rigid fillers because
306 of the glassification as discussed previously. Regarding the flow type to produce fibrous

307 dispersion, uniaxial flow would be the most effective [66], although other types of flow also
 308 have the capability to deform the droplets to some degree.

309 [FIG. 10]

310 Although T_g of PMMA is higher than that of PIBM, the drawdown force enhancement is
 311 pronounced by the PIBM addition. This would be attributed to the number and shape of the
 312 droplets, i.e., fibrous shape with high aspect ratio. The elongational stress in a suspension
 313 containing rigid fibers was discussed by the theoretical and experimental approaches. Among
 314 them, the slender-body theory was successfully developed to predict the elongational stress
 315 considering the excess deformation of a matrix between fibers [34], which was
 316 experimentally proved by Mewis and Metzner [28] and Laun [31]. According to the slender-
 317 body theory, elongational viscosity η_E of a suspension with long slender particles depends on
 318 the aspect ratio as well as the volume fraction of the particulate dispersion as expressed in the
 319 following equation,

$$320 \quad \eta_E = 3\eta_c + \frac{4}{3}\eta_c \frac{\phi_d \left(\frac{l}{d}\right)^2}{\ln\left(\frac{\pi}{\phi_d}\right)} \quad (2)$$

323 where η_c is the shear viscosity of a continuous phase, ϕ_d is the volume fraction of the
 324 dispersion, and l/d is the length-to-diameter ratio of fibers.

325 As indicated by this theory, localized excess stress generated by large shear deformation
 326 of a matrix located between neighboring fibers is responsible for the enhancement of
 327 elongational stress of a suspension. Since the distance between neighboring fibers is
 328 determined by the number of fibers, fine fibers with a high aspect ratio provide high
 329 elongational stress on average at the same volume fraction. Therefore, the blend with PIBM,
 330 which has a lot of fine fibers with a high aspect ratio, exhibits high elongational stress. In

331 other words, PIBM has a great ability to enhance the drawdown force, as compared with
332 PMMA.

333 Because the solidification temperature of polymers depends on various factors, such as
334 flow field, size and shape of the extrudate, extrusion temperature, stretch ratio, and molecular
335 characteristics, the drawdown force must be also sensitive to such conditions and material
336 characteristics. Here, the proposed mechanism is further confirmed using PP-random, which
337 has a lower T_c than PP homopolymer having a similar shear viscosity, *i.e.*, PP-M. T_c 's
338 evaluated by DSC at a cooling rate of 10 and 100 °C/min are 115.0 °C and 99.0 °C for PP-M
339 and 92.7 °C and 76.6 °C for PP-random. As seen in Fig. 11, the enhancement of the
340 drawdown force by blending both PIBM and PMMA is not so obvious when using PP-M. On
341 the contrary, this phenomenon is clearly detected when using PP-random. Because PP-
342 random has lower T_c than PP-M, the crystallization of PP-random after passing through a die
343 must take place slower than that of PP-M. As a result, the matrix between fibers deforms
344 greatly prior to the crystallization, resulting in the high level of the drawdown force, which is
345 enhanced at the extrusion with a long die because of a high aspect ratio of dispersions. This
346 result indicates that the prompt solidification of the fibrous dispersions of the acrylate
347 polymer provides localized shear deformation of the PP melt between the neighboring
348 acrylate fibers during uniaxial stretching, as explained by Laun [31]. As a result, excess stress
349 is generated owing to the large localized shear deformation, which is responsible for the high
350 level of drawdown force.

351 [FIG. 11]

352 The deformation of the dispersed phase in the non-stretched strand is further confirmed
353 by measuring the lateral expansion of the strand after dipping into a silicone oil bath at 170
354 °C. Because the uniaxial stretching was performed, the strand has a cylindrical shape. After
355 immersion into the bath, PP matrix as well as the dispersed phase is melted immediately.

356 Then, the interfacial tension tends to pull the dispersions back to the spherical shape.
357 Therefore, prolonged dispersions provide high level of the lateral expansion as well as the
358 vertical shrinkage. Based on this technique, the magnitude of the deformation is estimated
359 from the lateral expansion of the strands. Since there is no dispersed phase in the pure PP
360 system, the level of strand expansion for the pure PP is decided by the degree of chain
361 orientation. It is found that the strand expansion of PP-M (1.52 for $L/D=40/1$) is slightly
362 higher than that of PP-random (1.50 for $L/D=40/1$). Furthermore, the value of PP-
363 random/PIBM is much larger than that of pure PP-random as shown in Fig. 12. This is
364 reasonable because the interfacial tension between the matrix and dispersions dominantly
365 decides the shrinkage of the strands. Moreover, the strand expansion of the blend with PP-
366 random is found to be significantly larger than that with PP-M, which correlates with the
367 drawdown force enhancement. Considering that the drawdown force enhancement by the
368 acrylate polymers is pronounced for PP-random, especially when using a long die, PIBM and
369 PMMA droplets deform greatly in PP-random rather than in PP-M. This is owing to the slow
370 solidification of PP-random, demonstrating that the deformation of the dispersions occurs
371 even after passing through the die, which results in the high level of drawdown force.

372 [FIG. 12]

373 At present, we are studying the effect of material characteristics such as blend ratio,
374 interfacial tension, and molecular weight on the rheological properties and processability at
375 various processing operations. Furthermore, the effect of the die shape and entrance angle
376 should be investigated considering the industrial applications. Besides, not only rheological
377 properties but also mechanical properties in the solid state are interesting for the present
378 blend system. As well known, the addition of liquid crystalline polymers affects mechanical
379 properties for flexible polymers greatly [67-69]. Furthermore, oriented polymers obtained by
380 flow-induced crystallization show marked rigidity [70-72]. Therefore, the mechanical

381 properties in the solid state of this blend system, considering the molecular orientation as well
382 as the orientation of acrylate fibers, are worth for studying.

383

384 **IV. CONCLUSION**

385 Drawdown force enhancement of PP at capillary extrusion is demonstrated by blending
386 immiscible acrylate polymers such as PIBM and PMMA, which have significantly low shear
387 viscosity at the processing temperature of PP. It will be a new method to enhance the
388 drawdown force for PP without an increase in the shear viscosity in an extruder. The
389 mechanism of this phenomenon is found to be attributed to the prompt solidification of PIBM
390 and PMMA at the rapid cooling condition like the drawdown force measurement. The
391 dispersed droplets of the acrylate polymers deform to the flow direction in and near the die,
392 which is determined by the die geometry, interfacial tension with PP, and viscosity ratio.
393 Once their solidification takes place, they will act as rigid fibers. This situation occurs by the
394 difference in the cooling rate dependence of solidification temperatures; *i.e.*, the
395 crystallization temperature of PP is more sensitive to the cooling rate than the glass transition
396 temperature of the acrylate polymers. Consequently, the drawdown force is enhanced by the
397 excess stress generated by large shear deformation of a matrix between the solidified fibers.
398 Considering that most processing operations are carried out at rapid cooling conditions, this
399 phenomenon can be applicable to improve the processability.

400

401 **Acknowledgements**

402 The authors would like to thank Mitsubishi Rayon Co., Ltd., Japan Polypropylene Corp., and
403 Prime Polymer Co., Ltd. for their kind support of the materials.

404

405 **References**

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589

590 **Figure captions**

591

592 FIG. 1. Temperature dependence of oscillatory tensile moduli such as storage modulus E'
593 (closed circles) and loss modulus E'' (closed diamonds) for PP-H/PIBM (95/5) at 10 Hz. The
594 E'' curves for pure PP-H (open circles) and pure PIBM (open diamonds) are also plotted with
595 a vertical shift ($a = -1$). An SEM image of cryogenically fractured surface of the compressed
596 film is also shown.

597

598 FIG. 2. Master curves of frequency dependence of oscillatory shear moduli such as storage
599 modulus G' (circles) and loss modulus G'' (diamonds) for PP-H/PIBM (95/5) (closed
600 symbols), PP-H (open symbols), and PIBM (gray symbols) at the reference temperature of
601 190 °C.

602

603 FIG. 3. Steady-state shear stress σ (open symbols) and primary normal stress difference N_{11}
604 (closed symbols) for PP-H (circles) and PP-H/PIBM (95/5) (diamonds) at 190 °C. The data
605 for the blend are plotted with a horizontal shift ($a = 1$).

606

607 FIG. 4 Shear viscosity as a function of shear rate for PP-H (circles) and PP-H/PIBM (95/5)
608 (diamonds) at 190 °C.

609

610 FIG. 5. Transient elongational viscosity as a function of time at various Hencky strain rates at
611 190 °C for PP-H/PIBM (95/5). The solid line represents $3\eta^+(t)$ calculated from the
612 oscillatory shear modulus.

613

614 FIG. 6. Drawdown force of PP-H, PP-H/PIBM (95/5), and PP-H/PMMA (95/5) at a draw
615 ratio of 2.4. The applied shear rate at the die wall was 124 s^{-1} and the temperature was
616 controlled at $190 \text{ }^\circ\text{C}$.

617

618 FIG. 7. 2D-XRD patterns for the strand of PP-H and PP-H/PIBM (95/5) extruded from the
619 dies having $L/D = 40/1$ at $190 \text{ }^\circ\text{C}$ and stretched at a draw ratio of 4. The plot below each
620 image represents the azimuthal intensity distribution of (040) plane, indicated by the arrows
621 in the image.

622

623 FIG. 8. DSC cooling curves for PP-H, PP-H/PIBM (95/5), and PP-H/PMMA (95/5) at a
624 cooling rate of $10 \text{ }^\circ\text{C}/\text{min}$.

625

626 FIG. 9. Crystallization temperature T_c for PP-H (open circles) and glass transition
627 temperature T_g 's for PIBM (closed squares) and PMMA (closed diamonds) as a function of
628 cooling rate.

629

630 FIG. 10. SEM pictures of the cut surface of the strands for PP-H/PIBM (95/5) and PP-
631 H/PMMA (95/5) extruded from a die with $L/D = 10/1$ or $40/1$ without stretching; (a) end-
632 view, (b) center area of side-view, and (c) edge area of side-view. The cut surface was
633 immersed in acetone to remove the acrylate polymers. The arrows in the images represent the
634 flow direction.

635

636 FIG. 11. Drawdown force for the blends with 5 wt% of PIBM or PMMA stretched at a draw
637 ratio of 2.4. The temperature was controlled at $190 \text{ }^\circ\text{C}$.

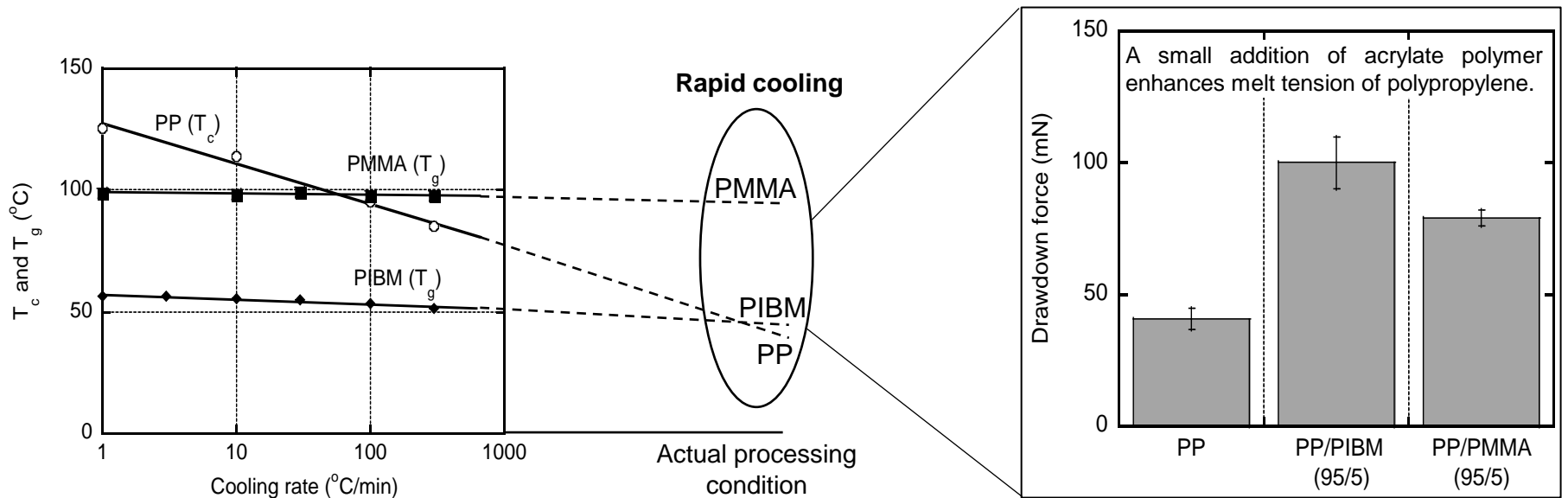
638

639 FIG. 12. Ratio of the strand diameter after dipping into silicone oil bath at 170 °C to that of
640 the original one for the blends of PP-M and PP-random with 5 wt% of PIBM and PMMA.

641 The strands were not stretched.

642

643 Table I. Zero-shear viscosity at 190 °C of the materials.



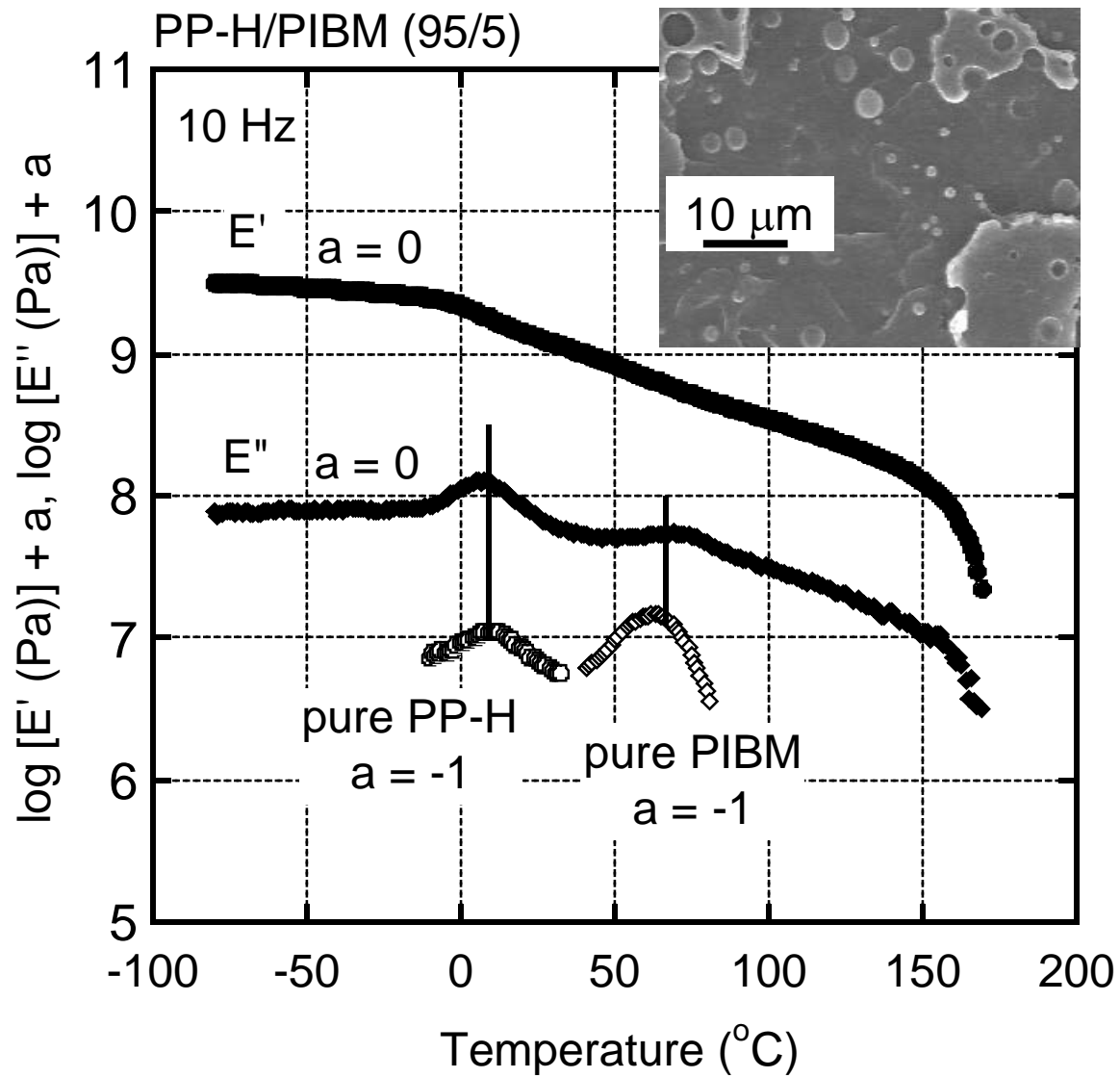
Prompt glassification
of acrylate polymer with fibrous shape
at rapid cooling



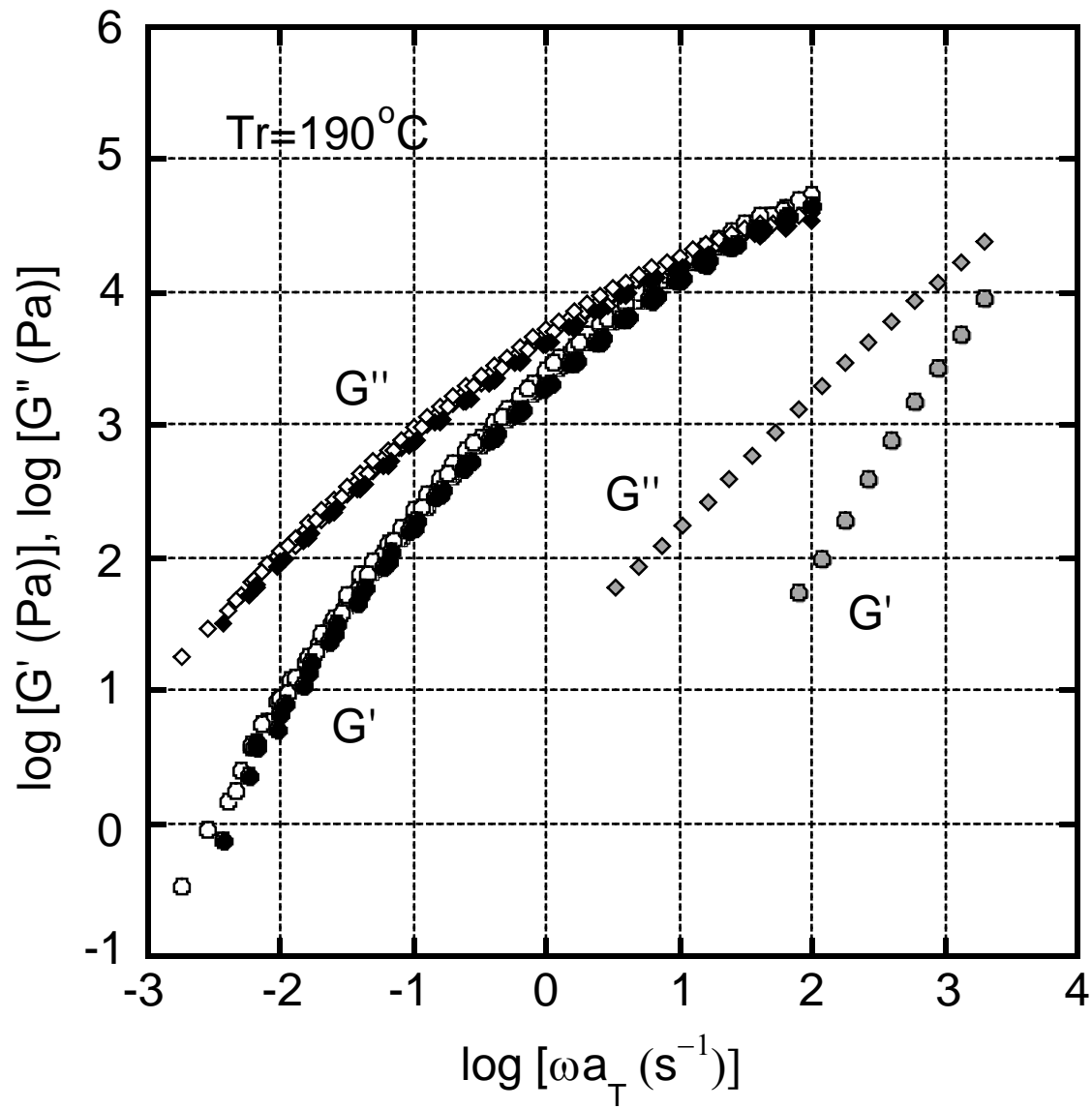
Localized
deformation
of PP melt



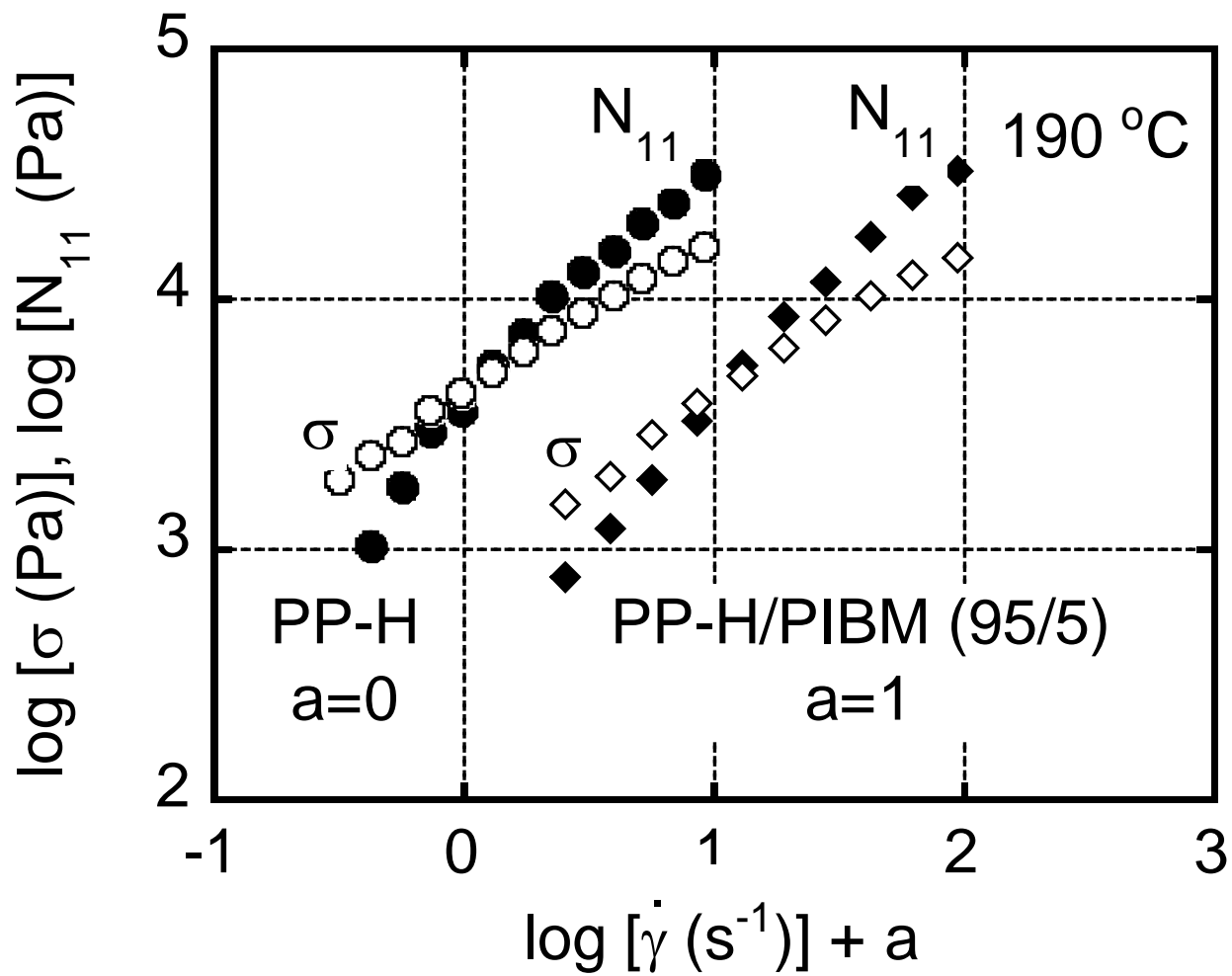
Enhancement
of drawdown force
(melt tension)



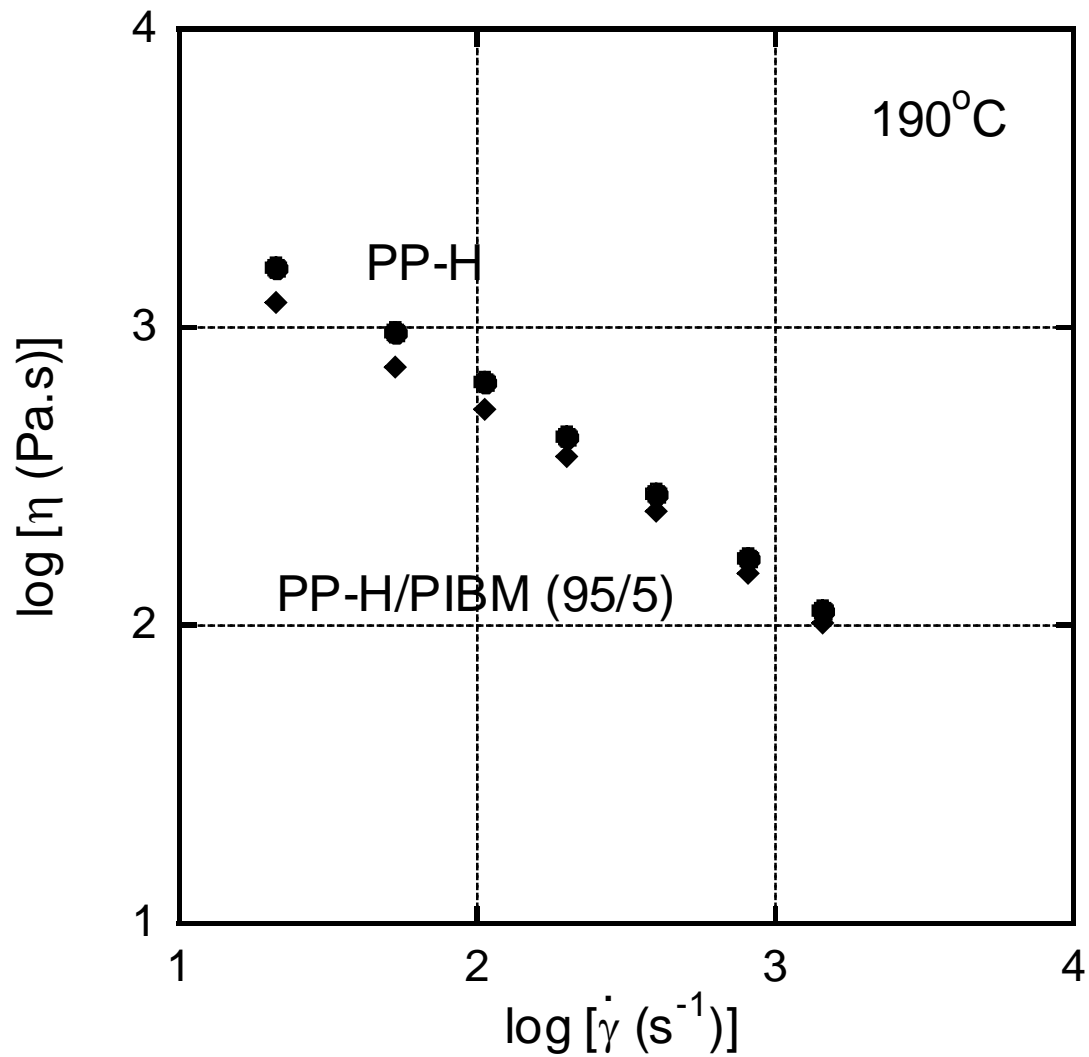
SEEMORK et al., FIG. 1



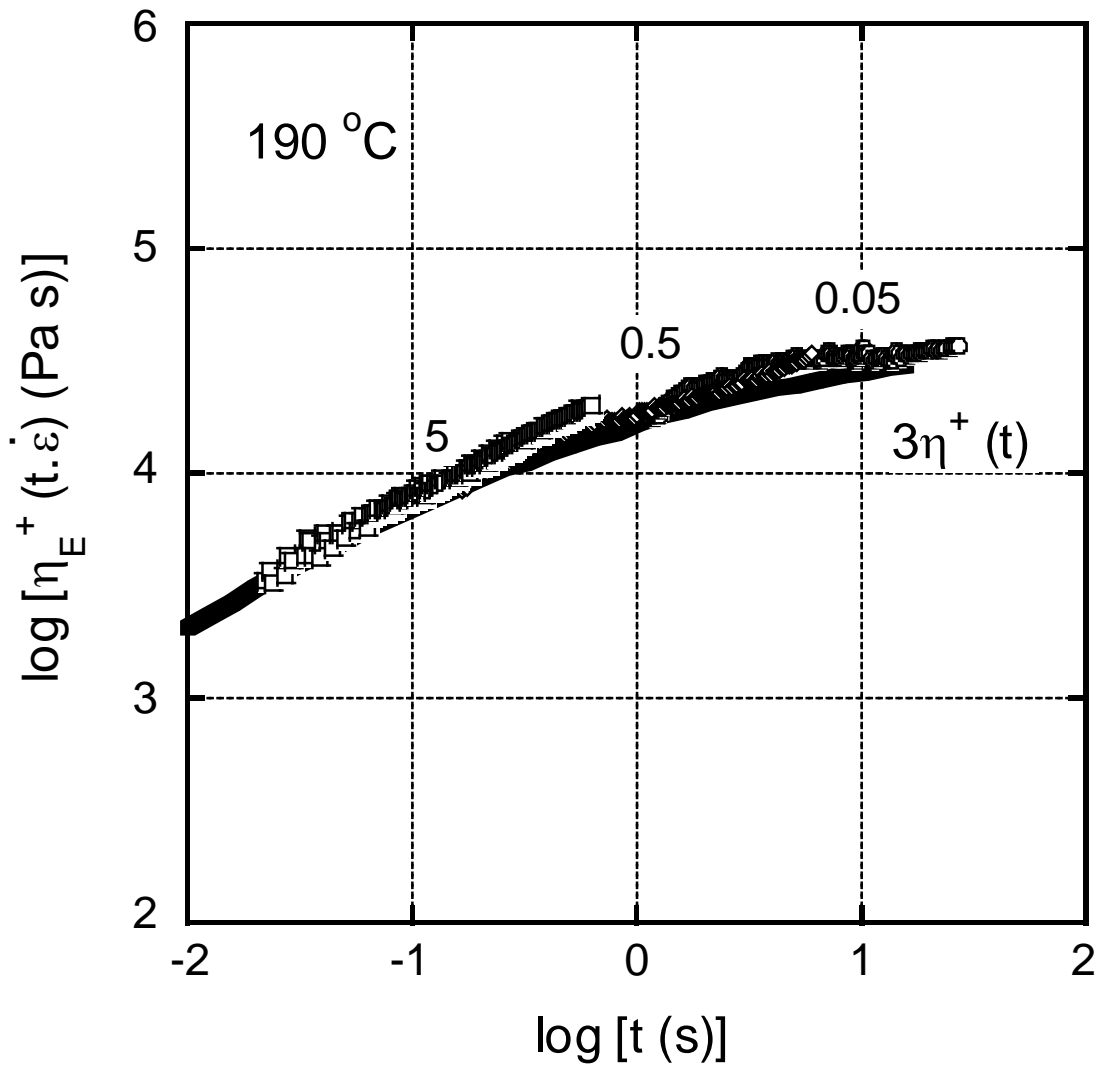
SEEMORK et al., FIG. 2



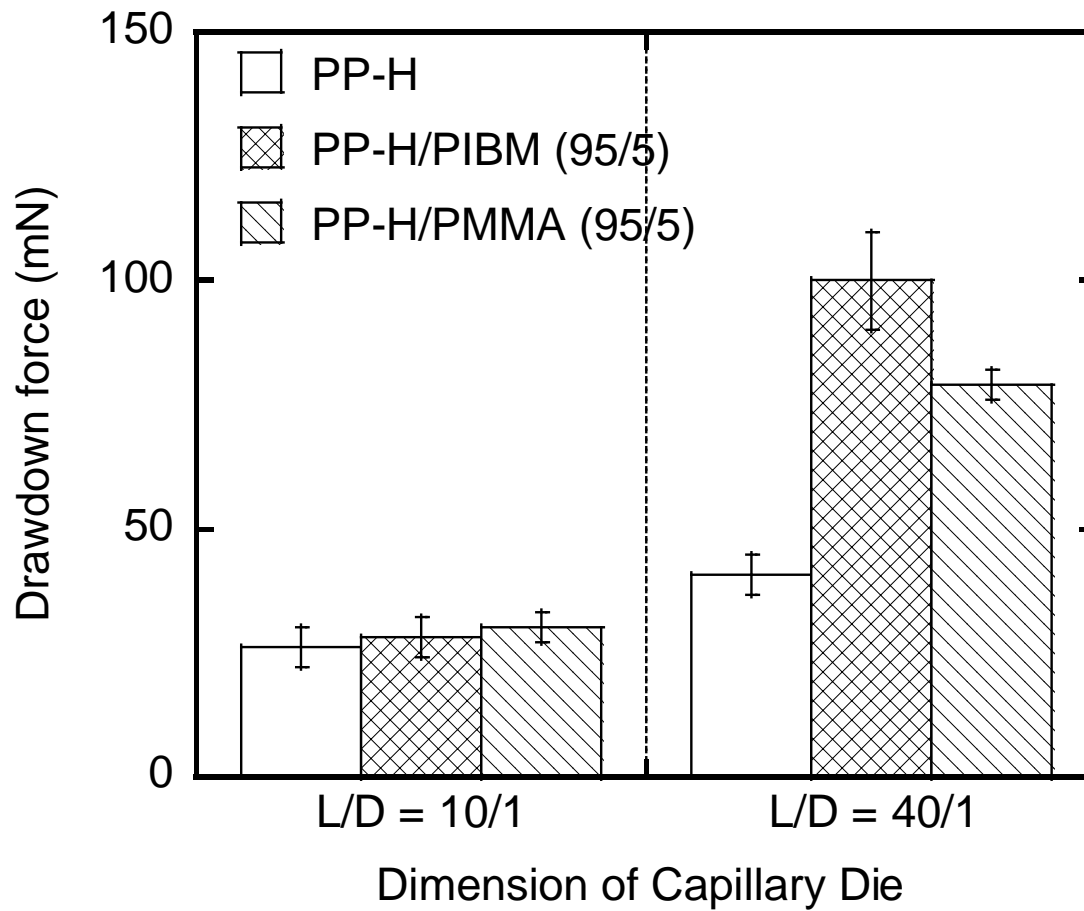
SEEMORK et al., FIG. 3



SEEMORK et al., FIG. 4

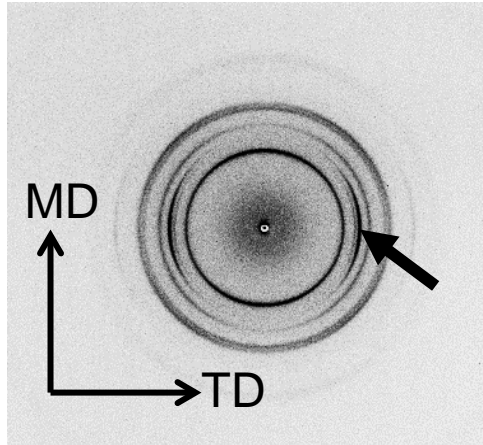


SEEMORK et al., FIG. 5

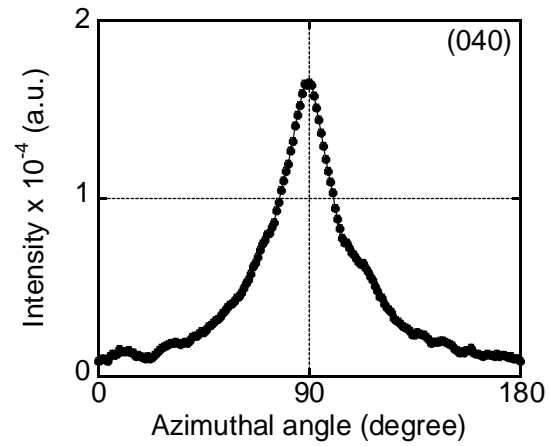
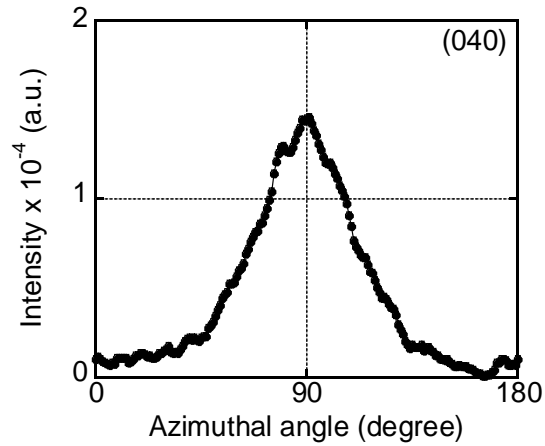
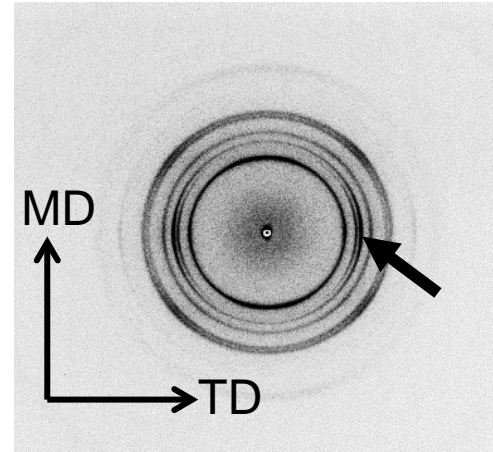


SEEMORK et al., FIG. 6

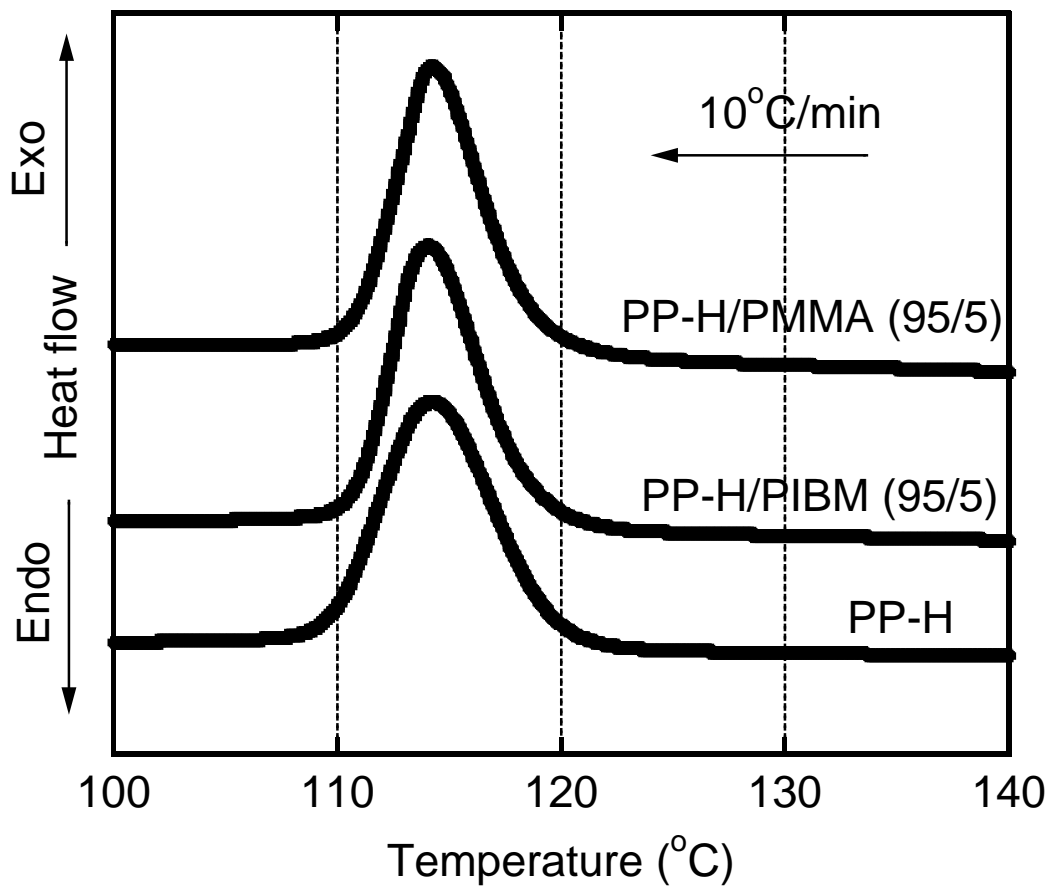
PP-H



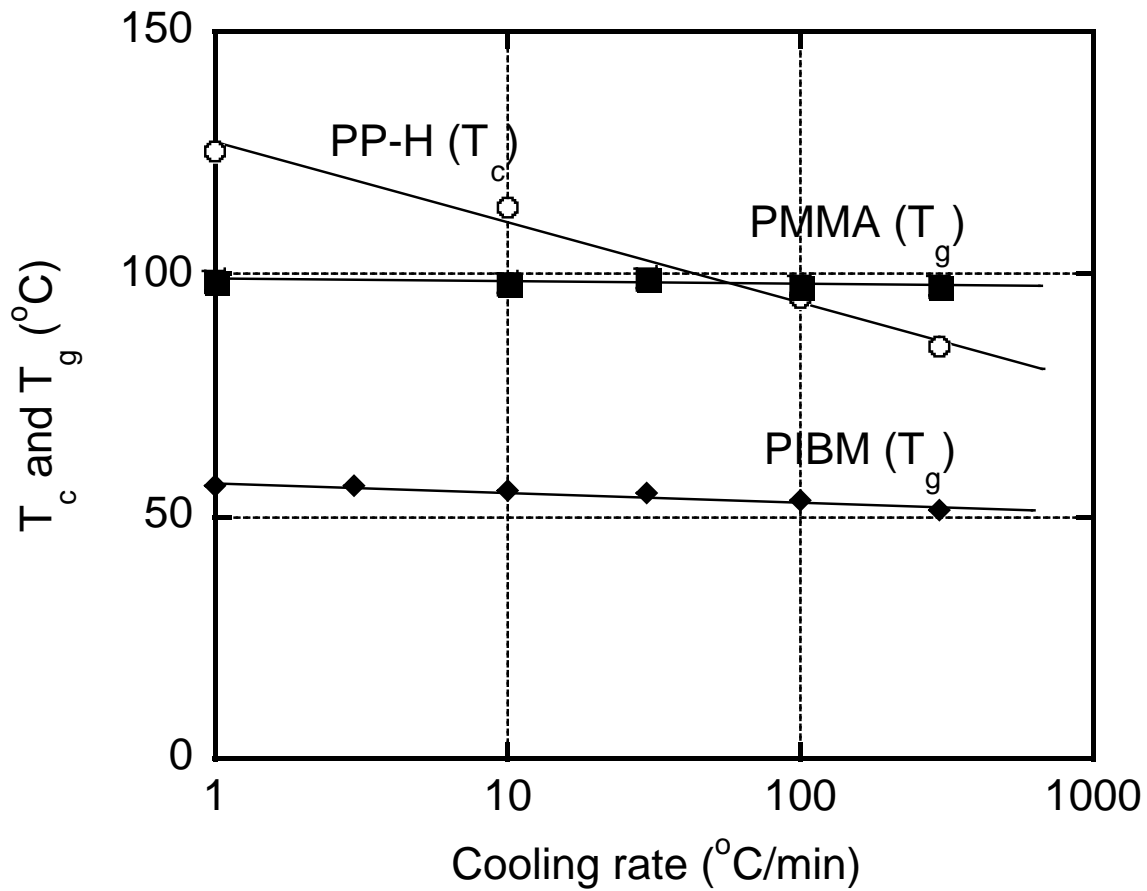
PP-H/PIBM (95/5)



SEEMORK et al., FIG. 7



SEEMORK et al., FIG. 8



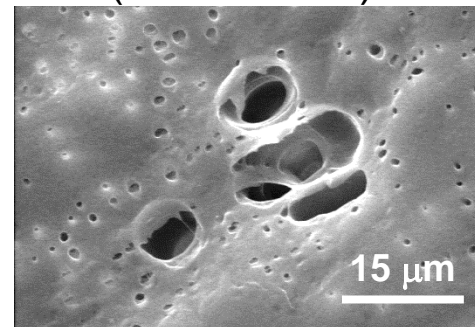
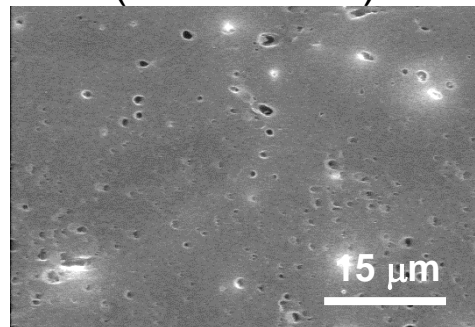
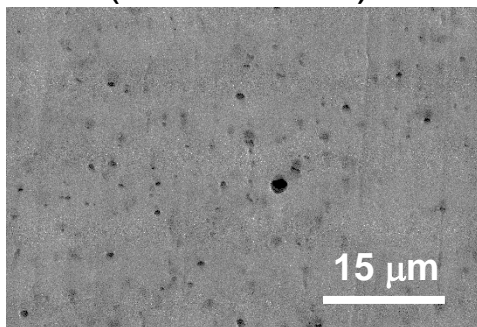
SEEMORK et al., FIG. 9

PP-H/PIBM (95/5)
(L/D = 10 /1)

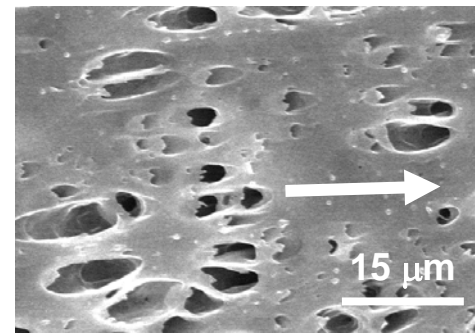
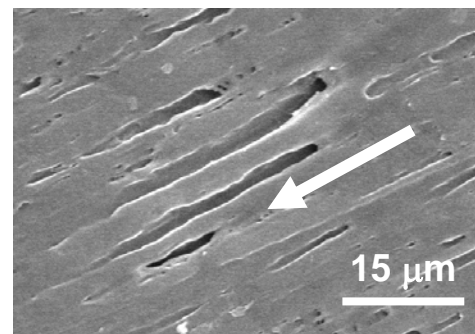
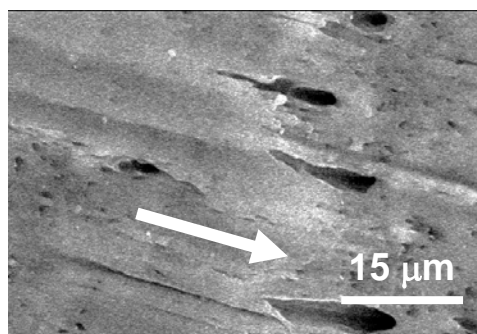
PP-H/PIBM (95/5)
(L/D = 40 /1)

PP-H/PMMA (95/5)
(L/D = 40 /1)

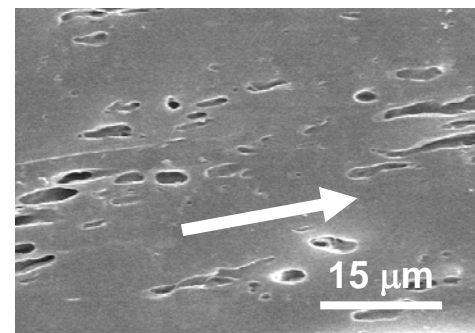
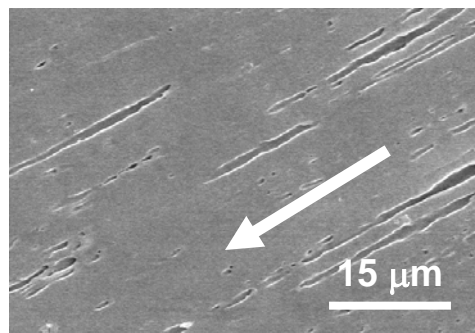
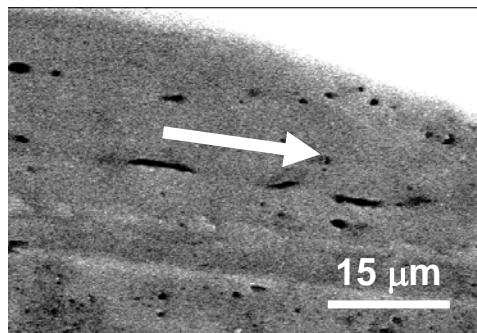
(a)



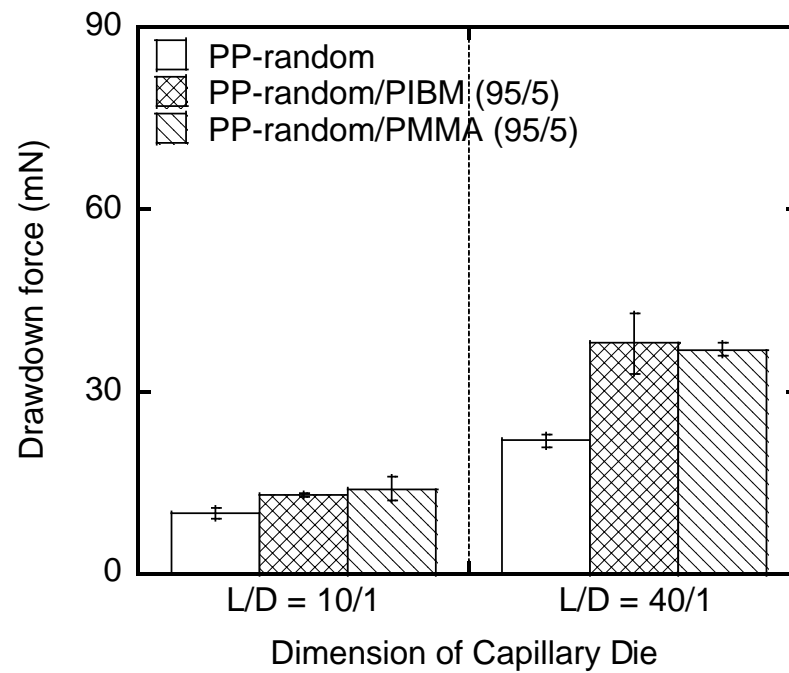
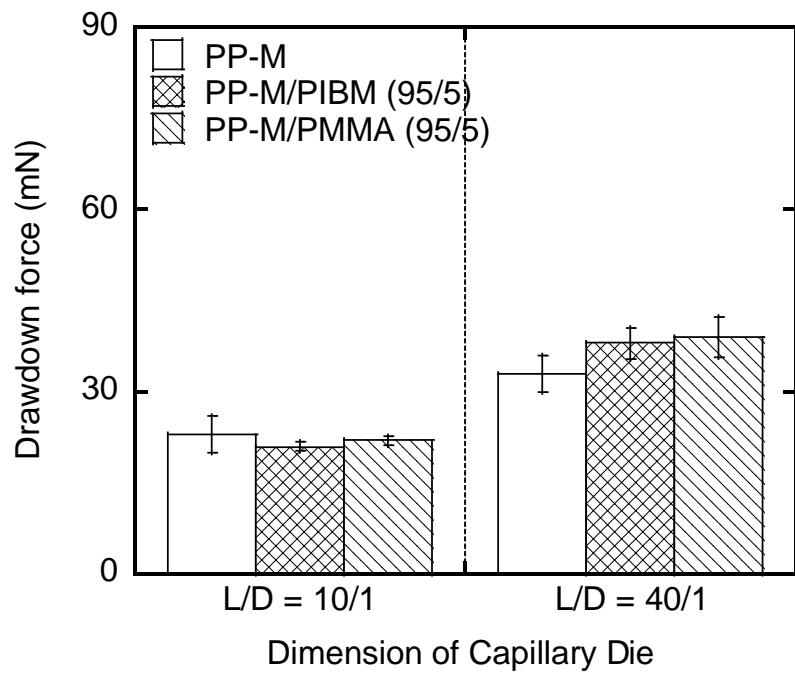
(b)



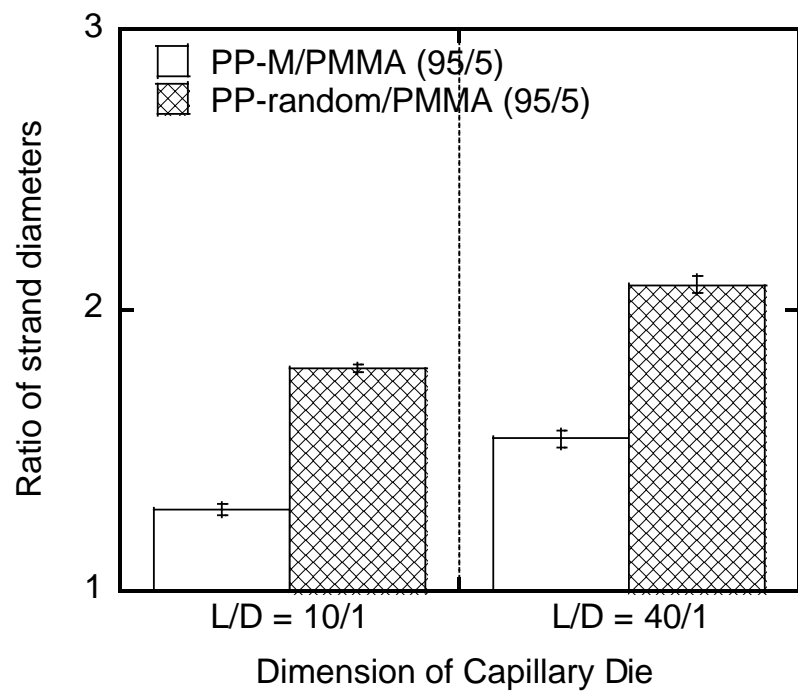
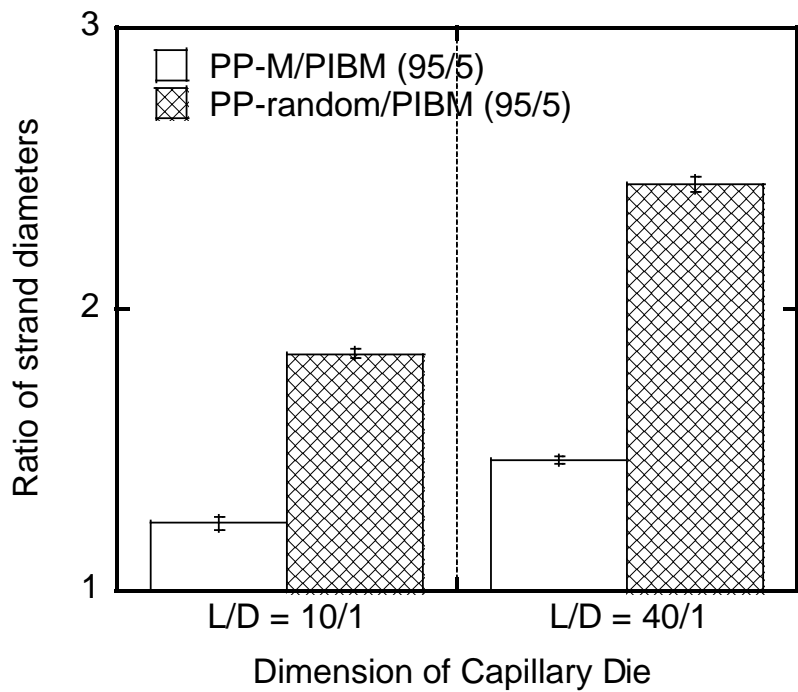
(c)



SEEMORK et al., FIG. 10



SEEMORK et al., FIG. 11



SEEMORK et al., FIG. 12

Table I. Zero-shear viscosity at 190 °C of the materials

Samples	η_0 (Pa s)
PP-H	9,850
PP-M	3,930
PP-random	4,930
PIBM	45
PMMA	280
PP-H/PIBM (95/5)	9,300
PP-H/PMMA (95/5)	9,500

SEEMORK et al., Table I